Improvement of Wood Properties by Impregnation with Multifunctional Monomers

LON J. MATHIAS, SOO LEE, JOHN R. WRIGHT, and STEPHEN C. WARREN

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

SYNOPSIS

Southern pine samples with different dimensions and bulk densities were impregnated with the multifunctional monomer ethyl α-hydroxymethylacrylate (EHMA) and 5 mol % of fluorinated or nonfluorinated crosslinking agent. The maximum impregnation yield (105% by weight) was achieved under vacuum with good improvement of water repellency.

Impregnation with EHMA plus another multifunctional monomer 2-vinyl-4,4-dimethyl-2-oxazolin-5-one (vinyl azlactone) was carried out to improve the mechanical properties of wood samples. Water repellency was also improved depending on the amount of vinyl azlactone in the monomer solution. A maximum of 41% antiswell efficiency (ASE) was obtained by impregnation with a 9 : 1 w/w mixture of EHMA and vinyl azlactone. Improvements of 38–54% in impact strength and 27–44% in compression modulus were achieved depending on the relative amount of vinyl azlactone incorporated. FT-IR and solution or solid-state NMR spectroscopy were used for chemical characterization of the polymers themselves and the wood–polymer composites.

INTRODUCTION

To reinforce the physical or mechanical properties of wood, techniques such as heat or pressure treatment, crosslamination (as in plywood), surface coating, and impregnation with reactive materials have been extensively evaluated. The most promising method for improving the specific properties of the wood cell wall material is chemical impregnation under vacuum or pressure. Compounds highly reactive to the hydroxyl groups of cellulose, hemicellulose, and lignin components of wood include epoxides, isocyanates, anhydrides, lactones, and diols. All have been examined for the reduction of equilibrium moisture content, one of the most important factors related to dimensional stability of wood.[1] Chemical impregnation also has potential for reducing the susceptibility of the wood to biological degradation. A simple acetylation by a dip process in acetic anhydride has been widely utilized to reduce swellability of wood in water.[2] Another widely studied system is the crosslinking of wood via impregnation with formaldehyde in the presence of acid

catalyst.[3] Several liquid monomers [e.g., methyl methacrylate (MMA) and styrene (St)] were also incorporated into wood samples with up to 160 wt % weight gain, and then polymerized in the lumens to improve wood's dimensional stability.[1] These systems were very effective in filling the cell lumens with polymers but not effective in penetrating the cell walls to any noticeable extent with polymer.[4]

To improve the penetration of monomers into cell walls, we chose the multifunctional monomer, ethyl α-hydroxymethylacrylate (EHMA), as a candidate. This monomer contains three different functionalities including an alcohol, ester, and polymerizable double bond. The hydroxyl group was expected to increase monomer hydrophilicity and hydrogen bonding capability with the various components of wood. Moreover, after or during the polymerization, intra- or intermolecular transesterification should occur through reaction of the hydroxyl groups of EHMA units and cellulose with monomer ester groups to form a very strong three-dimensional network that provides good dimensional stability to the wood–polymer composite. Further improvement in properties may be possible via crosslinking of the EHMA polymer using added or *in situ* formed diacrylate crosslinking agents. *In situ* network formation

of EHMA coupled with improved adhesion and binding to wood should provide enhanced toughness to the final composite.

We describe here wood impregnation with EHMA and diacrylate crosslinking agents in the presence of the water-soluble radical initiator, 2-(carbamoyl-azo)isobutyronitrile (V-30), which was found to be a good initiator while maintaining low viscosity for sufficient time to give good monomer incorporation at elevated temperature.[5] The EHMA–comonomer system containing the multifunctional monomer, 2-vinyl-4,4-dimethyl-2-oxazolin-5-one (vinyl azlactone), was also examined to improve the dimensional stability of wood. Generally, 2-oxazolin-5-ones are known to undergo ring-opening addition reaction with a variety of nucleophiles including water, alcohols, amines, and thiols.[6] With the vinyl azlactone, an acid-catalyzed Michael reaction also occurs with thiols.[7] The reactivity of vinyl azlactone, before or during vinyl copolymerization, opens possibilities for forming very rigid crosslinked polymers with material-containing hydroxyl groups like EHMA, poly(EHMA), or wood.

EXPERIMENTAL

Materials

V-30 initiator was obtained as a generous donation from Wako Chemical Co. and used without further purification. Vinyl azlactone was donated by 3M Chemical Co. and used as obtained. EHMA was synthesized by reaction of ethyl acrylate with formaldehyde in the presence of DABCO (1,4-diazabicyclo[2,2,2]-octane).[8] Fluorinated and nonfluorinated diacrylate crosslinking agents were prepared from fluorinated or nonfluorinated bisphenol-A-based epoxide and EHMA with a catalytic amount of BF_3–OEt_2.[5]

Wood samples (Southern pine) with different dimensions ($1 \times 1 \times \frac{1}{4}''$ for the water soaking test, $\frac{1}{4} \times \frac{1}{4} \times \frac{5}{2}''$ for impact strength testing, and $\frac{1}{2} \times 1 \times \frac{1}{16}''$ for the buckled plate test) and bulk densities (0.355 and 0.590 g/cm^3) were obtained from the Forest Products Laboratory, Forest Services, USDA, and used after drying at 105°C for 12 h.

Typical Impregnation Process

All wood for testing or impregnation was first oven-dried for 12 h in air at 105°C. Impregnation involved placing the wood samples (usually $1 \times 1 \times \frac{1}{4}''$ with wood fibers parallel to one of the long dimensions)

in a vacuum chamber (< 3 mmHg) at 50–60°C for 30 min. Monomer or a monomer mixture containing 1.5–3 mol % V-30 initiator was introduced into the vacuum chamber until the wood samples were covered. After 1–2 h of impregnation at 50–60°C (at that time most impregnated wood samples sank into the monomer), vacuum was released and the impregnation process carried out for another 30 min. Finally, wood samples were removed and wiped to remove excess monomer from wood surfaces. The wood samples were wrapped in aluminum foil and thermally polymerized at 80–115°C for 10–96 h. After unwrapping, the samples were dried in a vacuum oven at 45°C overnight to remove unreacted monomer. All data on weight and dimension change of wood samples were recorded at each step of the impregnation and cure procedure.

Characterization

Water repellency and dimensional stability were evaluated by a water soaking test with $1 \times 1 \times \frac{1}{4}''$ samples (grain parallel to smallest dimension) of untreated wood and wood–polymer composites using published procedures.[1] Sample volumes were calculated from the exterior dimensions measured to the nearest 0.001 cm with a microcaliper. Three samples for each treatment and the control were evaluated and results averaged. Water repellency was measured for short-term resistance to water uptake and is expressed as water-repellent effectiveness (WRE)[1] calculated from eq. (1).

$$WRE = \{(D_c - D_t)/D_c\} \times 100, \qquad (1)$$

where D_c = volume change (or water uptake) of control immersed in water for short times, usually 60 min, and D_t = volume change (or water uptake) of impregnated wood sample in water for the same time period.

The dimensional stability of impregnated wood samples was evaluated with antiswell efficiency (ASE) values using changes in tangential, radial, and longitudinal dimensions after 7 d of soaking in distilled water. Dimensional stability was expressed as ASE[1] determined from eq. (2) and (3).

$$S = (V_2 - V_1)/V_1 \times 100, \qquad (2)$$

where S = volumetric swelling coefficient, V_1 = wood volume of oven-dried sample (12 h, 105°C) before water soaking test, and V_2 = wood volume after water soaking test.
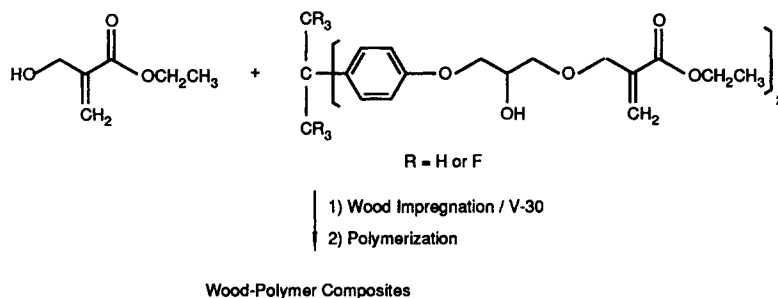
R = H or F

1) Wood Impregnation / V-30
2) Polymerization

Wood-Polymer Composites

Scheme 1   Wood impregnation with EHMA and diacrylate crosslinking agents in the presence of V-30.

$$ASE = (S_2 - S_1)/S_1 \times 100, \qquad (3)$$

where S_1 = volumetric swelling coefficient for treated wood and S_2 = volumetric swelling coefficient for untreated wood.

Relative impact strength was measured by an instrument (CS-137-053) made by Custom Scientific Instruments Inc. using $\frac{1}{4} \times \frac{1}{4} \times \frac{5}{2}''$ samples of wood and wood–polymer composites. Longitudinal toughness of wood–polymer composites was measured with the buckled plate test[9] using a 1020C Instron and $1 \times \frac{1}{2} \times \frac{1}{16}''$ samples. For these two non-ASTM tests, fibers were parallel to the long axis of the sample and fracture occurred perpendicular to

the fiber direction. The compression modulus (E) was calculated from eq. (4) using data from the buckled plate test.[9] For each of these tests, 9–10 untreated wood samples were used as controls, and 5–10 treated samples for each impregnation composition; values given in the tables are averages.

$$E = 12 P_c l^2 / \pi^2 w h^3, \qquad (4)$$

where P_c = maximum force, w = width of wood sample, l = length of wood sample, and h = thickness of wood sample.

Infrared spectra were obtained on powdered samples made into KBr pellets run on a Perkin-

Table I   Impregnation of EHMA into Southern Pine with 5 mol % Nonfluorinated or Fluorinated Diacrylate Crosslinking Agent

Sample No.	Wood Weight[a]	Final Weight[b]	% Wt. Incr.	Final Volume	% Vol. Change[c]	d (g/cm³)
GR4L-E1[d]	2.53 g	4.37 g	73%	3.93 cm³		1.11
GR4L-E2[d]	2.53	4.37	73	4.06		1.08
GR4L-E3[d]	2.54	4.45	75	3.98		1.12
Ave.	2.53	4.40	74	4.00	−4.17%	1.10
GR4L-F1[e]	2.42 g	4.89 g	102%	4.44 cm³		1.10
GR4L-F2[e]	2.42	4.99	106	4.42		1.13
GR4L-F3[e]	2.43	4.98	105	4.35		1.15
Ave.	2.42	4.95	105	4.40	2.59%	1.12

[a] After drying at 105°C for 12 h.
[b] After polymerization at 100°C for 12 h and drying at 45°C *in vacuo* for 2 h.
[c] Average data for original wood sample (GR4L)
 volume: 4.29 cm³
 weight: 2.53 g
 density: 0.59 g/cm³.
[d] Composition of nonfluorinated system:
 EHMA 45.00 g, 342.6 mmol
 Nonfluorinated bisepoxide 6.12 g, 18.0 mmol
 BF₃–OEt₂ catalytic amount.
[e] Composition of fluorinated system:
 EHMA 41.82 g, 312.0 mmol
 Fluorinated bisepoxide 9.95 g, 16.4 mmol
 BF₃-OEt₂ catalytic amount.

Elmer FT-IR 1600 Series spectrometer. Solution ^{13}C NMR spectroscopy was carried out at 75 MHz on a Bruker AC-300 while a Bruker multinuclear CP/ MAS probe on a Bruker MSL-200 was used for solid-state ^{13}C NMR acquisitions; both methods used standard acquisition parameters. Thermograms of wood–polymer composites were obtained with a DuPont 910 Differential Scanning Calorimeter (DSC) cell using crimped pans, a 951 Thermogravimetric Analysis (TGA) unit, and a 9900 data station with a 10°C/min heating rate under nitrogen flow. Thermal analysis involved small pieces of wood or wood–polymer composite sliced from the original samples with a razor blade and allowed to equilibrate for 1 d on the bench top. Scanning electron microscopy (SEM) was used to examine the impregnated polymers within the wood before and after sample fracture; interior portions were exposed by cutting with a razor blade, gold sputter coated, and examined with a JEOL SEM.

RESULTS AND DISCUSSION

Wood Impregnation with EHMA and Diacrylate Crosslinking Agents

Preformed or *in situ* generated diacrylate ethers from fluorinated or nonfluorinated bisepoxides and EHMA were shown to serve as efficient and reactive crosslinking agents for vinyl monomers.[5] By using such systems (shown in Scheme 1), wood impregnation was carried out at 50°C for 1 h under reduced
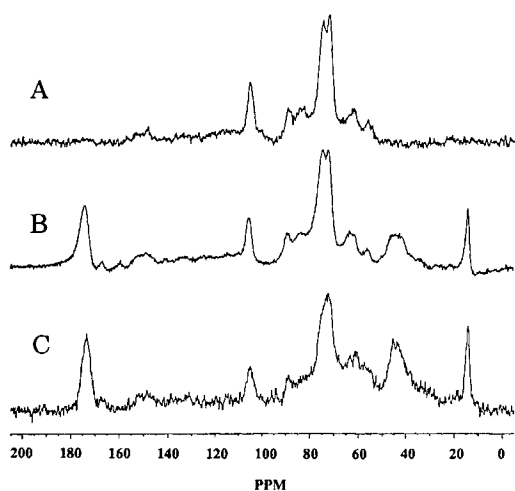
Figure 1 ^{13}C CP/MAS spectra of untreated wood (A), and wood impregnated with EHMA and 5 mol % of fluorinated (B) or nonfluorinated (C) diacrylate crosslinking agent in the presence of V-30.
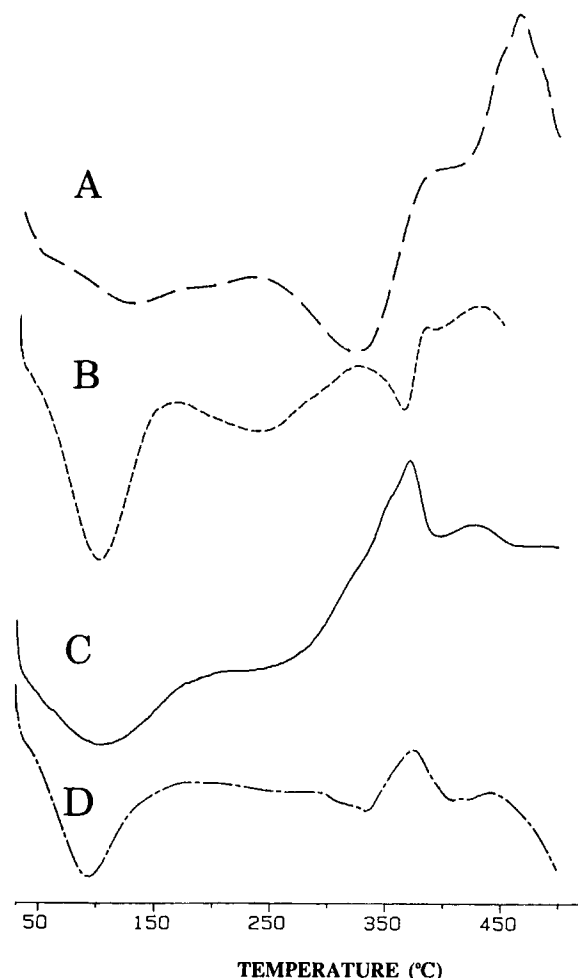
Figure 2 DSC thermograms (exotherm up) of nondried untreated wood (A), a physical mixture of wood and 102 wt % of poly(EHMA) crosslinked with 5 mol % fluorinated diacrylate crosslinking agent (B), and wood impregnated with EHMA and 5 mol % fluorinated (C, 102 wt % polymer uptake) or nonfluorinated (D, 73 wt % polymer uptake) diacrylate crosslinking agent (heating rate, 10°C/min).

pressure. A key factor affecting monomer incorporation in wood is the viscosity of the monomer solution. During impregnation at 50°C for 1 h, the viscosity of the monomer solution was low enough to give reasonably high monomer incorporation (70–110%, Table I) without gelation.

^{13}C CP/MAS NMR spectroscopy was used for preliminary confirmation of impregnation by EHMA and complete polymerization of EHMA inside the wood samples. The methyl carbons of poly(EHMA) were observed at 14.2 ppm and the ester carbonyl peaks around 173 ppm. Absence of double bond carbon peaks at 123 and 140 ppm (clearly seen in unpolymerized samples) provided
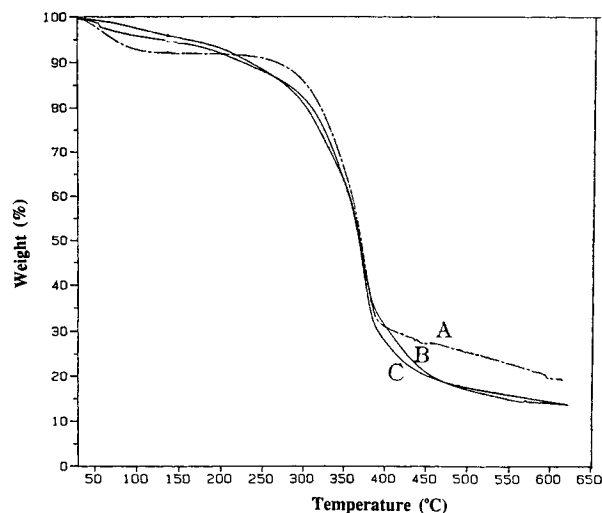
Figure 3 TGA thermograms of undried, untreated wood (A), and wood impregnated with EHMA and 5 mol % fluorinated (B, 102 wt % polymer uptake) or nonfluorinated (C, 73 wt % polymer uptake) diacrylate crosslinking agent (heating rate, 10°C/min).

Figure 4 Swelling of wood–polymer composites measured with the water soaking test; A: untreated wood oven-dried at 105°C for 12 h; B: wood impregnated with EHMA and 5 mol % fluorinated diacrylate crosslinking agent, 102 wt % polymer uptake; C: wood impregnated with EHMA and 5 mol % nonfluorinated diacrylate crosslinking agent, 73 wt % polymer uptake.

evidence for complete polymerization (Fig. 1). Weak peaks were seen between 120–140 ppm for aromatic carbons of the crosslinking agents although this region overlaps the lignin peaks and makes quantitation difficult.

Evaluation of chemical reaction and hydrogen bonding between ester or hydroxyl groups of poly(EHMA) and hydroxyl groups of wood components was attempted with DSC. Comparison was made of the thermograms of impregnated wood and a physical mixture of wood and crosslinked poly(EHMA) with the same overall composition as the impregnated wood sample (Fig. 2). The impregnated and cured wood samples show an endothermic peak around 200–230°C, that is not seen in the thermograms of wood alone and the mixture of wood and crosslinked poly(EHMA). This may in-
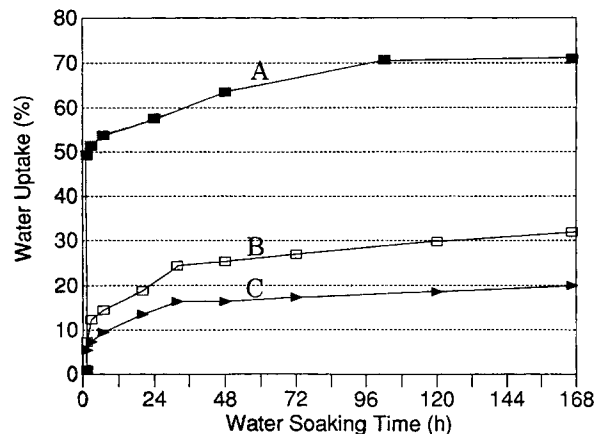
dicate some chemical interaction or binding between poly(EHMA) and wood, perhaps involving transesterification.

Thermal weight loss of these impregnated wood samples detected by TGA showed a reduction of residual moisture content (initial weight loss at $\geq 100°C$) and slightly lower thermal stability due to the tendency of ester groups of poly(EHMA) to transesterify and release ethyl alcohol (Fig. 3). IR and solid-state NMR were used to confirm the latter process. Onset of decomposition and overall thermal stability were surprisingly similar for the wood–polymer composites and unimpregnated wood, with all samples showing baseline instabilities in the DSC and rapid weight loss above 300°C.

Dimensional stability and water repellency were measured using a simple water soaking test. This test estimates not only water repellency (from the

Table II Water-Repellent Effectiveness of Wood Samples Impregnated with EHMA and 5 mol % Diacrylate Crosslinking Agents by the Water Soaking Test

	WRE	
Sample	From Water Uptake	From Volume Change
Wood impregnated with EHMA and fluorinated crosslinking agent	89	83
Wood impregnated with EHMA and nonfluorinated crosslinking agent	85	81

1 h immersion in water at 25°C.

data obtained for short-term water soaking) but also provides a measure of dimensional stability (from the data obtained for long-term water soaking). As shown in Table II, water repellency of impregnated wood samples was increased significantly. Water-

repellent effectiveness (WRE) values for impregnated wood–poly(EHMA) samples containing both diacrylate crosslinking agents were higher than 80%. The wood sample impregnated with EHMA and nonfluorinated diacrylate crosslinking agent showed
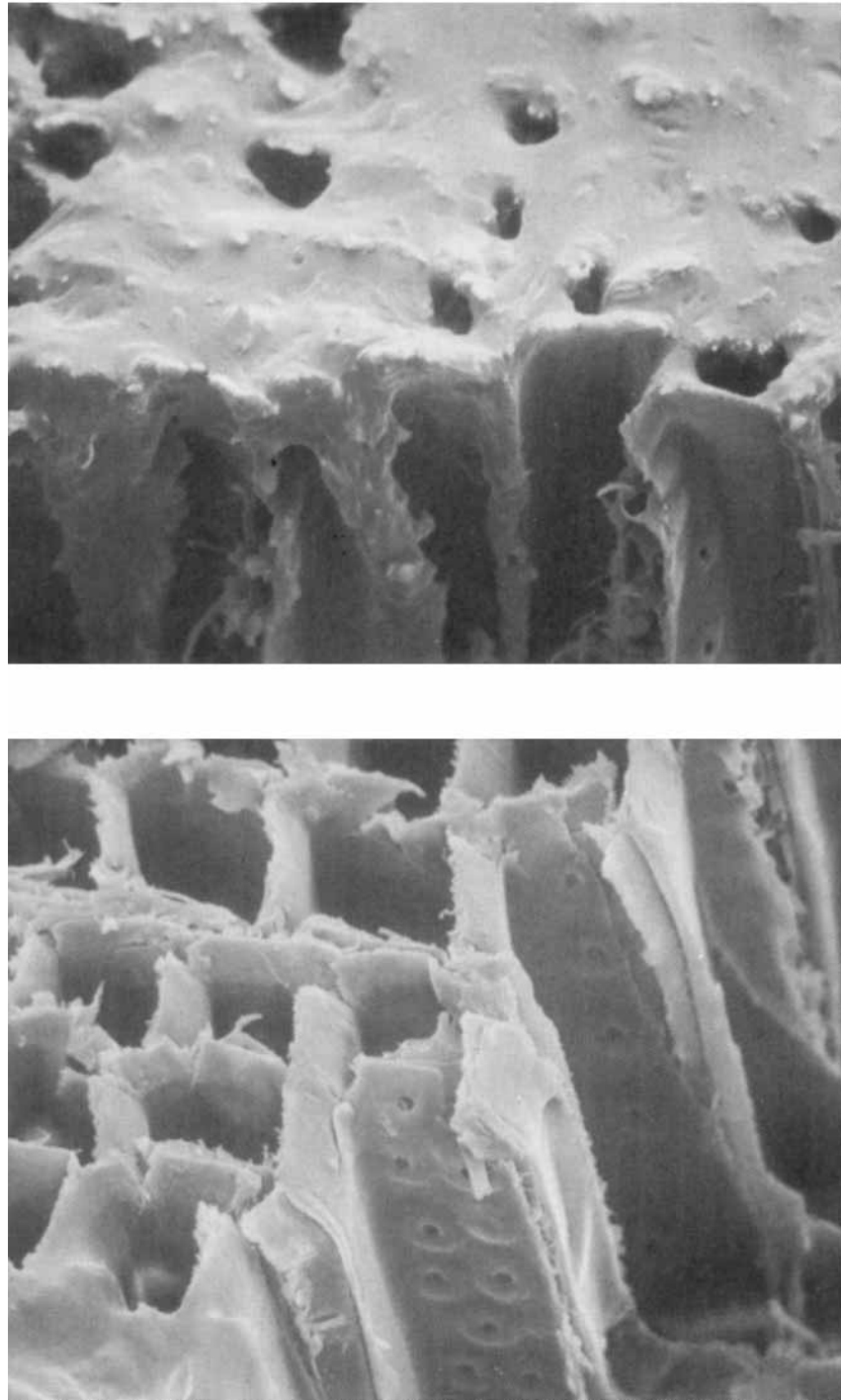

Figure 5   SEM photomicrographs (580X) of untreated wood (lower picture) and wood impregnated with EHMA and 5 mol % fluorinated diacrylate crosslinking agent (upper).

the better improvement in water repellency and dimensional stability (Figure 4).

Southern pine wood samples with lower density (0.355 g/cm^3) were also impregnated with EHMA and either the fluorinated or nonfluorinated diacrylate crosslinking agents and V-30. Because of the large void space in these wood samples, much higher impregnation yields (around 120% weight gain) were obtained than with denser wood samples. Both groups of wood-polymer composites showed very good dimensional stabilities. Even after three months in water at 25°C, only 4.7% and 5.1% volume changes were detected for wood-polymer composites impregnated with EHMA and fluorinated or nonfluorinated diacrylate crosslinking agent, respectively, versus a 19.3% volume change for untreated wood samples under the same condition. Water uptake (by weight gain) of both families of impregnated wood samples after 3 months was also reduced to less than 30% of that of untreated wood samples.

Finally, SEM photomicrographs of both groups of impregnated wood samples showed excellent incorporation of poly (EHMA) into the wood, although there was void space remaining in some of the lumens of several samples (Fig. 5). We attribute incomplete filling in these cases to physical difficulties associated with our impregnation procedure since most samples obtained showed complete lumen bulking.
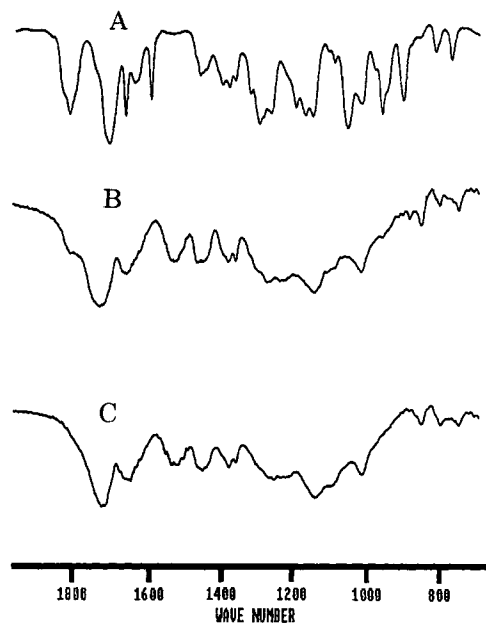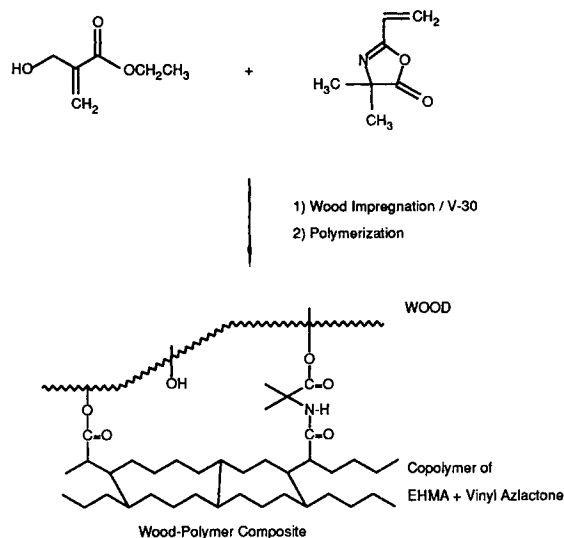

Figure 6 FT-IR spectra of 1 : 1 wt/wt mixture of EHMA and vinyl azlactone monomers (A), copolymer polymerized at 80°C for 24 h with V-30 (B), and copolymer subsequently treated at 120°C for 20 h (C).

Scheme 2 Wood impregnation with EHMA and vinyl azlactone in the presence of V-30.

Wood Impregnation with EHMA and Vinyl Azlactone

We next examined the comonomer system containing EHMA and vinyl azlactone in the expectation of improving, first, incorporation of the monomers and copolymers into the cell wall (compared to other vinyl monomers) and, second, the physical properties of the composite through enhanced interaction of the copolymer with the cell wall components and the lumen-filling matrix through better polymer–polymer interaction and crosslinking. Radical polymerization and copolymerization of vinyl azlactone produces polymers containing pendant azlactone groups that can easily react through ring-opening by nucleophiles to form derivatives containing amide plus ester, thioester, or a second amide linkage (depending on the nucleophile). We wished to examine the possibility of forming rigid materials by polymerizing vinyl azlactone with EHMA followed by thermally induced intermolecular attack of the hydroxyl groups of EHMA to give highly crosslinked products.

Model studies involved 1 : 1 EHMA–vinyl azlactone copolymerizations (not in wood composites) that resulted in strong, clear, and crosslinked polymers after complete conversion to copolymer at 80°C. While ring-opening of azlactones by nucleophiles generally requires the presence of base or acid catalyst,[7] we found that during the copolymerization of EHMA and vinyl azlactone at 80°C, the ring-opening reaction through attack by hydroxyl groups occurred spontaneously.[10] As shown in Figure 6, the

IR absorption band around 1810 cm^{-1} of the cyclic ester group of azlactone almost disappeared after heating at 80°C for 24 h. Thermal treatment at 120°C for an additional 20 h gave product that did not show any residual azlactone groups (Fig. 6), indicating essentially complete reaction.

This comonomer system was used for wood impregnation to obtain wood–polymer composites for evaluation of dimensional stability, impact strength, and compression modulus compared to untreated wood (Scheme 2). Impregnation with various feed ratios of EHMA and vinyl azlactone were carried out at 50°C for 2 h in the presence of 1.5–3 mol % of V-30 initiator. Polymerization at 80°C for 72 h gave wood–polymer composites with high impreg-

nation yields as measured by % wt gain after final cure and drying (Table III).

As shown in Table III, final impregnation yields before polymerization were dependent on the amount of vinyl azlactone in the monomer mixture. The maximum impregnation and weight gain in the intermediate and cured composites were obtained with an equal weight ratio of vinyl azlactone and EHMA. Weight losses of impregnated monomers during polymerization were also dependent on the amount of EHMA in the monomer solution. Roughly comparable values of final weight gain (after cure) were observed for azlactone contents of 25% and higher. The higher weight loss of impregnated monomers obtained for lower vinyl azlactone con-

Table III   Typical Southern Pine Impregnation Results with EHMA and Vinyl Azlactone Using 1.5 mol % of V-30 Initiator

Sample	% Azlactones[a]	Dried Wood[b]	Impregnated Wood[c]	Cured Composite[d]
40a	75%	W = 2.07 g V = 3.96 cm^3 d = 0.52	4.32 g	4.30 g (ΔW = 107.7%) 3.96 cm^3 (ΔV = −2.5%) 1.09 (Δd = 95.5%)
40b	75%	W = 2.01 g V = 3.96 cm^3 d = 0.51	4.29 g	4.25 g (ΔW = 111.4%) 4.00 cm^3 (ΔV = −2.2%) 1.06 (Δd = 98.5%)
40c	50%	W = 2.00 g V = 3.98 cm^3 d = 0.50	4.50 g	4.41 g (ΔW = 120.5%) 4.05 cm^3 (ΔV = −1.9%) 1.09 (Δd = 103.5%)
40d	50%	W = 2.04 g V = 4.01 cm^3 d = 0.51	4.52 g	4.48 g (ΔW = 119.6%) 4.05 cm^3 (ΔV = −2.1%) 1.11 (Δd = 104.2%)
40e	25%	W = 1.98 g V = 3.94 cm^3 d = 0.50	4.28 g	4.07 g (ΔW = 105.6%) 4.18 cm^3 (ΔV = 1.5%) 0.97 (Δd = 87.4%)
40f	25%	W = 2.07 g V = 4.02 cm^3 d = 0.52	4.39 g	4.16 g (ΔW = 101.0%) 4.25 cm^3 (ΔV = 2.8%) 0.98 (Δd = 81.5%)
40g	10%	W = 2.12 g V = 3.90 cm^3 d = 0.54	4.12 g	3.82 g (ΔW = 80.2%) 4.18 cm^3 (ΔV = 4.0%) 0.91 (Δd = 57.0%)
40h	10%	W = 2.11 g V = 3.85 cm^3 d = 0.55	4.11 g	3.77 g (ΔW = 78.7%) 4.17 cm^3 (ΔV = 2.3%) 0.90 (Δd = 58.8%)
40i	5%	W = 1.96 g V = 3.93 cm^3 d = 0.50	4.00 g	3.57 g (ΔW = 82.1%) 4.28 cm^3 (ΔV = 3.9%) 0.83 (Δd = 61.3%)
40j	5%	W = 1.99 g V = 3.97 cm^3 d = 0.50	4.00 g	3.57 g (ΔW = 79.4%) 4.14 cm^3 (ΔV = 0.3%) 0.86 (Δd = 64.0%)

[a] Amount of vinyl azlactone in total comonomer solution by weight.
[b] Southern pine (1 × 1 × 0.25″, end grain) after drying at 105°C for 12 h.
[c] Impregnated at 50°C for 2 h under vacuum (3 mmHg).
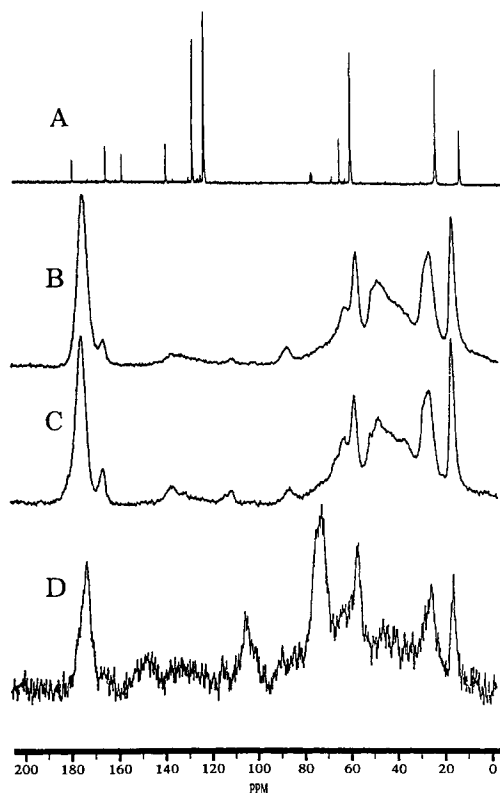[d] Polymerized at 80°C for 72 h, and then at 115°C for 24 h.

Figure 7   Solution ^{13}C NMR spectrum (in CDCl$_3$) of 1 : 1 mixture of EHMA and vinyl azlactone monomers (A), and ^{13}C CP/MAS spectra of 1 : 1 copolymers (B, polymerized at 80°C for 24 h; C, thermally treated at 120°C for 20 h), and wood impregnated with 1 : 1 weight ratio of EHMA and vinyl azlactone and heated at 80°C for 72 h (D).

tent (higher EHMA content) may be related to transesterification involving ester and hydroxyl groups of EHMA with each other and with wood components involving loss of ethyl alcohol during both impregnation and final cure processes.

Solution and solid-state ^{13}C NMR spectroscopy were used to characterize pure copolymers and wood–polymer composites (Fig. 7; see Fig. 1 for the spectrum of untreated wood). Disappearance of peaks around 123, 124, 128, and 140 ppm for double bond carbons of the monomers provides evidence for complete polymerization. Disappearance of peaks around 180 ppm for lactone carbons and 158 ppm for imino carbons of azlactone show that ring-opening reaction was essentially completed during polymerization even without added catalyst. These results are similar to those obtained from the neat copolymerization of vinyl azlactone and EHMA. ^{13}C CP/MAS NMR spectra of wood–polymer composites contained characteristic carbon peaks for ring-opened vinyl azlactone groups (24 ppm for CH$_3$), EHMA ester moieties (14.3 ppm for CH$_3$ and 174 ppm for ester carbons), and wood (56, 72, and 105 ppm for cellulose carbons).

Interestingly, DSC thermograms of wood–polymer composites polymerized at 80°C for 72 h all showed small exotherms at around 155°C (see Fig. 8). However, these transitions essentially disappeared for all the composites after subsequent thermal treatment at 115°C for 24 h. The ^{13}C CP/MAS spectra of these thermally treated samples showed a decrease in the peak intensity around 14 ppm
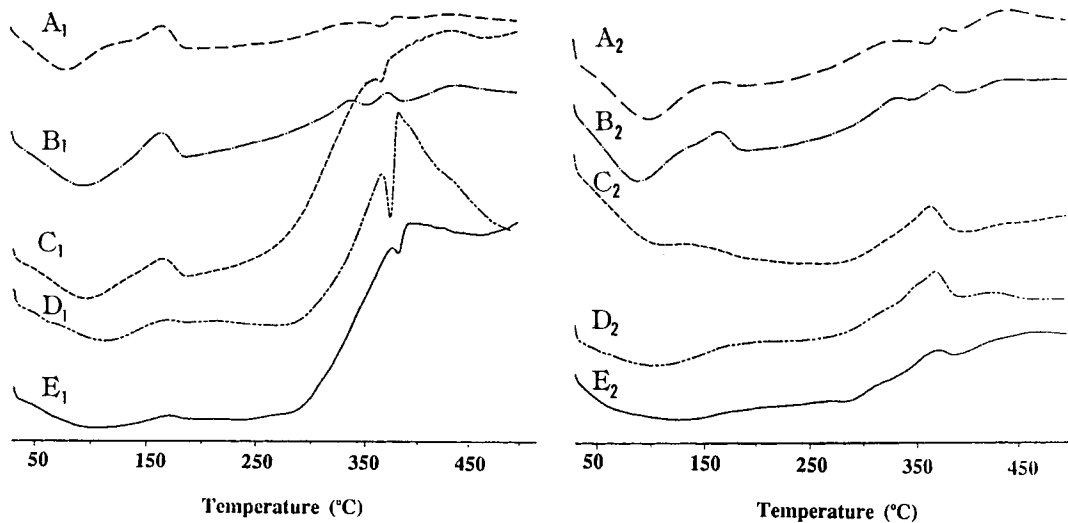

Figure 8   DSC thermograms of wood samples impregnated with EHMA and increasing amounts of vinyl azlactone: A, 5%; B, 10%; C, 25%; D, 50%; E, 75% (subscript 1 denotes wood samples polymerized at 80°C for 72 h, and subscript 2 denotes samples subsequently heated at 115°C for 20 h).
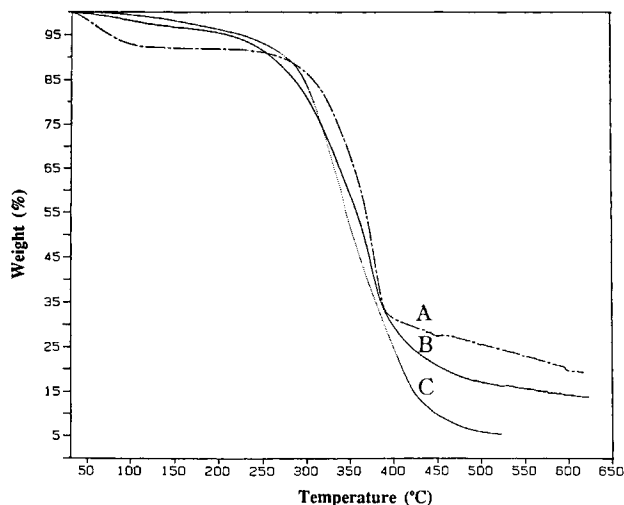
Figure 9 TGA thermograms of A: untreated wood; B: wood impregnated with 1 : 1 weight ratio of EHMA and vinyl azlactone (120% polymer uptake); and C: copolymer of 1 : 1 wt/wt EHMA and vinyl azlactone.

Figure 10 Swelling of wood–polymer composites measured with the water soaking test; A: untreated wood oven dried at 105°C for 12 h; and wood impregnated with EHMA and various amounts of vinyl azlactone: B, 10 wt %; C, 25 wt %; D, 50 wt %; E, 75 wt % vinyl azlactone.

(methyl carbon of the ester group), probably due to transesterification with partial loss of the ester groups. The region between 275–330°C in the DSC thermograms corresponds to depolymerization and decomposition as shown by rapid weight loss in the TGA plots (Fig. 9) for both wood and the composites.

The water soaking test used earlier to determine the WRE of wood–poly(EHMA) system was also applied to the wood samples impregnated with EHMA and vinyl azlactone. Most samples showed excellent improvement in water repellency based on either water uptake or dimensional change. The data in Table IV and Figure 10 indicates that vinyl azlactone may play an important role in improving water repellency. Increasing amounts (up to 75 wt %) of vinyl azlactone in the monomer mixture led to increases in the WRE value up to 98%.
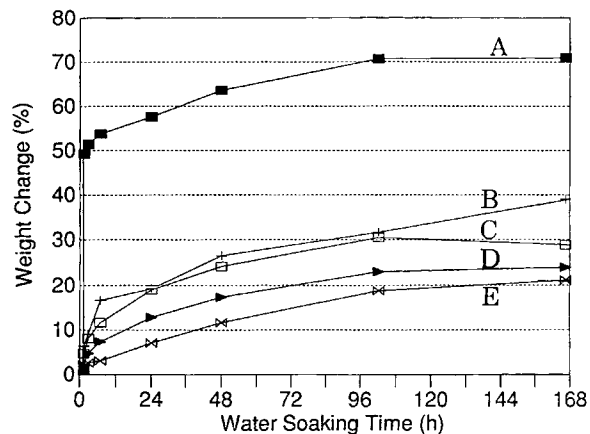
In contrast to water repellency (which is a measure of *rapid* moisture uptake), dimensional stability measures the *equilibrium* swelling with water. As shown in Table V, the ASE values for wood–polymer composites impregnated with EHMA and various ratios of vinyl azlactone varied randomly with the amount of vinyl azlactone.

Most samples showed significant gain in antiswell efficiency, indicating improved resistance to swelling on long-term exposure to water. Strangely, the wood sample impregnated with 25 : 75 EHMA–vinyl azlactone had a negative ASE value (−4.19). The reason for this decreased performance may be that some reaction took place of absorbed water with unopened azlactone rings in the impregnated copolymers. Such a reaction would generate pendent carboxylic acid groups that enhance further water uptake.

The impact strengths of impregnated wood samples were compared with that of untreated wood. As

Table IV Water-Repellent Effectiveness of Wood Samples Impregnated with EHMA and Various Ratios of Vinyl Azlactone in the Presence of 3 mol % V-30

	WRE	
Sample	By Water Uptake	By Volume Change
Wood + 90 : 10 EHMA–vinyl azlactone 95.2% wt polymer gain	86.93	85.54
Wood + 75 : 25 EHMA–vinyl azlactone 103.3% wt polymer gain	88.98	90.63
Wood + 50 : 50 EHMA–vinyl azlactone 106.2% wt polymer gain	93.02	93.95
Wood + 25 : 75 EHMA–vinyl azlactone 99.8% wt polymer gain	97.95	94.99

1 h immersion in water at 25°C

Table V ASE of Wood Impregnated with EHMA and Vinyl Azlactone after 7 d Immersion in Water at 25°C

Samples[a]	Swelling Coefficient (S)	ASE
Untreated wood[b]	14.3	—
Wood + 90 : 10 EHMA–vinyl azlactone	8.5	40.9
Wood + 75 : 25 EHMA–vinyl azlactone	11.1	22.6
Wood + 50 : 50 EHMA–vinyl azlactone	9.4	34.4
Wood + 25 : 75 EHMA–vinyl azlactone	14.9	−4.2

[a] Same samples as indicated in Table IV.
[b] Oven-dried at 105°C for 24 h.

shown in Table VI, the impact strength of all samples were improved compared to wood with a maximum (54%) seen for the 75 : 25 mixture of EHMA and vinyl azlactone. However, the amount of vinyl azlactone did not much affect the amount of improvement, and variations between compositions are

well within the standard deviations measured. The coefficient of variation (COV, equal to standard deviation divided by the average value) is less than 25.2% for the 6 samples measured for each composition. This is similar to experimental data reported with 50 samples of untreated wood (25% COV).[11]

Longitudinal toughness from the buckled plate test in Table VII for wood–polymer composites showed the strong reinforcing effect of the EHMA–vinyl azlactone copolymers. Increasing vinyl azlactone content led to increasing longitudinal compression modulus up to 24 GPa (45% improvement) compared to untreated wood. COVs of these measurement with 7 samples were comparable to those of experimental data for a different but related measurement obtained with 50 samples (28% COV).[11]

SEM microphotographs of these wood–polymer composites showed very high, uniform filling by the EHMA–vinyl azlactone copolymers of the lumen of wood. The surface of most composite samples (Fig. 11A) appeared continuous and the interior (Fig. 11B) of the samples showed almost no void space. In a few samples, however; volume shrinkage on polymerization and loss of monomer or ethanol during cure led to hollow cylinders partially filling the lumen (Fig. 11C). We believe these results indicate

Table VI Comparison of Relative Impact Strengths of Wood Samples Impregnated with EHMA and Vinyl Azlactone

Wood Samples	Relative Impact Strength[a]	COV (%)
Untreated wood[b]	0.45 ± 0.08	17
Wood + 75 : 25 EHMA–vinyl azlactone 65.7% wt polymer gain	0.69 ± 0.07 (+54%)	10
Wood + 50 : 50 EHMA–vinyl azlactone 70.1% wt polymer gain	0.62 ± 0.12 (+38%)	19
Wood + 25 : 75 EHMA–vinyl azlactone 75.7% wt polymer gain	0.64 ± 0.16 (+43%)	25

[a] Average data from six samples.
[b] Oven-dried at 105°C for 12 h.

Table VII Comparison of Longitudinal Toughness of Wood Samples Impregnated with EHMA and Vinyl Azlactone

Wood Sample (EHMA : Vinyl Azlactone)	Longitudinal Toughness[a]				
	Force (N)	COV (%)	Force/s.g.	E[b] (GPa)	ΔE
Untreated wood[c]	1060 ± 230	21	1990 ± 350	16.4	—
75 : 25 EHMA–vinyl azlactone 58.6% wt polymer gain	1350 ± 360	27	1400 ± 310	20.9	27%
50 : 50 EHMA–vinyl azlactone 65.4% wt polymer gain	1370 ± 410	30	1550 ± 520	21.2	29%
25 : 75 EHMA–vinyl azlactone 64.2% wt polymer gain	1530 ± 480	31	1640 ± 520	23.7	45%

[a] 3 mol % V-30 initiator, cured at 80°C for 72 h. Average data from seven samples; s.g. is specific gravity in column 3.
[b] Average compression modulus calculated from eq. (4).
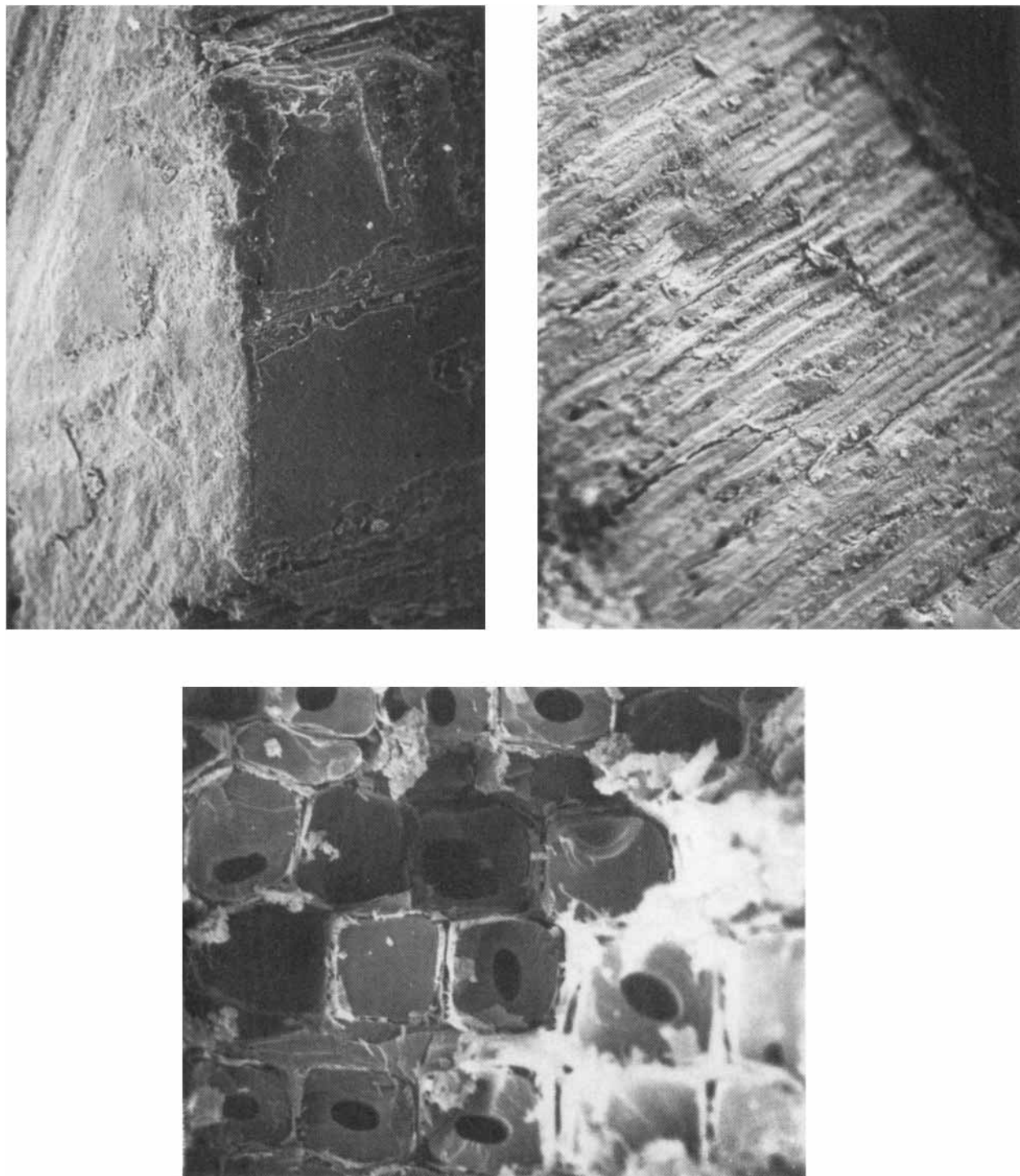[c] Nondried wood sample.

Figure 11 SEM photomicrographs of wood impregnated with 1 : 1 weight ratio of EHMA and vinyl azlactone; upper left picture, surface at 75×; upper right, interior at 136×; and lower, region with partially filled lumen at 700×.

that uniform lumen filling is readily attainable and good interaction of the lumen component with the cell wall material has been achieved with these systems.

CONCLUSIONS

Vacuum impregnation of Southern pine samples of various dimensions and bulk densities was carried

out using a multifunctional monomer EHMA and several coreactants. With 5 mol % of a fluorinated or nonfluorinated diacrylate crosslinking agent and V-30 initiator, thermally cured composites showed water repellency improvements up to 89% at 105% impregnation by weight.

Greater interaction of polymer and wood was obtained by impregnation with EHMA and another multifunctional monomer, vinyl azlactone. Composite formation using various ratios of vinyl azlactone to EHMA was carried out under similar conditions to that of EHMA. Water-repellency values of the wood–polymer composites were greatly improved with values ranging from 85–98%. Maximum antiswell efficiency (41% ASE) was obtained on impregnation with 9 : 1 w/w EHMA and vinyl azlactone, while other compositions gave ASE values from −4.19–34%. Improvements of 38–54% in impact strength and 27–44% in compression modulus were also achieved. SEM photomicrographs confirmed excellent impregnation with uniform lumen filling and good cell wall adhesion.

REFERENCES

1. R. M. Rowell and P. Peggy, *USDA, Forest Products Laboratory Gen. Tech. Rep. FPL-GTR-55.*, Madison, WI, (1987).
2. R. M. Rowell, A.-M. Tillman, and R. Simmonsen, *J. Wood. Chem. Tech.*, **6**(3), 427–448 (1986).
3. R. M. Rowell, *Wood Sci.*, **10**(4), 193–197 (1978).
4. K. I. Brebner, M. H. Schneider, and R. T. Jones, *Forest Prod. J.*, **38**(4), 55–58 (1988).
5. S. Lee, S. F. Thames, and L. J. Mathias, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 525–549 (1990).
6. A. K. Mukerjee and P. Kumar, *Heterocycles*, **16**, 1995 (1981).
7. J. K. Rasmussen, S. M. Heilmann, F. Palensky, H. K. Smith, Jr., and K. C. Melancon, *Makromol. Chem., Rap. Comm.*, **5**, 67–70 (1984).
8. L. J. Mathias and S. H. Kusefoglu, *Macromolecules*, **20**, 2326 (1987).
9. R. L. Brady, R. S. Porter, and J. A. Donovan, *J. Mater. Sci.*, **24**, 4138–4143 (1989).
10. L. J. Mathias and M. Jeno, *J. Polym. Sci., Polym. Chem.*, to appear.
11. U.S. Department of Agriculture, Forest Services, "Wood Handbook; Wood as an Engineering Material," USDA Tech. Bull. No. 282, Washington, D.C., p. 88, 1932.