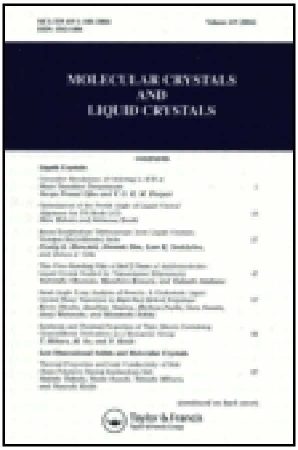

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Wood-Polymer Composites: Review of Processes and Properties

W. Dale Ellis [a]

[a] U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin, 53705-2398, USA

Version of record first published: 24 Sep 2006

To cite this article: W. Dale Ellis (2000): Wood-Polymer Composites: Review of Processes and Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 353:1, 75-84

To link to this article: http://dx.doi.org/10.1080/10587250008025649

Mol. Cryst. and Liq. Cryst., 2000, Vol. 353, pp. 75-84
Reprints available directly from the publisher
Photocopying permitted by license only

Wood-Polymer Composites: Review of Processes and Properties

W. DALE ELLIS

U.S. Department of Agriculture, Forest Service, Forest Products Laboratory,
One Gifford Pinchot Drive, Madison, Wisconsin 53705–2398 USA[*]

Wood-polymer composites (WPC) are made from wood and monomers that are polymerized inside the wood. Combining wood with polymer enhances the physical properties of the wood, allowing the composite to be tailored to specific applications. This paper reviews the processes and monomers used to make WPC, physical properties of WPC, and actual and potential applications. The characteristics of traditional monomers (methyl methacrylate and styrene) and new monomers are described, as are WPC surface hardness, water repellency, dimensional stability, abrasion resistance, and fire resistance. Current and potential uses for WPC range from hardwood flooring to furniture, sports equipment, parts for musical instruments, industrial applications, and construction materials.

Keywords: wood-polymer composites; monomers; wood; hardness; dimensional stability

INTRODUCTION

In general, any combination of wood and a polymer can be considered a wood–polymer composite (WPC). The term WPC has been used to describe a wide variety of materials, which include polymer filled with wood fiber and solid pieces of wood filled with polymer. This article focuses on WPC made from solid wood such as veneers or other small pieces of wood.

The process used to combine wood fibers with a polymer is different from that used to fill wood with plastic. There are limitations to the size of wood that can be treated successfully; large and thick specimens may not allow complete penetration of treatment chemical. To facilitate penetration, air is removed from the wood via a vacuum before treatment. Treatment

---

[*] The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain and not subject to copyright. The use of trade or firm names is for reader information and does not imply endorsement of any product or service.

chemicals are then pulled into the treating vessel to cover the wood and the vacuum is released. Wood is soaked in the chemicals at atmospheric or higher pressures for a designated period, and the wood is then removed from the treating vessel. Polymerization of the monomers in the wood is initiated by radiation or chemical catalysts and heat. For acrylate monomers, air is excluded from the process since it inhibits polymerization.

POLYMERIZATION METHODS

Radiation

Gamma radiation

Radiation-initiated polymerization is the most common method used to cure monomers in wood, although chemical curing is apparently a less expensive method for small-scale production. The major variables affecting polymerization rate and extent are monomer type, other chemical additives, wood species, and radiation dose rate[1]. In radiation polymerization of vinyl monomers, such as methyl methacrylate (MMA), cobalt 60 gamma ray dose rates of 56, 30, and 9 rad/sec produce exotherms at 120°C, 90°C, and 70°C, respectively, with reaction times of 5, 7, and 12 h, respectively, resulting in wood weight gain of 70% to 80%[2]. Additives such as alkenyl phosphonates and moisture in the wood increase the rate of polymerization[3]. High intensity radiation reduces the mechanical strength of the wood[4].

Electron beam

High energy electrons are another means of generating free radicals for the initiation of polymerization. Electron beam irradiation has been used to produce WPC using veneers impregnated with styrene, MMA, acrylonitrile, butyl acrylate, acrylic acid, and unsaturated polyesters[5-7].

Chemical Initiators

Peroxides

Free radicals for polymerization can be generated by thermal decomposition of peroxides, including t-butyl hydroperoxide, methyl ethyl ketone peroxide, lauroyl peroxide, isopropyl hydroperoxide, cyclohexanone peroxide, hydrogen peroxide, and benzoyl peroxide. The peroxides are added in amounts from about 0.2% to 3% by weight of monomer. The radicals differ in reactivity; for example, the phenyl radical is more reactive than the benzyl radical and the allyl radical is not reactive. Benzoyl peroxide appears to be used more frequently than are other peroxide initiators.

Vazo catalysts

The Vazo series of catalysts manufactured by the DuPont Company are white crystalline solids that are soluble in most vinyl monomers. Thermal decomposition produces two free radicals per catalyst molecule. The catalyst series consists of Vazo 52, Vazo 64, Vazo 67, and Vazo 88 (2,2'-azobis-(2,4-dimethylvaleronitrile), 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis-(2-methylbutyronitrile), and 1,1'-azobis-(cyclohexanecarbonitrile),

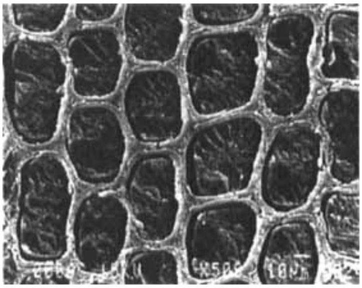

FIGURE 1 Void space at wood cell wall–polymer interface caused by shrinkage of monomer during polymerization.

respectively)[8]. The rate of free radical formation is dependent on the catalyst used and is controlled by regulating the temperature. The effective temperature range for Vazo 52 is 35°C to 80°C; for Vazo 64 and 67, 45°C to 90°C; and for Vazo 88, 80°C to 120°C. These catalysts are most frequently used in concentrations from ≤0.01% to 1.0% by weight of monomer. Vazo catalysts are generally preferable to peroxides because they are insensitive to shock, are non-oxidizing (i.e., do not bleach dyes incorporated in monomer), and can be easily handled and stored.

MONOMERS

Monomers used to make WPC include methyl methacrylate (MMA), styrene, unsaturated polyester resins, and new monomers such as polar esters. MMA has been the most commonly used monomer since 1965[9]. It is among the least expensive and most readily available monomers for WPC. MMA is used alone or in combination with other monomers, which are added to crosslink the polymer system. MMA must be cured in an inert atmosphere or at least in the absence of oxygen. Significant amounts of MMA can be lost during curing because of its relatively low boiling point (101°C). Also, shrinkage upon polymerization (about 20% by volume) can cause some distortion in wood[10] and also result in void space at the interface between the wood cell wall and the polymer (Fig. 1). The addition of crosslinking monomers such as di- and tri-methacrylates causes greater shrinkage of the polymer and thus larger void spaces[11].

Crosslinking agents frequently used with MMA and other vinyl monomers are trimethylolpropane triacrylate, trivinyl isocyanurate, trimethylolpropane trimethacrylate, ethylene glycol dimethacrylate, trimethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, and divinylbenzene. Crosslinking agents generally increase reaction rate and improve polymer physical properties [12].

Another monomer used to make WPC is styrene[13]. Like MMA, styrene is readily available and relatively inexpensive. It can be polymerized in wood using radiation, peroxides and heat, or 2,2'-azobisisobutyronitrile (AIBN)-type catalysis and heat techniques. Styrene is usually used with other monomers to change rate and extent of polymerization and to improve WPC physical properties through cross linking.

Unsaturated polyester resins are less expensive than MMA and they can be easily modified to produce special WPC properties. Many varieties of polyester resins are available as commercial products. Unsaturated polyester resins are used in combination with other monomers, particularly styrene. Styrene dilutes the resin, which makes it less viscous and more able to penetrate wood. Polyesters lower heat cure times and loss of styrene during curing[12].

Many new monomers have become available since the early stages of WPC research in the 1960s. These new monomers have properties that allow changes in the process for making WPC. Many new acrylate monomers have lower vapor pressures than do MMA and styrene, which reduces evaporation of the chemical from the wood prior to polymerization and permits polymerization in heated presses rather than heated chambers filled with nitrogen. Many of these monomers shrink less when polymerized than do MMA and styrene. The elimination of void space at the wood cell wall–polymer interface results in better WPC properties such as hardness.

Polar ester monomers having hydroxyethyl and glycidyl groups also reduce void space. Smaller voids have been found inside the polymer, suggesting better adhesion of the polymer to the inner surface of cell walls [1]. A combination of hexanediol diacrylate (HDDA) and hydroxyethyl methacrylate (HEMA) resulted in better adhesion of polymer to cell walls compared to HDDA alone (Fig. 2)[14].

The inherent brittleness of WPC made from acrylic compounds can be reduced by combining isocyanate compounds with acrylic monomers[5]. Fujimura[16] improved WPC properties by adding a blocked isocyanate to a mixture of MMA and 2-hydroxyethyl methacrylate. The isocyanate compound crosslinked the copolymer. Using an isocyanate with acrylate

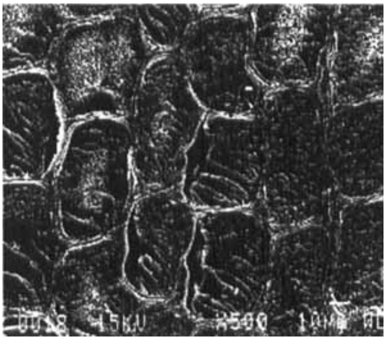

FIGURE 2 **Adhesion of polymer to cell walls in WPC made with HDDA and HEMA.**

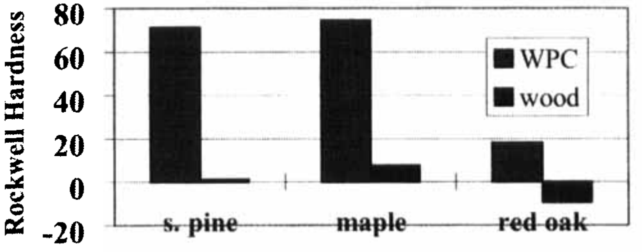

FIGURE 3 Hardness of pine, maple, and red oak solid wood and WPC made with polymer loads of 76%, 59%, and 52%, respectively.

monomers increased hardness and decreased WPC swelling in water[14].

Addition of an isocyanate compound to the styrene treating mixture improves the mechanical properties of wood–polystyrene composites. Polymethylene (polyphenyl isocyanate) forms a bridge between the wood and polymer interface. The isocyanate compound facilitates efficient stress transfer between the wood and polymer[17].

WPC PROPERTIES

Combining wood with polymer improves the physical properties of the wood, allowing the composite to be tailored for specific applications. Frequently targeted properties are hardness, dimensional stability, moisture exclusion, and resistance to abrasion, decay, weather, and fire. Other important properties are toughness, strength, and appearance.

Hardness

Hardness of a WPC depends on polymer hardness and loading. Polymer hardness is affected by the type of polymer, presence of crosslinking chemicals, and method and extent of polymerization. Polymer loading is affected by wood porosity and density; porous, low-density wood requires a high polymer load. Conversely, dense wood, such as the latewood of oak, accepts a very low polymer load. In general, the higher the polymer load the greater the WPC hardness (Fig. 3). Polymer loading is also affected by impregnation method and monomer properties, such as viscosity, boiling point (evaporation during cure), polarity, molecular weight, and shrinkage with polymerization.

Hardness values determined for untreated and MMA-treated red oak, aspen, and sugar maple indicate that the tangential face of untreated maple is harder than its radial face. The radial face of untreated oak was harder than its tangential face, but both oak and maple polymer composites showed no significant differences between radial and tangential faces[18]. Untreated wood hardness values were related to sample density, but not to corresponding hardness values for MMA-treated wood. For untreated pine and red oak, my research has shown that the radial face is harder than the tangential face and the longitudinal face the least hard. For pine and oak WPC, the tangential face is the hardest. Latewood of untreated oak is harder than earlywood, but latewood and earlywood of oak WPC show no significant difference in hardness.

Abrasion Resistance

The Taber wear index is weight loss (mg/1000 cycles) caused by an abrasive wheel turning on the specimen. The lower the weight loss value, the better the resistance to wear. In my research, maple veneers treated with combinations of HDDA and HEMA and an isocyanate have an average Taber wear index of 64 compared to 90 for untreated veneers. In other research, weight loss of alderwood and birchwood impregnated with MMA has been reported to be as much as 85% less than that of untreated wood[19]. Abrasion resistance of composites made from polystyrene and birch, alder, and spruce is comparable to that of natural oak wood[20].

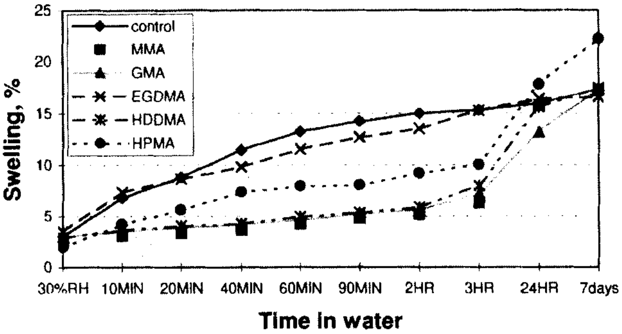

FIGURE 4 Swelling of maple WPC in water.

Dimensional Stability

Dimensional stability allows wood to resist changes in dimensions when subjected to changing moisture conditions. Many WPC are not dimensionally stable (Fig. 4). Given sufficient time in water or high humidity, most WPC will swell to the same extent as untreated wood.

Many researchers have tried to improve the dimensional stability of WPC. One approach has been to direct penetration and deposition of treatment chemicals into the wood cell walls to bulk the wood at or near its wet or green dimensions. Another method has been to react chemicals with hydroxyl groups in cell walls, decreasing the wood's affinity for moisture [21,22]. Dimensional stability is measured as percentage of swelling or as antiswell efficiency (ASE). ASE is the percent reduction in swelling of treated wood compared to untreated wood at equilibrium water or moisture saturated conditions. Polymers within the lumen do not make a significant contribution to dimensional stability compared to chemical interaction with wood cell wall components[23]. Such polymers slow moisture penetration, reducing the rate but not the extent of swelling (Fig. 5).

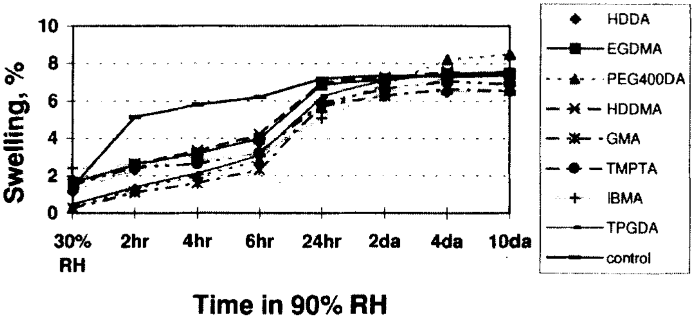

FIGURE 5 Swelling of pine WPC in 90% RH

Moisture exclusion efficiency (MEE), the ability to exclude moisture, is related to the rate at which the composite absorbs moisture and swells and not to the maximum extent of swelling or moisture uptake. MEE has apparently been mistaken for dimensional stability or ASE in studies in which the composite was not allowed to reach equilibrium with respect to moisture or water[21]. In WPC, the large void volume of wood filled with polymer reduces pathways for entrance of water and moisture. Although WPC absorb water and swell at a slower rate than does untreated wood, maximum swelling is usually almost the same as that of untreated wood.

Most vinyl monomers penetrate only the cell lumen, not the cell walls, and therefore do not cause wood swelling. Some monomers with hydroxyl groups will cause swelling. At 20°C, hydroxyethyl acrylate causes 14% swelling in maple, 9% in red oak, and 4% in southern pine. Other polar monomers result in little or no swelling at 20°C. Increasing the temperature to 105°C increases the extent of swelling; hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, and hydroxypropyl methacrylate result in 10% to 20% swelling[14,24]. These monomers could improve the dimensional stability of WPC.

Some dimensional stability can be obtained by reacting chemicals with the wood before impregnating it with monomers or by incorporating reactive chemicals in the monomer mixture. Chemical modification of wood prior to impregnation with a monomer improves dimensional stability compared to monomer treatments alone. Acetylation of wood using acetic anhydride produces good dimensional stability. The acetylated wood can then be made into a WPC with very good properties[25,26]. Lawniczak[4] found that adding isocyanates to styrene improved dimensional stability and strength of treated poplar wood. To improve monomer penetration, solvents have been used to swell the wood and carry the monomers into the cell walls[27]. The success of this approach has been limited.

Decay Resistance

Polymer impregnation has little effect on resistance to brown-rot decay of WPC prepared using MMA and several kinds of crosslinking monomers (1,3-butylene dimethacrylate, ethylene dimethacrylate, and trimethylolpropane trimethacrylate) and polar monomers (2-hydroxyethyl methacrylate and glycidyl methacrylate) added at 5%–20% concentration[10]. Most WPC are not decay resistant because the polymer merely fills the lumens and does not enter the cell walls, which makes the cell walls accessible to moisture and decay organisms. Using styrene or MMA in a methanol system allows some polymer to penetrate the cell walls. The amount of polymer in the cell wall plays an important role in resistance to decay. Some protection against biological degradation is possible at cell wall polymer contents of 10% or more[28]. Pentachlorophenol and tri-n-butyltin acrylates and methacrylates have been synthesized[29]. In tests on WPC made with these monomers, pentachlorophenol acrylate polymer provided no protection against decay. In contrast, tri-n-butyltin acrylate polymer at loads as low as 2% was effective at preventing decay by *Gloephyllum trabeum*[30].

Weather Resistance

To determine weathering characteristics, composites made from wood (birch and pine) and methyl methacrylate, styrene, and acrylonitrile were exposed in a Xenon-arc weatherometer for 1000 hours. These wood–plastic composites were more resistant to surface checking than were untreated controls. Composites made with styrene and acrylonitrile performed better than those made with MMA. At present, outdoor use of composites is not practical[31]. Composites treated with both cell-wall-modifying treatment (butylene oxide or methyl isocyanate) and lumen-fill treatment (MMA) resist the degradative effects of accelerated weathering in a weatherometer. The use of MMA in addition to cell wall-modifying chemical treatments provides added dimensional stability and lignin stabilization and improves resistance to weathering[32].

Fire Retardancy

The flammability of wood is enhanced by polymethyl methacrylate[33,34] but not affected by styrene and acrylonitrile[35]. Bis(2-chloroethyl) vinylphosphonate with vinyl acetate or acrylonitrile improves WPC fire retardancy, but it is less effective than poly(dichlorovinyl phosphate) or poly(di-ethyl vinylphosphonate). Wood impregnated with dimethylaminoethyl methacrylate phosphate salt and then polymerized in the presence of crosslinking agents has high fire retardancy[36], as does wood treated with trichloroethyl phosphate[37]. The addition of chlorinated paraffin oil to monomer systems provides fire retardancy[38]. The limiting oxygen index values of MMA-bis(2-chloroethyl)vinyl phosphonate copolymers and MMA-bis(chloropropyl)-2-propene phosphonate copolymer wood composites are much higher than that of untreated wood and other composites, indicating the effectiveness of phosphonates as fire retardants[39].

Dense smoke evolves from specimens treated with styrene-type monomers whereas those treated with MMA are essentially smoke free[40]. The presence of aromatic polymers, such as poly(chlorostyrene), and fire retardants with aromatic benzene rings in wood increased smoke evolution, flame spread, and fuel contribution in a modified tunnel furnace test[41]. In all specimens tested, smoke evolution increased markedly after the flame was extinguished.

Other Properties

The results of work on the mechanical properties of WPC leave little doubt that the strength properties of composites are generally enhanced compared to those of normal wood. Hardness, compressive strength, and impact strength of wood composites increase with increased monomer loading[42]. Crosslinking monomers increase static bending properties, compressive strength, and torsional modulus, and polar monomers improve dimensional stability and static bending properties but have no significant effect on compressive strength and torsional modulus[10].

APPLICATIONS

The major uses for WPC fall into four main categories: flooring, sports equipment, musical instruments, and furniture. Flooring, the largest volume use for WPC, includes solid plank flooring, top veneers of laminated flooring, and fillets for parquet flooring. Patents have been issued for golf club heads[43], baseball bats, hockey sticks[44], and parts of laminated skis. WPC is used for wind instruments[33], mouthpieces of flutes and trumpets[45,46], and finger boards of stringed instruments. A huge potential use is veneer laminates for furniture such as desk writing surfaces and tabletops[26,47].

References

[1] P. Aagaard, *Sven. Kem. Tidskr.* **79,** 501 (1967).

[2] V. I. Glukhov, G. V. Shiryaeva, *Plast. Massy.* **6,** 35 (1973).

[3] G. V. Shiryaeva, N. D. Prishchepa, V. I. Glukhov, V. T., Lebedev, V. L.Karpov, in *Proceedings, Tihany Symp. Radiat. Chem.* **3,** 783 (1972).

[4] M. Lawniczak, *Industria Lemnului* **4,** 141 (1972).

[5] T. Handa, I. Seo, T. Ishii, Y. Hashizume, *Polym. Sci. Technol.* **20,** 167 (1983).

[6] T. Handa *et al., Mokuzai Gakkaishi* **19,** 493 (1973).

[7] M. Gotoda, K. Yokoyama, and S. Toyonishi, *Nippon Genshiryoku Kenkyusho* **5026,** 08 (1970).

[8] Du Pont Company, *Technical Product Data.*

[9] J. A. Meyer, *For. Prod. J.* **15,** 362 (1965).

[10] H. Kawakami, H. Yamashina, K. Taneda, *J. HokkaidoFor. Prod. Res. Inst.* **306,** 10 (1977).

[11] H. Kawakami, K. Taneda, S. Ishida, J. Ohtani, *Mokuzai Gakkaishi* **27,** 197 (1981).

[12] D. L. Kenaga, *Wood Fiber* **2,** 40 (1970).

[13] I. F. Siau, J. A. Meyer, C. Skaar, *For. Prod. J.* **162** (1965).

[14] W. D. Ellis, J. L. O'Dell, *J. Appl. Polym. Sci.* (in press).

[15] R. Schaudy, E. Proksch, *Oesterr. Forschungszent. Seibersdorf* Report No. **4113** (1981).

[16] T. Fujimura, M. Inoue, I. Uemura, *Mokuzai Gakkaishi* **36,** 851 (1990).

[17] D. Maldas, B. V. Kokta, C. Daneault, *J. Appl. Polym. Sci.* **38,** 413 (1989).

[18] F. C. Beall, A. E. Witt, L. R. Bosco, *For. Prod. J.* **23,** 56 (1973).

[19] J. K. Miettinen, T. Autio, F. E. Siimes, T. Ollila, *Val Tek. Tutkimuslaitos, Julk.* **137,** 58 p (1968).

[20] J. Dolacis, *Modif. Svoistv Drev. Mater.* edited by K. A. Rotsens, (Zinatne, Riga, USSR, 1983), **37,** 107.

[21] W. E. Loos, *Wood Sci Technol.* **2,** 308 (1968).

[22] R. M. Rowell, R. Moisuk, J. A. Meyer, *Wood Sci.* **15,** 290 (1982).

[23] T. Fujimura, M. Inoue, *Mokuzai Gakkaishi* **37,** 719 (1991).

[24] W. D. Ellis, *Wood Fiber Sci.* **26,** 333 (1994).

[25] M. Wada, M. Fushitani, *Mokuzai Gakkaishi* **38,** 1035 (1992).

[26] M. Kakehi, Y. Yoshida, K. Minami, **JP 60242002** (1985).

[27] J. Maine, **US 3790401** (1974).

[28] T. Furuno, T. Uehara, S. Jodai, *Mokuzai Gakkaishi* **38,** 285 (1992).

[29] R. M. Rowell, in *Controlled Release Delivery Systems,* edited by T. J. Roseman and S. Z. Mansdorf (Marcel Dekker, Inc., New York, 1983), Chap. 23, p. 347.

[30] R. E. Ibach, R. M. Rowell, in *Proceedings, Int. Res. Group Wood Preserv.,* Doc. No. IRG/WP/95-30066 (1995).

[31] R. L. Desai, S. C. Juneja, *For. Prod. J.* **22,** 100 (1972).

[32] R. M. Rowell, W. C. Feist, W. D. Ellis, *Wood Sci.* **13,** 202 (1981).

[33] R. L. Calleton, E. T. Choong, R. C. McIlhenny, *Wood Sci. Technol.* **4,** 216 (1970).

[34] H. Lubke, J. Jokel, *Zesz. Probl. Postepow. Nauk. Roln.* **260,** 281 (1983).

[35] R. Schaudy, J. Wendrinsky, E. Proksch, *Holzforschung* **36,** 197 (1982).

[36] A. U. Ahmed, N. Takeshita, M. Gotoda, *Nippon Genshiryoku Kenkyusho* **5027,** 82 (1971).

[37] T. Autio, J. K. Miettinen, *For. Prod. J.* **20,** 36 (1970).

[38] V. K. Iya, A. B. Majali, *Radiat. Phys. Chem.* **12,** 107 (1978).

[39] M. G. S. Yap, Y. T. Que, L. H. L. Chia, H. S. O. Chan, *J. Appl. Polym. Sci.* **43,** 2057 (1991).

[40] J. F. Siau, J. A. Meyer, R. S. Kulik, *For. Prod. J.* **22,** 31 (1972).

[41] J. F. Siau, G. S. Campos, J. A. Meyer, *Wood Sci.* **8,** 375 (1975).

[42] H. Mohan, K. N. Rao, India, A. E. C., *Bhabha At Res Cent [Rep.], B.A.R.C.* **930,** 28 p. (1977).

[43] S. Katsurada, K. Kurahashi, **GB2141753** (1985).

[44] K. Yamaguchi, **JP57203460** (1982).

[45] K. Knotik, E. Proksch, **DE 2054730** (1971).

[46] K. Knotik, E. Proksch, K. Bresimair, **FR 2069273** (1971).

[47] J. Maine, **US 3560255** (1971).