

Approaches to the improvement of biological resistance of wood through controlled release technology

By **George C. Chen and Roger M. Rowell**

George C. Chen and Roger M. Rowell are with the Forest Products Services Laboratory of the United States Department of Agriculture, Madison, Wis. The presentation was given at the 13th international symposium on controlled release of bioactive material of the Controlled Release Society.

CONVENTIONAL wood preservatives such as CCA, creosote and pentachlorophenol are effective against decay fungi, marine borers and insects. But they are toxic to plants and mammals and cause environmental and health problems.

Controlled release is a new technology by

which to minimize the environmental and health hazards of treating wood with preservatives. This technology, if it were fully developed, would be able to release wood preservatives in an effective low dose leaving no free chemicals to leach into the environment.

While the concept of controlled release has been given wide application in medical drug delivery and limited application in controlling agricultural pests, weeds and fertilizer applications, very little research is being conducted to develop this technology for wood protection.

Our current work in wood protection relating to controlled release technology is the investigation of bonding fungicides to wood through reactive functional groups and im-

pregnating wood with polymers containing pendent fungicides.

Controlled release methods

Because of the porous and polymeric nature of wood, controlled release technology can be applied by the three methods described below.

Encapsulation — Encapsulation is limited to surface applications because the pore size of wood is too small for microcapsules to penetrate. Surface application of fungicides encapsulated in the form of film¹ or fungicidal capsules incorporated into paint² showed some protection against mildew.

New technology is underway to make nanocapsules. These may be small enough to allow some, if not deep, penetration into the wood structure. Another technique that may be developed in the future is the *in situ* encapsulation of bioactive compounds in the voids of wood. More research is needed in this area.

Filling bioactive polymers in the cell lumen — Cell lumens, creating voids in the wood, can be viewed as reservoirs for filling monomers or polymers. Filling the voids with bioactive polymers is used less often because of solubility problems. The low solubility of polymers and high viscosity of polymer solution result in a low loading of polymers in wood.

Nevertheless, bioactive polymers such as a tributyltin methacrylate/methyl acrylate copolymer and the tributyltin ester of methyl vinyl ether/maleic anhydride copolymer impregnated into wood with a retention (3 to 6 lb/ft³) of bioactive polymers showed good protection against marine borers after two years in the ocean.³

Filling the voids in wood with a monomer containing bioactive compounds followed by *in situ* polymerization or copolymerization with a carrier monomer using a catalyst can achieve a high loading of bioactive polymers in wood. A great deal of research has been conducted in this area. Pentachlorophenol,^{4,5,6} pentabromophenol, 8-hydroxyquinoline,⁶ and organotin acrylates^{6,7,8,9} and methacrylates have been synthesized and polymerized in wood with either methyl meth-

acrylate⁶ or glycidyl methacrylate.^{10,11,12} These wood-polymer composites have been found to be effective preservatives against marine borers. Biocidal methacrylates have also been applied in the form of surface film^{6,13,14} and found to be effective anti-fouling materials^{6,13,14} but less effective against mildew.⁴

Bonding biocides to cell wall polymers —

A great deal of research has been conducted in bonding reactive chemicals to wood cell-wall Polymers.¹⁵ The results have shown that after reacting with simple alkyl epoxides¹⁶ and isocyanates^{17,18} wood is not degraded by microorganisms or termites in laboratory tests^{16,17,19,20} and has resisted attack by marine organisms in the ocean for 7 years^{21,22} Bonding of non-toxic chemicals to wood generally requires a high loading of bonded chemicals (more than 20 percent weight gain) to give a good protection.

Bonding biocides containing reactive groups to cell wall polymers may give good protection against biodegradation at much lower loading of chemicals (from 1 to 5 percent weight gain) if the bonded biocides behave as a controlled release compound. Research in this area is the subject of our current investigations.

Current work on controlled release technology at Forest Products Laboratory

1. Bonding fluorophenyl isocyanates to wood. Polyhalogenated (trifluoro, tribromo, trichloro and pentachloro substituted) phenyl isocyanates react with methanol to form polyhalogenated phenyl methyl carbamates. In treated wood, 2,4,6-trifluorophenyl methyl carbamate was shown to be effective against fungal as well as termite attack while bromo and chloro analogues were not effective (**Fig. 1** and **Table 1**). Because of the effectiveness of fluorophenyl methyl carbamate in resisting biodegradation, wood bonded to fluorophenyl isocyanates and wood impregnated with fluorophenyl methyl carbamates are being evaluated for resistance to fungal decay.

Synthesis of fluorophenyl isocyanates,

fluorophenyl methyl carbamates and the bonding of fluorophenyl isocyanates to wood are described below.

Synthesis of 2,4,6-trifluorophenyl isocyanate²³. 1,1,3,3-tetramethylurea (0.9 ml, 7.52 mmoles) was added to a solution of phosgene (28.06 g, 283.65 mmoles) dissolved in benzene (80 ml). The resulting solution was stirred for 10 min. at which time 2,4,6-trifluoroaniline (4.4 g, 30.00 mmoles) was added. The solution was heated to a temperature of 60°C. for 2 hours and then refluxed for 1 hour while phosgene was bubbled in. After removing excess phosgene under reduced pressure, the clear upper layer solution was collected by recantation from the bottom oil layer, and the bottom oil layer was discarded. The solution was evaporated to give a yellow liquid (6.8 g, 131 percent).

The liquid was distilled to give an azeotropic mixture, b.p. 80°-134°C.; IR: max 2,276 cm⁻¹ (NCO); NMR (chloroform-d); 3.40, 3.27, 3.14 (2-proton triplets, H-3, 5, aromatic protons), 2.70 (6-proton singlet, benzene). An azeotropic mixture also resulted using dichloromethane or toluene as a solvent.

Pentafluorophenyl isocyanate was also synthesized by the same procedure. An azeotropic mixture of product and solvent was also obtained. An azeotropic mixture of benzene and trifluorophenyl isocyanate or

pentafluorophenyl isocyanate was used to prepare fluorophenyl methyl carbamates and to react with wood.

Synthesis of 2,4,6-trifluorophenyl methyl carbamate. 2,4,6-trifluorophenyl isocyanate, (1.0 g) in anhydrous methanol (70 ml) was refluxed for 2 hours to give white crystals after recrystallization from methanol, m.p. 102°-103°C.; IR (KBr) 1718 cm⁻¹ (CO, carbamate), 3250 cm⁻¹ (NH, bonded); NMR (chloroformed) (H-3.5, AR), 6.38 (1H, s, NH), 3.78 (3H, s, Me). Anal. calc. for C₈H₆NO₂F₃: C, 46.84 H, 2.95; N, 6.83. Found: C, 47.22; H, 3.12; N, 6.82.

Other fluorophenyl methyl carbamates were synthesized by the same procedure.

Bonding fluorophenyl isocyanates to wood. Five southern pine blocks ¾ × ¾ × ¾ in) were reacted at 110°C. for 2 hours at 150 lb/in² with 4 ml of trifluorophenyl isocyanate in 80 ml acetone. After reaction, the blocks were air-dried and then oven-dried at 75°C. overnight. The blocks were then extracted with acetone in a Soxhlet extractor for 6 hours, air-dried and oven-dried at 75°C. overnight, which give an average of 3.12 percent weight gain. The blocks were then conditioned at 27°C., 30 percent relative humidity for 3 weeks prior to soil-block testing.

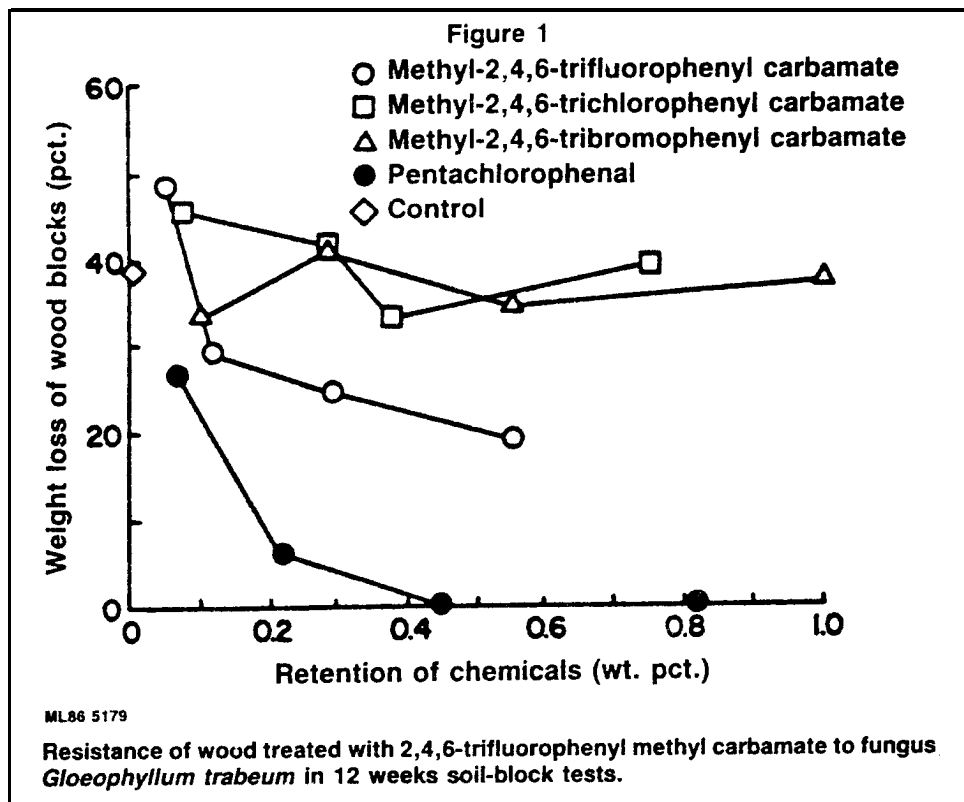
Same procedure was used for bonding other fluorophenyl isocyanates to wood.

Table 1
Percent weight loss of southern pine blocks
and percent survival of *Reticulitermes flavipes*
exposed to wood treated with carbamates in the 4 weeks termite tests

| Compound | Retention | Weight loss of blocks ^a (%) | Termite survival ^b |
|--|-----------|--|-------------------------------|
| Methyl 2,4,6-trifluorophenyl carbamate | 0.06 | 12.3 | 93.1 |
| | .59 | 0 | 0 |
| Methyl 2,4,6-trichlorophenyl carbamate | .07 | 13.9 | 91.4 |
| | .72 | 1.1 | 67.6 |
| Pentafluorophenyl | .0097 | 21.1 | 89.7 |
| | .097 | .3 | 14.6 |
| Control | | 24.8 | 92.6 |

^aFigures are average of three replicates.

^bBased on final live biomass.



Three levels of weight percent gain ranging from 1 to 8 percent were obtained by adjusting the concentrations of fluorophenyl isocyanate solution or reaction time to 6 hours.

2. Reaction of 8-hydroxyquinoline, pentachlorophenol or B naphthol with ethylene-maleic anhydride copolymer. An account will be presented of the synthesis and purification of these potentially bioactive polymers and a preliminary evaluation of their effect on fungal decay in treated wood.

References

1. Upsher, F. J. 1985. *Int. Biodeterior.* 21(3):211-214.
2. Noren, G. K.; Clifton, M. F.; Migdal, A. H. 1986. *J. Coatings Technol.*, 58(734): 31-39.
3. Andersen, D. M. 1979. Rep. No. DTNSRDC/SME-78/41. Bethesda, Md.:

David W. Taylor Naval Ship Res. and Develop. Center.

4. Pittman, C. U.; Lawyer, K. R. 1982. *J. Coatings Technol.* 54(690):41-46.
5. Pittman, C. U.; Ramachandran, K. S.; Lawyer, K. R. 1982. *J. Coatings Technol.* 54(690):27-40.
6. Rowell, R. M. *Proc.* 1981 ICRPS. 347-357.
7. Garg, B. K.; Corredor, J.; Subramanian, R. V. 1977. *J. Macromol. Sci. Chem.* A11(9):1567-1601.
8. Mendoza, J. A. 1977 Pullman, WA: Wash. State Univ. M.S. Thesis.
9. Montermoso, J. C.; Andrews, J. M.; Marinelli, L. P. 1958. *J. Polym. Sci.* 32(125): 523-525.
10. Subramanian, R. V.; Mendoza, J. A.; Garg, B. K. 1978 *Proc. ISCRBM.* Akron, Ohio: Univ. of Akron Press. 6.8-6.24.
11. Subramanian, R. V.; Mendoza, J. A.;

- Garg, B. K. 1981. *Holzforschung*. 35:253-259.
12. Subramanian, R. V.; Mendoza, J. A.; Garg, B. K. 1981. *Holzforschung*. 35:263-272.
13. Montemarano, J. A.; Dyckman, E. J. 1974 Proc. ICRPS. Akron, Ohio: Univ. of Akron Press, 21.1-21.9.
14. Subramanian, R. V.; Garg, B. K. 1977 Proc. ICRPS. Corvallis, OR: Ore. State Univ. Press. 154-164.
15. Rowell, R. M. 1975. *Am. Wood-Preserv. Assoc. Proc.* 71: 41-51.
16. Rowell, R. M.; Gutzmer, D. I. 1975. *Wood Sci.* 7(3):240-246.
17. Rowell, R. M. Ellis, W. D. 1979. *Wood Sci.* 12(1):52-58.
18. Ellis, W. D.; Rowell, R. M. 1984. *Wood Fiber Sci.* 16(3): 349-356.
19. Nilsson, T.; Rowell, R. M. 1982. Doc. No. IRG/WP/3211. Stockholm, Sweden: IRGWP. 6 p.
20. Rowell, R. M.; Hart, S. V.; Esenther, G. R. 1979. *Wood Sci.* 11(4):271-274.
21. Johnson, B. R.; Gutzmer, D. I. 1981. Res. Pap. FPL 399. Madison, Wis.: For Prod. Lab. 14 p.
22. Rowell, R. M. 1982. STFI Ser. A, No. 772, Stockholm, Sweden, For Prod. Res. Lab. 32-49.
23. Chen, G. C.; Rowell, R. M. 1984. U.S. Patent 4,477,389.