Wood–Polymer Composites Made with Acrylic Monomers, Isocyanate, and Maleic Anhydride

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ABSTRACT: Wood could provide better service in some applications if it were harder and more dimensionally stable. In this study, wood–polymer composites (WPC) made with different chemical combinations were evaluated for dimensional stability, ability to exclude water vapor and liquid water, and hardness. Pine, maple, and oak solid wood were combined with different combinations of hexanediol diacrylate, hydroxyethyl methacrylate, hexamethylene diisocyanate, and maleic anhydride. Treatment slowed the rates of water vapor and liquid water absorption. Although the resultant dimensional stability was not permanent, the rate of swelling of WPC specimens was less than that of unmodified wood specimens. In addition, WPC were harder than unmodified wood. The chemical combination of hexanediol diacrylate, hydroxyethyl methacrylate, and hexamethylene diisocyanate greatly decreased wetting and penetration of water into the wood. This chemical combination also gave the hardest and most dimensionally stable WPC. In general, WPC prepared using hydroxyethyl methacrylate were harder than specimens made without hydroxyethyl methacrylate and excluded water and moisture more effectively. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2493–2505, 1999

Key words: wood–polymer composite; water repellency; moisture exclusion; dimensional stability

INTRODUCTION

Natural beauty, durability, and versatility make wood the preferred material for many uses. In most circumstances, it is unnecessary to improve the properties of wood; but for some uses, better service could be obtained if wood were harder and more dimensionally stable. The density and hardness of wood can be increased by filling the wood voids with resins. Wood has been impregnated with water-soluble phenolic resins.[1,2] This treatment improves compressive strength properties and moisture-related shrinking and swelling. Phenolic resins penetrate and bulk the cell wall structure, preventing shrinkage of the wood upon drying.

Other researchers[3–11] have tried to dimensionally stabilize wood by treating it with acrylate or methacrylate monomers. Their success has been limited. Most efforts decreased the rate of dimensional change and the rate of swelling but did not increase dimensional stability. Most attempts to stabilize wood using monomers have failed because the monomers did not penetrate the cell walls or react with the wood.

Approaches taken to improve the dimensional stability of wood–polymer composites (WPC) have included (1) preswelling the wood with polar solvents and/or mixing polar solvents with mono-

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Table I Monomer Solutions for Wood–Polymer Composites

Monomer	Ratio (w : w)
HDDA	—
HDDA–DesN75	3 : 1
HDDA–MAn	3 : 1
HDDA–HEMA–MAn	1 : 2 : 1
HEMA–DesN75–MAn	2 : 1 : 1
HDDA–DesN75–MAn	2 : 1 : 1
HDDA–HEMA	1 : 1
HDDA–HEMA–DesN75	1 : 2 : 1
Control (untreated)	—

mers to swell the wood,[12,13] (2) swelling the wood with polar monomers to aid penetration into cell walls,[14] and (3) mixing reactive chemicals, such as an isocyanate, with the monomer for reaction with the wood to make it more hygrophobic.[15]

The polar monomers 2-hydroxyethyl methacrylate (HEMA) and glycidyl methacrylate (GMA) were added to methyl methacrylate (MMA) and the effects on the properties of the treated wood examined.[16,17] The WPC made from mixtures of MMA and HEMA or GMA had greater dimensional stability in high relative humidity and in water compared to WPC made from MMA without HEMA or GMA. Antiswell efficiency (ASE) was as high as 72%.

The objectives of our research were to evaluate the ability of combinations of hexanediol diacrylate, hydroxyethyl methacrylate, hexamethylene diisocyanate, and maleic anhydride to increase the density, hardness, water vapor exclusion, water repellency, and dimensional stability of wood.

MATERIALS

Description of Specimens

Southern Pine (species group), maple (*Acer saccharum*), and Red Oak (species group) specimens (2.5 by 2.5 by 0.6 cm, radial by tangential by longitudinal) were cut with growth rings parallel to an edge.

Treatment Chemicals

The chemical formulations were mixtures of acrylic monomers and an anhydride and/or an isocyanate (Table I). The monomers were hexanediol diacrylate (HDDA) and hydroxyethyl methacrylate (HEMA). Maleic anhydride (MAn) was used because it reacts with hydroxyl groups and with double bonds in acrylic monomers to form polymers. The isocyanate was hexamethylene diisocyanate (Desmodur N75 [DesN75]).* Chemicals were mixed by weight in the ratios shown in Table I. We used 0.5% 2,2′-azobis-(2-methylbutyronitrile) (Vazo 67), based on the weight of acrylate, to catalyze the polymerization reactions.

METHODS

Treatment of Specimens

The WPC specimens were dried for 18 h in an oven at 105°C, cooled 1 h in a desiccator over anhydrous calcium sulfate, and then weighed and measured in radial and tangential directions. Duplicate specimens of each wood species were placed in a container inside a vacuum chamber. The chamber and specimens were degassed using a pump to draw a vacuum to about −90 kPa. The vacuum was continued for 30 min, and the treating solution was then drawn by the vacuum into the chamber to cover the specimens. The vacuum was continued for an additional 10 min and then released to return the chamber to atmospheric pressure. After 18 h in treating chemicals at 22°C, specimens were removed from the chamber, and excess chemicals were wiped from their surfaces. Specimens were then placed between release paper and aluminum plates and cured in a press at 120°C and 68.9 kPa (10 lb/in^2) pressure for 10 min. Post-polymerization weights were measured for all specimens after drying at 105°C and cooling for 1 h in a desiccator over anhydrous calcium sulfate. Radial and tangential dimensions were measured. The percentage of polymer loading was calculated from dry weights of treated and untreated specimens.

Water Vapor Exclusion

Dry specimens were weighed, conditioned at 27°C and 30% relative humidity (RH), and then reweighed after reaching equilibrium moisture content. Specimens were then subjected to 90% RH

* The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

at 27°C and weighed after 2, 4, 6, 24, 48, 72, 96, and 168 h and 90 days. Moisture was calculated as the percentage of moisture based on the dry weight (weight of wood in WPC) of untreated specimen.

Water Exclusion

Specimens conditioned at 27°C, 30% RH were placed in distilled water and weighed after 10, 30, 60, and 90 min and 2, 3, 4, 5, 6, 7, 8, 24, and

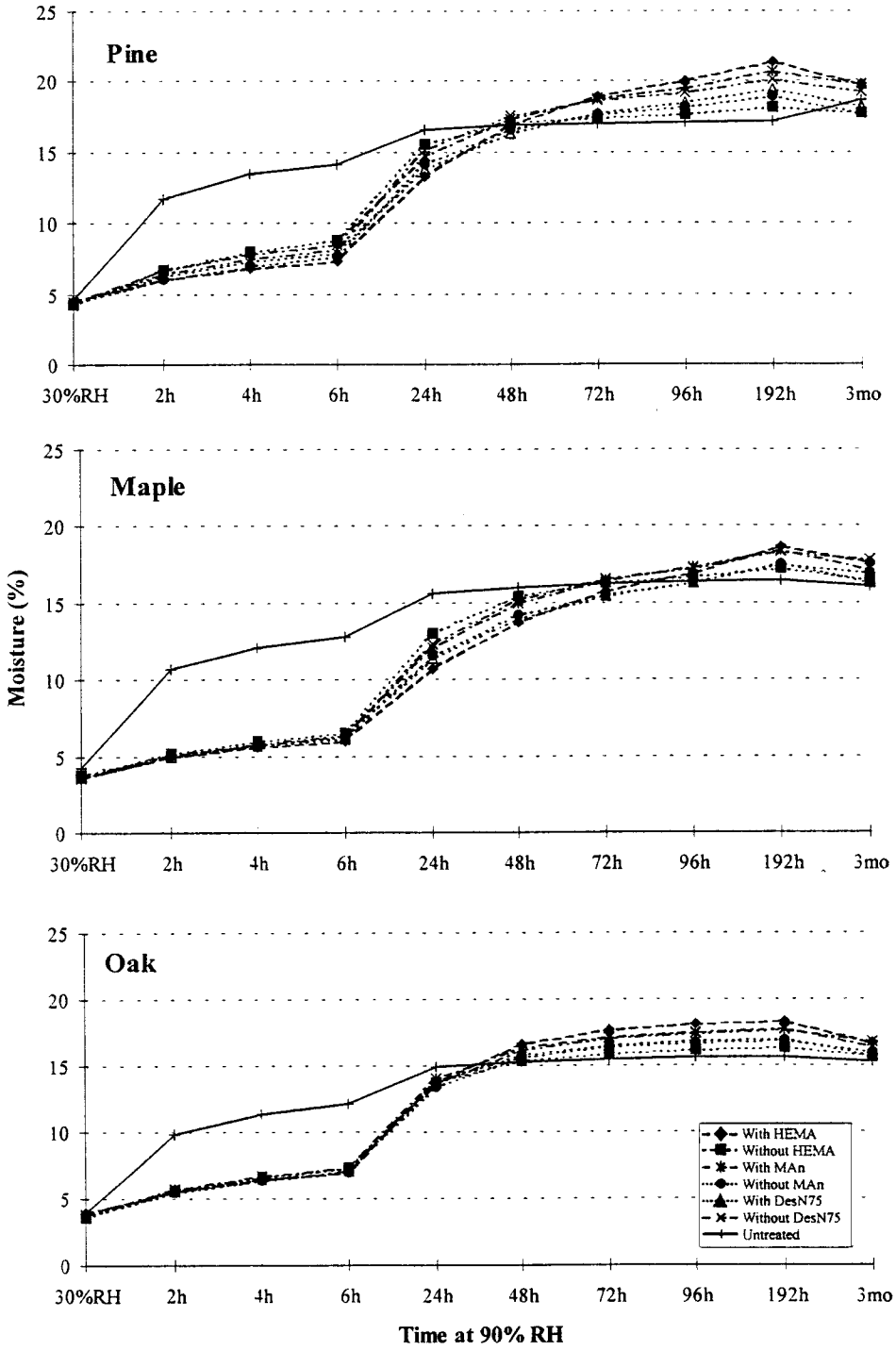

Figure 1 Weight gain of WPC from moisture sorption at 27°C and 90% relative humidity.

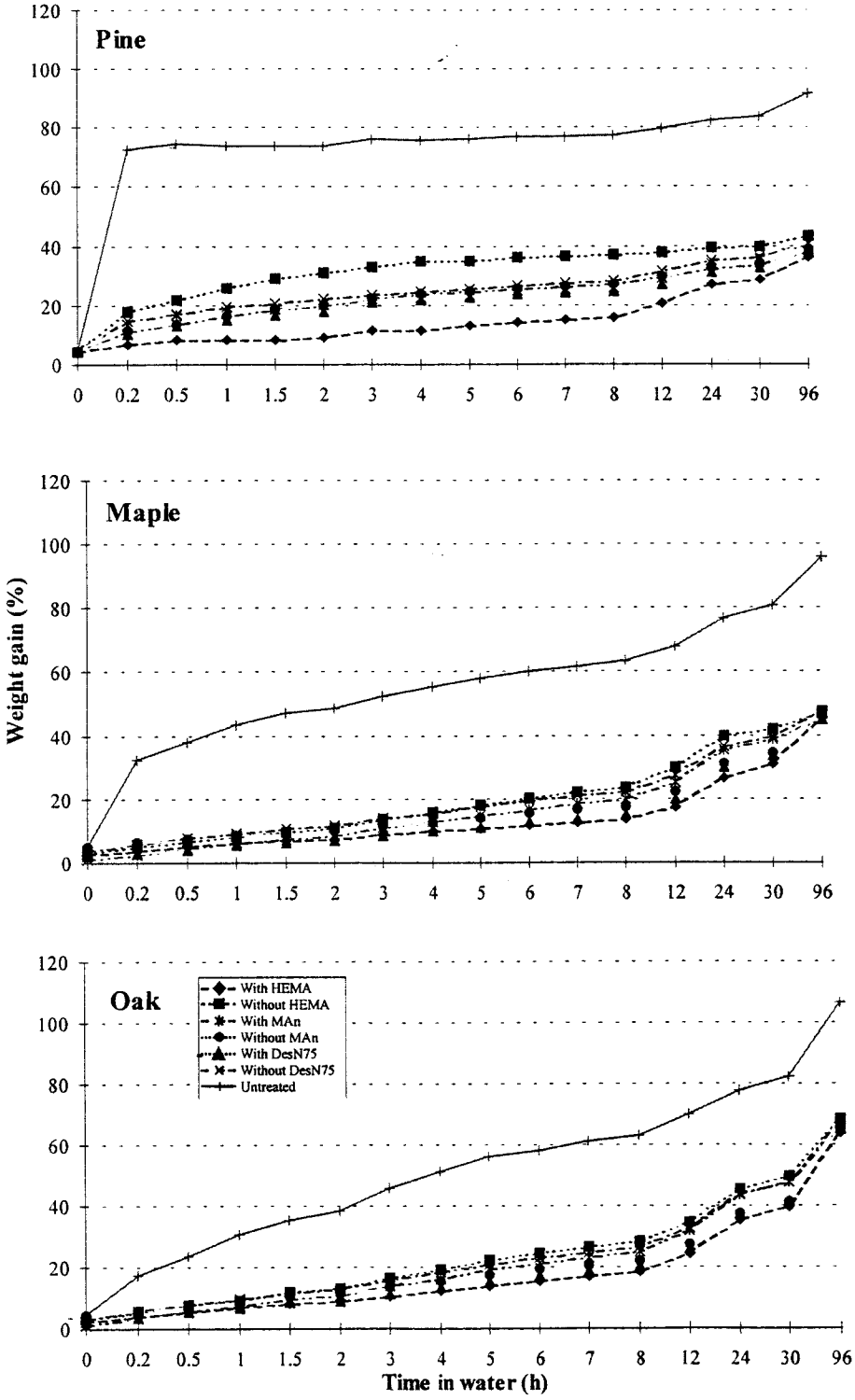

Figure 2 Weight gain of WPC in water.

96 h. The amount of water in the specimens was calculated as the percentage of the dry weight of untreated specimens. Cubes (5 mm) cut from specimens were soaked for 24 h in an aqueous solution of 0.3% methylene blue dye and 0.3% toluidine blue dye by weight in water. The color

Table II Weight Gain of Wood–Polymer Composites from Water Vapor

Treatment (Ratio)	Weight Gain (%)[a] at Various Times at 90% RH					
	24 h	48 h	72 h	96 h	192 h	3 mo
Pine:						
HDDA–DesN75 (3 : 1)	14.5	16.2	16.6	16.8	17.1	16.4
HDDA	14.6	16.4	16.7	16.9	17.3	16.7
HDDA–MAn (3 : 1)	16.2	17.6	18.0	18.4	19.2	18.3
HDDA–HEMA–MAn (1 : 2 : 1)	13.5	17.6	20.0	21.3	23.3	22.7
HEMA–DesN75–MAn (2 : 1 : 1)	12.3	16.2	18.6	19.8	21.0	18.4
HDDA–DesN75–MAn (2 : 1 : 1)	17.1	18.1	18.4	18.7	19.2	19.6
HDDA–HEMA (1 : 1)	16.3	19.0	19.8	20.2	20.7	19.4
HDDA–HEMA–DesN75 (1 : 2 : 1)	11.3	15.0	17.4	18.8	20.6	18.6
Control (untreated)	16.6	16.9	17.0	17.1	17.2	18.7
Maple:						
HDDA–DesN75 (3 : 1)	12.0	14.6	15.5	15.9	16.5	15.4
HDDA	12.9	15.3	16.1	16.4	16.8	16.5
HDDA–MAn (3 : 1)	12.7	15.6	17.7	17.3	18.1	17.5
HDDA–HEMA–MAn (1 : 2 : 1)	11.2	14.8	16.9	18.0	19.5	18.7
HEMA–DesN75–MAn (2 : 1 : 1)	10.1	13.4	15.6	16.9	18.5	16.1
HDDA–DesN75–MAn (2 : 1 : 1)	14.4	16.2	16.7	17.0	17.4	16.5
HDDA–HEMA (1 : 1)	12.4	15.1	16.5	17.4	18.8	18.4
HDDA–HEMA–DesN75 (1 : 2 : 1)	9.1	11.8	13.9	15.4	17.8	17.3
Control (untreated)	15.6	16.0	16.2	16.4	16.4	16.1
Oak:						
HDDA–DesN75 (3 : 1)	13.3	14.8	15.3	15.5	15.6	14.9
HDDA	13.3	15.0	15.5	15.8	15.8	15.4
HDDA–MAn (3 : 1)	13.8	15.8	16.5	16.8	17.2	16.4
HDDA–HEMA–MAn (1 : 2 : 1)	13.3	16.9	18.4	19.0	19.5	18.2
HEMA–DesN75–MAn (2 : 1 : 1)	14.5	16.9	17.5	17.8	17.7	15.2
HDDA–DesN75–MAn (2 : 1 : 1)	15.6	15.8	16.2	16.5	16.6	16.2
HDDA–HEMA (1 : 1)	14.4	16.9	17.8	18.1	18.2	17.0
HDDA–HEMA–DesN75 (1 : 2 : 1)	12.6	15.9	17.1	17.5	17.8	16.6
Control (untreated)	14.9	15.3	15.4	15.6	15.6	15.3

[a] Percentage of moisture in specimens based on untreated dry weight.

of the specimens was used to indicate the extent of wetting by and penetration of water.

Dimensional Stability

To measure swelling in water vapor, specimens were first dried at 105°C and measured in radial and tangential directions. We assumed that the longitudinal dimension remained constant. Next, specimens were conditioned to equilibrium moisture content at 27°C, 30% RH and remeasured. Finally, specimens were subjected to 27°C, 90% RH and measured after 2, 4, 6, 24, 48, 72, 96, and 168 h and 90 days. Radial and tangential measurements were used to calculate volumetric swelling at these specified intervals. Swelling was considered change in volume expressed as percentage of the volume of the dry treated specimen.

To measure swelling in liquid water, specimens conditioned at 27°C, 30% RH were placed in distilled water at room temperature and dimensions were measured at 10, 30, 60, and 90 min and 2, 3, 4, 5, 6, 7, 8, 24, and 96 h. Swelling was considered change in volume expressed as the percentage of volume of the dry treated specimen.

Hardness

Specimen hardness was measured using a Rockwell hardness tester with a 0.25-in (6.35-mm) ball indenter and 60 kgf (588.4*N*) of force (Rockwell

Table III Water Gain in Wood–Polymer Composites

Treatment (Ratio)	Water Gain (%) at Various Times[a]									
	0.5 h	1 h	2 h	4 h	6 h	8 h	12 h	24 h	30 h	96 h
Pine:										
HDDA–DesN75 (3 : 1)	14	18	27	35	36	37	39	40	40	43
HDDA	22	28	35	36	37	37	38	39	39	41
HDDA–MAn (3 : 1)	27	29	32	34	35	35	36	38	38	43
HDDA–HEMA–MAn (1 : 2 : 1)	9	9	11	13	15	17	21	28	30	39
HEMA–DesN75–MAn (2 : 1 : 1)	5	5	8	10	13	15	20	29	31	36
HDDA–DesN75–MAn (2 : 1 : 1)	26	29	31	35	37	38	39	41	42	46
HDDA–HEMA (1 : 1)	11	12	12	17	21	24	30	36	37	40
HDDA–HEMA–DesN75 (1 : 2 : 1)	7	7	6	7	9	9	11	15	17	30
Control (untreated)	74	74	74	76	77	77	80	83	84	92
Maple:										
HDDA–DesN75 (3 : 1)	5	7	8	11	14	16	22	34	39	48
HDDA	9	11	13	17	22	26	33	42	43	49
HDDA–MAn (3 : 1)	8	11	14	21	27	31	36	42	43	45
HDDA–HEMA–MAn (1 : 2 : 1)	5	6	7	10	12	14	18	29	34	45
HEMA–DesN75–MAn (2 : 1 : 1)	1	3	4	7	10	12	17	30	35	43
HDDA–DesN75–MAn (2 : 1 : 1)	4	6	9	13	18	22	29	41	44	47
HDDA–HEMA (1 : 1)	9	10	12	14	16	18	23	33	38	51
HDDA–HEMA–DesN75 (1 : 2 : 1)	6	7	7	8	9	9	11	15	17	42
Control (untreated)	38	44	49	55	60	63	68	77	81	96
Oak:										
HDDA–DesN75 (3 : 1)	6	7	10	14	18	20	26	38	42	69
HDDA	9	12	16	23	28	32	38	48	52	67
HDDA–MAn (3 : 1)	8	10	15	22	28	32	39	49	52	65
HDDA–HEMA–MAn (1 : 2 : 1)	5	7	9	12	16	19	25	37	41	62
HEMA–DesN75–MAn (2 : 1 : 1)	3	5	7	12	16	20	28	40	45	70
HDDA–DesN75–MAn (2 : 1 : 1)	6	8	12	19	25	29	36	47	52	73
HDDA–HEMA (1 : 1)	8	10	12	16	20	23	30	41	45	65
HDDA–HEMA–DesN75 (1 : 2 : 1)	5	6	7	9	10	12	15	24	27	59
Control (untreated)	23	31	39	51	58	63	70	78	82	107

[a] Percentage of water in specimens based on untreated dry weight.

scale L). Specimens were conditioned at 27°C, 65% RH before testing. For pine and oak specimens, hardness of earlywood and latewood of longitudinal, radial, and tangential faces was measured. For maple specimens, it was difficult to distinguish earlywood from latewood on the longitudinal face, so earlywood and latewood were not measured separately.

Electron Microscopy

Electron microscopy was used to examine polymer in longitudinal faces of the wood. We were particularly interested in the extent to which the polymer filled the cells and possible adhe-

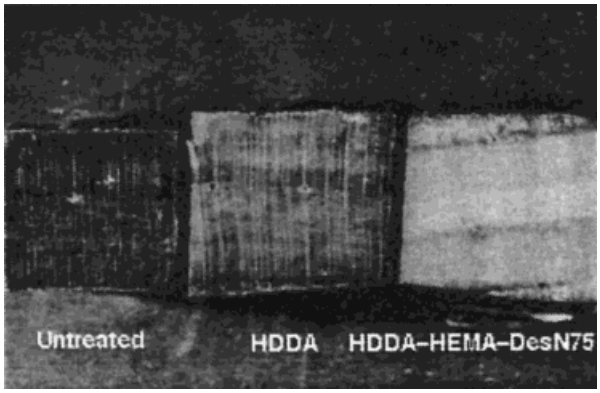

Figure 3 Effect of wetting with aqueous dye solution.

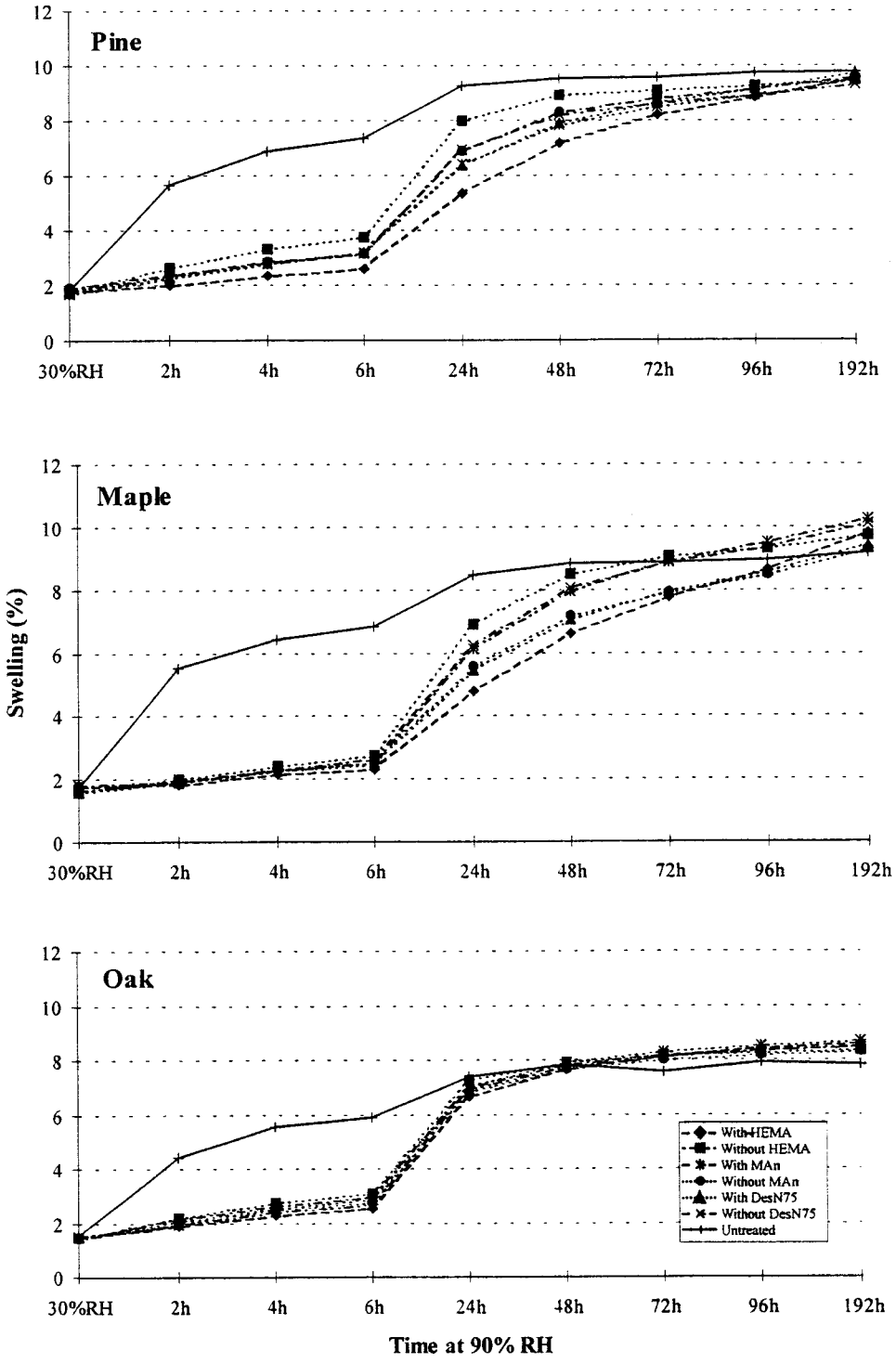

Figure 4 Swelling of WPC conditioned at 27°C and 90% relative humidity.

sion of the polymer to the cell wall. Since some monomers have the potential to penetrate and swell cell walls, we looked for swollen cell walls.

Analysis of Data

Data for each test were evaluated to separate the effects of each component in the monomer mix-

Table IV Volumetric Swelling of Wood–Polymer Composites in Water Vapor[a]

Treatment (Ratio)	Swelling (%) at 90% RH at Various Times					
	24 h	48 h	72 h	96 h	192 h	3 mo
Pine:						
HDDA–DesN75 (3 : 1)	8.3	9.5	9.8	9.9	10.2	9.9
HDDA	7.5	8.7	8.8	9.0	9.3	9.0
HDDA–MAn (3 : 1)	7.8	8.7	8.8	9.0	9.3	9.1
HDDA–HEMA–MAn (1 : 2 : 1)	4.8	6.5	7.4	7.9	8.7	9.2
HEMA–DesN75–MAn (2 : 1 : 1)	4.8	7.3	8.9	9.8	10.7	10.8
HDDA–DesN75–MAn (2 : 1 : 1)	8.3	8.9	8.9	9.1	9.2	8.9
HDDA–HEMA (1 : 1)	7.5	9.0	9.5	9.9	9.9	9.5
HDDA–HEMA–DesN75 (1 : 2 : 1)	4.2	6.0	7.1	7.8	8.8	8.1
Control (untreated)	9.3	9.5	9.6	9.8	9.8	9.6
Maple:						
HDDA–DesN75 (3 : 1)	6.1	7.8	8.3	8.6	9.1	9.0
HDDA	6.7	8.4	8.9	9.0	9.4	9.4
HDDA–MAn (3 : 1)	7.4	9.2	10.2	10.0	11.0	11.0
HDDA–HEMA–MAn (1 : 2 : 1)	5.2	7.4	8.7	9.5	10.5	10.8
HEMA–DesN75–MAn (2 : 1 : 1)	4.4	6.4	8.0	8.9	10.1	10.4
HDDA–DesN75–MAn (2 : 1 : 1)	7.5	8.6	8.9	9.1	9.4	8.8
HDDA–HEMA (1 : 1)	5.7	7.2	7.8	8.5	9.6	9.8
HDDA–HEMA–DesN75 (1 : 2 : 1)	3.8	5.4	6.6	7.6	9.1	9.1
Control (untreated)	8.5	8.8	8.9	8.9	9.2	9.1
Oak:						
HDDA–DesN75 (3 : 1)	7.2	7.8	7.9	8.1	8.1	8.1
HDDA	7.1	7.7	7.9	8.0	8.1	8.0
HDDA–MAn (3 : 1)	7.4	8.2	8.5	8.7	8.8	8.3
HDDA–HEMA–MAn (1 : 2 : 1)	6.4	7.4	8.1	8.5	8.8	9.0
HEMA–DesN75–MAn (2 : 1 : 1)	7.2	7.9	8.4	8.6	8.7	8.6
HDDA–DesN75–MAn (2 : 1 : 1)	7.3	8.0	8.4	8.3	8.4	7.9
HDDA–HEMA (1 : 1)	6.8	7.7	8.0	8.2	8.3	8.3
HDDA–HEMA–DesN75 (1 : 2 : 1)	6.4	7.5	8.1	8.4	8.6	8.2
Control (untreated)	7.4	7.8	7.6	7.9	7.8	7.8

[a] Percentage of swelling of specimens from oven dry to 90% relative humidity.

tures. For example, values for swelling of specimens in water were averaged according to the presence or absence of each ingredient, such as HEMA. Swelling values (eight values) for WPC made with monomer mixtures containing HEMA were averaged; then, swelling values (eight values) for WPC made with monomer mixtures not containing HEMA were averaged. The averaged values (average of eight values per species) were compared to show the effects of each component (HEMA, isocyanate, and maleic anhydride) on specific WPC properties.

In addition to calculations of data averages, data from WPC tests were used to determine which WPC formulations performed best.

RESULTS

Water Vapor Exclusion

The rate at which WPC absorbed water vapor was slower than that of untreated wood. The rate of water vapor absorption (measured by weight gain) appeared to depend on the species of wood and the monomers/polymer used to make the WPC. Approximately 48 h of exposure at 27°C and 90% RH were required for the pine WPC moisture content to equal that of untreated pine, and maple WPC required an average of 72 h for moisture weight gain to approach that of untreated maple (Fig. 1). Oak WPC were less effec-

Table V Volumetric Swelling of Wood–Polymer Composites in Water

Treatment (Ratio)	Swelling (%) at Various Times (h)									
	0.5	1.0	2	4	6	8	12	24	30	96
Pine:										
HDDA–DesN75 (3 : 1)	5	7	12	16	17	17	17	17	17	18
HDDA	8	11	14	15	15	15	15	15	15	15
HDDA–MAn (3 : 1)	9	10	11	12	12	12	12	12	12	12
HDDA–HEMA–MAn (1 : 2 : 1)	4	5	5	6	7	8	9	11	11	12
HEMA–DesN75–MAn (2 : 1 : 1)	4	5	5	6	8	9	11	14	14	14
HDDA–DesN75–MAn (2 : 1 : 1)	8	1	12	13	13	13	13	13	13	14
HDDA–HEMA (1 : 1)	4	5	5	7	9	11	14	16	16	16
HDDA–HEMA–DesN75 (1 : 2 : 1)	2	2	2	3	3	3	4	6	7	13
Control (untreated)	15	15	16	15	16	15	15	16	16	16
Maple:										
HDDA–DesN75 (3 : 1)	3	3	4	5	6	8	10	15	16	17
HDDA	4	4	6	8	1	11	15	17	17	18
HDDA–MAn (3 : 1)	4	5	7	10	12	14	14	15	15	16
HDDA–HEMA–MAn (1 : 2 : 1)	3	4	4	5	5	6	8	12	15	17
HEMA–DesN75–MAn (2 : 1 : 1)	3	3	4	5	6	6	9	13	14	16
HDDA–DesN75–MAn (2 : 1 : 1)	2	2	3	6	8	9	12	14	14	15
HDDA–HEMA (1 : 1)	4	4	5	6	7	8	10	14	16	18
HDDA–HEMA–DesN75 (1 : 2 : 1)	2	2	3	4	3	4	5	6	8	18
Control (untreated)	12	14	15	17	16	16	17	17	17	17
Oak:										
HDDA–DesN75 (3 : 1)	3	3	4	6	8	9	12	14	14	16
HDDA	3	4	6	10	12	13	14	15	15	16
HDDA–MAn (3 : 1)	2	3	5	8	11	12	13	13	14	15
HDDA–HEMA–MAn (1 : 2 : 1)	2	2	3	4	5	7	9	13	13	14
HEMA–DesN75–MAn (2 : 1 : 1)	2	3	4	5	7	9	12	13	14	14
HDDA–DesN75–MAn (2 : 1 : 1)	2	2	4	7	10	11	13	13	14	15
HDDA–HEMA (1 : 1)	3	3	4	5	7	8	11	14	15	16
HDDA–HEMA–DesN75 (1 : 2 : 1)	2	2	3	3	4	5	6	10	12	15
Control (untreated)	6	7	10	13	13	14	14	14	14	15

tive at excluding water vapor than were pine and maple WPC. After 24 h at 90% RH, the moisture weight gain of all oak WPC specimens was nearly the same as that of untreated oak (Fig. 1). Specimens treated with HDDA–HEMA–MAn had higher moisture weight gains than did WPC treated with other monomer mixtures (Table II). None of these monomer–polymer treatments of wood resulted in permanent water vapor excluding properties, but some decreased the rate at which WPC absorbed water vapor well below that of untreated wood.

Water Exclusion

Untreated pine, maple, and oak specimens absorbed 92, 96, and 107% water by dry weight, respectively (Table III). WPC made from pine, maple, and oak absorbed much less water than did untreated wood. Filling the voids of wood with polymer decreases the space available to hold water. The polymer hinders the access of water to wood cell walls, but water does eventually diffuse into the wood. Of the three species, pine absorbed the least water, and oak absorbed the most water. WPC made with HDDA–HEMA–DesN75 had the slowest rate of water absorption, up to 96 h in water; these specimens absorbed the least water compared to other WPC (Table III). The presence or absence of HEMA in the monomer formulation affected the amount of water absorbed by pine WPC (Fig. 2). WPC prepared without HEMA on

the average had the greatest increase in weight from water sorption, and WPC prepared from monomer mixtures containing HEMA absorbed the least water. The effect of HEMA on water sorption was similar in maple and oak WPC but not as great as the effect in pine (Fig. 2).

The 5-mm untreated cubes and WPC cubes soaked for 24 h in an aqueous dye solution showed a marked difference in water penetration (Fig. 3). The solution dyed the untreated wood uniformly. In specimens made with HDDA, the wood was dyed, but not the polymer. Specimens made with

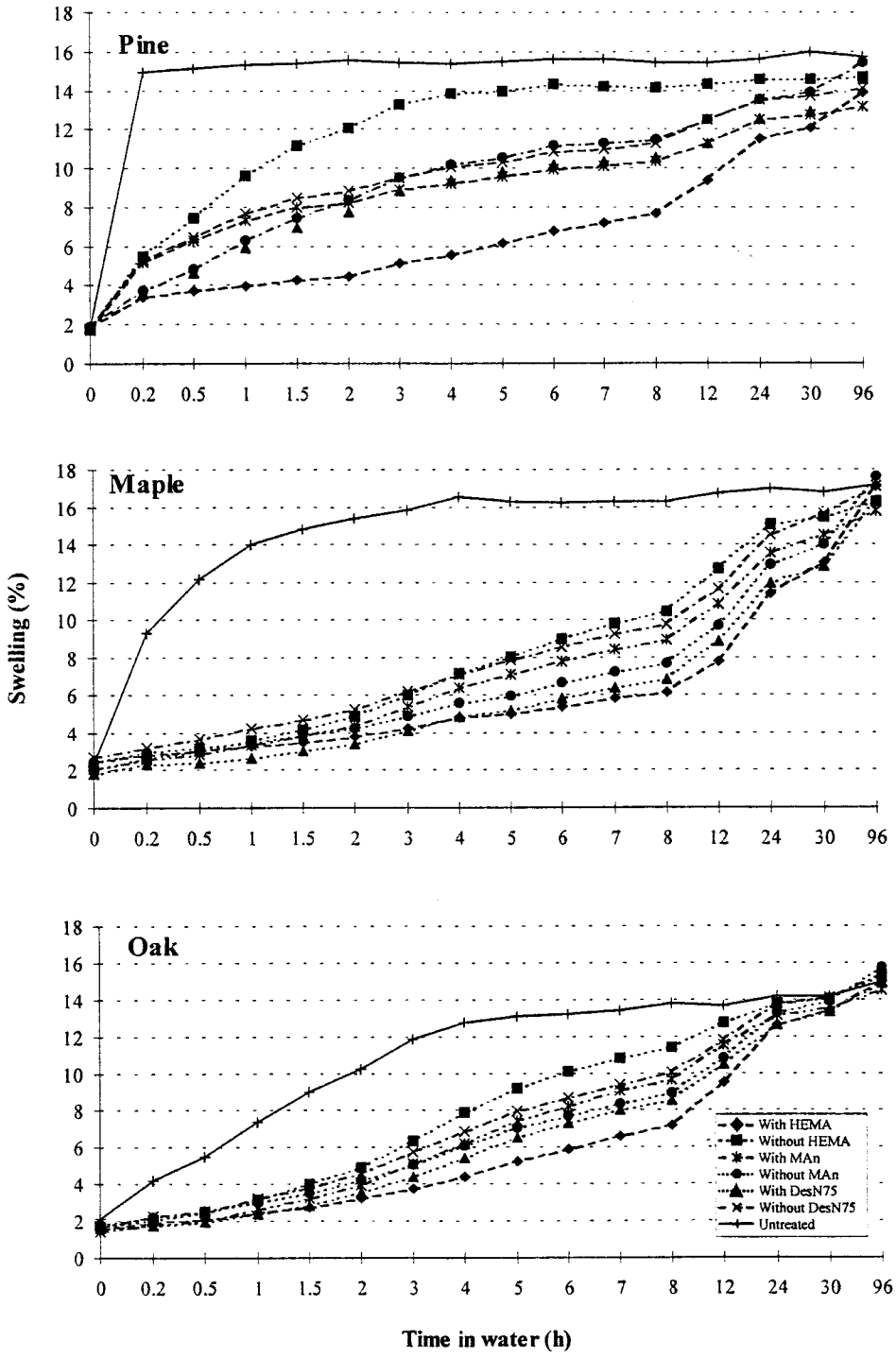

Figure 5 Volumetric swelling of WPC in water.

Table VI Rockwell Hardness of WPC Specimens

Treatment (Ratio)	Rockwell Hardness for Various Specimen Faces[a]								
	Pine			Maple			Oak		
	R	*T*	*L*	*R*	*T*	*L*	*R*	*T*	*L*
HDDA–DesN75 (3 : 1)	28	36	41	34	36	45	19	11	23
HDDA	29	29	37	38	39	47	20	11	27
HDDA–MAn (3 : 1)	28	29	29	32	32	49	19	9	22
HDDA–HEMA–MAn (1 : 2 : 1)	35	36	65	54	49	60	20	9	42
HEMA–DesN75–MAn (2 : 1 : 1)	31	42	66	50	44	56	9	9	31
HDDA–DesN75–MAn (2 : 1 : 1)	24	30	40	37	38	47	18	2	18
HDDA–HEMA (1 : 1)	40	46	51	39	38	49	16	11	28
HDDA–HEMA–DesN75 (1 : 2 : 1)	55	52	69	59	57	66	18	10	40
Control (untreated)	−2	−10	−13	−8	−7	−9	−7	−15	−21

[a] *R* is radial; *T*, tangential; and *L*, longitudinal. Indenter utilized a 0.25 in (6.35 mm) ball and 60 kgf (588.4*N*) of force. Hardness values based on Rockwell scale *L*.

HDDA–HEMA–DesN75 were slightly dyed on the outside, and the remaining part of the specimens, both wood and polymer, was not dyed (Fig. 3). This is a good indication that this treatment prevents wetting and penetration of water into the wood. However, it is not certain whether the dye was absorbed to the same extent as the solvent because of the chromatographic effect of wood.

Dimensional Stability

Swelling in Water Vapor

The chemical treatments and conditions used in this study did not swell the wood by any significant amount, indicating that the chemical did not diffuse into the cell walls. Consequently, no dimensional stability was attained through a bulking mechanism. Although the treatment did not result in permanent dimensional stability, the resultant moisture-excluding properties of WPC specimens enabled them to resist swelling for several hours at 90% RH. The reduction in the rate of swelling of WPC corresponded to the moisture-excluding capacity of the treatment. The rate of swelling appears to be dependent on the species of wood and the monomers or polymer used to make the WPC. All WPC specimens swelled more slowly than did the untreated specimens.

The percentage of volumetric swelling of pine WPC was less than that of untreated pine for up

Table VII Rockwell Hardness of WPC Averaged by Solution Components

Formulation	Rockwell Hardness				
	Pine		Oak		
	Earlywood	Latewood	Earlywood	Latewood	Maple[a]
With HEMA	58.2	66.9	33.6	37.0	57.9
Without HEMA	33.2	40.6	24.3	20.5	46.9
With DesN75	48.3	59.7	28.1	28.1	53.4
Without DesN75	43.2	47.8	29.8	29.4	51.4
With MAn	46.5	53.3	27.9	29.0	53.1
Without MAn	44.9	54.1	30.0	28.5	51.7

[a] Earlywood and latewood were not measured separately in maple specimens because it was difficult to distinguish earlywood from latewood on the longitudinal face.

to 96 h (4 days) at 90% RH; after that time, swelling of WPC was nearly the same as that of untreated specimens (Fig. 4). There were some small differences in swelling among the different treatments (Table IV). Among the pine WPC, those made with HEMA–DesN75–MAn swelled the most (11%), and those made from monomer mixtures containing HEMA swelled the least. In pine WPC made without HEMA, average volumetric swelling was greater than that of other species (Fig. 4).

Maple WPC showed less swelling than did untreated specimens for up to 48 h (Fig. 4). After 192 h at 90% RH, swelling of maple WPC was the same as or slightly greater than that of untreated wood. Polymer treatments affect the rate of swelling, but not the extent to which WPC swell. The HDDA–HEMA–DesN75 monomer mixture slowed the rate of swelling more than did other monomers (Table IV).

Oak WPC specimens were the least able of the three species to resist swelling. After 48 h, the extent of swelling of oak WPC was nearly the same as the maximum swelling of untreated specimens (Fig. 4). Generally, none of the treatments caused any significant reduction in swelling of specimens kept several days at 90% RH (Table IV).

Swelling in Liquid Water

Pine, maple, and oak WPC made with HDDA–HEMA–DesN75 swelled less, for up to 30 h in water, than did other specimens. After 96 h in water, all specimens, treated and untreated, showed little or no difference in the extent of swelling (Table V). The main difference observed between WPC and untreated specimens was the rate, not the extent, of swelling. The small untreated specimens used in this study swelled quickly in water; pine approached maximum swelling in less than 1 h and maple within 3 h, whereas untreated oak swelled more slowly, approaching maximum swelling after 8 h in water (Table V). The rate of swelling was slower for WPC specimens. The polymer in wood was more efficient at decreasing the rate of swelling in maple than in pine and oak (Fig. 5).

The presence of HEMA in the monomer formulations decreased the rate of swelling of WPC more than did any other ingredient (Fig. 5). The presence of an isocyanate (Desmodur N75) also helped decrease the rate of swelling of WPC in water. Specimens prepared with HDDA–HEMA–DesN75 had the slowest rate of swelling in water for all three species tested (Table V).

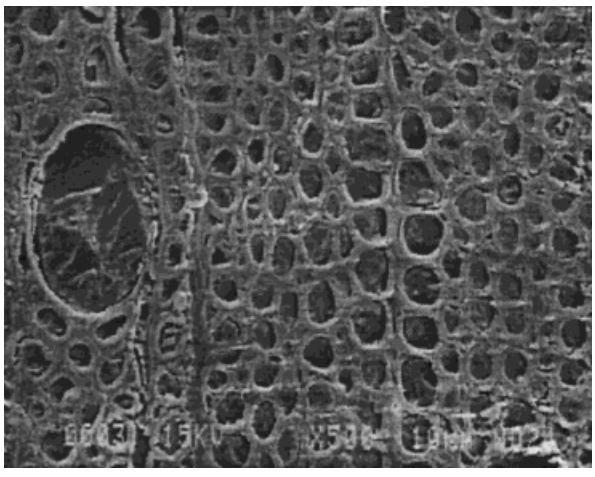

Figure 6 Effect of HDDA on adhesion of the polymer to cell walls in maple WPC.

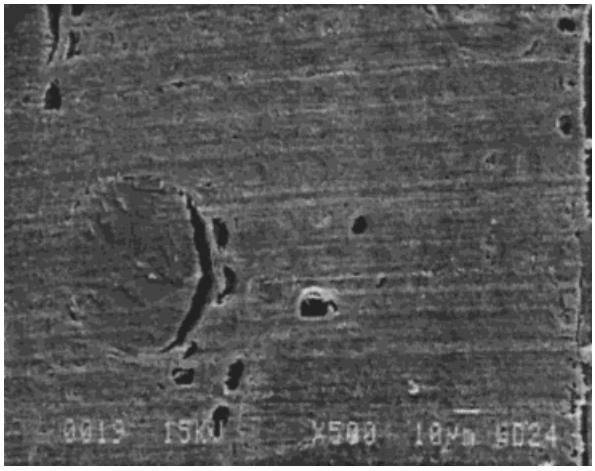

Figure 7 Effect of HDDA–HEMA–DesN75 on adhesion of the polymer to cell walls in maple WPC.

Hardness

Rockwell hardness was measured on radial, tangential, and longitudinal faces of specimens. The longitudinal face of WPC specimens was harder than the radial and tangential faces (Table VI). The Rockwell hardness values (scale L) of pine and maple WPC were greater than those of oak WPC. HDDA–HEMA–DesN75 (1 : 2 : 1) had the greatest effect on hardness (value of 69) on the longitudinal face of pine. For oak, the same treat-

ment resulted in average Rockwell hardness on the longitudinal face of 40. Maple WPC were harder than oak WPC. Of the maple WPC, specimens made with HDDA–DesN75 (3 : 1) had the lowest Rockwell hardness value (45) on the longitudinal face; but these specimens were, nevertheless, harder than oak WPC made with HDDA–HEMA–MAn (1 : 2 : 1), which had the highest Rockwell hardness (42) among the oak specimens (Table VI).

The WPC Rockwell hardness values were averaged according to presence or absence of specific components in the monomer formulations (Table VII). Using averaged values, the hardest WPC were those prepared from chemical formulations containing HEMA and the least hard, those WPC prepared without HEMA. The presence of HEMA increased hardness of all WPC specimens. The presence of DesN75 increased pine WPC hardness considerably and maple WPC hardness slightly, but it did not increase oak WPC hardness. There were no consistent changes in WPC hardness that could be attributed to the presence or absence of MAn.

Electron Microscopy

Electron micrographs of WPC prepared with HDDA indicated no adhesion between the polymer and cell walls. The polymer appeared to break and pull out of the cells (Fig. 6). In contrast, WPC prepared with HDDA–HEMA–DesN75 (1 : 2 : 1) had good adhesion between the polymer and cell walls (Fig. 7). The polymer completely filled the cells, except for small bubbles in the polymer itself.

CONCLUSION

Superior results were obtained with HDDA–HEMA–DesN75 (1 : 2 : 1). Wood–polymer composites (WPC) made with this chemical combination were the hardest, had the least discoloration with treatment, and had rates of moisture sorption and swelling in both water and water vapor that were lower than those of other WPC made in this study. The complete filling and adhesion of the HDDA–HEMA–DesN75 polymer in the wood contributed to these superior properties. Generally, WPC made from pine and maple were about equally hard, and both pine and maple WPC were harder than oak WPC. The hardest WPC were those made with HEMA in the formulation. This monomer increased hardness and water exclusion properties and decreased the rates of swelling in water and 90% relative humidity. The polarity of the HEMA monomer likely increases interfacial adhesion between the polymer and wood. It is this increased interfacial adhesion that improves water exclusion, decreases the rate of swelling, and increases hardness of WPC.

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