Holzforschung, Vol. 62, pp. 488–493, 2008 • Copyright © by Walter de Gruyter • Berlin • New York. DOI 10.1515/HF.2008.062

Synthesis of ethylene maleic anhydride copolymer containing fungicides and evaluation of their effect for wood decay resistance

George C. Chen*

USDA, Forest Service, Forest Products Laboratory, Madison, WI, USA

*Corresponding author.
Research Chemist USDA, Forest Service, Forest Products Laboratory, 1 Gifford Pinchot Dr., Madison, WI, USA
Fax: +1-608-231-9262
E-mail: gchen@fs.fed.us

Abstract

The aim of the present study was to combat wood decay based on the approach controlled-release biocides from polymers. The possibility of introducing polymer-bonded fungicides into the cell lumens was investigated. The synthesis of ethylene maleic anhydride copolymer containing pentachlorophenol (penta) and 8-hydroxy quinoline (8HQ) in N, N dimethyl formamide is described. It was demonstrated that the penta-bonded acrylate is a poly(ethylene co-dipentachlorophenyl diacrylate), which has a disubstituted pentachlorophenyl group linked through two acrylate ester bonds. The reaction of ethylene maleic anhydride copolymer with 8-hydroxy quinoline leads to products containing 44.8% poly(ethylene co-8-hydroxy quinolinyl acrylate) and 55.2% of unreacted poly(ethylene co-maleic anhydride). Wood impregnated with the polymers described prevented decay by a brown- and white-rot fungus, even after water leaching. Wood treated with the fungicide pentachlorophenol (penta) alone prevented only decay by a brown-rot fungus. An advantage is that high loading of penta in polymer can be achieved. Moreover, there is a slow-release effect on the active agent due to hydrolysis of ester bonds. The decay resistance of wood treated with poly(ethylene co-8-quinolinyl acrylate) was similar to that of wood impregnated with 8-hydroxy quinoline.

Keywords: copolymer; ethylene maleic anhydride; fungal decay resistance; fungicides; poly(ethylene co-8-hydroxy quinolinyl acrylate); poly(ethylene co-dipentachlorophenyl diacrylate); synthesis; wood.

Introduction

Controlled-release organotin polymers for antifouling in marine environments (Montemarano and Dyckman 1975) were the guide for many investigations in the field of wood decay prevention.

One approach is the in situ polymerization of monomers containing wood-decay biocides in the cell lumens. Wood was impregnated with monomers of acrylate and methacrylate-boned pentachlorophenol, pentabromophenol, 8-hydroxy quinoline and organotins, and the polymerization occurred in the cell lumens (Pittman et al. 1978, 1982a,b; Subramanian et al. 1981a,b; Rowell 1983, 1984; Ibach and Rowell 2001). Some of these composites were effective against wood decay fungi and marine borers (Pittman et al. 1978; Subramanian et al. 1981a,b; Ibach and Rowell 2001).

Another approach involves direct bonding of fungicides containing reactive functional groups to cell wall polymers. The fungicides are, e.g., flurophenyl isocyanates, isothiocyanates, p-toluene sulfonyl chloride and isocyanates. The fungicide-bonded wood was resistant against a brown-rot fungus at levels of 1–5% bonded chemicals (Chen et al. 1990; Chen 1992a,b).

A third approach works with polymer-bonded fungicides which are introduced into the cell lumens by impregnation. Little research has been conducted in this area. In the present study, synthesis of ethylene maleic anhydride copolymer was performed which contained pentachlorophenol or 8-hydroxy quinoline. The fungal resistance of the impregnated woods was tested.

Materials and methods

Synthesis

Poly(ethylene co-dipentachlorophenyl diacrylate), EMA-Penta Poly(ethylene co-maleic anhydride), EMA, 25.2 g, 2×10^{-1} mol (calculated as alternating ethylene and maleic anhydride repeating unit, M_w 100 000) and pentachlorophenol (53.2 g, 2×10^{-1} mol) in 200 ml N, N dimethyl formamide (DMF), dried over molecular sieve 4-Å for more than 1 day, were under reflux for 4 h. Hereafter, solvent was removed by a rotary evaporator and a viscous liquid was obtained. The liquid was triturated with 150 ml acetone, and the acetone-insoluble products (42.2 g) were recovered by filtration. The products were further extracted with acetone for 12 h in a Soxhlet extractor and a solid residue was obtained (38.4 g, 49% yield). TLC (thin layer chromatography) on silica plate and with acetone or methanol as a developing solvent showed that no pentachlorophenol was left in the products. The solid was recrystallized from hot or boiling acetone with stirring and yielded needle crystals. The crystals decomposed at 193–195°C and could not be characterized by nuclear magnetic resonance (NMR) because of low solubility in DMF or DMSO (dimethyl sulfoxide). The crystals were characterized by infrared (IR) spectroscopy.

Poly (ethylene co-8-quinolinyl acrylate), EMA-8HQ Poly (ethylene co-maleic anhydride), EMA, 25.2 g, 2×10^{-1} mol (calculated as alternating ethylene and maleic anhydride repeating unit, M_w 100 000) and 8-hydroxy quinoline (29.1 g, 2×10^{-1} mol) dissolved in 200 ml DMF, dried over molecular sieve 4-Å for more than 1 day, were under reflux for 4 h. Then, solvent was removed by a rotary evaporator and the resulting viscous liquid was triturated with acetone (100 ml) and additional acetone

(200 ml) was added. The acetone insoluble solid (38.7 g, 71% yield) was recovered by filtration and further extracted with acetone for 12 h in a Soxhlet extractor and 32.4 g solid was obtained. TC on silica plate and with acetone or methanol as a developing solvent revealed that no 8-hydroxy quinoline (8HQ) was present in the products. Decay resistance of wood was tested with the products without further purification.

Elemental analysis and infrared characterization

Elemental analysis of the products was performed by the Galbraith Laboratories, Inc. (Knoxville, TN, USA). The products were also characterized by a Galaxy Series FTIR 5000 in KBr.

Fungal decay evaluation

Wood was impregnated with EMA-Penta or the EMA-8HQ products (later determined to be a mixture of EMA-8HQ and EMA). The fungal decay resistance was evaluated by a 12-week laboratory soil-block fungal decay tests against the brown-rot fungus, *Gloeophyllum trabeum* (L: Fr.) Murr., MAD-617 and the white-rot fungus, *Trametes versicolor* (L. Fr.) Quel., MAD-697.

Loblolly pine (*Pinus taeda* L.) and sweetgum (*Liquidambar styraciflua* L.) sapwood blocks (19 mm in all anatomical directions) were selected according to the American Society for Testing Materials (ASTM) Standard D 1413-99 (ASTM 2000). Blocks were impregnated with pyridine solutions of ethylene maleic anhydride copolymer containing pentachlorophenol or 8-hydroxy quinoline at four concentration levels (0.5, 1.0, 2.5 and 5%, wt/wt) as well as pyridinesolutions of pentachlorophenol at the concentration levels of 0.5, 1.0 and 2.0% (wt/wt) or 8-hydroxy quinoline solution at concentration levels of 1.0 and 2.0% (wt/wt). Blocks treated with polymer-bonded penta or 8HQ were compared with those treated with penta or 8HQ to assay their effectiveness against fungal degradation.

For each test, 14 blocks of each wood were placed in a glass jar (500 ml capacity) and were evacuated in a desiccator (2.2–3 KPa for 30 min). The blocks were then impregnated in the desiccator with the treating solutions and the soaking time was 1 day. The blocks were dried in a fume hood for 3 days and then heated in an oven at 105°C for 1 day. In total, seven blocks per treatment were conditioned at 27°C and 30% relative humidity (RH) for 3 weeks. Another seven blocks were leached in 350 ml distilled water 6, 24 and 48 h and then every 24 h for 2 weeks according to the ASTM Standard D1413-99, section 12.3 (ASTM 2000). No analysis was made for the concentration of fungicide-bonded polymers in wood after leaching. After water leaching, the blocks were also conditioned at 27°C and 30% RH for 3 weeks. Soil-block fungal decay tests were conducted according to the ASTM Standard D1413-99 (ASTM 2000). Loblolly pine was tested against *G. trabeum* and sweetgum against *T. versicolor*. In total, five replicate blocks from each treatment, five controls and five blocks treated with solvent without leaching were tested during a 12-week period. The weight losses were determined. Threshold retention is defined as 2% weight loss, as estimated by a logarithmic plot of the retention vs. weight loss data.

Results and discussion

Synthesis

As will be demonstrated below, poly(ethylene co-dipentachlorophenyl diacrylate), shortly EMA-Penta, with disubstituted pentachlorophenyl – linked through two ester bonds – could be synthesized in high yield under reflux of EMA copolymer with pentachlorophenol for 4 h in DMF. The products from reaction of EMA with 8-hydroxy quinoline contained a nearly equimolar mixture of EMA and EMA-8HQ.

Elemental analysis

Poly(ethylene co-dipentachlorophenyl diacrylate), EMA-Penta The penta-bonded acrylate polymer contained 57.5% Cl (th. 55.33%), 30.7% C (th. 33.74%) and 2.72% H (th. 0.94%). Accordingly, the carbon content was 3.08% lower and hydrogen content was 1.78% higher than the theoretical values. Obviously, some impurities are responsible for the deviations. Infrared analysis revealed bands at 3428, 2696, and 2410 cm^{-1}, which were attributed to bonded OH absorptions of the carboxylic acids (Bellamy 1964). The impurity may be a poly(ethylene co-dicarboxylic acid) which was identified by proton NMR in the starting polymer. The 2.14% elevated chlorine content is an indication that more anhydride groups than ethylene groups are present in the polymer. The high chlorine content (57.5%) is proof that the copolymer is completely reacted with pentachlorophenol. The high content of pentachlorophenol in the acrylate copolymer is one of the advantages of this technique, as the controlled-release period will certainly be prolonged.

Poly(ethylene co-8-quinolinyl acrylate), EMA-8HQ Elemental analysis of the products resulted in 56.8% C (th. 66.43%), 6.5% H (th. 4.83%) and 2.3% N (th. 5.16%). Accordingly, the nitrogen content of the products was only 44.8% of the theoretical value and this finding means that the products contains only 44.8% of poly (ethylene co-8-quinolinyl acrylate) and the remaining 55.2% is an unreacted EMA copolymer. This interpretation is further supported by the IR analysis. The carbonyl band of the anhydride is very intense.

Infrared characterization

The assignments of IR bands of EMA (**1**), EMA-Penta (**2**), Penta (**3**), EMA-8HQ (**4**) and 8HQ (**5**) from Figure 2 are described in Table 1. Only the synthesized polymer (**2**) and (**4**) are described below.

EMA-Penta (**2**) (Figures 1 and 2, Table 1) was a major product from crystallization which showed the characteristic strong IR absorptions attributable to C-H stretching vibrations of the methylene group (2962 cm^{-1}), aromatic C=C stretching vibration (1535 cm^{-1}) and aromatic C-O stretching vibration (1425 cm^{-1}) (Colthup 1964; Conley 1970). In addition, an impurity that could not be removed by crystallization was also present. The impurity was visible at 3428, 2696 and 2410 cm^{-1} attributable to bonded OH absorptions of the carboxylic acid groups (Bellamy 1964). EMA-8HQ (**4**) (Figure 2, Table 1) is characterized by the strong IR absorptions attributable to asymmetric C-H stretching vibration of the methylene group (2948 cm^{-1}), asymmetric and symmetric stretching vibrations of the anhydride group (1788 and 1729 cm^{-1}) and ring vibration and CH deformation of the quinoline (1456, 1400, 1117, 950 and 754 cm^{-1}) (Bellamy 1964; Colthup 1964; Conley 1970). Another major polymer was

Table 1 Assignments of FTIR bands of poly(ethylene co-maleic anhydride) (EMA, **1**), poly(ethylene co dipentachlorophenyl diacrylate) (EMA-Penta, **2**), pentachlorophenol (**3**), poly(ethylene co-8-quinolinyl acrylate) (EMA-8HQ, **4**) and 8-hydroxy quinoline (**5**) from Figure 2.

Polymer or compound	Wave-number (cm^{-1})	Intensity	Assignment	References
Poly (ethylene co-maleic anhydride) **(1)**	3442, 3200, 2600	s	Bonded OH of the carboxylic acid group (impurity)	Bellamy 1964; Cothup 1964; Conley 1970
	2962	s	Asymmetric C-H stretching vibration of the methylene group	
	1715	s	C=O stretching vibration of the anhydride group	
	1197	s	C-C stretching vibration	
Poly (ethylene co-dipenta-chlorophenyl diacrylate) **(2)**	3428, 2696 2410	s	Bonded OH of the carboxylic acid group (impurity)	Bellamy 1964; Cothup 1964; Conley 1970
	2962	s	Asymmetric C-H stretching vibration of the methylene group	
	1535	s	Aromatic C=C stretching vibration	
	1425	s	Aromatic C-O stretching vibration	
	765, 718	m	Aromatic C-Cl stretching vibrations	
Pentachlorophenol **(3)**	3418	s	OH stretching vibration	Conley 1970
	1546, 1418	s	Aromatic C=C stretching vibration	
	1383, 1307	s	Aromatic C-O stretching vibration	
	770, 709	m	C-Cl stretching vibration	
Poly (ethylene co-8-quinolinyl acrylate) **(4)**	3429	s	Bonded OH absorption of carboxylic acid (impurity)	Bellamy 1964; Colthup 1964; Conley 1970
	2948	s	Asymmetric C-H stretching vibration of the methylene group	
	1788, 1729	s	Asymmetric and symmetric stretching vibrations of the anhydride group	
	1456, 1400 1117, 950 754	s	Ring vibration and CH deformation of the quinoline	
8-hydroxy quinoline **(5)**	3200	s	OH stretching vibration	Bellamy 1964
	3047	s	CH stretching vibration	
	1580	s	C=C stretching vibration	
	1508	s	C=N stretching vibration	
	1287, 1223 781, 742	s	Ring vibration and CH deformation	

the unreacted EMA which is characterized by the strong carbonyl absorptions at 1788 and 1729 cm^{-1} attributable to asymmetric and symmetric C-O stretching vibrations of the anhydride group (Bellamy 1964; Colthup 1964; Conley 1970). Beside the above two polymers, the products also contained poly(ethylene co-diacrylic acid), as indicated by the IR absorption at 3429 cm^{-1} attributable to bonded OH absorption of the carboxylic acid group (Bellamy 1964).

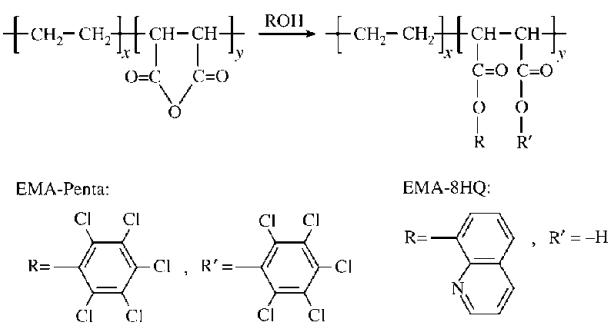

Figure 1 Synthesis of ethylene maleic anhydride copolymer containing pentachlorophenol (EMA-Penta) or 8-hydroxy quinoline (EMA-8HQ).

Fungal decay evaluation

Wood impregnated with EMA-Penta resisted decay by a brown- and white-rot fungus, even after water leaching, whereas wood impregnated with a mixture of EMA-8HQ and EMA could only resist decay by a brown-rot fungus. The weight loss of pinewood impregnated EMA-Penta (Table 2) and exposed to *G. trabeum* was at a retention level of 0.62 mmol/100 g wood below the defined threshold weight loss of 2%. For leached wood, the threshold retention was estimated to be 1.9 mmol/100 g wood. The threshold retention of non-leached pentachlorophenol treated wood was 1.17 mmol/100 g wood compared to 1.13 mmol/100 g wood for leached wood. The control and solvent treated blocks had weight losses of 30.6 and 28.5%, respectively. These decay tests prove that EMA-Penta treated wood and non-leached pinewood performed better than penta treated wood, but EMA-Penta was slightly less effective after water leaching.

With regard to penta-bonded polymer decayed by *T. versicolor* (Table 2), the threshold retention for non-leached wood was 2.67 mmol/100 g wood. After leaching, the threshold retention was 2.63 mmol/100 g wood. The threshold retention of pentachlorophenol treated and

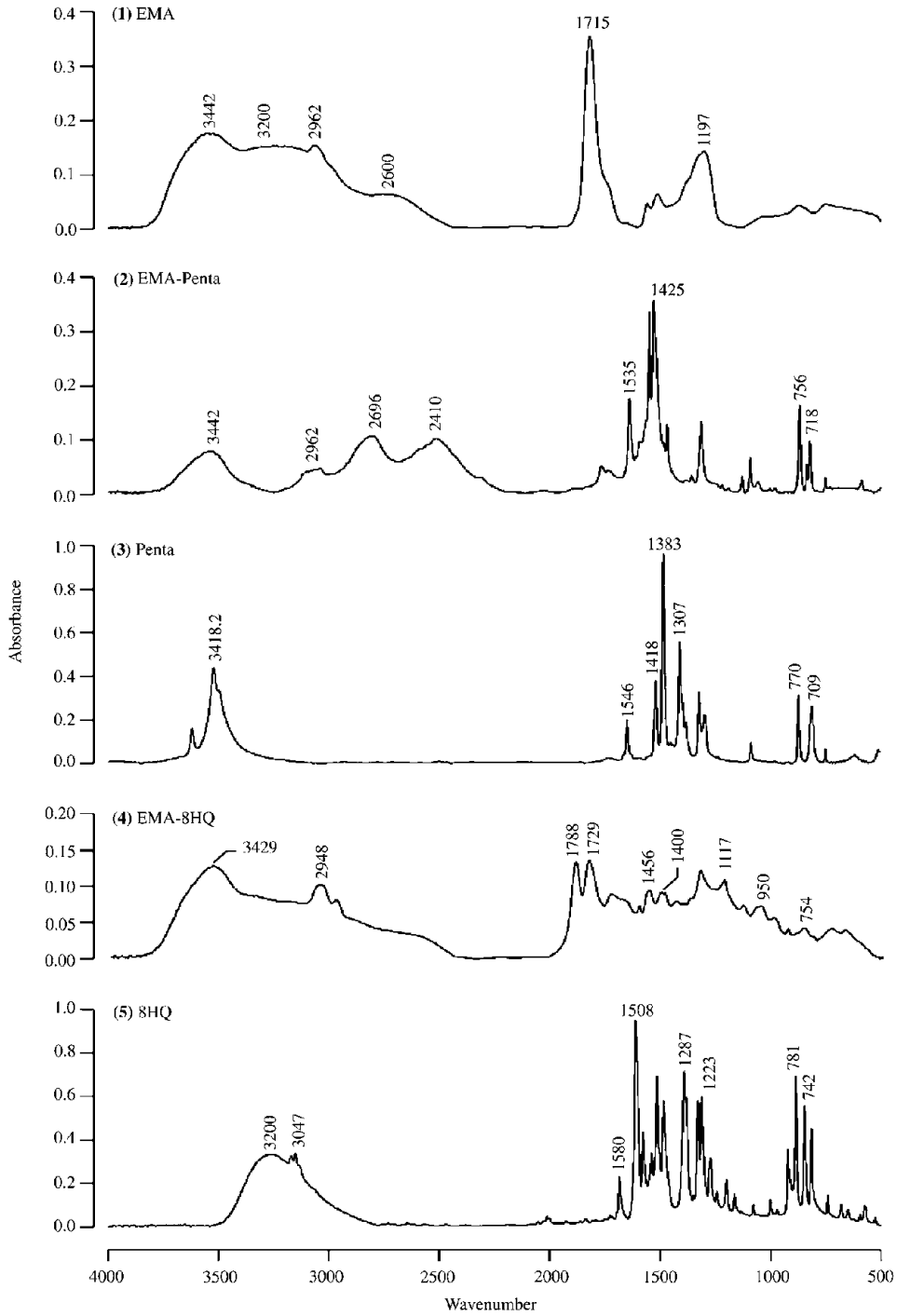

Figure 2 Infrared absorption of (**1**) Poly(ethylene co-maleic anhydride) (EMA), (**2**) Poly(ethylene co-dipentachlorophenyl diarcrylate) (EMA-Penta), (**3**) Pentachlorophenol (Penta), (**4**) Poly(ethylene co-8-quinolinyl acrylate) (EMA-8HQ) and (**5**) 8-hydroxy quinoline (8HQ).

non-leached wood was 2.1 mmol/100 g wood, while leaching made the treatment ineffective. The control and solvent treated blocks had 36.8 and 32.7% weight losses, respectively. The decay tests with *T. versicolor* indicated that EMA-Penta in sweetgum wood was more effective than pentachlorophenol, because it remained effective after water leaching. Clearly, decay protection with EMA-Penta has the advantage that high loading of penta can be achieved, and the release of penta from polymers is slow. For release, the pentachlorophenyl group has to be hydrolyzed by acids or enzymes (Pittman et al. 1982a). For commercial applications, penta was introduced to wood by hydrophobic petroleum solvents, which act as a barrier to water and thus retard leaching of penta during service.

In the case of impregnated pinewood with the mixture of EMA-8HQ and EMA (Table 2), the threshold retention against *G. trabeum* was 3.13 mmol/100 g wood (non-leached) and 3.20 mmol/100 g wood (leached). A treatment with 8-hydroxy quinoline resulted in a threshold retention below 1.21 mmol/100 g wood (non-leached). The control and solvent alone treated samples had 30.6 and 28.5% weight losses caused by *G. trabeum*. With regard to the degradation with *T. versicolor* (Table 2),

Table 2 Effect of poly(ethylene co-dipentachlorophenyl diacrylate), shortly EMA-Penta; pentachlorophenol, shortly Penta; poly(ethylene co-8-quinolynyl acrylate), shortly EMA-8HQ; and 8-hydroxi-quinolin, shortly 8-HQ, on weight losses of pine blocks decayed by *Gloeophyllum trabeum* and sweetgum blocks decayed by *Trametes versicolor* in a 12-week soil-block fungal decay test.

Treatment and concentration of solution (%)	Retention (mmol/100 g wood)		Weight loss (%)[a] by			
			Gloeophyllum trabeum		*Trametes versicolor*	
	Pine	Sweet gum	Non-leached	Leached	Non-leached	Leached
Solvent (pyridine)			28.5 (4.6)		32.7 (6.8)	
Control			30.6 (5.0)		36.8 (2.5)	
EMA-8HQ 0.5	0.62	0.60	1.7 (1.2)	26.4 (4.4)	36.1 (1.9)	34.5 (5.7)
EMA-8HQ 1.0	1.14	0.98	0.3 (0.2)	3.7 (2.7)	22.2 (8.8)	32.8 (4.2)
EMA-8HQ 2.5	2.56	1.98	0.1 (0.1)	0 (0)	2.2 (1.3)	13.0 (3.1)
EMA-8HQ 5.0	4.72	3.12	0.8 (0.2)	0 (0)	1.3 (0.2)	0 (0)
Penta 0.5	0.75	0.73	6.2 (12.2)	2.5 (4.4)	35.1 (2.8)	52.4 (4.0)
Penta 1.0	1.37	1.17	0.4 (0.7)	0.1 (0.1)	23.3 (7.0)	45.7 (10.1)
Penta 2.0	2.46	2.34	0.1 (0.1)	0.1 (0.1)	0.6 (0.6)	50.1 (7.0)
EMA-8HQ 0.5	0.62	0.58	16.5 (1.3)	12.3 (4.1)	41.0 (8.7)	46.0 (6.0)
EMA-8HQ 1.0	1.04	1.03	14.5 (2.3)	7.1 (1.1)	38.3 (5.7)	51.1 (6.1)
EMA-8HQ 2.5	2.34	2.28	4.4 (2.0)	6.7 (2.6)	40.7 (8.8)	42.0 (7.2)
EMA-8HQ 5.0	3.64	3.22	0 (0)	0.8 (0.4)	34.4 (3.2)	38.4 (4.6)
8-HQ 1.0	1.21	1.30	1.7 (0.9)		42.6 (8.8)	
8-HQ 2.0	2.46	2.30	0.1 (0.1)		25.4 (9.7)	

[a]Average of five replicates.
Data in parentheses are standard deviations.

sweetgum wood impregnated mixture of EMA-8HQ and EMA revealed a threshold retention below 2.3 mmol/100 g wood (unleached). Thus, neither the polymeric mixture nor 8-hydroxy quinoline alone was effective against *T. versicolor*.

Conclusions

Fungicides can be bonded to polymers through hydrolizable linkages, such as ester and amide bonds, or non-hydrolizable linkages, such as hydrocarbons and ethers. The phenoxide anion of pentachlorophenol or 8-hydroxy quinoline in the investigated polymers is susceptible to hydrolysis and will release fungicides from polymers in treated wood. Wood impregnated with poly (ethylene co-dipentachlorophenyl diacrylate), EMA-Penta, is suited to slow-release wood protection.

EMA-Penta in wood prevents decay by both brown- and white-rot fungus, even after water leaching. Pentachlorophenol treated wood is effective only against a brown-rot fungus. There is a pronounced slow-release effect in this case due to enzyme-catalyzed hydrolysis of the acrylate ester bonds. On the other hand, the decay resistance of wood treated with a mixture of EMA-8HQ and EMA is similar to that of wood treated with 8-hydroxy quinoline alone.

Acknowledgements

Infrared analysis was provided by the analytical unit of the Forest Products Laboratory (FPL) and fungal decay tests were performed by Rebecca Schumann of the FPL.

References

ASTM (2000) D1413-99. Standard method of testing wood preservatives by laboratory soil-block cultures. American Society for Testing Materials (ASTM), West Conshohocken, PA.

Bellamy, L.J. The Infrared Spectra of Complex Molecules. Richard Clay and Company, Ltd., Bungay, Suffolk, 1964. pp. 277–282.

Chen, G.C., Rowell, R.M., Ellis, W.D. (1990) Fungal resistance of southern pine impregnated with methyl fluorophenyl carbamates or reacted with fluorophenyl isocyanates. Wood Fiber Sci. 22:165–172.

Chen, G.C. (1992a) Fungal resistance of loblolly pine reacted with methyl or phenyl isothiocyanate. Holzforschung 46:77–80.

Chen, G.C. (1992b) Fungal resistance of loblolly pine reacted with para-toluene sulfonyl chloride or isocyanate. Wood Fiber Sci. 24:161–167.

Colthup, N.B., Daly, L.H., Wiberley, S.E. Introduction to Infrared and Raman Spectroscopy. Academic Press, New York, 1964. pp. 195–277, 291–318.

Conley, R.T. Infrared Spectroscopy. Allyn and Bacon Inc., Boston, MA, 1970. pp. 87–202.

Ibach, R.E., Rowell, R.M. (2001) Wood preservation based on in situ polymerization of bioactive monomers. Part 2. Fungal resistance and thermal properties of treated wood. Holzforschung 55:365–372.

Montemarano, J.A., Dyckman, E.J. (1975) Performance of organomettalic polymers as anti-fouling materials. J. Paint Technol. 47:59–61.

Pittman, C.U. Jr, Stah, G.A., Winters, H. (1978) Synthesis and mildew resistance of vinyl acetate and ethyl acrylate films containing chemically anchored fungicides. J. Coating Technol. 50:49–56.

Pittman, C.U. Jr, Ramachandran, K.S., Lawyer, K.R. (1982a) Synthesis of fungicidal monomers, polymers, and lattices. J. Coating Technol. 54:39–40.

Pittman, C.U. Jr, Lawyer, K.R. (1982b) Preliminary evaluations of the biological activity of polymers with chemically bound biocides. J. Coating Technol. 54:41–46.

Rowell, R.M. (1983) Bioactive polymer-wood composites. In: Controlled Release Delivery Systems. Eds. Roseman, T.J., Mansdorf, S.Z. Marcel Dekker Inc., New York. pp. 347–357.

Rowell, R.M. (1984) Bonding of toxic chemicals to wood. Appl. Biochem. Biotechnol. 9:447–453.

Subramanian, J.A., Mendoza, J.A., Garg, B.K. (1981a) Wood preservation by organotin polymers. I. In situ polymerization of organotin monomers. Holzforschung 35:253–259.

Subramanian, J.A., Mendoza, J.A., Garg, B.K. (1981b) Wood preservation by organotin polymers. II. Improvement in strength and decay resistance. Holzforschung 35:263–272.

Received June 12, 2007. Accepted January 31, 2008.
Previously published online February 28, 2008.