

Short Note

Synthesis and evaluation of phosphotriamidates in wood for thermal and fungal decay protection

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Introduction

It is estimated that there are almost 500 000 residential structure fires every year attended by US fire departments. These fires killed approximately 3700 people in 1995 (Hoebel 1998). Proper treatment of wood products with fire retardants would reduce the damages to buildings and save lives. Phosphate fire retardants have been used in wood products (Juneja 1972; Juneja and Richardson 1974; AWP standard 2004); however, they decrease the wood strength over time (LeVan and Winandy 1990; LeVan et al. 1990). One method to minimize the strength loss is to replace phosphate with phosphoramidates (phosphoramides) as fire retardants. The P-N bonds in aromatic and some aliphatic phosphoramidates are stable to alkaline and some acidic conditions (Chao et al. 1995) and have been shown to be better dehydration agents and phosphorylation catalysts for cellulose (Langley et al. 1980). It has been demonstrated that phosphoramidates in cellulose promote retention of phosphorus in char and increase char yield after pyrolysis (Hendrix et al. 1972; Pandya and Bhagwat 1981).

Our previous studies proved that wood reacted with phosphoramidates produced in situ from phosphorus pentoxide and aromatic and aliphatic amines at 115°C had an elevated resistance to thermal and fungal degradation. Wood treated in this way degraded thermally at lower temperatures in the range of 254–304°C at maximum pyrolysis rate loss (control 377°C) and char yields increased to 32.0–44.7% (control 20.1%) (Lee et al. 2004a). Phosphoramidate reacted wood prevents decay by a brown-rot fungus *Gloeophyllum trabeum* (Pers.: Fr.) Murr. MAD-617 at concentrations of 8.1–19.2 mmol/100 g wood. Wood destruction by the white-rot fungus *Trametes versicolor* (L.: Fr.) Quel. MAD-697 was also prevented at concentration levels between 2.9 and 13.3 mmol/100 g wood (Lee et al. 2004b). However, the

preparation of treated woods needs 4–24 h reaction time in *N,N*-dimethylformamide and it is too complicated for practical applications.

The objective of this study was to evaluate the possibility of simplification of the process. The question in focus was simply whether phosphotriamidates impregnated wood would be as effective concerning fire resistance and fungal decay as phosphoramidate bonded wood.

Experimental

Phosphotriamidates were synthesized under the reflux of phosphoryl oxychloride with aliphatic and aromatic amines in chloroform (Audrieth and Toy 1942). They were characterized by a Galaxy Series FTIR 5000 spectrophotometer in KBr and ¹H-NMR spectrometry (instrument: Avance DPX 250) in d-chloroform or d₆-DMSO. Only the infrared (IR) and NMR spectra of a new triphenyl ethyl phosphotriamidate (TEP) will be reported here.

Elemental analysis was performed by the Galbraith Laboratories, Inc. (Knoxville, TN, USA). The melting points of phosphotriamidates were determined by a Thomas Hover model capillary melting point apparatus (Arthur H. Thomas Co., Philadelphia, PA, USA). Thermal analysis of a loblolly pine wood block impregnated with phosphotriamidates (0.1 mmol/100 g wood) was performed on a thermal gravimetric analyzer (TGA) (model: Perkin Elmer TGA 7; Perkin Elmer Life and Analytical Sciences, Inc., Waltham, MA, USA). The conditions were N₂; heating rate of 20°C min⁻¹ from 50°C to 600°C.

Reaction of phosphoryl oxychloride with amine in a 1:6 molar ratio has a higher yield of phosphotriamidate than a molar ratio of 1:3. In both reactions, 3 mol of pyridine was the catalyst. The yield and melting point of phosphotriamidates are triphenyl phosphotriamidate (TPP) 64%, 210°C (211–214°C); tri-*p*-toluidyl phosphotriamidate (TTP) 85%, 198°C (195–198°C); tribenzyl phosphotriamidate (TBP) 86%, 98–99°C (98–99°C); TEP 73%, 88–90°C and tricyclohexyl phosphotriamidate (TCP) 36%, 243°C (245–246°C). The melting points of TPP, TTP, TBP and TCP were close to those reported in the literature (values shown in parentheses according to Audrieth and Toy 1942). Elemental analysis of a new compound (TEP) was C 68.96%, H 7.44% and N 9.85%. The theoretical values are C 70.74%, H 7.42% and N 10.31%.

IR absorption of TEP (Figure 1) with P-N absorption at 698–725 cm⁻¹ (A) and symmetric and asymmetric stretching vibrations of P-N at 859–915 cm⁻¹ (A), P=O absorption at 1088 cm⁻¹ (B) and C-N absorptions at 1166–1190 cm⁻¹ (C) (Colthup et al. 1964; Conley 1966; Thomas 1974).

¹H NMR of TEP in d-chloroform (ppm) (Figure 1) was 2.1–2.2 (d, 1H, amino proton), 2.65–2.75 (m, 2H, β-methylene protons), 2.9–3.2 (m, 2H, α-methylene protons) and 7.2–7.4 (m, 5H, aromatic protons).

Fungal decay tests were evaluated by a 12-week laboratory soil-block decay test. Brown rot fungus: *G. trabeum* for loblolly pine (*Pinus taeda* L.) blocks. White rot fungus: *T. versicolor* for sweetgum (*Liquidambar styraciflua* L.) blocks. Sapwood blocks from each wood species (19 mm in all anatomical directions)

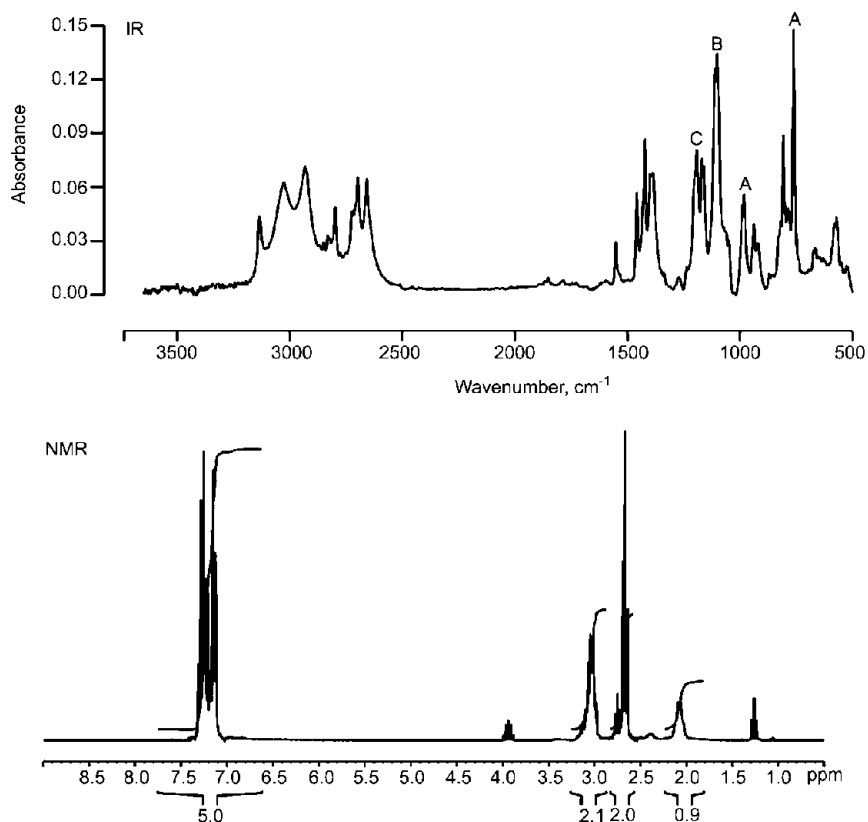


Figure 1 FTIR spectrum and ^1H NMR spectrum of triphenyl ethyl phosphotriamidate (TEP).

were selected according to the ASTM (2000) Standard D1413-99. Blocks were impregnated with methanol solutions of phosphotriamidates as well as aqueous solutions of boric acid at five concentration levels: 22.6, 11.3, 5.7, 1.6 and 0.8 mmol/100 g solution. Boric acid was included because it has well documented activity against a range of decay fungi.

For each test, 14 blocks of each wood species were situated in a glass jar and placed in a desiccator with a vacuum at 2.2–3.0 KPa for 20 min. They were then impregnated with one of the solutions indicated above in MeOH and soaked for 1 day. After soaking, the blocks were dried in a fume hood for 1 day and then heated in an oven at 60°C for 1 day. Seven blocks per treatment were conditioned at 27°C and 30% relative humidity (RH) for 3 weeks. Another seven blocks per treatment were leached in 350 ml of distilled water which was changed after 6, 24 and 48 h and then every 24 h for 2 weeks, according to the ASTM Standard D1413-99 (ASTM 2000).

No analysis was made for phosphotriamidate concentrations in wood, and the effect of water leaching was not assessed, either. After leaching, the blocks were conditioned at 27°C and 30% RH for 3 weeks. Five replicate blocks from each treatment, five controls and five blocks treated with solvent alone (with and without water leaching) were tested for decay resistance over 12 weeks exposure to one of the two decay fungi. The extent of fungal attack was determined by weight loss. Solution concentration was expressed as mmol of chemical/100 g solution. Retention of phosphotriamidates in wood blocks is not reported in Table 1.

Results and discussion

Thermal analysis

Phosphorus compounds, including phosphates and phosphoramidates, can alter the pyrolysis pathway of

cellulose and hemicelluloses in wood by favoring a dehydration pathway leading to more char and less volatile compounds (Shafizadeh 1984; Sekiguchi and Shafizadeh 1984). For this reason, phosphorus compounds were investigated extensively as fire retardants for textiles and wood products (Toy and Walsh 1987).

Thermal gravimetric analysis in nitrogen at 600°C of wood impregnated with phosphotriamidates (0.1 mol/100 g wood) revealed that the treated wood decomposes at temperatures in the range of 275–280°C at maximum rate loss. The control without impregnation decomposes at 380°C (Table 2). From the point of view of fire protection, it is important, however, that the char yields increased to 33.7–40.2% (control 16.9%) (Table 2). Diammonium phosphate treated wood, a known fire retardant, had a temperature of 295°C at the maximum rate loss and yielded 39.6% char. This indicates that the pyrolysis pathway of wood treated with phosphotriamidates was similar to that found in the case of most phosphorus compounds, which increase dehydration and lead to higher char yields and less volatile compounds. The aromatic phosphotriamidates resulted in higher char yields than those produced by the aliphatic phosphotriamidates. The char yields of TPP (40.2%) and TTP (38.9%) are comparable to those woods that are treated with diammonium phosphate (39.6%) and phosphotriamidate bonded wood (40.4–44.7%).

Fungal decay resistance

None of phosphotriamidates impregnated woods are as resistant to fungi as wood treated with boric acid. Wood impregnated with TBP and TEP at 22.6 mol/100 g wood

(without leaching) diminished weight losses caused only by *G. trabeum* (8.5% and 11.8%, respectively) (Table 1). The control had 64.2% weight loss, and wood blocks treated with methanol solvent alone without and with leaching had 59.8% and 54.8% weight losses, respectively. Wood impregnated with TPP and TEP at 22.6 mmol/100 g wood (without leaching) decrease weight losses caused by *T. versicolor* to 7.4% and 9.6%, respectively (Table 1). The control had 22.5% weight loss, and wood treated with methanol solvent alone without and with leaching, had 48.5% and 46.9% weight losses, respectively. This indicates that methanol as solvent promotes the weight loss of wood blocks by *T. versicolor*. The removed extractives by methanol may be an explanation for this effect. After leaching, none of phosphor-triamidates treated woods were resistant against fungi. This observation is in contrast to phosphoramidate bonded wood (Lee et al. 2004b), the decay preventing effect of which does not depend only on the toxicity.

Table 2 Thermal gravimetric analyses of pinewood impregnated with phosphor-triamidates (0.1 mol/100 g wood).

Treatment	T max (°C)	Char yield (%)
Control	380	16.9
Diammonium phosphate	295	39.6
TPP	280	40.2
TTP	275	38.9
TBP	280	36.9
TEP	290	34.8
TCP	280	33.7

T max: temperatures at maximum pyrolysis rate loss. Char yields: obtained at 600°C in nitrogen as protecting gas.

Conclusions

Previous studies showed that phosphoramidates (phosphoramides) – produced in situ and which are chemically bonded with the wood matrix – provided thermal and fungal decay resistance to the modified wood. A simple

Table 1 Effect of phosphor-triamidates on weight losses of pine blocks exposed to *Gloeophyllum trabeum* and sweet gum blocks exposed to *Trametes versicolor* in a 12-week soil-block fungal decay test.

Treatment	Concentration of solution (mmol/100 g)	Weight loss(%) ^a by			
		<i>Gloeophyllum trabeum</i>		<i>Trametes versicolor</i>	
		Non-leached	Leached	Non-leached	Leached
Boric acid	0.8	53.4 (8.1)	51.8 (3.1)	28.5 (13.8)	39.4 (9.3)
	1.6	30.0 (4.7)	50.2 (4.1)	8.7 (3.5)	37.1 (7.1)
	5.7	5.2 (5.2)	58.6 (5.2)	0.3 (0)	39.2 (8.2)
	11.3	2.8 (1.3)	59.8 (5.2)	1.2 (0)	39.4 (4.0)
	22.6	0.9 (0.3)	43.3 (4.8)	0.5 (0)	33.6 (4.3)
TPP	0.8	54.0 (11.6)	58.9 (7.4)	28.8 (6.3)	44.3 (11.9)
	1.6	61.0 (4.8)	60.3 (3.7)	27.5 (5.8)	38.6 (7.8)
	5.7	55.8 (8.5)	60.1 (7.3)	20.1 (4.6)	38.0 (8.4)
	11.3	44.4 (8.9)	60.8 (4.2)	18.8 (4.8)	22.7 (5.1)
	22.6	23.2 (10.0)	58.6 (5.2)	7.4 (5.4)	16.0 (3.1)
TTP	0.8	52.8 (3.7)	50.8 (2.7)	39.5 (12.9)	35.9 (2.4)
	1.6	51.0 (7.5)	60.0 (5.7)	35.6 (14.7)	32.7 (5.0)
	5.7	54.2 (7.7)	58.8 (6.2)	40.0 (5.9)	32.5 (8.5)
	11.3	44.4 (8.9)	50.4 (3.4)	33.9 (15.1)	37.2 (3.4)
	22.6	23.2 (10.0)	55.3 (4.6)	19.3 (1.9)	21.6 (7.5)
TBP	0.8	52.5 (8.6)	56.0 (5.4)	35.8 (8.7)	46.4 (3.1)
	1.6	57.9 (4.8)	61.2 (8.6)	39.8 (4.4)	46.9 (7.2)
	5.7	45.5 (9.5)	53.2 (8.8)	38.3 (5.7)	38.4 (12.0)
	11.3	26.9 (18.2)	41.4 (2.1)	37.1 (6.4)	38.1 (4.7)
	22.6	8.5 (6.4)	25.5 (6.6)	29.2 (4.2)	41.4 (9.4)
TEP	0.8	43.6 (7.0)	47.8 (4.2)	46.6 (13.7)	37.8 (9.4)
	1.6	43.1 (7.8)	47.1 (4.5)	36.7 (5.8)	35.5 (7.4)
	5.7	33.8 (7.8)	31.1 (3.4)	36.0 (11.8)	34.5 (7.4)
	11.3	17.6 (3.30)	34.1 (5.6)	29.2 (4.2)	38.2 (7.1)
	22.6	11.8 (3.1)	13.4 (3.1)	9.6 (6.0)	24.1 (4.8)
TCP	0.8	56.4 (8.3)	49.4 (6.1)	39.4 (6.8)	36.8 (6.5)
	1.6	48.6 (11.6)	43.2 (6.6)	40.5 (2.9)	42.4 (7.0)
	5.7	45.2 (11.3)	58.8 (6.8)	38.0 (4.3)	41.4 (4.6)
	11.3	46.4 (8.1)	56.3 (7.4)	27.8 (3.4)	30.6 (8.5)
	22.6	26.8 (17.3)	56.8 (6.8)	20.4 (4.2)	28.6 (3.7)
Solvent only (methanol)		59.8 (5.7)	54.8 (6.8)	48.5 (6.4)	46.9 (16.8)
Control		64.2 (3.4)		22.5 (2.6)	

^aAverage of five replicates. Standard deviations are in parentheses.

impregnation of wood with this substance class would have advantages. The objective of this study was a comparative assessment of treated woods with phosphortriamidates and phosphoramidates. Thermal gravimetric analysis revealed that impregnation with phosphortriamidates at the level of 0.1 mol/100 g wood changes the thermal properties of wood: the temperatures at the maximum pyrolysis rate loss were lowered to 275–290°C (control 380°C) and char yields increased to 33.7–40.2% (control 16.9%). However, only a few of the phosphortriamidates partially protected the wood against fungal decay. A simple impregnation with phosphortriamidates helps as a fire retardant but not as a fungicide.

Acknowledgements

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