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Fungal decay resistance of wood reacted with phosphorus pentoxide-amine system

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Abstract

Resistance of wood reacted in situ with phosphorus pentoxide-amine to the brown-rot fungus *Gloeophyllum trabeum* and white-rot fungus *Trametes versicolor* was examined. Wood reacted with either octyl, tribromo, or nitro derivatives were more resistant to both fungi. Threshold retention values of phosphoramide-reacted wood to white-rot fungus *T. versicolor* ranged from 2.9 to 13.3 mmol, while these for brown-rot fungus *G. trabeum* ranged from 8.1 to 19.2 mmol. Wood reacted with phosphoramide tested to be more resistant to white-rot than brown-rot attack.

Keywords: brown-rot; *Gloeophyllum trabeum*; phosphoramide; threshold retention; *Trametes versicolor*; white-rot.

Introduction

Wood is subject to biodegradation by a variety of microorganisms, but the greatest damage is often caused by decay fungi, because they can rapidly cause structural failure. Many treatments are available to prevent or retard the destructive action of decay fungi. However, more than 5.2 billion in annual losses in the United States are estimated to result from fungal deterioration (Powell et al. 1992). Microbial attack of wood has traditionally been controlled through the use of wood preservatives. Effective broad-spectrum fungicides, such as creosote, pentachlophenol, and chromated copper arsenate, inhibit enzymes of many metabolic pathways, and are currently used to protect wood from decay. However, these toxic preservatives have been subjected to public criticism by their broad toxicity. The result has been an increased demand for the development of low toxicity alternatives or safe non-toxic treatments to prevent wood deterioration (Illman and Highley 1989).

The organophosphorus fungicides, such as phosphoramides are primarily active against fungal caused plant diseases such as powdery mildew (O'Brien 1960; Matolcsy et al. 1988). Phosphorus-containing flame retardants were also found to be strong inhibitors of both mildew and decay organisms (Bullock et al. 1964). However, there was little found in the literature about the properties of phosphoramide-reacted wood.

Phosphoramide is prepared in situ by reacting phosphorus pentoxide with amines which then reacts with wood. Phosphoramide compounds alter thermal degradation of reacted wood, promote retention of phosphorus in the char residue, and increase char yields after pyrolysis (Lee et al. 1998, 1999). In order to obtain a better understanding the potential for use of phosphoramides as wood preservatives, a series of novel phosphoramides were synthesized to react with wood, and the reacted-wood specimens were further tested for their fungal resistance.

Materials and methods

Chemical modification of wood

Loblolly pine (*Pinus taeda* L.) and sweetgum (*Liquidambar styraciflua* L.) sapwood blocks of dimensions 19×19×19 mm (radial×tangential×longitudinal) were reacted with phosphorus pentoxide and one of twelve different amines including alkyl, halophenyl, and phenyl amines (Table 1).

Thirty specimens of loblolly pine or sweetgum blocks were dried at 60°C for 1 day, cooled 30 min in a glass desiccator over dry agent, and then weighed. The blocks were transferred to a flask and placed in a desiccator under vacuum at 2.1 to 3.3 kPa for 30 min and then impregnated with dried N, N-dimethylformamide (DMF, 200 ml, dried over a 4 Å molecular sieve for more than 1 day) and held for 15 min. At the end of this process, the vacuum was slowly released to atmospheric pressure and the flask containing the blocks was removed from the treating desiccator. Phosphorus pentoxide, amine and wood (based on 1-4,anhydroglucopyranose equivalent) in a molar ratio of 1:3:1 were calculated, and the required chemicals weighed, and then slowly added to the flask. The reaction of loblolly pine was continued at 115°C for 7, 8, or 10 h to yield 3 different weight gains. Sweetgum was also reacted at 115°C for 1, 2, or 4 h to yield 3 different weight gains. In order to remove unreacted chemical, the specimens from each treatment were extracted with 900 ml acetone in a Soxhlet extractor for 12 h. The extracted specimens were then air-dried for 1 day, and leached in 900 ml distilled water daily for 14 days. After leaching, the specimens were heated in an oven at 60°C for 24 h. The extent of reacted chemical was calculated as weight retention determined by the difference in oven-dried weight of the specimen before modification (W_1) and after leaching (W_2) according to the following equations:

$$\text{Weigh retention}_1\ (\%) = [(W_2 - W_1)/W_1] \times 100 \quad (1)$$

$$\text{Weight retention}_2\ (\text{mmol/100g wood}) = [(W_2 - W_1)/\text{Molecular weight of one substituted phosphoramide}]/(W_1/100) \times 1000 \quad (2)$$

After being reacted in the various phosphorus pentoxide and

amine systems, wood blocks were investigated for fungal resistance.

Analysis

Bond formation between wood and phosphoramides was identified by Fourier Transform Infrared Analysis (FTIR). Selected specimens were analyzed by a Wattson Model 5000 FTIR spectrophotometer to obtain 2 cm^{-1} resolution spectra over the 4000 to 400 cm^{-1} region. The solid potassium bromide (KBr) method was used for comparison of specific functional groups in unmodified and phosphoramide modified wood. X-ray microanalysis (EDXA) was performed on selected modified and unmodified specimens with a Tracor Northern 5500 energy dispersive spectrometer. Dried specimens were cut in the radial direction and mounted on specimen holders with a mixture of silver paint and cellulose cement. The specimens were transferred to a high vacuum evaporating unit and coated with carbon. Changes in unmodified and modified specimens of wood cells reacted with chemicals were examined by EDXA, and the chemical distribution on wood cells were detected by X-ray maps.

Decay tests

Decay resistance was assessed according to procedures described in ASTM standard D1413-76 (ASTM 1994). *Gloeophyllum trabeum* (Pers.:Fr.) Murr. (Madison-617), a brown-rot fungus, was used with loblolly pine blocks, and *Trametes versicolor* (L.:fr.) Quel. (Madison-697), a white-rot fungus, was used with sweetgum blocks. Five replicate blocks from each treatment and 5 control blocks were tested for decay resistance over a 12-week period. Before and after incubation, the blocks were dried at 60°C for 24 h and weighed. Weight loss was expressed as a percentage of the initial oven-dried weight of the specimen. The extent of fungal attack was determined by oven dried weight loss, and the weight loss values were the means ± standard deviation (SD) for 5 replicate blocks after 12-week of incubation. Chemical retention in wood that resulted in weight loss by decay of less than 2% was considered to be the threshold retention for fungal attack.

Results and discussion

Characterization of reacted wood

Bond formation between wood and phosphoramides was evidenced by the characteristic infrared absorption by P–OH, P=O and P–N groups in loblolly pine wood fiber reacted with the propyl and butyl derivatives (Figure 1). The P–OH group in the modified wood absorbed at 2480 cm^{-1} as a result of P–OH stretching vibration, at 1240 cm^{-1} as a result of P=O vibration, and at 926 cm^{-1} as a result of P–N asymmetric stretching vibration (Colthup et al. 1964). P–N bond formation is clearly visible in wood reacted with phosphoramide.

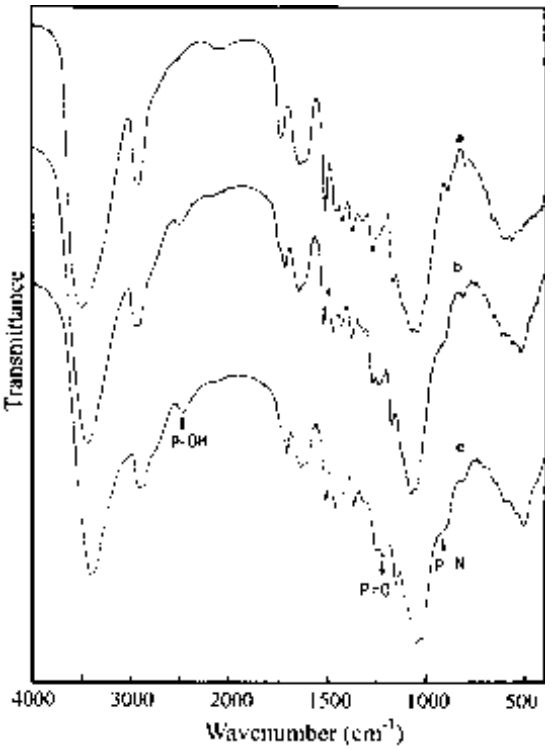

Figure 1 FTIR spectra of control pine wood and pine wood reacted with PPAM and PBAM at 50 mmol/100 g wood retention: (a) control; (b) PPAM; (c) PBAM.

Figures 2–3 show the SEM and EDXA distribution map of phosphorus and chlorine from PCAN-reacted wood. The results reveal that both chemical elements are retained in the reacted wood, indicating that chemical bonds were formed as a result of the reaction of wood and phosphoramide. Moreover, denser phosphorus and chlorine distributions were observed around the cell lumen of S_3 layer, suggesting that the reaction between phosphoramide and wood was uneven. Different phosphorus and chlorine counts were also present at different positions of the cell wall (S_2) and cell middle lamella (Fig-

Table 1 Chemicals reacted with wood through phosphorus pentoxide and amines system.

Chemical	Structure	Molecular weight	Abbreviation
Phosphorus pentoxide	P_2O_5	141.94	P
Propylamine	$C_3H_7NH_2$	59.11	PAM
Butylamine	$C_4H_9NH_2$	73.14	BAM
Hexylamine	$C_6H_{13}NH_2$	101.19	HAM
Octylamine	$C_8H_{17}NH_2$	129.25	OAM
4-Fluoroaniline	$C_6H_4FNH_2$	111.12	FAN
4-Chloroaniline	$C_6H_4ClNH_2$	127.57	CAN
4-Bromoaniline	$C_6H_4BrNH_2$	172.03	BAN
2,4,6-Tribromoaniline	$C_6H_2Br_3NH_2$	329.83	TBAN
Aniline	$C_6H_5NH_2$	93.13	AN
p-Anisidine	$C_6H_4OCH_3NH_2$	123.16	ASD
p-Toluidine	$C_6H_4CH_3NH_2$	107.16	TLD
4-Nitroaniline	$C_6H_4NO_2NH_2$	138.13	NAN

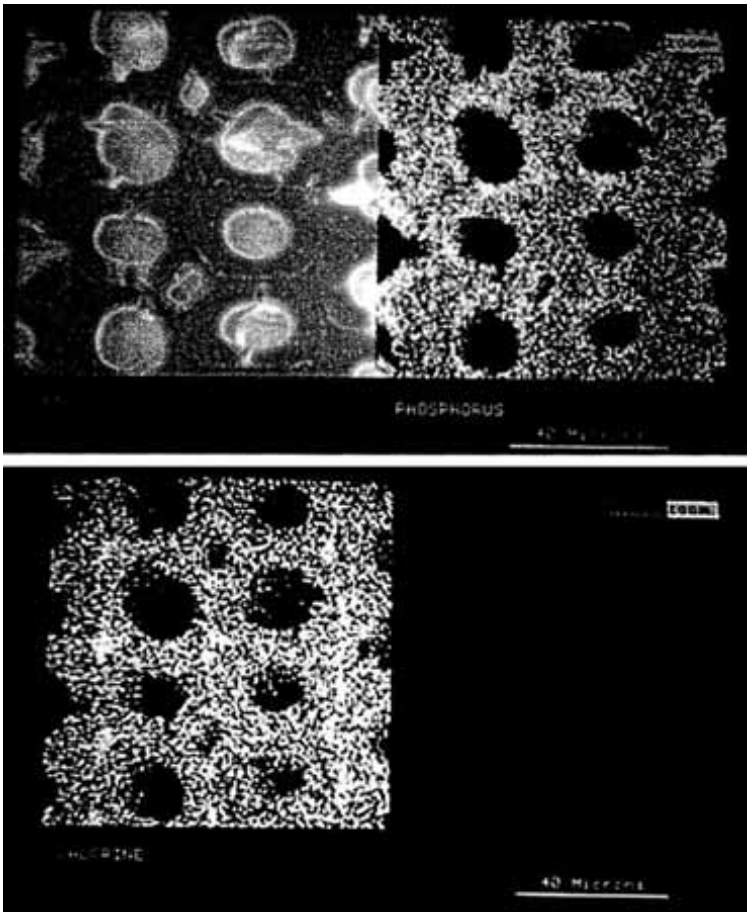

Figure 2 EDXA distribution map of loblolly pine reacted with PCAN at 50 mmol/100 g wood retention, leached (1000×).

ure 2). Evaluation of the P and Cl counts of the reacted wood in the EDXA analysis spectra (Figure 3) revealed that there was more Cl than P present in the cell middle lamella with a count ratio of Cl to P of nearly 2, suggesting that these reactive chemicals were able to react preferably with lignin in wood. The results also provided further evidence that the reaction between wood components and chemical was uneven.

Wood decay tests

Brown rot fungus Exposure of loblolly pine wood reacted with alkyl phosphoramides revealed threshold retentions with *G. trabeum* for octyl and hexyl derivatives of 13 and 13.3 mmol per 100 g wood (Table 2). For the butyl derivative at 18.7 mmol of chemical in wood, weight loss was 2.6%. The propyl derivative at 20.4 mmol suffered 12% weight loss. Based on the same molar ratio of chemical to wood, wood specimens reacted with octyl derivative had a lower weight loss than those of wood specimens reacted with hexyl, butyl, and propyl derivatives, indicating that the octyl derivative was the most effective, followed by hexyl and butyl derivatives, while propyl derivative was ineffective at the retentions tested. The results also indicated that increasing alkyl group size in phosphoramide resulted in better fungal resistance, a pattern that is similar to that observed for alcohols and aliphatic acids tested in an agar-flask method by Baechler (1947).

Threshold retentions for wood reacted with monohalo-

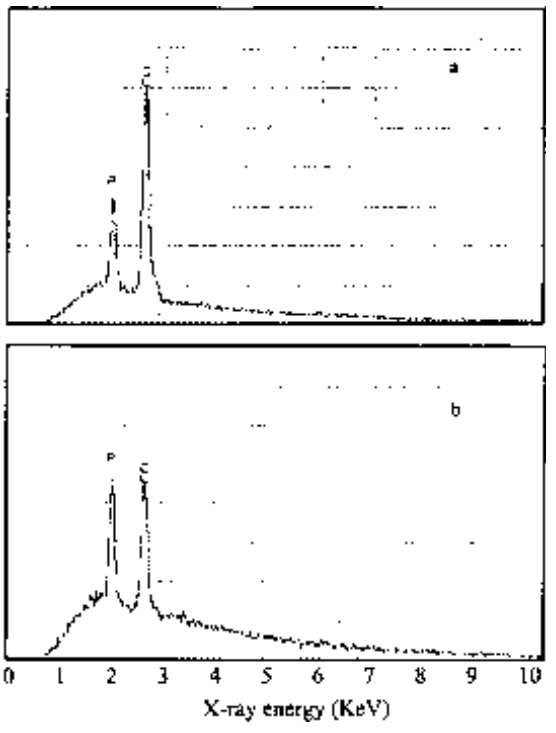

Figure 3 EDXA spectrum of loblolly pine reacted with PCAN at 50 mmol/100 g wood retention, leached (1000×): (a) middle lamella; (b) cell wall (S2).

Table 2 Soil-block decay test of loblolly pine reacted with phosphorus pentoxide-amine system and inoculated with *Gloeophyllum trabeum* for 12 weeks.

Treatment	Weight retention[1] (%)	Weight loss[2] (%)
Control	–	46.8±2.0
PPAM	2.8 (6.0)	32.8±2.7
	5.9 (12.4)	16.8±1.5
	9.7 (20.4)	12.0±1.0
PBAM	4.7 (8.9)	23.1±3.1
	7.3 (13.5)	13.5±2.2
	10.0 (18.7)	2.6±0.5
PHAM	5.6 (8.6)	2.3±0.2
	8.4 (13.3)	1.2±0.3
	11.8 (18.7)	1.5±0.3
POAM	5.8 (7.8)	2.2±0.1
	9.9 (13.0)	0.6±0.1
	12.6 (16.8)	0.3±0.1
PFAN	6.0 (9.5)	3.5±0.4
	7.2 (11.3)	1.7±0.5
	10.5 (17.0)	1.6±0.7
PCAN	5.4 (7.9)	2.5±0.5
	8.7 (12.7)	1.2±0.2
	15.9 (23.7)	1.9±0.4
PBAN	9.5 (11.6)	3.0±0.8
	14.5 (17.0)	1.7±0.1
	25.4 (30.9)	2.2±0.1
PTBAN	8.7 (6.3)	3.6±0.7
	11.5 (8.1)	1.7±0.8
	15.8 (11.4)	1.6±0.5
PAN	4.5 (8.1)	28.2±3.0
	10.7 (19.3)	12.7±1.8
	12.2 (22.5)	3.0±0.2
PASD	3.2 (4.8)	40.1±2.7
	8.7 (12.9)	24.3±4.1
	16.9 (24.8)	5.9±1.5
PTLD	8.7 (13.9)	2.3±0.2
	11.8 (19.2)	1.7±0.1
	16.0 (26.0)	1.5±0.1
PNAN	4.4 (6.1)	2.5±0.8
	6.8 (9.3)	1.4±0.5
	11.3 (15.8)	1.3±0.1

[1] Values in parentheses are mmol/100 g wood.
[2] Values are means of 5 specimens±SD.

phenyl phosphoramides and exposed to *G. trabeum* were 11.3, 12.7, and 17.0 mmol for fluoro, chloro, and bromo derivatives, respectively. The results indicated that the fluoro derivative was the most effective followed by chloro and bromo derivatives. Similar results were also observed in wood modified with *p*-toluene sulfonyl chloride and fluoro, chloro, and bromo anilines (Chen 1994). The threshold retention was 8.1 mmol for wood reacted with tribromo derivative (Table 2). Generally, wood reacted with halophenyl phosphoramides was effective in preventing attack by the brown-rot fungus. In particular, wood reacted with the tribromo derivative, based on the same molar ratio of chemicals in reacted wood, was the most resistant to decay among these four treatments. The results also indicated that increasing bromine substitution on the phenyl ring increased efficacy against fungal attack. Stamm and Seborg (1943) reported that increasing the degree of halide substitution in the reacting chemicals can increase the toxicity of reacted wood. There are three bromine substituents in the aryl group of the tribromo derivative. Therefore, higher substitution of bromine in this compound might account for its higher toxicity.

Threshold retentions with *G. trabeum* were 9.3, 19.2 mmol for nitro and 4-methyl derivatives, respectively, while anilino and anisole derivatives were ineffective for wood reacted with phenyl phosphoramides containing electron withdrawing and donating groups on the phenyl ring (Table 2). The nitro derivative was the most effective, followed by 4-methyl and anilino derivatives, while the anisole derivative was the least effective. Whether electron donating or withdrawing groups affect the fungitoxicity still remains to be investigated.

White-rot fungus Decay tests of sweetgum wood reacted with alkyl phosphoramides gave threshold retentions with *T. versicolor* of 4.7, 5.9 and 11.2 mmol for octyl, hexyl and butyl derivatives, respectively (Table 3). The propyl derivative at 13.3 mmol of weight retention of chemical had 2.4% weight loss. The octyl derivative was the most effective, followed by the hexyl and butyl derivatives, whereas the propyl derivative was the least effective. Similar results were obtained with brown-rot fungus, indicating that the size of the alkyl group in phosphoramide has similar effectiveness against the decay types. However, wood reacted with alkyl phosphoramides were more resistant to white-rot decay than brown-rot decay.

When wood was reacted with monohalophenyl phosphoramides, threshold retentions with *T. versicolor* were 5.6, 4.5, and 6.3 mmol for fluoro, chloro, and bromo derivatives, respectively (Table 3). It was difficult to conclude whether the chloro derivative was more effective than the fluoro derivative because only one concentration was assessed. The threshold retention value for the tribromo derivative was 3.5 mmol, while that for the monobromo derivative was 6.3 mmol. Data also revealed that wood reacted with the tribromo derivative was the most resistant to white-rot fungal decay among all the halophenyl phosphoramide-reacted woods tested. All reacted woods provide better resistance to white-rot fungi than brown-rot fungi.

For wood reacted with phenyl phosphoramides containing electron withdrawing and donating groups, threshold retentions of reacted woods with *T. versicolor* were 2.9, 5.0, 5.2, or 9.9 mmol when treated with nitro, anilino, 4-methyl or 4-methoxy derivatives, respectively (Table 3). The nitro derivative was the most effective, followed by the anilino and 4-methyl derivatives, while the 4-methoxy derivative was the least effective. The results also failed to reveal whether electron withdrawing or donating groups affected fungitoxicity as observed in the brown-rot test. Further investigations will be required.

Wood reacted with phosphoramides tested to be more resistant to white-rot than brown-rot attack. Threshold retention values of phosphoramide-reacted woods to white-rot fungus *T. versicolor* ranged from 2.9 to 13.3 mmol, while these for brown-rot fungus *G. trabeum* ranged from 8.1 to 19.2 mmol.

Table 3 Soil-block decay test of sweetgum reacted with phosphorus pentoxide- amine system and inoculated with *Trametes versicolor* for 12 weeks.

Treatment	Weight retention[1] (%)	Weight loss[2] (%)
Control	–	37.5±3.5
PPAM	1.3 (2.8)	13.5±3.7
	4.4 (9.2)	3.1±0.6
	6.3 (13.3)	2.4±0.7
PBAM	2.7 (5.0)	12.1±0.6
	4.7 (8.8)	6.9±0.4
	6.0 (11.2)	2.0±0.1
PHAM	3.8 (5.9)	2.0±0.1
	5.8 (9.0)	0.1±0.1
	8.1 (12.6)	0.1±0.1
POAM	3.5 (4.7)	2.1±0.1
	6.0 (8.0)	0.1±0.1
	9.2 (12.3)	0.1±0.1
PFAN	3.6 (5.6)	2.1±0.5
	6.6 (10.5)	0.4±0.1
	9.0 (14.4)	0.5±0.1
PCAN	3.1 (4.5)	1.9±0.5
	7.1 (10.5)	0.8±0.1
	10.0 (14.7)	0.9±0.2
PBAN	5.2 (6.3)	2.1±0.5
	9.4 (11.4)	0.6±0.2
	14.1 (17.1)	0.9±0.2
PTBAN	4.8 (3.5)	2.0±0.4
	6.9 (5.1)	0.7±0.2
	15.3 (11.2)	0.6±0.1
PAN	2.8 (5.0)	2.1±0.6
	4.3 (7.6)	0.1±0.1
	7.8 (13.8)	0.1±0.1
PASD	4.6 (7.0)	3.9±0.2
	6.6 (9.9)	0.4±0.1
	12.1 (18.2)	0.1±0.1
PTLD	3.3 (5.2)	2.0±0.4
	4.4 (7.1)	0.2±0.1
	9.2 (14.8)	0.4±0.1
PNAN	2.1 (2.9)	1.9±0.6
	3.2 (4.5)	0.4±0.1
	7.8 (10.7)	0.4±0.1

[1] Values in parentheses are mmol/100 g wood.
[2] Values are means of 5 specimens±SD.

Conclusions

The deterioration of wood caused by decay fungi can be effectively prevented by treating with phosphorus pentoxide-amine system. Wood reacted with either octyl, tribromo, or nitro derivative was more effective than other treatments in both the brown-rot and white-rot decay test. Wood reacted with phosphoramide was less effective in resisting attack by brown-rot fungi and was more effective in resisting attack by white-rot fungi.

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Received March 24, 2003