

# Dimensional Stability of Wood–Polymer Composites

Yaolin Zhang,<sup>1,2</sup> S. Y. Zhang,<sup>1,2</sup> Dian Qing Yang,<sup>1</sup> Hui Wan<sup>1</sup>

<sup>1</sup>Forintek Canada Corp., 319 rue Franquet, Sainte-Foy, Quebec, Canada G1P 4R4

<sup>2</sup>Faculty of Forestry and Environmental Management, University of New Brunswick Fredericton, P.O. Box 44555, 28 Dineen Drive, Fredericton, New Brunswick, Canada E3B 6C2

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**ABSTRACT:** Wood–polymer composites (WPC) were prepared by impregnation of polymeric monomers in wood and *in situ* polymerization. Three polymeric chemicals were chosen for this study: methyl methacrylate (MMA), hydroxyethylene methacrylate (HEMA), and ethylene glycol dimethacrylate (EGDMA). The effects of polymeric monomers and their combinations on moisture adsorption (*M*), anti-moisture adsorption efficiency (AME), liquid water uptake (*D*), water repellency efficiency (WRE), longitudinal, radial, tangential, and volumetric swelling properties (*S*) after soaking, and anti-swelling efficiency (ASE) were investigated. It was found that *M* was different for different methacrylate combinations and depended not only on the composition of the impreg-

nants, but also on wood properties. Liquid water uptake was similar regardless of the formulation of the WPC. Wood–polymer composites with high MMA content displayed enhanced dimensional stabilities, but WPCs with high HEMA content did not. Tangential and volumetric ASEs were strongly dependent on the type of treatment. Mold growth tests showed that wood treated with HEMA alone had no surface mold growth, and wood treated with MMA alone also showed less mold growth than did the control samples. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5085–5094, 2006

**Key words:** adsorption; composites; monomers; polymerization; stabilization

## INTRODUCTION

Wood is a porous material consisting of various cell structures composed primarily of biopolymers (carbohydrate polymers of cellulose and hemicellulose and phenolic polymers of lignin) and minor amounts (5%–10%) of extractives. Wood is anisotropic longitudinally, radially, and tangentially. Wood also swells differently in each of these three principal directions when it absorbs moisture. In general, tangential swelling is in the range of 8%–12%, radial swelling reaches 4%–6%, and swelling in the longitudinal direction is less than 1%. Different moisture contents of wood affect wood mechanical properties such as tension, bending, and compression strength.<sup>1–2</sup> Because of this, attempts are often made to modify wood chemically in order to improve its dimensional stability and mechanical properties. Wood can be modified in several ways, including chemical modification by small organic molecules, formation of wood–polymer composites by impregnation of solid wood with water-soluble, thermosetting resin sys-

tems or organic vinyl monomers followed by *in situ* polymerization, resin treatment of compressed wood, thermal compression, and thermal treatment.<sup>3–4</sup>

The technique used here to improve the properties of solid wood was formation of a wood–polymer composite (WPC) by impregnating wood with polymeric monomers (such as methacrylates, acrylates, styrene, or unsaturated polyesters) or with thermoset resins (such as epoxy resin, phenol formaldehyde, urea formaldehyde, and melamine–formaldehyde resin), followed by *in situ* polymerization by radiation or catalyst-thermal treatment. In thermoset resin impregnation, the chemicals are able to enter the cell wall or react with the hydroxyl groups of wood components, such as phenol formaldehyde resin, thus improve the dimensional stability of wood.<sup>5–7</sup> However, these treatments generally reduce the bending strength and toughness of wood. For the commonly used polymeric impregnation monomers, such as methyl methacrylate and styrene, the WPC generally exhibits enhanced strength properties and hardness while displaying relatively poor dimensional stability because these monomers are mostly confined to the lumen and are not in the cell wall.<sup>8–11</sup>

The multifunctional monomer hydroxyethylene methacrylate (HEMA) was chosen as a candidate for improving the penetration of monomers into cell walls. This monomer contains four function group an alcohol, an ether, an ester, and a polymerizable double bond. The hydroxyl group was expected to increase

Correspondence to: H. Wan (hui.wan@qc.forintek.ca).

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monomer hydrophilicity and hydrogen-bonding capability with various components of wood. During or after polymerization, intermolecular transesterification would occur through reaction of the hydroxyl groups of the HEMA units with wood components (cellulose, hemicellulose and lignin) to form a strong three-dimensional network that could provide good dimensional stability to the resulting WPC. Further improving properties might be possible via crosslinking of the polymeric monomers through the addition of the dimethacrylate crosslinking agent ethyleneglycol dimethacrylate (EGDMA). Many studies of polymer-impregnated wood have centered on vinyl monomers, particularly methyl methacrylate (MMA), for several reasons: (1) low viscosity, (2) availability, and (3) enhancement of wood properties after impregnation and polymerization. However, MMA has some undesirable properties, such as high vapor pressure, which tends to result in monomer depletion on the surface before polymerization, and high volumetric shrinkage upon polymerization.

Wood of a given species can be identified by its unique features, in particular its cellular structure.<sup>12</sup> Wood species are usually divided into two categories: softwoods and hardwoods. Hardwoods, such as oak, maple, birch, and fruit trees, have broad leaves and are deciduous, whereas softwoods, such as pine, spruce, and fir, are conifers. The softwood cellular structure is relatively simple and mainly consists of longitudinal tracheid cells, whereas the hardwood structure is more complex. The major structural difference between hardwoods and softwoods is that hardwoods have vessel elements. Hardwoods have three types of vessel arrangements for the earlywood/latewood transition: (1) earlywood/latewood transition abrupt, a band of large early vessels next to a band of much smaller latewood vessels, such as is found in oaks; (2) earlywood/latewood transition gradual, in which large earlywood vessels gradually decrease to smaller latewood vessels, as seen in black walnut; and (3) vessels uniform in size across the entire growth ring (earlywood/latewood). Sugar maple has distinct growth rings in which the earlywood/latewood transition is not clear because of the small portion of latewood. Its vessels are evenly distributed, and their diameters are small.

The wood species, its anatomic structure, impregnation parameters (vacuum, pressure, temperature), and intrinsic properties of the monomer are important factors in the impregnation of monomers into wood.<sup>13-15</sup> Hardwood sapwood is appropriate for impregnation because the internal flow of impregnants inside the wood takes place mainly through vessels of relatively large diameter.<sup>15</sup> Incremental increases in pressure at a certain point enhance the retention of impregnants, and applying a vacuum prior to pressurization accelerates impregnation.<sup>13,15</sup>

In the present study, sugar maple wood-polymer composites were prepared by impregnation of combinations of MMA, HEMA and EGDMA, chosen with a mixture design, followed by *in situ* thermal polymerization. This study aimed to evaluate the effects of various combinations of MMA, HEMA, and EGDMA on moisture adsorption, water uptake, and dimensional stability of wood and to discover whether HEMA and EGDMA can improve dimensional stability.

## MATERIALS AND METHODS

### Materials

Wood samples were chosen from defect-free boards of sugar maple wood donated by BOA-FRANC (Sainte-Georges, Quebec, Canada), a wood flooring company. End-matched samples with dimensions of 55 × 70 × 4.5 mm (longitudinal × tangential × radial) were obtained in an alternating pattern of treated and control specimens.

2,2'-Azobis(2,4-dimethylvaleronitrile) [Vazo 52; (CH<sub>3</sub>)<sub>2</sub>C(CN)N=NC(CH<sub>3</sub>)<sub>2</sub>(CN)], a free-radical source, was donated by Dupont Specialty Chemicals (Wilmington, DE), and 0.5 wt % Vazo 52 was used based on the weight of the mixture of polymeric monomers. Methyl methacrylate [MMA; H<sub>2</sub>C=C(CH<sub>3</sub>)COOCH<sub>3</sub>], 2-hydroxyethyl methacrylate [HEMA; H<sub>2</sub>C=C(CH<sub>3</sub>)COOCH<sub>2</sub>CH<sub>2</sub>OH], and ethylene glycol dimethacrylate [EGDMA; H<sub>2</sub>C=C(CH<sub>3</sub>)COOCH<sub>2</sub>CH<sub>2</sub>OOC(CH<sub>3</sub>)C=CH<sub>2</sub>] were in part generously donated by Degussa Canada Inc. (Montreal, Quebec, Canada) and Degussa Corp. (Wilmington, DE) and in part bought from Monomer and Polymer Lab. (Philadelphia, PA) and used without further purification. The combinations of MMA : HEMA : EGDMA that made up the formulations were determined by a mixture design and are listed in Table I.

TABLE I  
Chemical Composition of Impregnants

Combination	Composition <sup>a</sup> (weight fraction)			PR <sup>b</sup> (%)
	MMA	HEMA	EGDMA	
1	1	0	0	43.15
2	0	1	0	52.03
3	0	0.900	0.100	50.56
4	0.900	0	0.100	49.44
5	0.500	0.500	0	57.76
6	0	0.950	0.050	59.11
7	0.450	0.450	0.100	54.27
8	0.950	0	0.050	49.18
9	0.475	0.475	0.050	53.14

<sup>a</sup> Vazo 52 was added at 0.5% wt based on the mixture of monomers.

<sup>b</sup> Detailed information in Zhang et al.<sup>16</sup>

### Preparation of composites

The sugar maple wood samples whose moisture content was approximately 8% were oven-dried at 105°C for 24 h to a constant weight. Samples were placed into an impregnation case. The appropriate monomer mixture was introduced into the case to immerse the sample. The impregnation procedure, which was determined on the basis of previous studies,<sup>13-15</sup> was as follows: (1) vacuum of 635 mm Hg (25 in Hg) for 15 min, (2) 550 kPa (80 psi) for 15 min, (3) wiping off excess chemicals after release of pressure and wrapping in aluminum foil, and (4) *in situ* polymerization in a compression mold press at 60°C for 5 min, at 100°C for 15 min, and at 120°C for 20 min. At least 15 specimens were treated with each type of impregnation.

### Scanning electron microscopy

Scanning electron microscopy (SEM) was used to examine the impregnated and control wood samples. The interior portions of radial and tangential planes were exposed by cutting with a surgery blade, carbon coated, gold-sputter-coated, and examined with a JEOL JSM 6400 SEM (Tokyo, Japan) at different magnifications.

### Moisture adsorption

Both the control and WPC samples were oven-dried at 105°C for 24 h and placed in a conditioning chamber at 65% relative humidity and a temperature of 21°C for 6 weeks. The samples (7 replicates) were weighed after oven drying and at the end of the 6-week conditioning period.

### Water uptake and dimensional stability

Both control and treated samples (5 replicates) were immersed side by side in water at 21°C in a tray with water running at 20 mL/s for 7 days. A plastic frame was used to ensure that no sample floated on the water surface. The sample dimensions were determined by two measurements each of length, width, and thickness at marked positions on the specimen, and the weights of the specimens were recorded after oven drying and after soaking with excess water wiped from surfaces. Swelling (longitudinal, radial, and tangential) and antiswelling (longitudinal, radial and tangential) efficiency were calculated with data acquired from the WPC and control samples. What is referred to in this article as the polymer retention (PR) of the samples was determined previously.<sup>16</sup>

Anti-moisture adsorption efficiency (AME) was determined using the following equation:

$$AME (\%) = (M_c - M_{WPC})/M_c \times 100 \quad (1)$$

where  $M$  is the moisture adsorption, and the subscripts  $C$  and  $WPC$  are the control and solid wood-polymer composite samples, respectively.  $M$  was calculated as:

$$M (\text{wt } \%) = (w_m - w_0)/w_0 \times 100 \quad (2)$$

where  $w_0$  is the initial weight of the oven-dried sample, and  $w_m$  is the weight after 6 weeks at 65% relative humidity and 21°C.

Similarly, water repellency efficient (WRE) was defined as:

$$WRE (\%) = (D_c - D_{WPC})/D_c \times 100 \quad (3)$$

where  $D$  is the water uptake of a sample, and subscripts  $C$  and  $WPC$  are the control and treated samples, respectively.  $D$  was expressed as:

$$D (\text{wt } \%) = (w_{\text{soak}} - w_0)/w_0 \times 100 \quad (4)$$

where  $w_0$  is the initial weight of the oven-dried sample and  $w_{\text{soak}}$  is the weight after immersion in water for 7 days at 21°C.

The swelling coefficient ( $S$ ) was calculated as:

$$S (\%) = (\alpha_{\text{soak}} - \alpha_0)/\alpha_0 \times 100 \quad (5)$$

where  $\alpha$  is the the sample volume or single-direction dimension (longitudinal, tangential, or radial),  $\alpha_{\text{soak}}$  is the sample volume or single-direction dimension after soaking, and  $\alpha_0$  is the volume or single-direction dimension of the oven-dried sample.

Antiswelling efficiency (ASE) was calculated as:

$$ASE_{\alpha} (\%) = (S_{\alpha-c} - S_{\alpha-WPC})/S_{\alpha-c} \times 100 \quad (6)$$

where  $S_{\alpha-c}$  is the swelling coefficient for the control sample,  $S_{\alpha-WPC}$  is the swelling coefficient for the WPC sample, and the subscript  $\alpha$  is the volume or single dimension (longitudinal, tangential, or radial).

The PR was calculated as follows:

$$\% \text{ PR} = (Den_{WPG-dry} - Den_{wood-dry})/Den_{wood-dry} \times 100 \quad (7)$$

where  $Den_{WPG-dry}$  and  $Den_{wood-dry}$  are the oven-dry densities of WPC and wood, respectively.

The data were analyzed using analysis of variance, regression analysis, analysis of covariance, and Student's  $t$  test. Analysis of covariance was the method used to remove the variability in the experiment by accounting for the variability in the wood properties that could not be controlled by the design structure, such as swelling properties, moisture adsorption, and liquid water uptake of untreated wood. Mixed models and general linear models were used for data analysis.<sup>17</sup>

### Evaluation of mold growth resistance

To evaluate resistance to mold growth, samples of  $50 \times 30 \times 4\text{--}4.5$  mm cut from five specimens in each test group were used. An incubator was filled with water to a depth of 50 mm. Test panel samples were randomly placed on two mesh racks in the incubator. The relative humidity inside the incubator was 100%. This incubator was then put in a growth chamber set at  $25^\circ\text{C}$ . The samples in the incubator were inspected for mold growth on two surfaces after 8 weeks.

Mold growth was visually rated on a scale from 0 to 5 where:

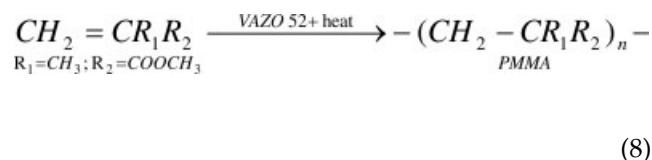
1. 0 = no mold growth;
2. 1 = trace mold growth (< 5% mold coverage);
3. 2 = little mold growth (5%–25% mold coverage);
4. 3 = moderate mold growth (25%–50% mold coverage);
5. 4 = heavy mold growth (50%–75% mold coverage);
6. 5 = very heavy mold growth (> 75% mold coverage).

### RESULTS AND DISCUSSION

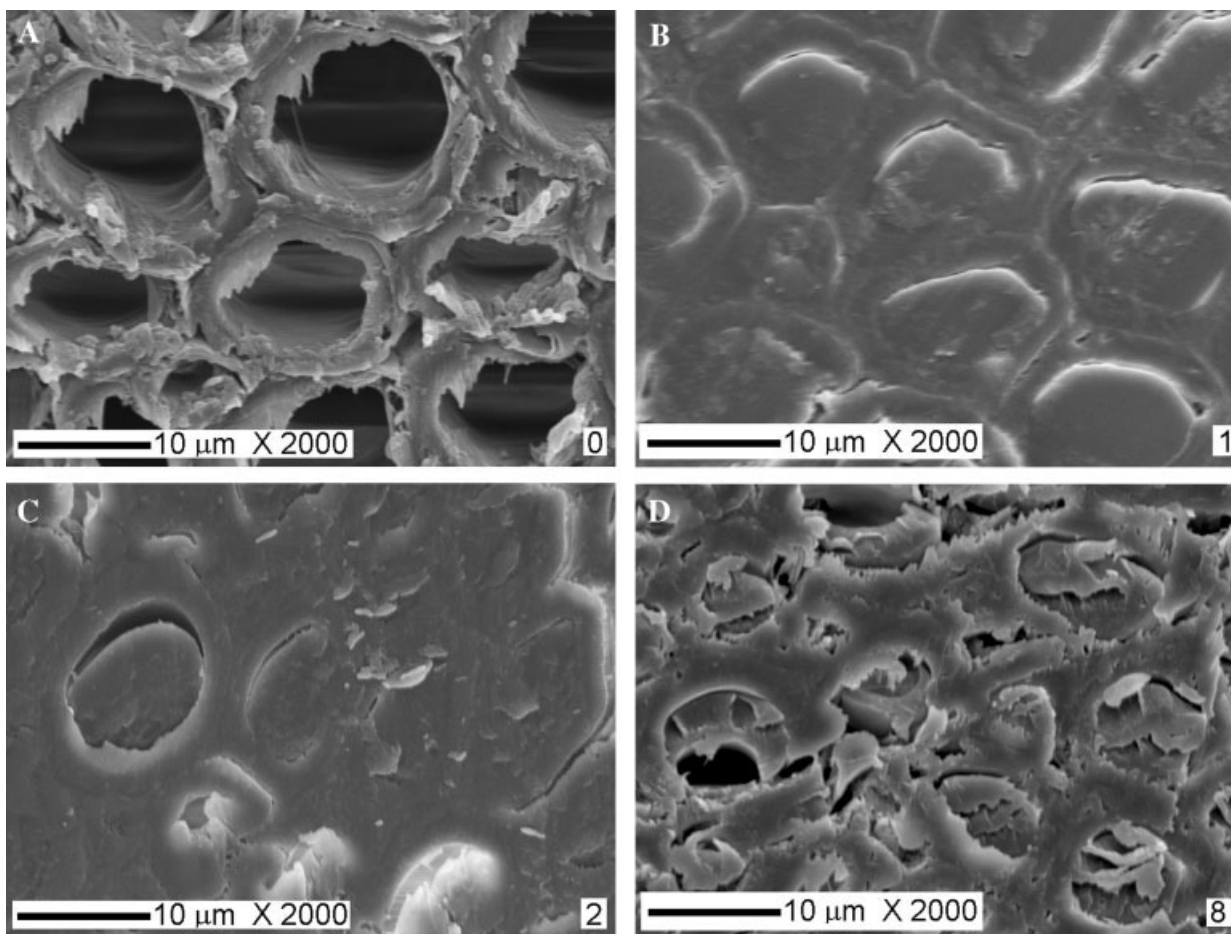
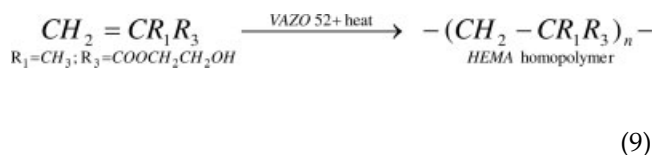
#### Polymer structures and morphology of wood–polymer composites

WPCs were formed by *in situ* polymerization after vinyl monomer impregnation of sugar maple via a catalyst-thermal procedure. Different polymer structures were formed after *in situ* polymerization for different monomers combinations as follows:

Combination 1 (100% MMA)—



Combination 2 (100% HEMA)—



**Figure 1** SEM micrographs of different formulations of MMA:HEMA:EGDMA combinations by weight as described in Table I (0, 1, 2, and 8 are the control sample, combination 1, combination 2, and combination 8, respectively).



**TABLE III**  
**AME of Different Treatments**

Combination	Mean (%)			Error (%)	
	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>	II-I <sup>d</sup>	III-I <sup>e</sup>
1	31.50 (4.50)	32.25	34.89	2.37	10.77
2	17.93 (5.16)	18.18	17.32	1.36	-3.40
3	11.26 (4.44)	11.35	12.46	0.77	10.67
4	30.73 (4.87)	30.27	32.60	-1.51	6.08
5	24.41 (2.64)	25.71	22.26	5.34	-8.83
6	13.03 (3.39)	12.53	9.49	-3.83	-27.21
7	24.58 (4.19)	25.08	23.96	2.04	-2.53
8	32.82 (1.77)	32.71	33.30	-0.35	1.47
9	24.50 (3.81)	23.58	23.87	-3.76	-2.56

<sup>a</sup> Arithmetic mean of AME with standard deviation in parentheses.

<sup>b</sup> Adjusted mean of AME by  $M_C$  as covariate at a mean of 10.42%.

<sup>c</sup> Adjusted mean of AME by PR as a covariate at a mean of 50.79%.

<sup>d</sup> (Mean II - mean I)/mean I  $\times$  100.

<sup>e</sup> (Mean III - mean I)/mean I  $\times$  100.

group in MMA; one ether, one hydroxyl and one ester group in HEMA; and two ether and two ester groups in EGDMA), different combinations of copolymers have different  $M$  capacities. HEMA is more hydrophilic than MMA because the former has more hydrophilic groups in its molecular unit. Composites with high HEMA content had higher  $M_{WPC}$  values than did those with high MMA content, as shown in Table II. These findings were similar to those of Rowell,<sup>18</sup> according to whom modification of wood by the application of propylene oxide, butylene oxide, and acetic anhydride makes the treated wood more hydrophobic, as shown by the lower equilibrium moisture contents of the treated versus the control samples. The composition of impregnants and the  $M_{WPC}$  adjusted by  $M_c$  used as a covariate can be described (with an  $R^2$  value of 0.95) as:

$$M_{WPC} = 7.29x_1 + 9.22x_2 + 7.67x_3 \quad (12)$$

where  $x_1$ ,  $x_2$ , and  $x_3$  are the weight fractions of MMA, HEMA, and EGDMA, respectively, in the system, with the conditions that  $x_1 + x_2 + x_3 = 1$  and  $0 \leq x_3 \leq 0.1$ .

Equation (8) is consistent with our analysis that WPC with a high HEMA content had higher moisture adsorption than those with a high MMA content.

A high  $M_{WPC}$  resulted in a low AME. Table III shows the AME values of the WPC samples. These analyses also showed that the AME of WPC was strongly dependent on the composition of the copolymers. High HEMA content (combinations 2, 3, and 6) resulted in the lowest AME values, whereas samples with a high MMA content (combinations 1, 4 and 8) had the highest AME values, because HEMA is more hydrophilic than MMA.

### Water uptake and water repellency efficiency

Water uptake of the WPC and control samples is shown in Table IV. The  $D_c$  was around 84 wt %, and  $D_{WPC}$  was in the range of 34.55–39.35 wt %, showing that the water uptake values of the composites ( $D_{WPC}$ ) were greatly reduced compared to those of the control samples. Because of the effects of wood variability and polymer retention on water uptake of WPC, the adjusted  $D_{WPC}$  values were also determined and are presented in Table IV. Water in wood can be in two forms: (1) free water, held in cell cavities, mainly in cell lumens and vessels, which are free of interaction with the hydrophilic groups of the cell walls; and (2) bound water, held in the cell walls by hydrogen bonds. In our study, most polymers in WPC resided in cell cavities, such as vessels and lumens,<sup>16</sup> and, by occupying a large portion of the cell lumens and vessels, reduced the volume that could be occupied by free water. From Table IV it can be seen that an increased PR resulted in a lower  $D_{WPC}$  for each treatment. High-HEMA-content WPC (combinations 2, 3, and 6) had a higher PR, whereas high-MMA-content samples (combinations 2, 3, and 6) had lower PR. However, HEMA is much more hydrophilic than MMA. Franson and Peppas<sup>19</sup> investigated equilibrium water uptake of polymethacrylates and found that water uptake for copolymers of HEMA and MMA increased with the amount of HEMA. More specifically, water uptake of the copolymers of HEMA and MMA increased from 15.5%, for a copolymer with a 1 : 1 HEMA–MMA mole ratio, to 41.4%, for a copolymer with a 9 : 1 HEMA–MMA mole ratio. Water uptake of pure HEMA polymer reached 59%. Franson and Peppas<sup>19</sup> also found that EGDMA-crosslinked HEMA polymer gained less water than did samples without

**TABLE IV**  
 **$D_{WPC}$  of Different Treatments**

Combination	PR (%)	Mean (%)			Error (%)	
		I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>	II-I <sup>d</sup>	III-I <sup>e</sup>
1	43.15	39.35 (2.07)	37.94	38.09	-3.59	-3.19
2	52.03	37.13 (1.71)	37.44	37.12	0.84	-0.03
3	50.56	37.84 (1.42)	37.92	37.40	0.19	-1.17
4	49.44	37.09 (2.33)	36.44	36.10	-1.74	-2.65
5	57.76	34.69 (1.69)	35.23	35.68	1.55	2.84
6	59.11	35.33 (0.62)	35.38	36.98	0.17	4.70
7	54.27	35.44 (3.69)	37.14	35.53	4.78	0.26
8	49.18	35.62 (2.98)	34.19	35.38	-4.02	-0.67
9	53.14	34.55 (0.89)	34.55	35.10	0.00	1.57
Control		84.43 (5.64)				

<sup>a</sup> Arithmetic mean of  $D_{WPC}$ , standard deviation in parentheses.

<sup>b</sup> Adjusted mean of  $D_{WPC}$  by  $D_C$  as covariate at a mean value of 84.43%.

<sup>c</sup> Adjusted mean of  $D_{WPC}$  by PR as a covariate at a mean value of 50.79%.

<sup>d</sup> (mean II - mean I)/mean I  $\times$  100.

<sup>e</sup> (mean III - mean I)/mean I  $\times$  100.

**TABLE V**  
WRE of Different Treatments

Combination	Mean (%)			Error (%)	
	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>	II-I <sup>d</sup>	III-I <sup>e</sup>
1	56.80 (2.45)	54.93	59.62	-3.30	4.96
2	55.87 (1.30)	55.67	55.89	-0.36	0.04
3	54.84 (1.95)	55.06	55.81	0.45	1.81
4	53.65 (5.90)	56.61	55.85	5.52	4.11
5	59.55 (3.20)	58.24	57.33	-2.19	-3.72
6	59.81 (2.18)	58.17	56.09	-2.74	-6.23
7	56.20 (3.76)	56.08	56.00	-0.21	0.36
8	59.40 (1.10)	59.50	59.94	0.17	0.90
9	59.03 (1.98)	59.01	57.81	-0.03	-2.06

<sup>a</sup> Arithmetic mean of WRE with standard deviation in parentheses.

<sup>b</sup> Adjusted mean of WRE by  $D_C$  as covariate at a mean of 84.43%.

<sup>c</sup> Adjusted mean of WRE by PR as a covariate at a mean of 50.79%.

<sup>d</sup> (Mean II - mean I)/mean I  $\times$  100.

<sup>e</sup> (Mean III - mean I)/mean I  $\times$  100.

EGDMA. Water adsorption of poly(methyl methacrylate) was around 2%. These two factors counteract each other, resulting in a similar  $D_{WPC}$  for all treatments (34.55%–39.35% for initial  $D_{WPC}$ , 34.19%–37.94% for  $D_{WPC}$  adjusted by  $D_C$ , and 35.10%–38.09% for  $D_{WPC}$  adjusted by PR).

The water repellency efficiency (WRE) values of all the composites are listed in Table V. Similarly, the adjusted WREs are also presented in Table V, adjusted in order to take into account the effects of the variability of wood and the PR. Table V shows that when adjusted for  $D_C$  (84.43%), wood treated with MMA alone had the lowest WRE (54.93%) among all the treatments. However, when adjusted for PR (50.43%), MMA-treated wood had one of the highest WREs among all the treatments. Nevertheless, the WREs of all the WPC were very similar. This also indicates that all treatments resulted in similar improvements in the reduction of liquid water uptake.

**TABLE VI**  
Swelling Coefficients of Different Treatments

Combination	$S_v$	$S_T$	$S_L$	$S_R$
1	16.75 (0.61)	9.04 (1.05)	0.39 (0.13)	6.69 (1.07)
2	18.80 (1.30)	9.39 (1.35)	0.32 (0.17)	8.25 (2.84)
3	20.53 (0.94)	13.07 (0.85)	0.37 (0.14)	6.81 (1.60)
4	18.11 (1.44)	9.20 (1.17)	0.28 (0.12)	7.86 (1.08)
5	19.84 (1.79)	10.84 (1.61)	0.39 (0.20)	7.75 (2.29)
6	21.08 (1.60)	12.16 (1.28)	0.37 (0.20)	7.54 (1.64)
7	19.05 (1.46)	9.93 (1.35)	0.44 (0.12)	7.83 (1.32)
8	17.39 (1.00)	8.91 (1.14)	0.36 (0.17)	7.41 (1.62)
9	19.67 (1.32)	9.56 (1.37)	0.34 (0.19)	8.84 (1.54)
Control	19.59 (1.30)	10.06 (1.69)	0.44 (0.13)	8.22 (1.66)

Standard deviations are in parentheses.

**TABLE VII**  
 $S_v$  of Different Treatments (%)

Combination	Mean (%)			Error (%)	
	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>	II-I <sup>d</sup>	III-I <sup>e</sup>
1	16.75 (0.61)	17.16	16.63	2.43	-4.96
2	18.80 (1.30)	18.64	18.80	-0.86	-0.04
3	20.53 (0.94)	20.05	20.49	-2.33	-1.81
4	18.11 (1.44)	18.38	18.01	1.46	-4.11
5	19.84 (1.79)	19.77	19.94	-0.35	3.72
6	21.08 (1.60)	21.10	21.24	0.10	6.23
7	19.05 (1.46)	18.90	19.06	-0.79	0.36
8	17.39 (1.00)	18.11	17.37	4.16	-0.90
9	19.67 (1.32)	19.32	19.72	-1.78	2.06

<sup>a</sup> Arithmetic mean of  $S_v$  with standard deviation in parentheses.

<sup>b</sup> Adjusted mean of  $S_v$  by  $S_{VC}$  as covariate at a mean of 19.59%.

<sup>c</sup> Adjusted mean of  $S_v$  by PR as a covariate at a mean of 50.79%.

<sup>d</sup> (Mean II - mean I)/mean I  $\times$  100.

<sup>e</sup> (Mean III - mean I)/mean I  $\times$  100.

### Dimensional stability

The swelling coefficients ( $S$ ) for the WPC and control samples are shown in Table VI. Table VI shows that  $S_{L-WPC}$ ,  $S_{R-WPC}$ ,  $S_{T-WPC}$ , and  $S_{V-WPC}$  actually depended on the different treatments. However, the  $S_L$  and  $S_R$  for WPC could not be differentiated among the different treatments if the wide standard deviations were considered. In the following, only  $S_{T-WPC}$  and  $S_{V-WPC}$  were analyzed further. To consider the effects of the variability of the wood and PR on  $S_V$  and  $S_T$ , analysis of covariance was performed, and the adjusted values are shown in Tables VII and VIII.

Considering the covariate effect, the adjusted  $S_V$  and  $S_T$  of the WPC presented in Tables VII and VIII show

**TABLE VIII**  
 $S_T$  of Different Treatments (%)

Combination	Mean (%)			Error (%)	
	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>	II-I <sup>d</sup>	III-I <sup>e</sup>
1	9.04 (1.05)	9.13	7.71	0.96	-14.70
2	9.39 (1.35)	10.44	9.41	11.23	0.17
3	13.07 (0.85)	10.03	13.75	-23.27	5.22
4	9.20 (1.17)	9.20	8.97	0.01	-2.47
5	10.84 (1.61)	10.68	13.91	-1.52	28.31
6	12.16 (1.28)	11.67	9.59	-4.06	-21.14
7	9.93 (1.35)	9.95	9.91	0.22	-0.22
8	8.91 (1.14)	9.60	9.17	7.72	2.91
9	9.56 (1.37)	9.81	10.47	2.57	9.49

<sup>a</sup> Arithmetic mean of  $S_T$  with standard deviation in parentheses.

<sup>b</sup> Adjusted mean of  $S_T$  by  $S_{TC}$  as covariate at a mean of 10.06%.

<sup>c</sup> Adjusted mean of  $S_T$  by PR as a covariate at a mean of 50.43%.

<sup>d</sup> (Mean II - mean I)/mean I  $\times$  100.

<sup>e</sup> (Mean III - mean I)/mean I  $\times$  100.

TABLE IX  
ASE<sub>V</sub> and ASE<sub>T</sub> of Different Treatments

Combination	ASE <sub>V</sub> (%)	ASE <sub>T</sub> (%)
1	12.07 (5.29)	8.52 (4.41)
2	4.91 (4.36)	-7.03 (5.99)
3	-1.68 (1.50)	-8.38 (3.70)
4	5.84 (6.58)	7.70 (7.99)
5	-0.99 (5.43)	-5.47 (6.23)
6	-7.62 (3.81)	-16.08 (3.86)
7	3.62 (4.52)	0.42 (5.42)
8	6.87 (4.24)	3.33 (2.73)
9	1.82 (3.07)	2.16 (6.18)

Standard deviations are in parentheses.

that WPC with a high MMA content (combinations 1, 4, and 8) had lower  $S_{V-WPC}$  and  $S_{T-WPC}$  than did those with a high HEMA content. In fact, treatment with MMA alone resulted in the lowest  $S_V$  and  $S_T$  among all the treatments and the control, and treatment with a high content of HEMA resulted in the highest  $S_V$  and  $S_T$  among all the treatments and the control. This means that MMA-treated wood achieved the best dimensional stability among all the treated woods and had better dimensional stability than the untreated wood, whereas the dimensional stability of the samples treated with HEMA at a higher content was inferior to that of the untreated wood.

Linear regression analysis also showed that  $S_{V-WPC}$  and  $S_{T-WPC}$  adjusted with control samples as covariates depended on the formulation of impregnants ( $R^2 = 0.96$ ) as:

$$S_{V-WPC} (\%) = 17.89x_1 + 20.86x_2 + 17.86x_3 \quad (13)$$

$$S_{T-WPC} (\%) = 9.49x_1 + 10.98x_2 + 6.68x_3 \quad (14)$$

where  $x_1$ ,  $x_2$ , and  $x_3$  are the weight fractions of MMA, HEMA, and EGDMA, respectively, in the system, with the conditions that  $x_1 + x_2 + x_3 = 1$  and  $0 \leq x_3 \leq 0.1$ .

These equations also prove that the addition of a high content of HEMA resulted in higher  $S_{V-WPC}$  and  $S_{T-WPC}$  than those of the untreated samples (19.59% for the  $S_V$  of untreated wood and 10.06% for the  $S_T$  of untreated wood).

ASE<sub>V</sub> and ASE<sub>T</sub> are presented in Table IX. Table IX shows that different combinations of impregnants had distinct effects on ASE<sub>V</sub> and ASE<sub>T</sub>, where wood treated with MMA alone (combination 1) possessed the highest ASE<sub>V</sub> (12.07%) and ASE<sub>T</sub> (8.5%), whereas combination 6 (95 wt % HEMA and 5 wt % EGDMA) resulted in the lowest ASE<sub>V</sub> (-7.62%) and ASE<sub>T</sub> (-16.08%). The adsorption of water by acrylic polymers is accompanied by volumetric swelling. Increasing the hydrophilic component (HEMA) in the copolymer of HEMA and MMA enhanced the water uptake capacity, and then resulted in increased swelling.<sup>19</sup> Peppas<sup>20</sup> indi-

cated that volumetric swelling in water of pure HEMA polymer reached around 40%. Therefore, high contents of HEMA in a copolymer resulted in high swelling after adsorption of water. High contents of HEMA gave lower or negative values of ASE<sub>V</sub> and ASE<sub>T</sub> compared to controls. These results contradict our assumptions that HEMA treated wood would react with hydrophilic groups of wood and have improved dimensional stability. Even though some formulations enhanced the ASE<sub>V</sub> and ASE<sub>T</sub> of WPCs, these improvements were limited as the highest values of ASE<sub>V</sub> and ASE<sub>T</sub> were only 12.07% and 8.52%, respectively. These values are much lower than those of wood modified by formaldehyde, acetic anhydride, methyl isocyanate, and thermoset resins (epoxy resin, phenolic-formaldehyde resin, melamine-formaldehyde resin, thiourea-formaldehyde etc.).<sup>18,21-25</sup> This indicates that methacrylates (MMA, HEMA, and EGDMA) do not alter the hygroscopic characteristics of wood, a finding supported by the results of many other studies showing that dimensional stabilization of wood by acrylate or methacrylate monomers is less effective.<sup>7,26</sup>

### Mold growth

Mold fungi are a heterogeneous and poorly defined group of fungi.<sup>27</sup> Mold growth on wood can cause severe discoloration, which can be a variety of colors but is most often green-gray or black. Even though mold ordinarily only grows on wood surfaces and does not diminish the structural integrity of the wood because mold fungi are not capable of degrading lignin, cellulose, or hemicellulose, it makes wood aesthetically unacceptable.<sup>28-29</sup> In addition, mold growth may have detrimental effects on health, including allergies and irritations caused by breathing spores or other tiny fragments, contact with moldy surfaces, or ingestion.<sup>30-32</sup> There are several strategies for preventing attacks by mold on wood, including (1) application of fungicide to kill mold, (2) chemical modification of the wood to make the food source of mold unusable, and (3) preventing the wood from becoming wet.<sup>33</sup> Taylor et al.<sup>34</sup> found that bleach and other low-toxicity biocides can minimize surface microflora but cannot inhibit all the fungi present. Price et al.<sup>35</sup> pointed out that wood preserved with a variety of copper complexes as well as with chromated copper arsenate (CCA) is sometimes subject to mold growth on the surface, particularly when moisture levels exceed about 20%. Şolpan and Güven,<sup>36</sup> who investigated oak, cedar, beech, and spruce preserved by *in situ* polymerization of ally glycidyl ether with acrylonitrile and methyl methacrylate, found that this treatment protected the samples against biodegradation.

The average levels of mold growth on treated and untreated sugar maple samples are shown in Figure 2. Not all the surfaces of the treated wood showed a

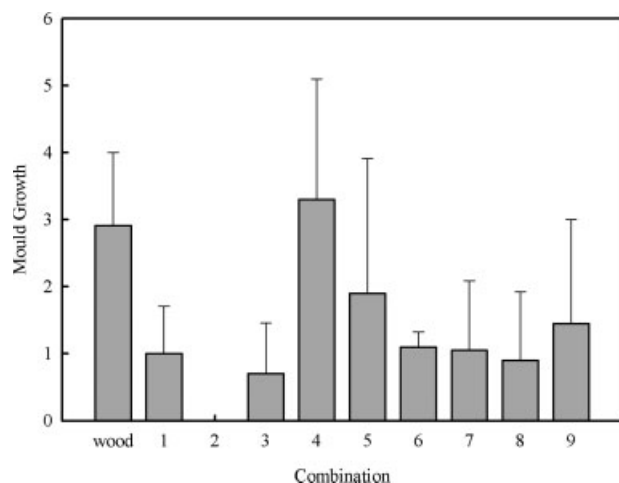


reduction in mold growth compared with that in the control samples. Three methods were used to account for the possible effect of the variability of wood on mold infestation: (1) analyses of covariance to test if the wood itself had a significant impact on mold growth, using growth on the end-matched untreated sample as covariate, (2) analysis of the ratio of mold growth on WPC to that of mold growth on the end-matched untreated sample, and (3) analysis of differences in mold growth between treated and untreated samples. The results are listed in Table X. Wood treated with HEMA alone had no mold growth on the surface. With adjusted means, the sugar maple treated with only MMA had less mold growth (1.68) than did the control sample (2.91), even though MMA is usually considered as a nonbioactive monomer for resistance to decay.<sup>37</sup> The results with all three methods showed that the WPCs with a high HEMA content (combinations 2, 3, and 6) had less mold growth on their surfaces than did those with a high MMA content, which means HEMA is bioactive against mold growth. The mechanism of anti-mold growth in HEMA needs further investigation.

## CONCLUSIONS

Impregnation of wood with various polymer mixtures altered the moisture adsorption ( $M$ ) properties of the resulting wood-polymer composites, with MMA-treated wood having the lowest  $M$  and WPCs with higher HEMA contents displaying higher moisture adsorption. This resulted in MMA-treated wood having the highest AME and the samples treated with higher HEMA contents having lower AMEs.

The 100 wt % MMA treatment showed the highest water uptake among all the treatments. However, this



**Figure 2** Impact of chemical formulation on sugar maple (1–9 refer to combinations 1–9 of MMA:HEMA:EGDMA by weight as described in Table I; wood refers to the control sample).

**TABLE X**  
Mold Growth (MG) of WPC and Control Samples

Combination	Mean (%)		Ratio <sup>c</sup>	Error <sup>d</sup>
	I <sup>a</sup>	II <sup>b</sup>		
1	1.00 ± 0.71	1.68	0.70 ± 0.45	-0.40 ± 0.65
2	0.00 ± 0.00	0.02	0.00 ± 0.00	-2.90 ± 0.96
3	0.70 ± 0.76	0.90	0.31 ± 0.35	-1.80 ± 1.04
4	3.35 ± 1.78	3.26	1.05 ± 0.55	0.15 ± 1.67
5	1.50 ± 1.66	0.85	0.62 ± 0.84	-2.10 ± 2.61
6	1.10 ± 0.22	0.68	0.29 ± 0.07	-2.80 ± 0.76
7	1.05 ± 1.04	1.25	0.42 ± 0.38	-1.45 ± 1.23
8	0.90 ± 1.02	1.36	0.55 ± 0.57	-1.00 ± 1.37
9	1.45 ± 1.55	1.20	0.40 ± 0.38	-2.05 ± 1.42
Control	2.91 ± 1.09			

<sup>a</sup> Arithmetic mean of MG.

<sup>b</sup> Adjusted mean of MG by MG of untreated wood as covariate at a mean of 2.91.

<sup>c</sup> Ratio is MG of WPC divided by MG of end-matched control.

<sup>d</sup> Difference is MG of WPC minus MG of end-matched control.

study found that all formulations resulted in a similar impact on  $D$  and in similar WREs.

Different combinations did not significantly improve dimensional stability. Volumetric swelling ( $S_V$ ) and tangential swelling ( $S_T$ ) were slightly improved by high-MMA-content impregnations, but not by high-HEMA-content treatments, which resulted in positive values of  $ASE_V$  and  $ASE_T$  for high-MMA-content combinations, but negative values of  $ASE_V$  and  $ASE_T$  for most HEMA-treated woods. This indicates that WPC with high HEMA content have reduced dimensional stability compared to untreated sugar maple.

Different combinations did have significant effects on mold growth. Wood treated with HEMA alone grew no mold on the surface, whereas treatment with MMA treatment reduced mold growth.

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