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Low polymer levels containing bioactive monomer polymerized *in situ* provide resistance to *Gloeophyllum trabeum*

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ABSTRACT

Wood preservation based on *in situ* polymerization of potentially bioactive monomers has been studied. Tributyltin oxide acrylate (TBTOA) and pentachlorophenol acrylate (PCPA) were synthesized. Wood samples were treated at 2%, 5%, 10%, 15% and 20% by weight solutions with varying amounts of crosslinker (trimethylolpropane trimethacrylate, TMPTM) and polymerized *in situ* in wood samples (2.54 cm x 2.54 cm x 0.635 cm). Methyl methacrylate (MMA) also was run at the same concentrations as a non-bioactive monomer comparison. Soil block testing was performed on acetone leached samples using *Gloeophyllum trabeum* in a standard ASTM test for 12 weeks. TBTOA was effective at all levels except when using greater than or equal to 10% crosslinker concentrations. PCPA showed some efficacy with 0% crosslinker present, but otherwise it gave no more protection than the MMA controls alone. This is probably due to the stable ester linkage formed in the polymer. Further investigation is underway to synthesize and biologically evaluate new bioactive monomers at low polymer levels for wood protection.

Key words: *Gloeophyllum trabeum*, *in situ* polymerization, pentachlorophenol acrylate, tributyltin oxide acrylate, methyl methacrylate, wood preservation

INTRODUCTION

Wood used in soil contact may require a preservative treatment to prevent degradation by decay fungi and insects. We are investigating an alternative to conventional preservative treatments through a method that involves *in situ* polymerization of monomers having covalently-bonded potentially-bioactive moieties.

There are two types of wood polymer composites that can be formed with wood: 1) nongrafted bulk polymer formation in the void structure of wood (Rowell, 1983); and 2) monomer or polymer grafting to reactive groups on the cell wall polymers (Rowell, 1975 and 1984). Therefore, there are two ways of introducing bioactive polymers into wood and we have chosen to pursue the first.

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The cell lumens can be filled by impregnation with bioactive polymers, but there tends to be a solubility problem. Polymers have low solubility, high viscosity, and large molecular size, therefore making it difficult to penetrate wood with polymer. It is possible instead to synthesize a monomer with a bioactive group, fill the wood with it, and then *in situ* polymerize or copolymerize with a carrier monomer using a catalyst. This results in a higher loading of the bioactive polymer into the wood.

Pentachlorophenol (Pittman and Lawyer, 1982; Pittman et al., 1982; Rowell, 1983), pentabromophenol (Rowell, 1983), 8-hydroxyquinoline (Pittman and Lawyer, 1982; Pittman et al., 1982), and tributyltinoxide (Andersen, 1979; Rowell, 1983; Mendoza, 1977; Montemarano and Cohen, 1976; Subramanian et al., 1981) acrylates and methacrylates were synthesized and polymerized in wood with either methyl methacrylate or glycidyl methacrylate. There was no increase in wood volume, indicating little or no cell wall penetration (Rowell, 1983). Rowell found all the levels of MMA (methylmethacrylate)-PCPM (pentachlorophenol methacrylate) and MMA-PBPM (pentabromophenol methacrylate) treatments were not much different than MMA alone in weight loss during the soil block test with *Gloeophyllum trabeum*. Thus, the biodegradation resistance is likely due to the moisture barrier and increase in density due to the polymer and not the release of the toxic chemical. Pentachlorophenol (PCP) and pentabromophenol (PBP) esters were stable and did not release the active biocide. All levels of MMA-TBTOM (tributyltin methacrylate) were effective, showing no weight loss when attacked by the brown-rot fungi.

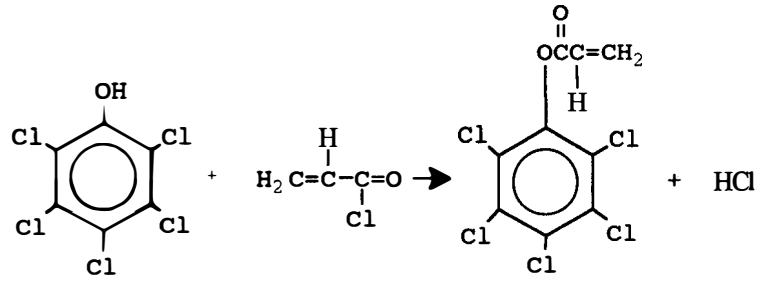
Treatment of wood with methacrylate polymers has its advantages and disadvantages. Advantages are a decreased rate of moisture pick-up and better mechanical properties, including an increase in modulus of elasticity and rupture, higher fiber stress or proportional limit, higher work to the maximum load, higher maximum crushing strength, and increased hardness index over untreated wood (Langwig et al., 1968; Rowell et al., 1982). The disadvantages are the high weight increase and high cost of treatment.

Past work shows that it is possible to have controlled release of a bioactive group, but that at such high loading of polymer it is not cost effective. Therefore, we have pursued this technology treating samples at high levels of bioactive acrylate, but at lower overall weight gains of bulk polymer.

MATERIAL AND METHODS

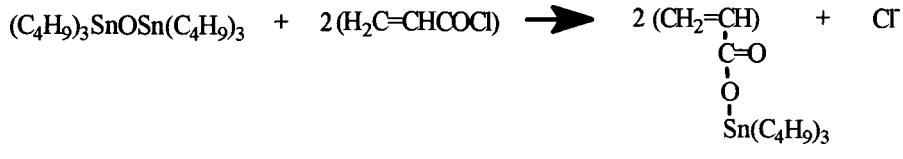
Synthesis of Acrylate Monomers

Pentachlorophenol Acrylate (PCPA):



Pentachlorophenol acrylate was prepared according to the literature (Rowell, 1983) with some modifications. Dry chloroform (500 ml), 66.63 g (0.25 mol) of pentachlorophenol (PCP), and 41.8 ml (0.30 mol) of triethylamine (TEA) were placed into a 1000 ml three-neck round-bottom flask and stirred until the pentachlorophenol dissolved. Acryloyl chloride (24.4 ml (0.30 mol)) was added dropwise to this mixture with mechanical stirring while cooled by an ice bath. The rate of addition was such that the temperature did not exceed 35° C. The solution was stirred two more hours at room temperature after all the acryloyl chloride was added. The chloroform solution was washed once with 1000 ml of ice water and twice with 1000 ml water, separated from the water, and then dried over sodium sulfate over night. The solution was filtered and then the chloroform was removed under reduced pressure at 50° C. The resulting solid was recrystallized from hot ethyl ether. Upon cooling, white crystals (72.54 g) were obtained (mp 81° C; 91% yield). Thin layer chromatography (TLC) on silica-gel-coated TLC sheets in a solvent system of hexane/chloroform (1:1 v/v) showed an Rf of 0.76 for PCPA and Rpcp of 1.9. The Rf of PCP was 0.41. Short-wave ultraviolet (UV) light was used to locate the compounds on TLC plates.

Tri-n-Butyltin Acrylate (TBTOA):



Tri-n-butyltin acrylate was synthesized according to literature (Rowell, 1983; Mendoza, 1977; Montermosa et al., 1958) with some modification. Tri-n-butyltin oxide (TBTO), 202.6 g (173.2 ml, 0.34 mol) was dissolved in 500 ml of carbon tetrachloride. Acrylic acid, 48.9 g (46.5 ml, 0.34 mol) and boiling chips were added to the solution. The mixture was refluxed for 3 hours and then allowed to cool before adding sodium sulfate to remove the water by-product. After filtering off the sodium sulfate, the carbon

tetrachloride was removed under reduced pressure, resulting in a crystalline solid. The solid was recrystallized by dissolving it in hot hexane, followed by cooling, filtration and washing with cold hexane. The resultant white needlelike crystalline material (TBTOA) yielded 175.9 g (71.7%) with a melting point of 74° C (lit. mp 74° C) (Kotrelev, 1961). TLC was not performed since TBTO esters do not respond to UV light.

Preparation of Treating Solutions

Solutions were prepared (Appendix 1) just prior to treating with each retention. **(A)** and **(B)** were separate runs. The catalyst used was 2,2'-Azobis-(2,4-dimethylvaleronitrile) from Polysciences, Inc.[2] Methyl methacrylate (MMA), the crosslinker (trimethylolpropane trimethacrylate, TMPTM), as well as the rest of the solvents used to synthesize and treat were all ordered from Aldrich.

Wood Treatments

The AWPA standard method of testing wood preservatives by laboratory soil-block cultures (AWPA E10-91) was followed with a few modifications. Southern yellow pine samples (2.54 cm X 2.54 cm X 0.635 cm) were dried at 105° C in a forced-draft oven for 24 hours, cooled for 1 hour at room temperature in a glass dessicator over phosphorus pentoxide and then weighed. (Subsequent weighings were performed in the same way.) They were then placed in a treating chamber and the system was evacuated for 30 minutes with a water aspirator (28 mm Hg). The selected solution was admitted into the treating chamber until the solution covered all the samples, and held for 5 minutes. Samples were held in place with a glass weight to prevent floating. The vacuum was released and the chamber was brought to atmospheric pressure. The samples were allowed to soak for 30 minutes in the solution, removed, wiped of excess solution, weighed, wrapped immediately in aluminum foil and then placed in a 52° C oven, flushed with nitrogen and left for 18 hours to allow polymerization. The foil was removed and samples weighed. The samples were oven dried at 105° C for 24 hours and then weighed. Eight samples were treated with each solution. Seven of the samples were put into the soil-block test and one sample was used for further analysis such as SEM, x-ray microanalysis, chlorine or tin analysis.

Leaching

Leaching was performed to remove any unpolymerized monomer on all samples. Samples (8 of each retention) were placed in a soxhlet extractor fitted with a 250 ml flat bottom flask. They were extracted with acetone for 2 hours. Samples were removed, dried in a forced-draft oven at 105° C for 24 hours and then weighed.

[2] 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.

Soil Block Tests

The standard soil block test was performed according to ASTM D 1413 (Standard Method of Testing Wood Preservatives by Laboratory Soil-Block Cultures, l976). Wood samples were placed in test with the brown-rot fungus *Gloeophyllum trabeum* (Madison 617). This fungus was selected because it is particularly tolerant to phenolic and arsenic compounds. Two untreated controls were removed after 6, 8 and 10 weeks to monitor fungal activity. Remaining samples were then removed after 12 weeks, oven dried at 105° C, and weighed. The extent of decay was determined by percent weight loss.

Scanning Electron Microscopy (SEM) and X-ray Microanalysis

Scanning Electron Microscopy (SEM) was performed on selected samples with a Joel 840 instrument. Longitudinal sections were gold coated and the earlywood and latewood were observed at X150 and X250 magnifications, respectfully. Representative pictures were taken of the earlywood as well as the latewood.

X-ray microanalysis was performed on selected samples with a Tracor Northern 5500 energy dispersive spectrometer. Cross sections were carbon coated and observed at various magnifications. Representative pictures were taken of the earlywood as well as the latewood. Video and x-ray maps were stored on disks and slides taken.

Pentachlorophenol and Tin Analysis

Weight percent of pentachlorophenol was determined by AWPA Standard Method A5-94 (5. Determination of chloride for calculating pentachlorophenol in solution or wood).

To determine weight percent of tin, wood samples were ground, wet ashed according to AWPA Standard Method A7-93 (Digestion Method #5 Perchloric Acid), and then analyzed using Atomic Absorption Spectroscopy (Perkin Elmer 5100PC).

RESULTS AND DISCUSSION

The average percent weight gains from treating wood blocks with PCPA and TBTOA, and the weight loss from soil block testing of all the samples are presented in Table 1 along with their standard deviations. Weight percent of PCP in the PCPA treated samples and tin in the TBTOA treated samples are also presented in Table 1.

The controls each had high weight losses (greater than 60%) which is expected due to the change in configuration of the wood samples (2.54 cm x 2.54 cm x 0.635 cm instead of the 1.9 cm x 1.9 cm x 1.9 cm standard). The configuration of the test samples was changed to allow for complete monomer penetration, polymerization, leaching, and a thinner sample for the decay test.

MMA and the crosslinker TMPTM were separately treated and used as non-bioactive monomer comparisons to see if there was any biological resistance from the polymers. The results for MMA indicate that at low polymer weight gains (less than 23%), the polymer gives little protection (greater than 53% weight loss) as a moisture barrier. For the crosslinker TMPTM alone, the polymer weight gains are higher (less than 42%) which gives slightly more protection (greater than 43% weight loss) than the untreated controls.

A plot of crosslinker percentage versus weight loss from biological testing for 0%, 2% and 5% PCPA is presented in Figure 3. The data is tightly gathered, so a plot of the regressions of percent weight loss on crosslinker percentage for 0%, 2%, and 5% PCPA data sets was performed and is presented in Figure 5. An analysis of variance was performed that contrasted the overall averages of percent weight loss for the 0%, 2%, and 5% cases. In column 2 of Table 2 the least-squares means[3] associated with this analysis are given. A Bonferroni multiple comparison test was used to test for a monomer percent effect. At a .05 significance level, there is no statistical difference between 0%, 2%, and 5% PCPA with varying amounts of crosslinker. This is indicated in column three of Table 2 by the fact that all three of the monomer percentages are "covered" by the letter A.

Table 2: Least-squares means and Bonferroni multiple comparison for 0%, 2%, and 5% PCPA

Monomer	Percent Weight Loss	Bonferroni groupings[4]
0% PCPA	49.5	A
2% PCPA	49.0	A
5% PCPA	47.8	A

A plot of crosslinker percentage versus percent weight loss from biological testing for 0%, 2% and 5% TBTOA is presented in Figure 4. An analysis of variance was performed that contrasted the overall averages of percent weight loss for the 0%, 2% and 5% cases. In column 2 of Table 3 the least-squares means associated with this analysis are given. A Bonferroni multiple comparison test was used to test for a monomer percent effect. The results are presented in column 3 of Table 3. Thus, at a .05 significance level there is a statistical difference in the effects of 0%, 2%, and 5% TBTOA.

Table 3: Least-squares means and Bonferroni multiple comparison for 0%, 2%, and 5% TBTOA.

Monomer	Percent Weight Loss	Bonferroni groupings
0% TBTOA	49.5	A
2% TBTOA	27.3	B
5% TBTOA	14.4	C

[3] In experiments in which every material is not equally subjected to all possible experimental conditions, raw means are not directly comparable. Instead they must be adjusted by the technique of "least-squares means" before comparisons can be made (SAS/STAT User's guide, Version 6, GLM procedure).
In this data set, one of the 5% PCPA observations was discarded as an outlier so the least-squares means will differ slightly from raw means.
[4] Material "covered by the same letter" cannot be statistically distinguished at a .05 significance level.

From the weight loss data (Table 1) we can see that TBTOA was biologically effective (less than 1.5% weight loss) at all levels, except when using increasing amounts of crosslinker. Increasing the amount of crosslinker with TBTOA decreases its effectiveness (up to 41% weight loss) against biological attack. The amount of crosslinker that is most effective is 5%, because beyond 5% there may be a barrier or trapping of the tin in the polymer. This may be due to the fact that there is more crosslinking making the TBTO less soluble or less prone to hydrolysis. SEM shows that the TBTOA polymer is smooth and at 20% TBTOA/5% crosslinker the polymer is evenly distributed in the earlywood (Figure 8) and the latewood (Figure 9), and the lumens are full.

Various amounts of PCPA, TBTOA, and MMA were run with no crosslinker to see the effect on polymerization. A plot of all the no crosslinker data is provided in Figure 1. Linear regressions (percent weight loss from biological testing as a function of monomer percentage) were fitted separately for each of the monomers. All three regression lines had slopes that were not statistically different from zero. An analysis of variance was performed that contrasted the overall averages of percent weight loss for the MMA, PCPA, and TBTOA. In column 2 of Table 4 the least squares means associated with this analysis are given. A Bonferroni multiple comparison test was used to test for a monomer effect. The results are presented in column 3 of Table 4. Thus, at a .05 significance level, there is a statistical difference between MMA, PCPA, and TBTOA with no crosslinker.

PCPA with no crosslinker data shows a low level (less than 35% weight loss) of biological resistance, but it is very scattered (Table 1). This may be due to pentachlorophenol being more accessible or less bound when there is no crosslinker present, but the standard deviations are very high. This indicates that there is uneven treating or not complete polymerization of this monomer. Samples were leached with acetone to remove any unpolymerized monomer. Thus, the unpolymerized PCPA should be completely leached with acetone, but the possibility exists that it has entered the cell wall and is not leached out. SEM shows that the polymer is somewhat crystalline in appearance and even at the high loading of 20% PCPA/5% crosslinker, the polymer in the earlywood (Figure 6) and latewood (Figure 7) is the exception and not the rule, indicating uneven treatment.

Table 4: Least-squares means and Bonferroni multiple comparison for MMA, PCPA, and TBTOA with no crosslinker.

Monomer	Percent Weight Loss	Bonferroni groupings
MMA	62.7	A
PCPA	19.2	B
TBTOA	1.3	C

Various amounts of PCPA, TBTOA, and MMA were also run with 5% crosslinker to see the effect on polymerization. A plot of all of the 5% crosslinker data is provided in Figure 2. Linear regressions (percent weight loss from biological testing as a function of monomer percentage) were fitted separately for each of the monomers. The MMA and PCPA regression lines had slopes that were negative and statistically different from zero. The TBTOA slope was not statistically different from zero. An analysis of variance was

performed that contrasted the overall averages of percent weight loss for MMA, PCPA and TBTOA. In column 2 of Table 5 the least-squares means associated with this analysis are given. A Bonferroni multiple comparison test was used to test for a monomer effect. The results are presented in column 3 of Table 5. Thus, at a .05 significance level, there is a statistical difference between MMA, PCPA, and TBTOA with 5% crosslinker.

TBTOA did very well in the soil block test (less than 1.5% weight loss) at both 0% and 5% crosslinker, but with no crosslinker present, there was a greater percent weight loss from the leaching with acetone than for the 5%. This indicates that with 5% crosslinker present, a more complete polymer matrix is formed resulting in a slower controlled release system. Non-crosslinked linear polymers are often removed by solvent extraction while crosslinked polymers are not. Thus, crosslinking results in a less soluble polymer that is more resistant to leaching. PCPA polymer treated wood had less weight loss from the leaching with acetone than TBTOA polymer treated wood. The ester linkage formed with PCP does not release or hydrolyze as readily as that formed with TBTO.

Table 5: Least-squares means and Bonferroni multiple comparison for MMA, PCPA, and TBTOA with 5% crosslinker.

Monomer	Percent Weight Loss	Bonferroni groupings
MMA	57.0	A
PCPA	43.5	B
TBTOA	1.1	C

CONCLUSION

Complete polymerization of bioactive monomers polymerized *in situ* in wood is possible at low polymer weight gains as indicated by resistance to acetone leachings. PCPA and TBTOA were both polymerized in wood with as low as 2% solution.

PCPA polymer is still not effective as a preservative with *in situ* polymerization. This is due to the stable ester linkage formed in the polymer. TBTOA is effective with *in situ* polymerization due to the release of TBTO through hydrolysis. TBTOA with 5% crosslinker present results in a less soluble polymer that is more resistant to leaching. Thus, the biological effectiveness of a bioactive polymer depends upon not only the toxicity of the bioactive group, but also the properties of the linkage between the bioactive group and the polymer.

Further research needs to be done on the mechanism of effectiveness of *in situ* polymerized bioactive monomers. Continued investigations are underway to synthesize and evaluate new bioactive monomers at low polymer levels for the protection of wood to both biological and thermal degradation.

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APPENDIX 1

Pentachlorophenol Acrylate (PCPA):

%PCPA	PCPA (g)	Acetone (ml)	0.4% Catalyst (g)	%TMPTM (ml)	
				(A) 0%	**(B)** 5%
2	4	196	0.8	0	10
5	10	190	0.8	0	10
10	20	180	0.8	0	10
15	30	170	0.8	0	10
20	40	160	0.8	0	10

%PCPA	PCPA (g)	Acetone (ml)	0.4% Catalyst (g)	%TMPTM (ml)
2	4	196	0.8	10 (20)
2	4	196	0.8	20 (40)
2	4	196	0.8	30 (60)
2	4	196	0.8	40 (80)
2	4	196	0.8	50 (100)

%PCPA	PCPA (g)	Acetone (ml)	0.4% Catalyst (g)	%TMPTM (ml)
5	10	190	0.8	10 (20)
5	10	190	0.8	20 (40)
5	10	190	0.8	30 (60)
5	10	190	0.8	40 (80)
5	10	190	0.8	50 (100)

Tri-n-Butyltin Acrylate (TBTOA):

%TBTOA	TBTOA (g)	Acetone (ml)	0.4% Catalyst (g)	TMPTM (ml) **(A)** 0% **(B)** 5%	
2	4	196	0.8	0	10
5	10	190	0.8	0	10
10	20	180	0.8	0	10
15	30	170	0.8	0	10
20	40	160	0.8	0	10

%TBTOA	TBTOA (g)	Acetone (ml)	0.4% Catalyst (g)	%TMPTM (ml)
2	4	196	0.8	10 (20)
2	4	196	0.8	20 (40)
2	4	196	0.8	30 (60)
2	4	196	0.8	40 (80)
2	4	196	0.8	50 (100)

%TBTOA	TBTOA (g)	Acetone (ml)	0.4% Catalyst (g)	%TMPTM (ml)
5	10	190	0.8	10 (20)
5	10	190	0.8	20 (40)
5	10	190	0.8	30 (60)
5	10	190	0.8	40 (80)
5	10	190	0.8	50 (100)

Methylmethacrylate (MMA):

% MMA	MMA (ml)	Acetone (ml)	0.4% Catalyst (g)	TMPTM (ml) **(A)** 0% **(B)** 5%	
2	4	196	0.8	0	10
5	10	190	0.8	0	10
10	20	180	0.8	0	10
15	30	170	0.8	0	10
20	40	160	0.8	0	10

Trimethylol propane trimethacrylate (TMPTM):

% TMPTM	TMPTM (ml)	Acetone (ml)	0.4% Catalyst (g)
10	20	200	0.8
20	40	200	0.8
30	60	200	0.8
40	80	200	0.8
50	100	200	0.8

Acetone Treated: Samples were treated with 200 ml acetone.
Acetone Leached: Samples were not treated, but were leached with acetone.

Table 1 Average percent weight gain after leaching, average weight loss of treated Southern Yellow Pine in soil block test with *Gloeophyllum trabeum*, weight percent PCP in PCPA treated samples and weight percent tin in TBTOA treated samples.

Treatment	Average weight gain (%) after leaching	Standard Deviation	Average weight loss in 12 weeks (%)	Standard Deviation	Weight % PCP	Weight % Sn
Control	*N/A	*N/A	63.90	2.98	-	-
Acetone Treated	-0.41	0.23	66.67	4.34	-	-
Acetone Leached	-1.12	0.13	62.70	5.35	-	-
TMPTM						
10%	13.31	0.58	55.93	1.81	--	-
20%	21.96	0.33	52.42	2.03	-	-
30%	29.87	0.94	49.04	4.42	-	-
40%	36.65	1.05	46.65	4.04	-	-
50%	41.83	1.19	43.40	2.16	-	-
MMA (0%TMPTM)						
2%	0.87	0.28	59.59	1.62	-	-
5%	1.14	0.17	63.84	3.45	-	-
10%	1.47	0.28	61.72	4.16	-	-
15%	3.29	0.58	65.87	1.16	-	-
20%	4.79	0.26	62.68	4.15	-	-
MMA (5%TMPTM)						
2%	7.89	0.47	60.10	1.93	-	-
5%	10.78	0.45	58.67	2.56	-	-
10%	13.83	0.99	58.55	1.26	-	-
15%	17.63	1.00	54.11	1.82	-	-
20%	22.85	1.54	53.63	2.49	-	-
TBTOA (0%TMPTM)						
2%	1.41	0.45	1.19	0.13	-	0.42
5%	3.55	0.60	1.26	0.22	-	0.91
10%	5.20	0.74	1.30	0.10	-	1.23
15%	8.26	1.22	1.23	0.12	-	2.50
20%	9.15	0.40	1.32	0.06	-	2.20
TBTOA (5%TMPTM)						
2%	9.23	0.46	1.21	0.09	-	0.71
5%	11.39	0.50	1.18	0.11	-	1.18
10%	13.98	0.57	1.04	0.16	-	1.89
15%	18.31	0.68	1.14	0.12	-	2.38
20%	22.03	0.82	1.16	0.05	-	2.92

Cont. on page 13

Treatment	Average weight gain (%) after leaching	Standard Deviation	Average weight loss in 12 weeks (%)	Standard Deviation	Weight % PCP	Weight % Sn
TMPTM (2% TBTOA)						
10%	14.59	0.55	2.99	1.82	-	0.76
20%	24.31	0.73	11.25	5.19	-	0.66
30%	32.59	0.60	41.14	5.08	-	0.36
40%	38.11	0.59	40.56	6.00	-	0.39
50%	42.30	0.43	40.69	2.61	-	0.33
TMPTM (5% TBTOA)						
10%	16.56	0.66	1.46	0.14	-	1.04
20%	26.92	0.27	2.90	0.98	-	0.99
30%	34.29	0.53	11.35	4.31	-	0.90
40%	41.26	0.69	21.46	3.90	-	0.76
50%	46.21	0.66	34.82	3.90	-	0.78
PCPA (0%TMPTM)						
2%	1.04	0.33	35.79	17.48	0.89	-
5%	3.14	0.44	8.31	7.79	2.81	-
10%	6.91	1.00	14.77	15.48	5.82	-
15%	12.72	1.27	22.16	12.80	8.84	-
20%	19.13	1.10	15.22	7.48	12.80	-
PCPA (5%TMPTM)						
2%	8.00	0.28	60.71	2.27	1.28	-
5%	9.72	0.57	49.40	5.38	2.59	-
10%	13.72	0.49	44.49	3.31	4.78	-
15%	18.87	0.82	38.34	6.19	8.67	-
20%	22.31	1.68	24.59	5.06	8.51	-
TMPTM (2% PCPA)						
10%	13.06	0.44	56.89	3.38	1.15	-
20%	22.51	0.34	54.80	1.00	1.15	-
30%	29.54	0.37	49.27	3.51	0.67	-
40%	35.93	0.45	41.08	0.77	0.92	-
50%	41.75	1.10	42.77	3.50	0.79	-
TMPTM (5% PCPA)						
10%	15.19	0.35	49.99	6.01	2.85	-
20%	23.93	0.39	51.76	2.38	2.78	-
30%	29.82	0.52	51.35	1.44	2.22	-
40%	36.97	0.94	43.86	2.42	2.11	-
50%	41.39	0.88	39.42	1.75	1.96	-

* N/A = Not Applicable

Figure 1.–Solution percentage vs. weight loss with 0% crosslinker for PCPA, TBTOA, and MMA

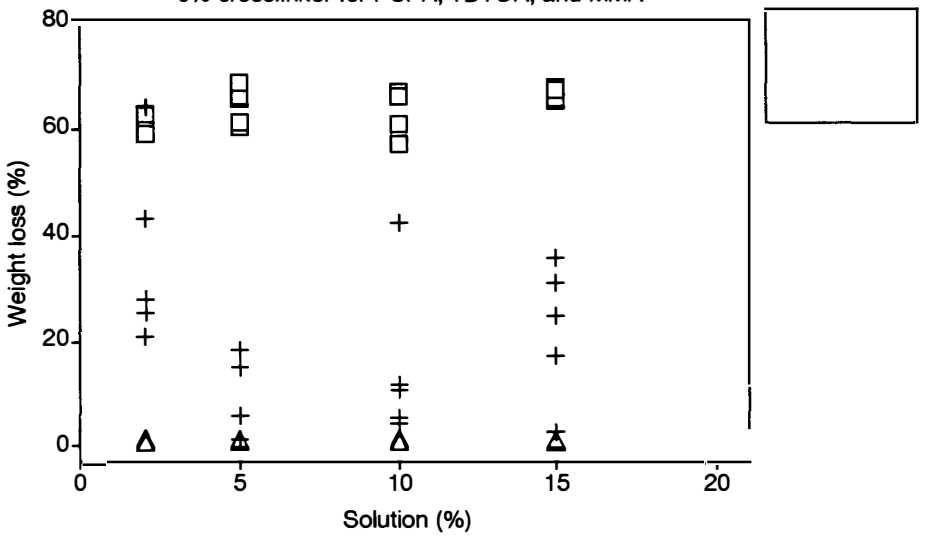

Figure 2.–Solution percentage vs. weight loss with 5% crosslinker for PCPA, TBTOA, and MMA

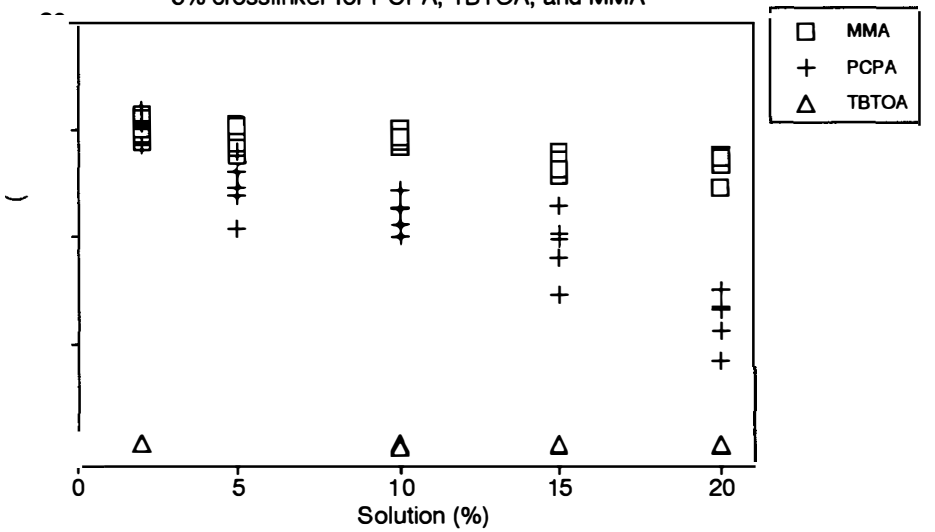

Figure 3.–Crosslinker percentage vs. percent weight loss for 0%, 2% and 5% PCPA

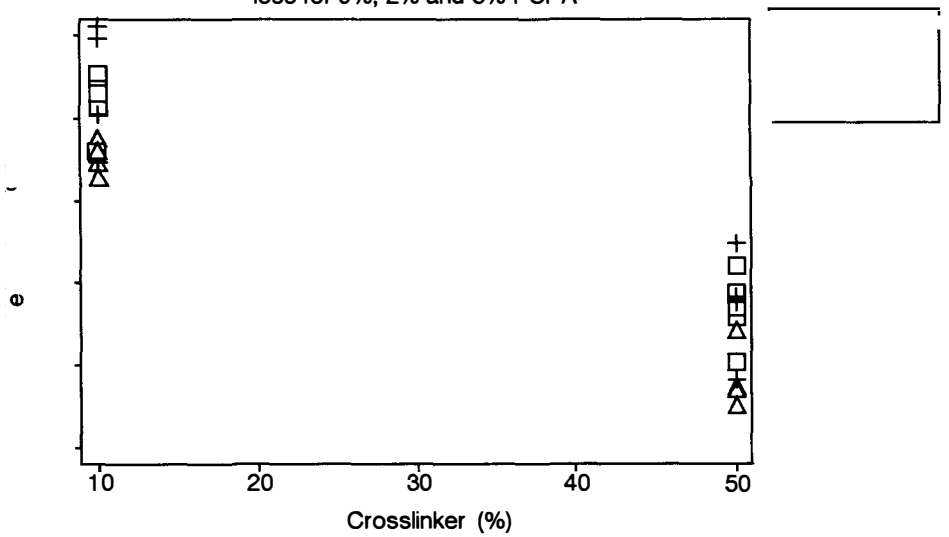

Figure 4.–Crosslinker percentage vs. percent weight loss for 0%, 2% and 5% TBTOA

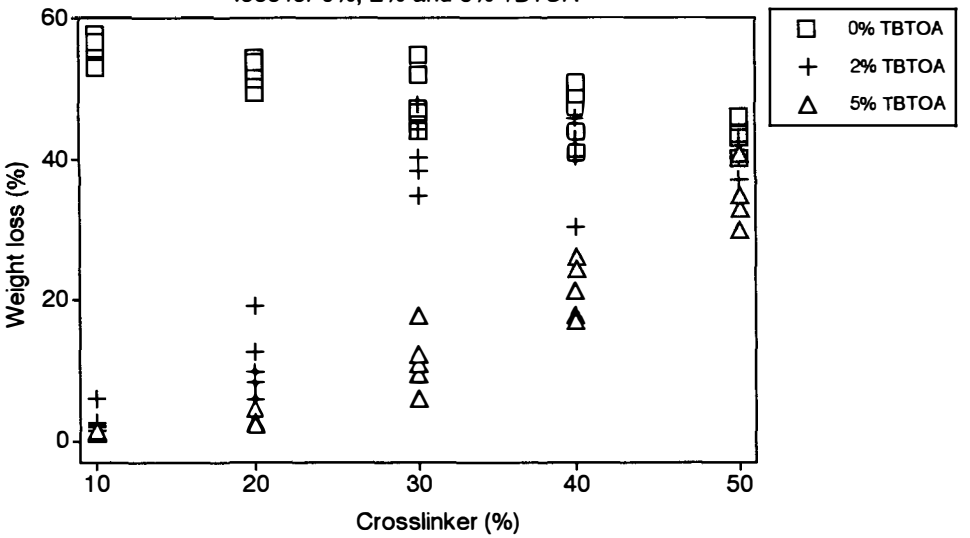

Figure 5.--Plot of the regressions of percent weight loss on crosslinker percentage for 0%, 2%, and 5% PCPA

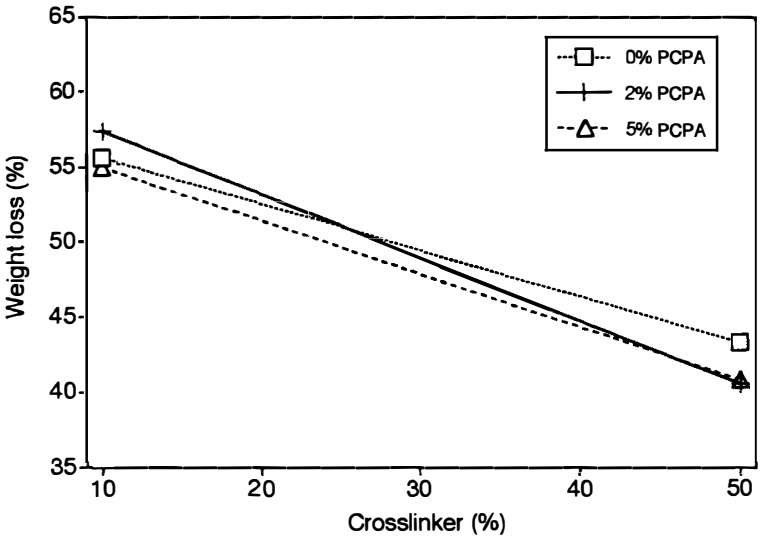

Figure 6. SEM of earlywood at 20% PCPA/5% crosslinker loading (150x).

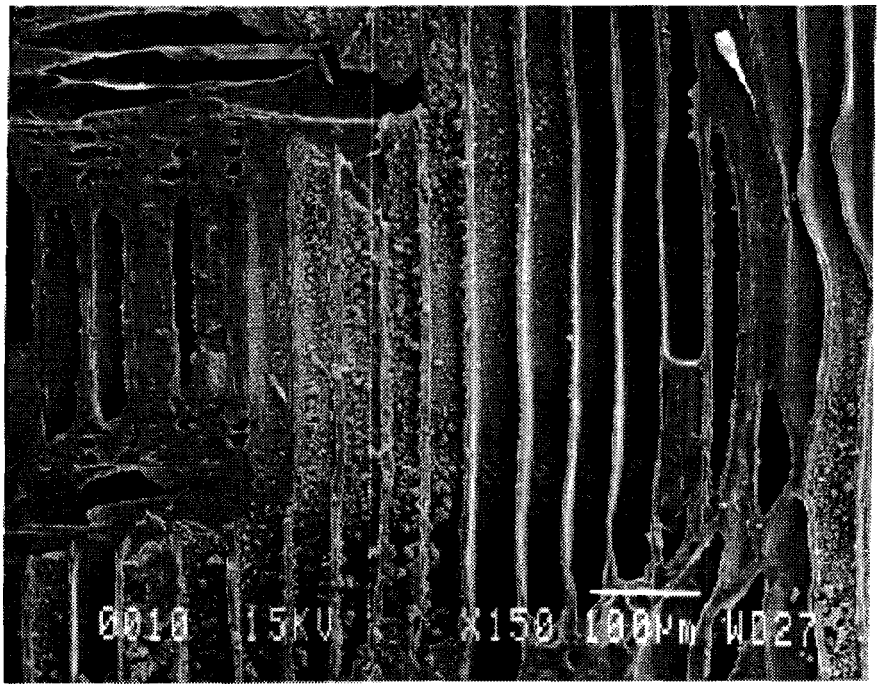

Figure 7. SEM of latewood at 20% PCPA/5% crosslinker loading (250x).

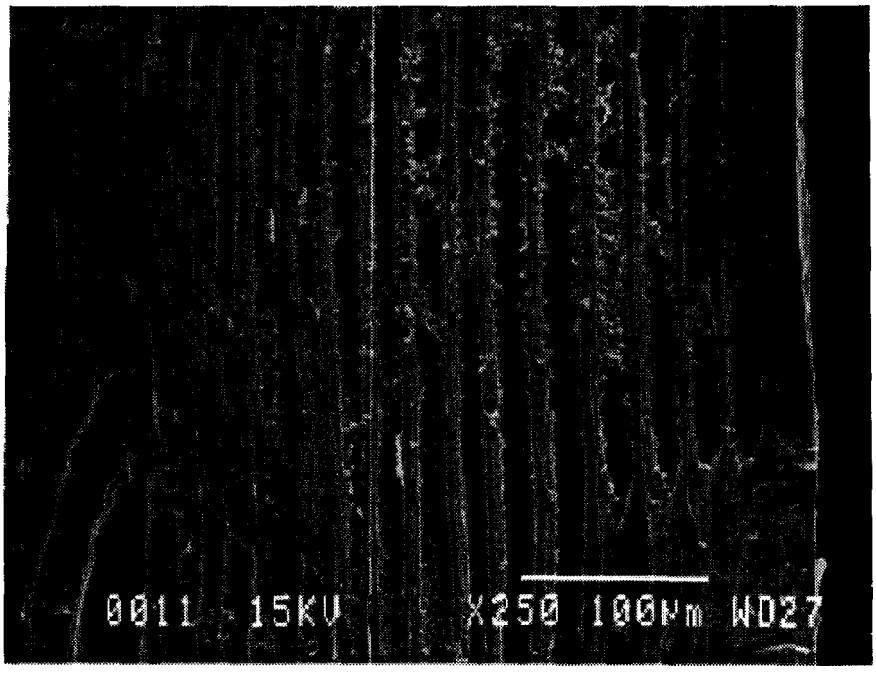

Figure 8. SEM of earlywood at 20% TBTOA/5% crosslinker loading (150x).

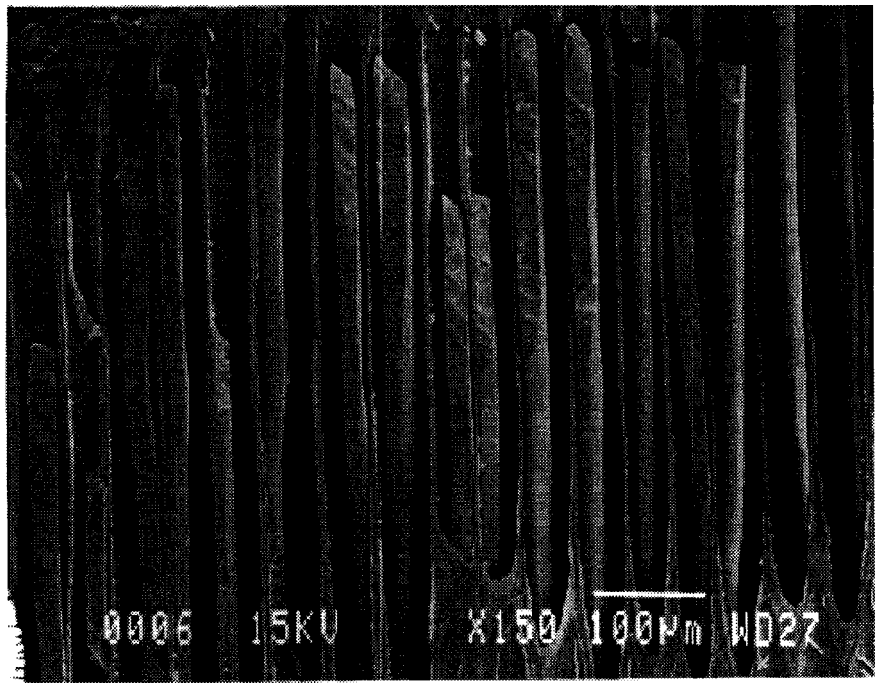

Figure 9. SEM of latewood at 20% TBTOA/5% crosslinker loading (250x).