

Wood Preservation Based on *In situ* Polymerization of Bioactive Monomers

Part 2. Fungal Resistance and Thermal Properties of Treated Wood¹⁾

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Keywords

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Brown-rot fungi

Summary

This paper is the second in a two-part series on *in situ* polymerization of bioactive monomers as an alternative to conventional preservative treatments. In this part of the study, bioactive monomers were evaluated for their ability to provide resistance to decay and protection against fire. Five bioactive monomers were synthesized: (1) pentachlorophenolyl acrylate (PCPA), (2) tributyltin acrylate (TBTA), (3) 8-hydroxyquinolyl acrylate (HQA), (4) 5,7-dibromo-8-hydroxyquinolyl acrylate (DBHQA), and (5) diethyl-N,N-bis (acryloxyethyl) aminomethyl phosphonate (Fyrol 6 acrylate, F6A). Southern pine sapwood samples were treated with acrylate solutions at different retention levels and with various amounts of crosslinker (trimethylolpropane trimethacrylate, TMPTM), then polymerized *in situ*. Methyl methacrylate (MMA) was used as the control. Biological resistance to the brown-rot fungus *Gloeophyllum trabeum* was determined on acetone-leached and unleached samples. PCPA showed some biological efficacy in the absence of crosslinker, but otherwise provided no more protection than did MMA alone.

TBTA was biologically effective at all retention levels except with crosslinker concentration $\geq 10\%$. HQA was biologically effective at $\geq 2\%$ retention. F6A was not biologically effective, although unleached wood treated with 10% F6A and 5% or no crosslinker showed some resistance to decay. The 5% DBHQA plus 5% crosslinker treatment was biologically effective in both leached and unleached wood. The effects of the highest treatment level of each monomer, after polymerization, were also evaluated by thermogravimetric analysis. All treatments provided some resistance to fire. The best treatment was 10% F6A, which resulted in the lowest mass loss (67.0%) and the lowest maximum temperature of pyrolysis (308.5 °C).

Introduction

In situ polymerization of bioactive monomers is one possibility for preserving wood from biodegradation. The bioactive group is attached to a vinyl monomer (in this case acrylate) and polymerized in the voids or lumens of the wood. This technology presumes that hydrolysis of the bioactive compound occurs with time, therefore working as a controlled release mechanism that holds the toxicant in place longer than does conventional treatment. Previous work on using bioactive methacrylates for preserving wood was performed at high (+ 100%) polymer loadings (Rowell 1983). This method was effective but expensive. To be cost-effective, the challenge is to achieve effective polymerization at low polymer loadings.

The standard ASTM D 1413 soil block test (ASTM 1976) was used to determine the decay resistance of treated wood. Southern pine sapwood was chosen because of its abundant use in many outdoor applications. The brown-rot fungus *Gloeophyllum trabeum* was chosen because it is particularly tolerant to phenolic and arsenic compounds.

Since the test compounds Fyrol 6 and 5,7-dibromo-8-hydroxyquinoline (DBHQ) are currently used as tire retar-

dants, treated wood products were tested for potential flame resistance by thermogravimetric analysis (TGA). In this method, a sensitive balance is used to measure weight change as a function of temperature (Billmeyer 1984). TGA gives the amount of char or residue and also the maximum temperature of pyrolysis. Although TGA is a small-scale (3-7 mg) laboratory test, it gives reproducible results (Camino and Costa 1988).

Materials and Methods

Sample preparation

Test solutions (1%, 2%, 5%, 10%, 15%, and 20%) were prepared just prior to treatment of southern pine sapwood specimens (2.54 by 2.54 cm cross section by 0.635 cm axial). The test compounds

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were (1) pentachlorophenol acrylate (PCPA), (2) tributyltin acrylate (TBTA), (3) 8-hydroxyquinolyl acrylate (HQA) (polymer and monomer), (4) 5,7-dibromo-8-hydroxyquinolyl acrylate (DBHQA) (polymer and monomer), and (5) diethyl-N,N-bis(acryloxyethyl) aminomethyl phosphonate (Fyrol 6 acrylate, F6A) (polymer and monomer). A crosslinking agent, trimethylolpropane trimethacrylate (TMPTM), was added to the monomers at various concentrations (5 %, 10 %, 20 %, 30 %, 40 %, and 50 %). The catalyst was 0.4% 2,2'-azobis-(2,4-dimethylvaleronitrile) (Polysciences, Inc., Wainington, PA). Specimens treated with methyl methacrylate (MMA), a nonbioactive monomer, and solvent (acetone)-leached specimens served as controls. After vacuum impregnation, the monomers were polymerized *in situ* in the wood at 52 °C as described in Part 1 of this series.

The chemicals were obtained from commercial suppliers and used without further purification; Fyrol 6 was obtained from Akzo Chemical Inc. (Dobbs Ferry, NY) and the other chemicals from Aldrich Chemical Company (Milwaukee, WI).

Biological evaluation

The standard soil block test was performed according to ASTM D 1413 (ASTM 1976). Wood specimens were exposed to the brown-rot fungus *Gloeophyllum trabeum* (Madison 617) for 12 weeks, oven dried at 105 °C, and weighed. The extent of decay was determined by percentage of mass loss.

Specimens treated with unpolymerized acrylate (HQA) and bioactive monomer (HQ) alone were sterilized with methyl bromide instead of autoclaved because of the low melting points of these compounds. Methyl bromide is commonly used to sterilize soil and to fumigate lumber and timber. Specimens were placed in the treating apparatus, the top was sealed, the container was filled with methyl bromide gas for 20 min. and the apparatus remained under a fume hood for 3 days. The apparatus was then flushed with air for 5 h and specimens were transferred to a sterile flow hood for placement in soil block bottles. Soil block tests were performed in three 12-weeks runs.

Elemental and thermogravimetric analyses

For elemental analysis, mass percentage of pentachlorophenol was calculated after determining the amount of chloride in PCPA-treated specimens by AWP Standard Method A5-94 (AWPA 1994). To determine tin content, TBTA-treated specimens were ground, wet ashed using perchloric acid (AWPA Standard Method A7-93, AWPA 1993) and analyzed by atomic absorption spectroscopy using a Perkin Elmer 5100PC. For phosphorous content, F6A-treated specimens were ground, wet ashed using a CEM Model MDS-2000 Microwave with peroxide-nitric acid (AWPA Standard Method A7-93, AWPA 1993). and analyzed by electrothermal atomization graphite furnace atomic absorption spectroscopy using a Perk-Elmer 5100PC. Bromine content of DBHQA-treated specimens was determined by Volhard's method using potassium thiocyanate (Vogel 1961).

Thermogravimetric analysis (TGA) was performed on an omniTherm TGA 1000 machine with a computer-controlled interface II connected to a thermal analysis software system (PL Thermal Sciences, Chicago, IL). Specimens were ground to greater than 100 mesh with a Wig-L-Bug and stored in a dessicator until use. Approximately 3 to 7 mg of sample was used for each run. Runs were performed at 200 °C-500 °C under nitrogen flow (20 ml/min) at a ramp rate of 20.0 °C/min. Specimens with the highest percentage of mass gain per treatment were analyzed.

Methods of analysis

Data were analyzed by analysis of variance (ANOVA), Bonferroni multiple comparison test, Wilcoxin test, and Student's t-test.

Results and Discussion

Biological evaluation

Effectiveness of decay resistance was measured in terms of percentage of wood mass loss. The most effective treatments resulted in < 5 % mass loss; moderately effective treatments, > 5 % but < 30 % mass loss; and ineffective treatments, > 30 % mass loss.

MMA, TMPTM, and controls

The solvent-leached and untreated controls had high mass losses (> 60 %), which was expected because of the configuration of the wood specimens (2.54 by 2.54 cm cross section by 0.635 cm axial as opposed to standard 1.9 by 1.9 by 1.9 cm). Test sample configuration was changed to allow for complete monomer penetration, polymerization, and leaching, and to facilitate the soil block test for wood decay.

MMA alone and the crosslinker TMPTM alone were used as non-bioactive monomer controls to determine whether polymerization provided resistance to decay. The results for MMA indicate that at low polymer weight gains (< 23 %), the polymer provided little protection as a moisture barrier (> 53 % mass loss). Polymer weight gains were higher for TMPTM alone (< 42%), resulting in slightly more protection (> 43 % mass loss) compared to untreated controls.

PCPA, TBTA, and MMA

Various amounts of PCPA, TBTA, and MMA without crosslinker were tested to determine the effect of the absence of crosslinker on polymerization (Fig. 1). Linear regressions (percentage mass loss determined from soil block test as a function of monomer percentage) were fitted separately for each monomer. The slopes of all three regression lines were not statistically different from zero. Results of an analysis of variance (ANOVA) and a Bonferroni multiple comparison test showed significant ($p = 0.05$) differences between the monomers (Table 1).

PCPA without crosslinker provided little resistance to decay (135 % mass loss), and resistance was not uniform

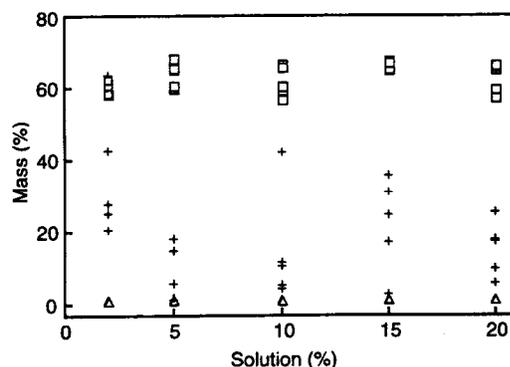


Fig. 1. Mass loss of samples treated with various solutions of MMA (□), PCPA (+), and TBTA (Δ) without crosslinker.

Table 1. Least-squares means and Bonferroni multiple comparison for various monomers with and without crosslinker

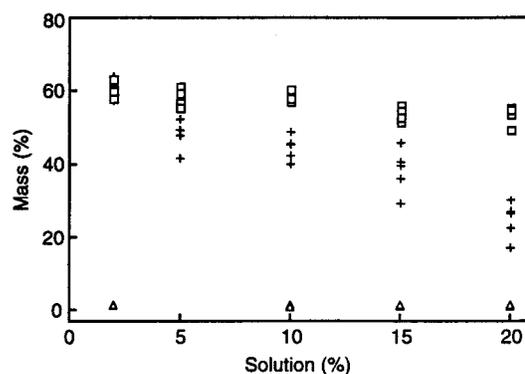
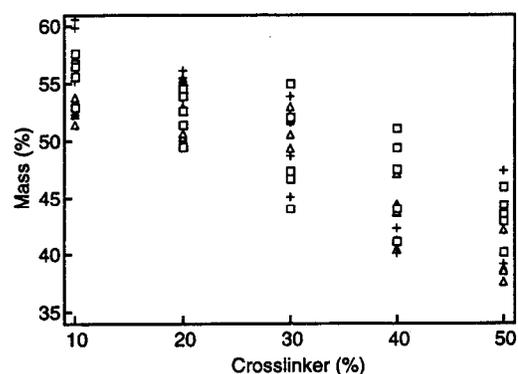
| Monomer | Crosslinker (%) | Mass loss (Least-squares analysis ^a) (%) | Bonferroni grouping ^b |
|----------|-----------------|--|----------------------------------|
| MMA | 0 | 62.7 | A |
| PCPA | 0 | 19.2 | B |
| TBTA | 0 | 1.3 | C |
| MMA | 5 | 57.0 | A |
| PCPA | 5 | 43.5 | B |
| TBTA | 5 | 1.1 | C |
| 0 % PCPA | 0-50 | 49.5 | A |
| 2 % PCPA | 0-50 | 49.0 | A |
| 5 % PCPA | 0-50 | 47.8 | A |
| 0 % TBTA | 0-50 | 49.5 | A |
| 2 % TBTA | 0-50 | 27.3 | B |
| 5 % TBTA | 0-50 | 14.4 | C |

^aSince every test material was not equally subjected to all possible experimental conditions, raw means were adjusted by least-squares means analysis. In this data set, an outlying data point for 5 % PCPA was discarded; thus, the least-squares means differed slightly from the raw means.

^bTest monomers in the same grouping were not different at the 0.05 level of significance.

throughout the sample. This may have been due to the greater accessibility or lower binding of pentachlorophenol in the absence of crosslinker. However, the high standard deviations indicate uneven treating or incomplete polymerization of this monomer. All unpolymerized PCPA monomer should have been completely removed from the specimens when they were leached.

Results of tests of PCPA, TBTA, and MMA with 5% crosslinker are shown in Figure 2. Slopes of regression lines for MMA and PCPA were negative and statistically different from zero. The TBTA slope was not statistically different from zero. The ANOVA and Bonferroni multiple comparison test showed significant differences ($p = 0.05$) between the monomers. Although both TBTA with 5% crosslinker and TBTA without crosslinker were effective in providing decay resistance (< 1.5 % mass loss), wood treated with TBTA without crosslinker had a greater percentage

**Fig. 2.** Mass loss of samples treated with various solutions of MMA (□), PCPA (+), and TBTA (Δ) with 5% crosslinker.**Fig. 3.** Mass loss of samples treated with various solutions of PCPA as a function of crosslinker concentration (□) = 0 %, (+) = 2 %, (Δ) = 5 % PCPA).

of mass loss from leaching with acetone (Table 2). This indicates that a more complete polymer matrix is formed in the presence of 5 % crosslinker, resulting in a slower controlled release system. As opposed to crosslinked polymers, non-crosslinked linear polymers are often removed by solvent extraction. Thus, crosslinking results in a less soluble polymer that is more resistant to leaching.

Table 2. Effects of TBTA treatment and acetone leaching on sample mass

| Control or treatment solution | Crosslinker (%) | Weight gain (%) | Mass loss from leaching (%) | Mass loss from decay ^a |
|-------------------------------|-----------------|-----------------|-----------------------------|-----------------------------------|
| Leached controls | | -1.1 | 1.1 | 62.7 |
| 2% | 0 | 1.4 | 1.7 | 1.2 |
| 5% | | 3.6 | 2.1 | 1.3 |
| 10% | | 5.2 | 4.5 | 1.3 |
| 15% | | 8.3 | 5.6 | 1.2 |
| 20% | | 9.2 | 6.8 | 1.3 |
| 2% | 5 | 9.3 | 1.2 | 1.2 |
| 5% | | 11.4 | 1.5 | 1.2 |
| 10% | | 14.0 | 2.3 | 1.0 |
| 15% | | 18.3 | 3.0 | 1.1 |
| 20% | | 22.0 | 2.8 | 1.2 |

^a Soil block test.

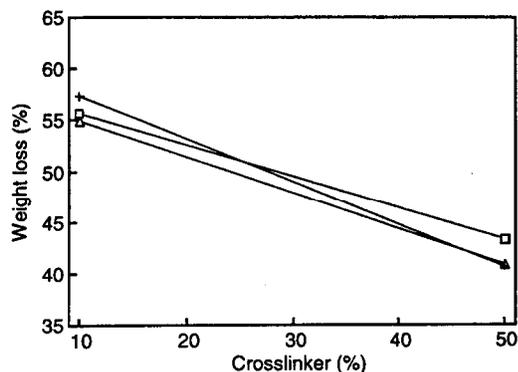


Fig. 4. Relationship of mass loss to crosslinker concentration for various PCPA solutions (□ = 0 %, + = 2 %, △ = 5 % PCPA).

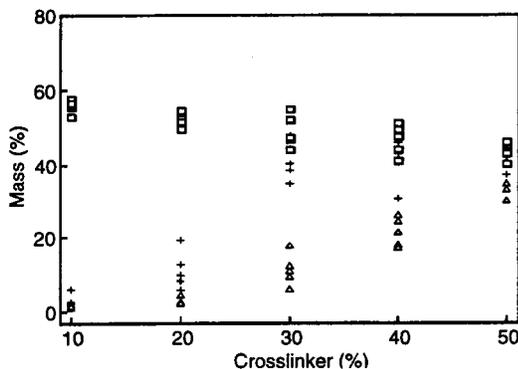


Fig. 5. Mass loss of samples treated with various solutions of TBTA as a function of crosslinker concentration (□ = 0 %, + = 2 %, △ = 5 % TBTA).

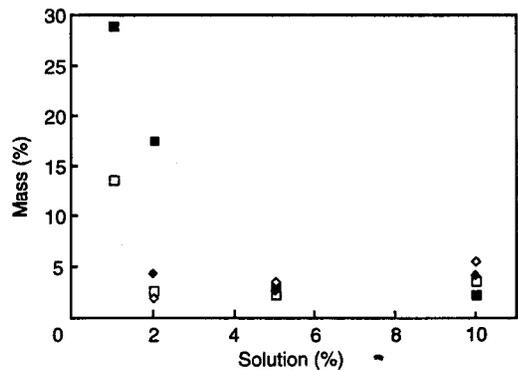


Fig. 6. Mass loss of leached (◆ = 0 %, ■ = 5%) and unleached (◇ = 0 %, □ = 5%) samples treated with various solutions of HQA, with and without crosslinker.

Figure 3 shows the effect of various concentrations of crosslinker for different PCPA solutions; results of linear regressions are shown in Figure 4. The ANOVA and Bonferroni multiple comparison test showed no significant ($p = 0.05$) differences between the 0 %, 2 %, and 5 % solutions (Table 1).

The effect of various concentrations of crosslinker for different TBTA solutions is shown in Figure 5. The ANOVA

and Bonferroni multiple comparison test showed significant ($p = 0.05$) differences between the 0 %, 2 %, and 5 % solutions (Table 1). Increasing the amount of crosslinker decreased TBTA effectiveness against decay ($\leq 41\%$ mass loss) (Fig. 5). The 5 % concentration of crosslinker was the most effective. Beyond this amount, there may be a barrier or trapping of tin in the polymer, possibly as a result of greater crosslinking, which makes TBTO less soluble or less prone to hydrolysis.

HQA

No crosslinker - For the 2 % HQA solution without crosslinker, mass loss was greater in the leached sample than in the unleached sample (Fig. 6). The difference between the leached and unleached samples was significant at a 0.02 level (Wilcoxon test), but the difference between the standard deviations (2.01 and 0.1) was significant at a 0.01 level. This variability may have been caused by incomplete polymerization at the low solution concentration and subsequent leaching of the polymerized monomer. In the unleached sample, unpolymerized monomer may have provided some biological resistance. The polymer is very soluble, as shown by hot acetone leaching (Part 1 of series), so that at low polymer weight gains, it is subject to leaching.

For 5 % and 10 % HQA without crosslinker, mass loss was greater in the unleached samples, contrary to expectation. However, the standard deviation for both of these samples was low (0.1). The unleached samples would be expected to have some unpolymerized monomer. The difference in mean percentage of mass loss was significant ($p = 0.01$).

5 % crosslinker - For 1% and 2 % HQA with 5 % crosslinker, mass loss was greater in the leached samples. This difference was only marginally significant for 1 % HQA. The p -value for Student's t -test was 0.07 and that for the Wilcoxon test 0.10. Thus, the difference between leached and unleached 1 % HQA samples was significant at a 0.10 level but not a 0.05 level; for 2 % HQA samples, the difference was significant at a 0.01 level.

For 5 % and 10 % HQA with 5 % crosslinker, mass loss was greater in the unleached samples. For 5 % HQA, the difference between unleached and leached samples was not significant ($p = 0.05$); however, the standard deviations of these leached and unleached samples (2.0 and 0.2, respectively) were significantly different ($p = 0.01$). Since the samples were true replicates, this difference in standard deviations is not attributable to replication. For 5 % HQA, as for 1 % and 2 % HQA, the high standard deviations suggest that leaching may have been uneven. For 10 % HQA, the difference in mass loss of unleached and leached samples was significant ($p = 0.01$), possibly as a result of the small sample number. The standard deviation for leached 10 % HQA samples was low (0.3), which indicates that the polymer may be more leach resistant at a higher percentage weight gain.

Comparison of no crosslinker and 5% crosslinker - Leached 2 % HQA samples with 5 % crosslinker had significantly ($p = 0.01$) greater mass loss than those without crosslinker. For the leached 5 % HQA sample with 5 %

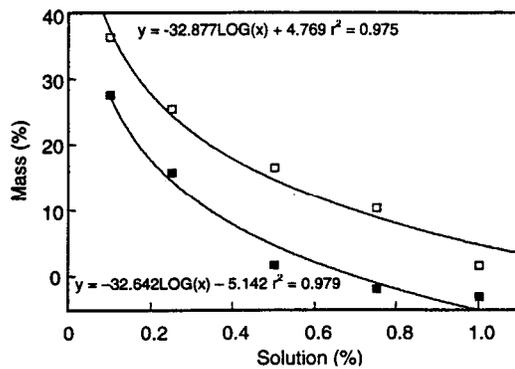


Fig. 7. Mass loss of samples treated with various solutions of HQ (□) and HQA (■) monomer.

crosslinker, mean mass loss (2.9 %) was close to that of the sample without crosslinker (2.6 %). The difference was not significant at a 0.05 level. However, the standard deviations for these samples were significantly different at a 0.01 level; the standard deviation for the sample with 5 % crosslinker was 2.0 and that of the sample without crosslinker, 0.1.

The leached 10 % HQA sample without crosslinker had greater mass loss (4.0%) than the sample with 5 % crosslinker (2.1%); this difference was significant at a 0.01 level. This suggests that crosslinking at higher weight percentage levels produces a more stable polymer. For lower HQA concentrations (2% and 5 %), samples without crosslinker had less mass loss than those with 5 % crosslinker but the standard deviations were higher, indicating uneven treatment or leaching.

For unleached samples, the 2% HQA sample without crosslinker had less mass loss than the sample with 5% crosslinker, but difference between the standard deviations was significant ($p = 0.05$), indicating uneven treatment at low solution concentrations. The 5 % and 10 % HQA samples with 5 % crosslinker had less mass loss than samples without crosslinker; differences were significant at a 0.01 level.

Comparison of HQ and HQA - Mean mass loss of HQ and HQA (unpolymerized) samples as a function of bioactive monomer concentration is shown in Figure 7. Since variance changed with the percentage of bioactive monomer, it was not appropriate to analyze this data by ANOVA. Thus, HQ and HQA samples were tested for differences per each solution concentration. All tests showed significant differences: 0.05 (Student's t -test), 0.03 (t -test), 0.0002 (t -test), 0.008 (Wilcoxon test), and 0.008 (Wilcoxon test) for the 0.1, 0.25, 0.5, 0.75, and 1.0 HQ solutions, respectively. Thus, HQA samples had less mass loss in the soil block test than did samples with the bioactive starting material (HQ) at all solution levels.

F6A

Results for F6A are shown in Figure 8. For 1 % and 2 % F6A, mass loss was significantly greater in the samples without crosslinker ($p = 0.009$) compared to those with 5 % crosslinker ($p = 0.001$). For 5 % and 10 % F6A, there was

Table 3. Amount of PCP, tin, phosphorous, and bromine in treated wood samples

| Treatment solution | No TMPTM | 5 % TMPTM |
|--------------------|--------------|-----------|
| PCPA | Weight % PCP | |
| 2 % | 0.9 | 1.3 |
| 5 % | 2.8 | 2.6 |
| 10 % | 5.8 | 4.8 |
| 15 % | 8.8 | 8.7 |
| 20 % | 12.8 | 8.5 |
| TBTA | Weight % Sn | |
| 2 % | 0.4 | 0.7 |
| 5 % | 0.9 | 1.2 |
| 10 % | 1.2 | 1.9 |
| 15 % | 2.5 | 2.4 |
| 20 % | 2.2 | 2.9 |
| F6A | Weight % P | |
| 1 %, leached | 0.1 | 0.1 |
| 1 %, unleached | 0.1 | 0.1 |
| 2 %, leached | 0.1 | 0.1 |
| 2 %, unleached | 0.1 | 0.1 |
| 5 %, leached | 0.2 | 0.1 |
| 5 %, unleached | 0.3 | 0.2 |
| 10 %, leached | 0.3 | 0.3 |
| 10 %, unleached | 0.5 | 0.4 |
| DBHQA | Weight % Br | |
| 1 %, leached | — | 0.3 |
| 1 %, unleached | — | 0.4 |
| 2 %, leached | — | 0.5 |
| 2 %, unleached | — | 0.6 |
| 5 %, leached | — | 0.9 |
| 5 %, unleached | — | 1.2 |

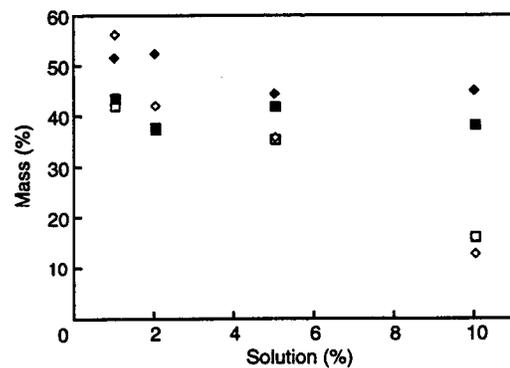


Fig. 8. Mass loss of leached (◆ = 0%, ■ = 5%) and unleached (◇ = 0%, □ = 5%) samples treated with various solutions of F6A, with and without crosslinker.

no significant difference ($p = 0.05$) between the sample without crosslinker and that with 5 % crosslinker. For 10 % F6A, the unleached samples showed some biological effect (13.0 % and 16.4 % mass loss for samples with and without crosslinker, respectively.)

For 1% and 2 % F6A, there was no difference between leached and unleached samples ($p = 0.05$). Mass loss was greater in leached 5 % and 10 % F6A samples with and without crosslinker ($p = 0.05$ and 0.0001, respectively) compared to unleached samples. The effect of leaching on mass loss is corroborated by the higher weight percentage

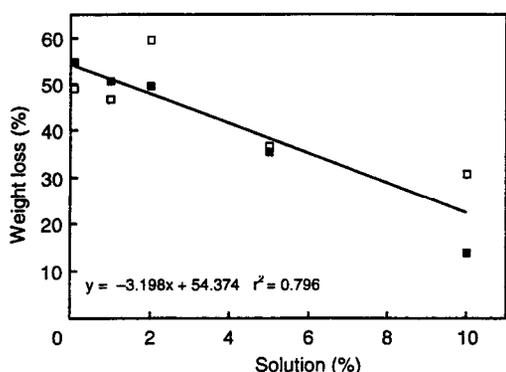


Fig. 9. Relationship of mass loss to solution concentration for various F6 (□) and F6A (■) monomer solutions.

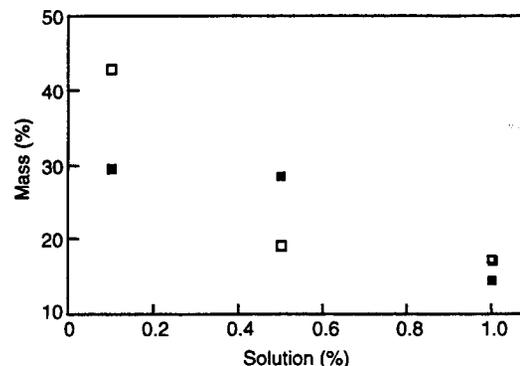


Fig. 11. Mass loss of samples treated with various solutions of DBHQ (□) and DBHQA (■).

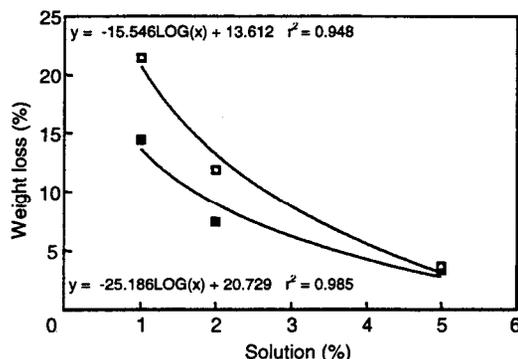


Fig. 10. Relationship of mass loss to solution concentration for leached (□) and unleached (■) samples treated with DBHQA and 5% crosslinker.

of phosphorous in the unleached 5% and 10% F6A samples (Table 3).

Mean mass loss of F6 and F6A samples as a function of bioactive monomer concentration is shown in Figure 9. At the 0.1%, 1%, and 5% levels of bioactive monomer, there was no difference between F6 and F6A at a 0.05 significance level. At the 2% level, F6A samples showed less mass loss than F6 samples at a 0.006 significance level. At the 10% level, F6A samples showed less mass loss than F6 samples at a 0.0001 significance level.

DBHQA

The effects of different concentrations of DBHQA, with and without crosslinker, on mass loss are shown in Figure 10. For 1% and 2% DBHQA, leached samples showed greater mass loss than unleached samples at the 0.002 and 0.007 significance levels; for 5% DBHQA, leached and unleached samples were not different at a 0.05 significance level. Treatment with 5% DBHQA was biologically effective for both leached and unleached samples although the standard deviation of the leached sample was higher than that of the unleached sample (1.5 versus 0.6).

Mean mass loss of DBHQ and DBHQA samples as a function of bioactive monomer concentration is shown in Figure 11. At the 0.1% bioactive level, DBHQA samples

showed lower mass loss than DBHQ samples, but the difference was marginal because the standard deviation of DBHQA was high (13.6). The p-value for a test that does not assume equality of standard deviations is 0.09. At the 0.5% bioactive level, DBHQ samples showed lower mass loss than DBHQA samples at a 0.02 significance level. At the 1% bioactive level, there was no significant difference between DBHQ and DBHQA.

Elemental and thermogravimetric analyses

Elemental microanalysis

Data on percentage of weight gain of PCP, tin, phosphorus, and bromine in samples treated with PCPA, TBTA, F6A, and DBHQA, respectively, with and without crosslinker are shown in Table 3.

The percentage weight gain of PCP in PCPA-treated samples was calculated from the amount of chlorine. The threshold for decay resistance of PCP is 2.56 kg/m³. The lowest weight percentage of PCP in the treated samples (0.9%) equated to 4.48 kg/m³. Although bioactivity was expected at this PCP level, this as well as much higher levels provided little biological protection, as evidenced by weight loss nearly equal to that of untreated samples.

In TBTA-treated samples, the weight percentage of tin (Sn) and biological efficacy depended on the amount of crosslinker present in the samples.

For unleached F6A-treated samples, biological efficacy was apparent at the highest level of treatment (10% F6A) with and without crosslinker (16.4% and 13.9% mass loss, respectively), which equates to 0.4% and 0.5% weight percentage gain of phosphorus, respectively. Biological efficacy was apparently due to the acrylate rather than the amount of phosphorus present at these low levels, since the F6-treated samples had the highest weight percentage of phosphorus and had higher percentage mass losses in the soil block test.

For 5% DBHQA with crosslinker, increasing the weight percentage of bromine tended to increase biological efficacy in both leached and unleached samples (0.9% and 1.2% Br, respectively).

Table 4. TGA results for control and treated samples

| Sample | Treatment | Mass loss (%) | Residual (%) | Temperature (°C) |
|---------|---------------------------|---------------|--------------|------------------|
| DAP | 10% | 52.6 | 47.4 | 278.0 |
| F6A | 10 %/5 % TMPTM, unleached | 67.0 | 33.0 | 308.5 |
| TMPTM | 50 %, leached | 72.7 | 27.3 | 381.4 |
| DBHQA | 5 %/5 % TMPTM, unleached | 73.2 | 26.8 | 369.2 |
| TBTA | 20 %/5 % TMPTM, leached | 73.2 | 26.8 | 327.9 |
| PCPA | 20 %/5 % TMPTM, leached | 73.7 | 26.3 | 365.1 |
| HQA | 10 %/5 % TMPTM, leached | 75.5 | 24.5 | 377.3 |
| MMA | 20 %/5 % TMPTM, leached | 77.4 | 22.6 | 379.7 |
| Control | None | 77.6 | 22.4 | 383.8 |

Thermogravimetric analysis

Heat initially breaks down wood chemically by pyrolysis or thermal degradation. When oxygen is present, the pyrolysis products (gases and charcoal) then unite with oxygen under certain conditions to ignite, which initiates combustion. Thermal decomposition and composition of the products are influenced by many physical and chemical factors, such as temperature, type of atmosphere, size and texture of the cellulose sample, crystallinity, and presence of impurities such as metals (Soares *et al.* 1995). Fire retardant chemicals incorporated in wood retard pyrolysis by minimizing the heat of combustion or by insulating the wood from the heat of fire (Kubler 1980). The mechanism of many fire retardants for wood is to reduce mass loss and/or the maximum temperature of pyrolysis compared to that of untreated controls.

The highest percentage weight gains for each treatment were analyzed by TGA. Results are shown in Table 4. Although a good screening method for many fire retardants for wood, TGA is not the best method for evaluating halogenated fire retardants. Therefore, the results may not be a true picture of the efficacy of brominated compounds as fire retardants. Brominated compounds may actually be good fire retardants for reducing flammability, but the data do not show that such compounds reduce mass loss.

The control had 77.6 % mass loss and a maximum temperature of pyrolysis of 383.8 °C. Diammonium phosphate (DAP), an effective fire retardant, was tested for comparison; mass loss was 52.6% and maximum pyrolysis temperature 278.0 °C. Of the synthesized acrylates, F6A resulted in the lowest mass loss (67.0 %) and lowest pyrolysis temperature (308.5 °C). Mass loss was lower in the crosslinker (72.7 %) than in the control, but maximum temperature of pyrolysis (381.4 °C) was almost as high as that of the control.

Mass loss was lower in samples treated with DBHQA, TBTA, and PCPA (73.2 %, 73.2 %, and 73.7 %, respectively) compared to the control (77.6%). Maximum temperature of pyrolysis was also lower than that of the control. TBTA-treated samples had the lowest maximum temperature of pyrolysis (327.8 °C), followed by PCPA (365.1 °C) and DBHQA (369.2 °C).

The HQA-treated samples showed only a slight decrease in mass loss (75.5 %) and maximum pyrolysis temperature (377.3 °C) compared to the control. MMA provided about

the same level of protection as did the control: 77.4 % mass loss and 379.7 °C maximum temperature of pyrolysis.

The F6A and TBTA spectra did not show a hemicellulose peak. The DBHQA, HQA and MMA spectra showed only a small hemicellulose shoulder at approximately 350 °C; the control, TMPTM, and PCPA spectra showed a hemicellulose shoulder at this temperature. Softwoods sometimes do not show a hemicellulose peak in TGA because of their chemical composition, whereas hardwoods almost always show a hemicellulose peak. An explanation for the variability of these spectra (treated and control) may be the small sample size.

Conclusion

Wood samples were examined biologically and thermally after *in situ* polymerization of five potentially bioactive acrylate monomers. Wood treated with TBTA, HQA, and DBHQA showed resistance to decay. Tests are being conducted on other fungi and extended to termite resistance.

All treatments provided some fire protection, but were not as effective as DAP. Higher loading of the fire retardant chemical may increase thermal efficacy. This study tested only flame resistance by TGA instrumentation, which uses a small sample size. Further research is needed on other fire tests for treated wood, such as the cone calorimeter.

Treatments that combine biological resistance to decay and protection against fire have commercial potential. Treatment levels needed for biological effectiveness and fire protection are different, but treatments can be designed for specific end-use properties. Another area for further research is the mechanism by which treatment provides biological protection.

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