Effect of Impregnation and In-Situ Polymerization of Methacrylates on Hardness of Sugar Maple Wood

Yaolin Zhang,[1,2] S. Y. Zhang,[1,2] Ying Hei Chui,[2] Hui Wan[1]

[1]*Forintek Canada Corporation, Sainte-Foy, Quebec, Canada G1P 4R4*
[2]*Faculty of Forestry and Environmental Management, University of New Brunswick, New Brunswick, Canada E3B 6C2*

ABSTRACT: The improvement of Brinell hardness of sugar maple (*Acer saccharum* Marsh.) samples through impregnation and in-situ polymerization of methyl methacrylate, 2-hydroxylethyl methacrylate, and ethylene glycol dimethacrylate monomers was investigated. The formulation combinations were determined by a mixture design. Sugar maple samples were impregnated with these mixtures by a vacuum and pressure process and polymerized *in situ* by a catalyst-thermal procedure. The effects of the monomers and their combinations on Brinell hardness and hardness modulus were analyzed. Chemical impregnation enhanced both Brinell hardness and hardness modulus. A significant relationship between hardness modulus and Brinell hardness was found. Modulus of elasticity of sugar maple was also improved through impregnation with methacrylates. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1674–1683, 2006

Key words: Brinell hardness; composites; wood; in-situ polymerization; impregnation

INTRODUCTION

Most Canadian coniferous species and some important hardwoods are not sufficiently dense and resistant to wear for use in the flooring, high-end furniture, and cabinet markets. Hardness implies the ability of a material to resist deformation. There is a wide variety of hardness assessment procedures available, including static indentation, scratch, plowing, rebound, damping, cutting, abrasion and erosion tests.[1,2] Hardness is a routinely measured mechanical characteristic that is sensitive to structural parameters as well as to mechanical behavior.[3–5] A classical method used to measure hardness is the static indentation test, which involves forcing a hard tool of known geometry into the sample body. The hardness of the sample is then defined as the ratio of the applied force to the size of the resulting indentation. Brinell hardness is defined as the ratio of the applied force to the actual area of surface contact, whereas Meyer hardness is the ratio of the applied force to the projected contact area.

For an elastic material, the size of the indentation is measured under load because deformations of this kind of material are not permanent, whereas for a plastic material, the area of the permanent indentation is measured after releasing the applied load. Wood behaves visco-elastically. Doyle and Walker[6] suggested that the contact area of the indentation be used to calculate the Brinell or Meyer hardness for several reasons: (1) there might be difficulties in measuring the impression, especially for shallow indentations where the imprint is unclear; (2) the sample material adjacent to the edge of the tool could become densified, which would exaggerate the size of the permanent indentation; and (3) a less permanent indentation occurs using green wood than dry wood, which would result in the false conclusion that green wood is harder than dry wood, if a permanent indentation was used to calculate hardness. Recently, nanoindentation techniques have become common for the investigation of mechanical properties of thin films and small volume materials.[7–13] Wimmer and coworkers[14,15] applied this technique to the study of wood cell mechanics, such as hardness and modulus of elasticity. Later, Gindl et al.[16,17] also adopted nanoindentation to study the mechanical properties of wood cell walls. Hardness was found to vary not only within a tree ring, but also within a single tracheid. The hardness of the radial S_2 layer was higher than that of the cell corner middle lamella.[14,15] The hardness of a developing tracheid was lower than that of mature tracheid, but the lignin content in the wood cell showed no statistically significant effect on the hardness of mature wood cells. These studies indicate that the structure of wood

cells affects hardness because of their heterogeneous cell-wall structure.

One of the techniques used to improve the properties of solid wood, which has received considerable attention in the past few decades, is the impregnation of wood with vinyl monomers such as methyl methacrylate (MMA), styrene (ST), or unsaturated polyester, and with thermoset resins including epoxy, phenol formaldehyde, urea formaldehyde, and melamine formaldehyde, followed by in-situ polymerization by radiation or catalyst-thermal treatments.[18–26] The resulting products are generally known as wood–polymer composite (WPC). In thermoset resin chemical impregnation, chemicals that enter the cell wall or react with hydroxyl groups of wood components, such as phenol formaldehyde resin, improve the dimensional stability of wood.[18–20] However, these treatments generally reduce bending strength and toughness of wood. For the more commonly used monomers, such as MMA and ST, the WPCs generally exhibit enhanced strength properties and hardness, while displaying a relatively poor dimensional stability due to the fact that these monomers do not react with wood components and are mostly confined to the lumen and are not in the cell walls.

Wood is anisotropic longitudinally, radially, and tangentially.[27] Wood anatomy indicates that wood structures vary with wood species. Trees are classified into softwoods and hardwoods. Hardwoods have vessels that are responsible for water transport, but softwoods do not. Furthermore, hardwoods can be subcategorized by the diameters and distributions of these vessels, such as ring-porous hardwood, semi-ring-porous hardwoods, and diffuse-porous hardwoods. In ring-porous woods, such as oak and elm, the pores formed in the earlywood zone have a diameter considerably larger than those in the latewood. In diffuse porous woods, such as sugar and red maples, the pores have the uniform diameters and distributions across the entire growth ring. This results in differences in mechanical properties of woods. Holmberg[28] investigated the hardness of Scots pine using loads applied at angles between 0 and 90° against the wood grain direction, and showed that hardness is greatly dependent on load direction, and that at a certain angle, hardness is fairly proportional to wood density. Hirata et al.[29] studied the hardness of woods with distinguished earlywood and latewood in the annual ring, and hardness distribution in radial and tangential sections. Hardness of earlywood was found to be lower than that of latewood, and there was no large variation in the hardness for agathis, a tropical coniferous wood with no clear growth ring. The hardness distribution reflected the density distribution of the wood surface. Ellis and O'Dell[24] measured the hardness of the softwood pine and the hardwoods oak and maple. They found that hardness was different in

radial, tangential, and longitudinal directions, and that hardness differences between different directions varied with wood species. The hardness of maple was similar in different directions, but pine and oak had very different hardnesses in different directions, especially in the radial and longitudinal directions. These studies indicated that woods without clear growth rings, such as sugar maple and red maple, should have less variation in hardness. Ellis and O'Dell[24] also indicated that WPC prepared with vinyl monomer and other chemicals could improve hardness in all directions and compensate for the large variations in hardness of untreated wood of some species, such as pine and oak.

Many studies have been reported to improve wood hardness through impregnation of monomers into wood and in-situ polymerization to form WPC.[20–26] These studies have shown that the hardness of WPC depends on the nature of impregnants, their retention, and the natural hardness of the wood. All WPC samples tested in these studies were found to be harder than their corresponding untreated wood samples.

The relationships between hardness and other mechanical properties were initially established for metals because of their better-known structural and mechanical properties. Subsequently, similar relationships were derived for polymers and other materials.[3–5] Tabil et al.[1] correlated Meyer hardness to the hardness modulus for alfalfa cubes by a binomial model. Zamfirova et al.[4] found that the Vickers micro-hardness of polyolefin is proportional to Vickers micro-hardness modulus on a logarithmic scale. Lewis[30] established a relationship between Janka hardness and the hardness modulus for wood-based materials, and noted that there was an advantage in determining the hardness value indirectly from the hardness modulus, especially for small indentations.

Despite the research carried out to date on WPC, much work is still needed to reduce manufacturing costs and improve performance of the final product in service. A solution to improve the mechanical properties and dimensional stabilities of WPC is to increase the degree of penetration of the chemicals into the wood cell wall. To realize this goal, the multifunctional monomer hydroxyethylene methacrylate (HEMA) was used in this study. HEMA contains four different functionalities, including alcohol, ether, ester, and a polymerizable double bond. The hydroxyl group in this compound was expected to increase monomer hydrophilicity and hydrogen bonding capability with various components of wood. During or after in-situ polymerization, the hydroxyl groups of HEMA units and wood components (cellulose, hemicellulose, and lignin) could participate in chemical reactions that would provide good dimensional stability to the WPC. Further improvements in properties may be possible by crosslinking reactions via the addition of
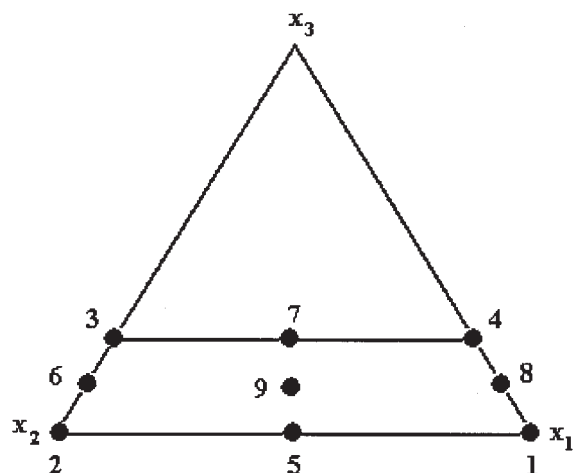
Figure 1 The mixture design (extreme vertices: 1–4; midpoints of edges: 5–8; and centroids of faces: 9).

ethylene glycol dimethacrylate (EGDMA). Many studies have used MMA because of its low viscosity, availability, and ability to improve wood properties after in-situ polymerization. However, MMA has some undesirable properties, such as high vapor pressure during treatment, which leads to monomer depletion on the surface before polymerization, and high volumetric shrinkage upon polymerization.

The objective of this research was to investigate the effects of MMA, HEMA, and EGDMA and of their combinations on some properties of WPC, including impregnability and hardness, and to arrive at an optimal impregnant formulation. The effects of these monomers and of their combinations on monomer retention by volume (MR_v) and polymer retention (PR) have been investigated previously.[31] It was found that the impregnation of sugar maple with different combinations of the three methacrylates results in similar MR_v values, showing that these three methacrylates have similar impregnabilities into sugar maple when applied with a vacuum–pressure process. Most impregnants are located in the vessel and lumen. PR depends on the combination of impregnants and is inversely proportional to wood density. This article focuses on the effects of monomers and formulation combinations on Brinell hardness, and evaluates the relationship between hardness and hardness modulus.

EXPERIMENTAL

Materials

Wood samples were cut from defect-free boards of sugar maple. End-matched samples with dimensions of 55 × 70 × 4.5 mm^3 (longitudinal × tangential × radial) were obtained in an alternating pattern of treated and control specimens. 2,2′-Azobis (2,4-dim-

ethylvaleronitrile) (0.5%; Vazo 52), a free radical source, was used based on the weight of the monomer mixture. Methyl methacrylate (MMA), 2-hydroxyl-ethyl methacrylate (HEMA), and ethylene glycol dimethacrylate (EGDMA) were used without further purification. The combinations of MMA:HEMA:EGDMA were determined by a mixture design as shown in Figure 1, and are listed in Table I. Further details on the mixture design are given elsewhere.[31]

Preparation of composite specimens

The sugar maple wood samples, conditioned at ~8% moisture content, were oven-dried to a constant weight at 105°C for 24 h. Samples were then placed into an impregnation reactor. Impregnation solutions were introduced into the reactor to immerse the samples. The impregnation procedure was vacuumed at 635 mmHg (25 in.) for 15 min followed by pressure at 550 kPa (80 psi) for 15 min. After impregnation, pressure was released, excess chemicals were wiped from the sample surface, and the treated samples were wrapped in aluminum foil. The treated samples were *in-situ* polymerized in a hot press without compression in three steps: (a) 60°C for 5 min, (b) 100°C for 15 min, and (c) 120°C for 20 min. A minimum of 15 specimens were treated for each impregnant combination. This three-step process was found appropriate for obtaining complete polymerization of impregnated samples. There was no exothermic and/or endothermic peak in the temperature range 25–200°C with a heating rate of 20°C/min for the treated wood after in-situ polymerization, as determined by a DSC 2910 Differential Scanning Calorimeter from TA Instruments, Inc. (DE). The WPC samples were then sanded to remove excess polymers from their surfaces. All data on weight and dimension of wood samples were recorded before impregnation and after polymerization.

TABLE I
Chemical Composition of Impregnants[a]

Combination	MMA (weight fraction)	HEMA (weight fraction)	EGDMA (weight fraction)
1	1	0	0
2	0	1	0
3	0	0.900	0.100
4	0.900	0	0.100
5	0.500	0.500	0
6	0	0.950	0.050
7	0.450	0.450	0.100
8	0.950	0	0.050
9	0.475	0.475	0.050

[a] Vazo 52 was added at 0.5 wt % based on the mixture of monomers.

Scanning electron microscopy

Scanning electron microscopy (SEM) was used to examine the impregnated and control samples. The interior portions of the radial–tangential plane, obtained by cutting with a surgery blade, were coated with carbon and gold before being observed with a JEOL JSM 6400 SEM (Tokyo, Japan).

Measurement of density profile

The density distributions of the samples were measured with a commercial X-ray density profiler (QMS Density Profiler, Model QDP-01X, Quintek Measurement Systems, Inc., Oak Ridge, TN). The density data were collected through the thickness of 50.8×50.8 mm^2 (2×2 in.) specimens at 0.02-mm increments. The 50.8×50.8 mm^2 (2×2 in.) specimens were equilibrated at 21°C and 65% relative humidity before the X-ray density scan. The data from 0 to 0.2 mm for each end surface of 50.8×50.8 mm^2 were removed so as to make sure that the X-ray beams passed through the entire surface of 50.8×50.8 mm^2.

Relative thickness positions from 0 to 1 are used to present the data.

Hardness tests

Hardness tests were performed on untreated and treated sugar maple samples using a universal test machine (Alliance RT/50 system, MTS Systems Corp., Eden Prairie, MN). The size of hardness test specimens was $55 \times 70 \times 4.5$ mm^3. During the test, the indenter (an 11.3-mm-diameter steel ball), attached to the loading platen of a test machine, was lowered to the surface of the test specimen. A preload of 1–2 N was applied to stabilize the test specimen. The applied load was then increased at such a rate so as to reach a target load of 1000 N in 15 s, and was maintained at this force for 25 s. The actual contact area under indentation was used to calculate the hardness of the specimen. The load-deformation data were collected at a sampling rate of 10 data points per second. Brinell hardness was calculated using eq. (2) shown later. The hardness modulus was calculated as the slope of load versus indentation response within the 20–60% indentation range. At least 10 specimens were tested for each monomer combination.

Modulus of elasticity

Flexural properties were evaluated as a function of different treatments using a Rheometrics Solids Analyzer RSA II with a transducer of 10 N. The samples were cut into rectangular bars, 55×6–8×1.0–1.5 mm^3 in longitudinal $\times$ tangential $\times$ radial directions, respectively. The tests were carried out at 25°C with a strain rate of 0.002/s and a measurement time of 1 s. The modulus was calculated from the slope of the stress–strain curve. Duplicate measurements were performed for different treatments and controls.

Analysis of test data

The PR of the treated specimens was calculated as follows:

$$\%PR = \frac{Den_{WPC-dry} - Den_{wood-dry}}{Den_{wood-dry}} \times 100 \quad (1)$$

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

Brinell hardness was calculated from eq. (2):

$$H_B = \frac{F}{(\pi D/2)(D - (D^2 - d^2)^{1/2})} = \frac{F}{\pi Dh} \quad (2)$$

where H_B is the Brinell hardness (N/mm^2), F is the maximum applied force (N), D is the diameter of the steel ball (mm), d is the diameter of the indentation under load (mm),

$$= \sqrt{D^2 - (D - 2h)^2} = 2\sqrt{Dh - h^2}$$

and h is the indentation depth (mm).

Data were analyzed by analysis of variance (ANOVA), Student's t-test, and analysis of covariance. Analysis of covariance was applied as a method to remove the variability in the experiment that could not be controlled by the design structure, such as the hardness and hardness modulus of untreated wood. Mixed models and general linear models were used for the analyses.

RESULTS AND DISCUSSION

Polymer retention

PR values for different treatments are presented in Table II. Different treatments have a definite impact on the PR. Previous studies[32] showed that higher wood density results in lower PR. In our case, PR was also affected by wood density.[31] The analysis of covariance removed this variability by accounting for wood density as a covariate.[33] With covariant analysis (mixed model), the adjusted means of PR for different treatments at a mean wood density of 700 kg/m^3 are presented in Table II.

After considering the pretreated wood density as a covariate at 700 kg/m^3, it became clear that the estimated value of PR is dependent upon the treatment. In general, a higher content of MMA in the mixed impregnants results in lower PR. This is because the density of the MMA monomer is lower than those of

Combination	Mean[a] (%)		Deviation[b]
	I	II	(%)
1	43.4 (5.4)	42.0 (1.1)	3.36
2	50.7 (6.4)	53.1 (1.1)	−4.81
3	48.0 (6.9)	53.3 (1.1)	−11.09
4	45.1 (7.7)	49.1 (0.8)	−8.78
5	56.0 (5.1)	57.5 (1.1)	−2.66
6	59.4 (5.3)	59.1 (1.1)	0.54
7	50.9 (8.9)	54.2 (0.8)	−6.38
8	49.2 (2.4)	46.6 (1.1)	5.46
9	53.3 (5.2)	53.7 (0.8)	−0.92

[a] I is arithmetic PR mean of each treatment and II is adjusted PR mean of treatments with $Den_{wood-dry}$ used as covariate, at a mean of $Den_{wood-dry}$ (700 kg/m^3).
[b] (Mean PR − adjusted mean PR)/mean PR × 100%.

other monomers (HEMA and EGDMA). It appears that there was higher depletion of MMA due to its higher vapor pressure during high temperature *in-situ* polymerization.

Linear regression analysis shows that a linear model, shown in eq. (3), can be used to describe the relationship between the weight fractions of methacrylate impregnants and PR with a R value of 0.79 based on the adjusted PR values.

$$PR = 44.70x_1 + 54.56x_2 + 66.33x_3 + 21.28x_1x_2 \quad (3)$$

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

Equation (3) confirms that WPC with high MMA content had lower PR than that with high HEMA content.

Morphology of WPC and untreated wood

Figure 2 shows the electron micrographs of the cross sections of treated and untreated wood samples. There were vessels and lumens of untreated sugar maple cells available for chemical filling, shown in Figure 2(0). The impregnation of methacrylates into sugar maple was mainly achieved by vessel and lumen filling, as shown in Figure 2(1–9).
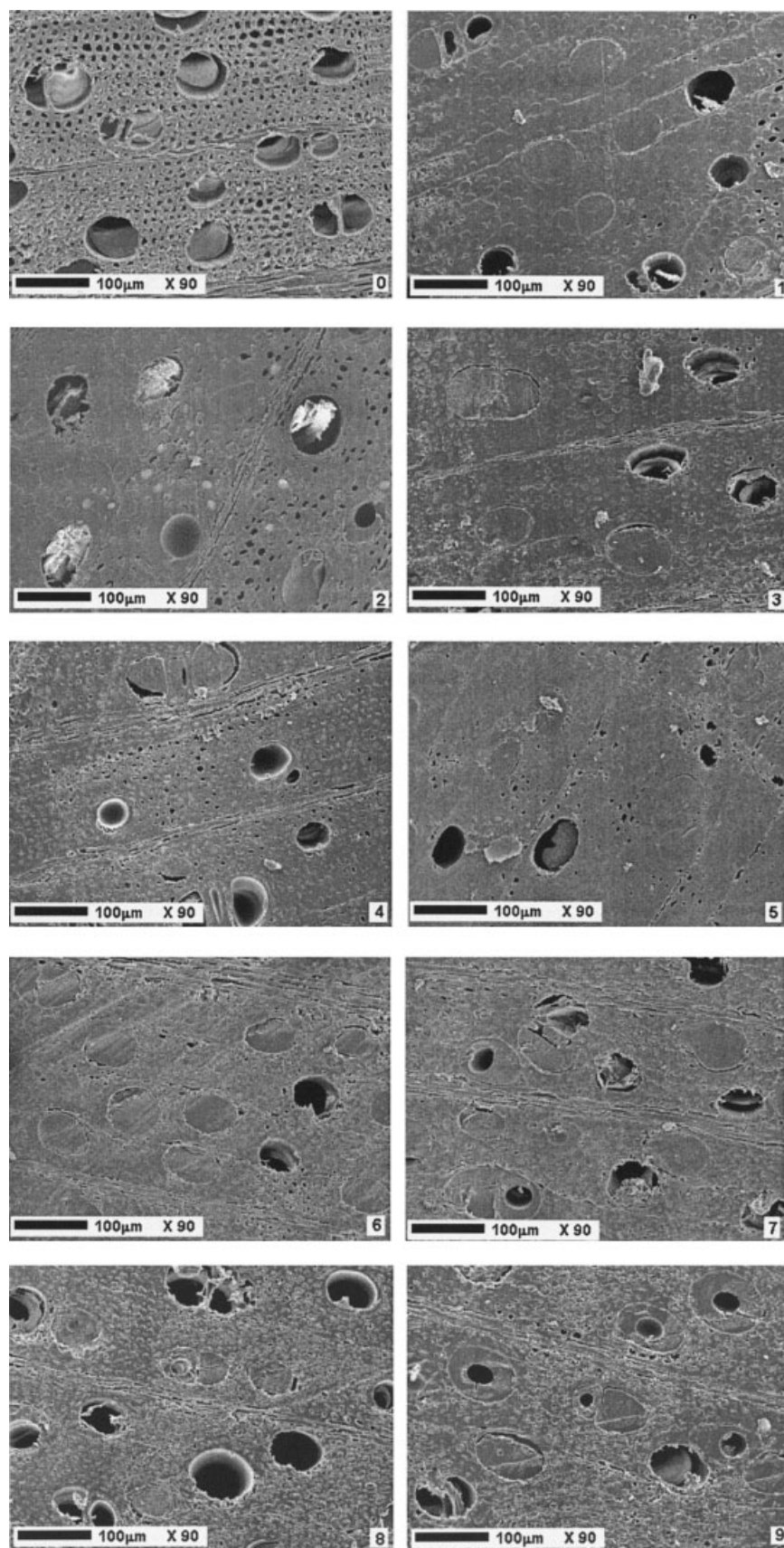
Density profiles

The results of density measurements for different treatments are summarized in Figure 3. WPCs had much higher densities than control samples. It can be found that for different treatments, the density profiles were different. Other treatments showed asymmetric density profiles with low core density except high MMA content combinations (1 and 4). However,

there were small variations in density from two sides to the center. The standard deviation of density through thickness accounted for 3% of the variation, comparing with the average density. This indicated that monomers penetrated all the wood and after in-situ polymerization, the polymers were still evenly distributed in the wood.

Brinell hardness

The average Brinell hardness (H_B) values of untreated wood and WPC for each combination are shown in Table III. WPCs were harder than untreated wood. Impregnation of methacrylates into sugar maple enhances hardness, but does not have distinct effects on dimensional stability because it does not penetrate into the cell wall, as shown by Zhang et al.,[34] in which WPCs with high MMA content obtained the best dimension stability among all the treatments, and improve dimensional stability (12.07% for volumetric antiswell efficiency), and higher HEMA treated sample does not improve the dimension stability. This is consistent with an earlier observation by Wright and Mathias[35] that surface hardness is influenced more by lumen filling than cell wall penetration of chemicals.

Improvement in hardness was also dependent on the natural hardness of the wood. Analysis of covariance was applied in this case, where end-matched sugar maple control and treatment samples were assumed to have the same hardness, and hardness of the end-matched control sample was used as a covariate to adjust the mean of hardness. It was found that H_B of untreated wood samples has a definite interaction with H_{B-WPC} for different treatments, as shown in Table IV. To eliminate the effect of wood density, the H_{B-WPC} was adjusted using the H_B of untreated wood as a covariate at a value of 14.45 N/mm^2. The adjusted mean hardness values are shown in Table III. It can be seen that different chemical compositions had varying degrees of impact on Brinell hardness (deviation was from −6.18% to 0.65%). The formulations containing 90 wt % HEMA and 10 wt % EGDMA had the two highest hardness values, whereas formulations with 90 wt % MMA and 10 wt % EGDMA gave the lowest hardness values. A comparison of the difference in adjusted means of H_{B-WPC} in Table III shows that high MMA content treatments (combinations 1, 4, and 8) were significantly different from other treatments. High MMA content (combinations 1, 4, and 8) gave the lowest hardness values among all the treatments, which is a result of the low PR when compared with other treatments. It was expected that the addition of EGDMA would increase the hardness of WPC. However, this occurred only in high HEMA content systems (combinations 2, 3, and 6), neither in high MMA content systems (combinations 1, 4, and 8) nor the

Figure 2 SEM micrographs of different formulation combinations (numbers refer to combinations 1–9 of MMA:HEMA: EGDMA by weight, as described in Table I, number 0 refers to control sample).
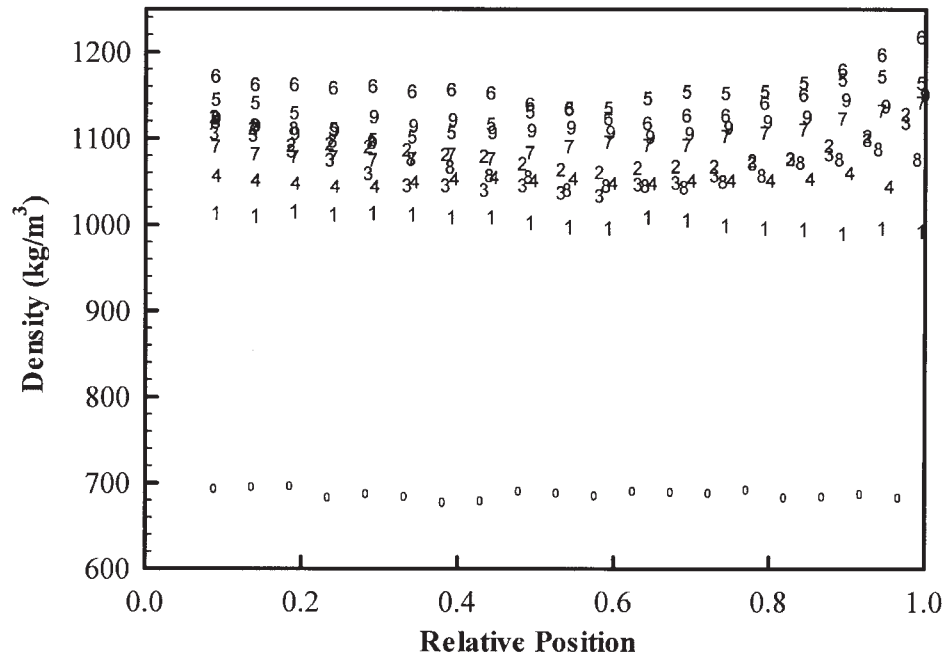
Figure 3 Density profile as a function of thickness (0, untreated wood; numbers 1–9 indicate WPCs with different formulation combinations, as described in Table I).

HEMA and MMA mixture systems (combinations 5, 7, and 9).

Based on the adjusted mean of $H_{B\text{-WPC}}$, a quadratic model can be used to describe the relationship between weight fraction of methacrylate impregnants and HB-WPC with a R2 value of 0.95, as shown in eq.(4).

$$H_{B\text{-WPC}} = 36.40x_1 + 37.74x_2 + 50.76x_3$$
$$+ 5.71x_1x_2 - 27.81x_1x_3 \quad (4)$$

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

Equation (4) shows that whether the addition of EGDMA increases the hardness or not depends not only on the amount of EGDMA, but also on the interactions among component impregnants.

Hardness modulus

The hardness modulus (M_H) values for the different combinations and controls are shown in Table V. WPC samples had higher values of $M_{H\text{-WPC}}$ (1404–1607 N/mm) than did untreated wood samples (635 N/mm). End-matched controls were used as covariates to see if the M_H of untreated wood masked the WPC results. The results presented in Table IV clearly show that there were interactions between the M_H of

TABLE III
$H_{B\text{-WPC}}$ **of Different Treatments (N/mm²)**

Combination	Mean I[a]	Mean II[b]	Deviation[c]	Grouping[d]
1	36.0 (1.4)	36.5 (0.8)	−1.39	A
2	37.7 (1.8)	37.8 (0.8)	−0.11	B
3	37.1 (3.2)	39.4 (1.1)	−6.18	B
4	35.3 (2.7)	35.7 (0.7)	−1.36	A
5	39.0 (1.7)	38.8 (0.9)	0.56	B
6	37.0 (3.8)	38.1 (0.7)	−2.81	B
7	38.4 (2.2)	38.1 (0.5)	0.91	B
8	35.4 (1.0)	35.4 (0.8)	0.08	A
9	38.6 (1.5)	38.3 (0.7)	0.65	B
Control	14.5 (2.7)			

Values in parentheses indicate standard deviation.
[a] I is arithmetic H_B mean of each treatment.
[b] II is adjusted H_B mean of treatments with H_B of wood control used as covariate at mean of 14.45 N/mm².
[c] (Mean $H_{B\text{-WPC}}$ − adjusted mean $H_{B\text{-WPC}}$)/mean $H_{B\text{-WPC}}$ ×100.
[d] Test treatments in the same grouping were not different at 0.05 significance level.

TABLE IV
Test of Fixed Effects

Source	NDF	DDF	Type III F	Pr > F
$H_{B\text{-WPC}}$				
K	9	102	65.91	<0.0001
$H_{B\text{-wood}} \times$ K	9	102	3.64	0.0006
$M_{H\text{-WPC}}$				
K	9	102	21.27	<0.0001
$M_{H\text{-wood}} \times$ K	9	102	6.50	<0.0001

NDF, numerator degrees of freedom; DDF, denominator degrees of freedom; K, different combinations, shown in Table I.

TABLE V
$M_{H\text{-WPC}}$ **of Different Treatments (N/mm)**

Combination	Mean[a] I	II	Deviation[b]	Grouping[c]
1	1440 (89)	1521 (44)	−5.60	A
2	1581 (169)	1515 (44)	4.14	A
3	1521 (209)	1589 (43)	−4.44	A
4	1428 (158)	1503 (32)	−5.29	A
5	1607 (167)	1556 (43)	3.19	A
6	1588 (227)	1549 (42)	2.49	A
7	1582 (176)	1536 (30)	2.87	A
8	1404 (103)	1489 (44)	−6.09	A
9	1584 (109)	1525 (31)	3.72	A
Control	635 (133)			

[a] Data in parentheses indicate standard deviation. I is arithmetic mean of $M_{H\text{-WPC}}$ of each treatment and II is adjusted mean with M_H of wood control as covariate at mean of 643.86 N/mm.
[b] (Mean $M_{H\text{-WPC}}$ − adjusted mean $M_{H\text{-WPC}}$)/mean $M_{H\text{-WPC}}$ ×100.
[c] Test treatments in the same grouping were not different at 0.05 significance level.

untreated samples and different treatments ($P < 0.0001$). The adjusted means of $M_{H\text{-WPC}}$ are also given in Table V. Based on the adjusted means of $M_{H\text{-WPC}}$, although combination 3 (90 wt % HEMA and 10 wt % EGDMA) gave the highest value for M_H, combinations with high MMA contents (95 and 90%) generated the lowest values. In general, there is no significant difference in hardness modulus between the treatments. All the treatments generated similar improvements in hardness modulus.

Relationship between Brinell hardness and hardness modulus

Student's t-test shows that M_H versus H_B of WPC and untreated sugar maple had a strong relationship. Figure 3 shows a plot of M_H versus H_B of WPC and untreated wood. It can be seen that hardness modulus increased with Brinell hardness. Linear regression analyses showed that both linear and quadratic models gave similar predictions. The empirical linear relationship between H_B and M_H can be expressed, with a R^2 value of 0.96, as:

$$M_H = 45.04 H_B - 140.96 \quad (5)$$

Most of the data fall within the 95% confidence limit. This shows that there exists a strong linear relationship between M_H and H_B. As Lewis[30] noted, there could be an advantage to obtain the hardness value indirectly from the hardness modulus, especially for shallow indentations. Since the hardness modulus can be read from the test machine, the use of hardness modulus as a substitute for hardness measurement

reduces variation during hardness measurements and allow for a more efficient hardness calculation.

Modulus of elasticity in bending

According to Gibson and Ashby,[36] at small strains (2%), the behavior of wood is linear–elastic in all three directions (longitudinal, tangential, and radial), while moduli of elasticity in the three directions are different with the modulus of elasticity in the longitudinal direction which is much higher than those in the tangential and radial directions. The tangential and radial directions have similar modulus of elasticity. The treated and untreated wood all show linear–elastic behavior below a strain of 0.2%, and the moduli of elasticity of different treatments are given in Figure 4. Because the vessels and lumens in WPC were filled with polymers after impregnation, stress–strain properties of WPC depended not only on the wood components, their structure, and their morphology, but also on the properties of impregnated polymers, their morphology, and their interaction with wood components. The atactic polymers were obtained after in-situ polymerization for different treatments. Formulation combinations 1, 2, and 5 formed linear polymers, while the other combinations formed nonlinear polymers, including combinations 6, 8, and 9 with 5% crosslinking agent EGDMA, and combinations 3, 4, and 7 with 10% crosslinking agent EGDMA. The intimate contact between polymers and wood cells (filled vessels and lumen) restricted the spatial motion of treated wood components, resulting in an increase in MOE. When the MOE results were adjusted to account for wood variability, the adjusted MOE of WPC was within the range 14,890–16,040 MPa (Table VI). However, the differences between various groups were not statistically significant. Analysis of the ratio of WPC MOE to end-matched control sample MOE also showed that different treatments generated similar improvements (1.16–1.31).

In consideration of the cost, viscosity and process abilities of monomers, and performance of resulted WPCs (hardness and dimension stabilities), it would be better to adopt the high MMA content combination to treat wood so as to improve the dimensional stability and hardness.

CONCLUSIONS

Impregnation of methacrylates into sugar maple resulted in vessel and lumen filling. PR in sugar maple was strongly dependent on the composition of the impregnant, with high MMA content, giving the lowest values among all the treatments. Brinell hardness (H_B) and hardness modulus (M_H) were generally enhanced through impregnation and in-situ polymerization. WPC with different monomers and their differ-
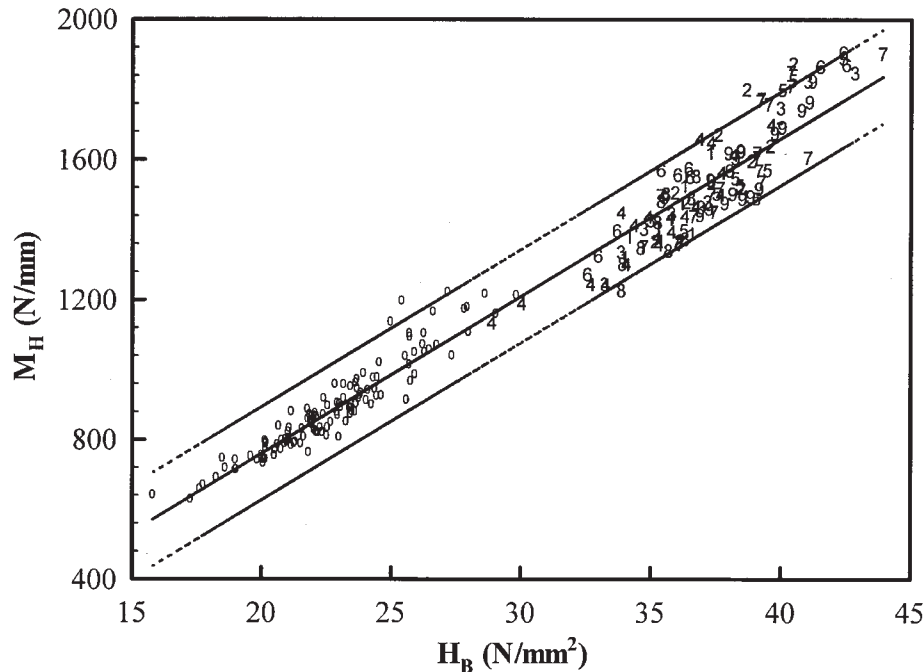
Figure 4 Hardness modulus as a function of Brinell hardness (0, untreated wood; numbers 1–9 indicate WPCs with different formulation combinations, as described in Table I; —(solid line) indicates the predicted value with eq. (5); . . . . . (dotted line) indicates 95% confidence limits for the individual observations).

ent combinations improved both Brinell hardness and hardness modulus. Addition of a crosslinker such as EGDMA did not always enhance H_B and M_H. This may indicate that composite morphology formed during *in-situ* polymerization affects the performance of WPCs. An empirical relationship between H_B and M_H

was established, in which M_H was proportional to H_B for both WPC and untreated sugar maple. The Brinell hardness could be indirectly determined by hardness modulus.

Modulus of elasticity was enhanced through impregnation and in-situ polymerization. Different treatments had the same impact on the modulus of elasticity.

TABLE VI
Modulus of Elasticity (MOE) of WPC and Control Samples

Combination	Mean ($\times 10^4$ MPa)[a] I	II	Ratio[b]	Difference[c] ($\times 10^3$ MPa)
1	1.49 (0.00)	1.511	1.21 (0.03)	2.59 (0.28)
2	1.51 (0.06)	1.534	1.23 (0.09)	2.83 (0.97)
3	1.47 (0.08)	1.492	1.19 (0.04)	2.39 (0.51)
4	1.54 (0.05)	1.604	1.31 (0.02)	3.64 (0.26)
5	1.61 (0.09)	1.569	1.23 (0.00)	2.99 (0.21)
6	1.56 (0.09)	1.527	1.20 (0.04)	2.59 (0.50)
7	1.42 (0.03)	1.489	1.21 (0.01)	2.48 (0.01)
8	1.60 (0.05)	1.506	1.16 (0.05)	2.20 (0.70)
9	1.55 (0.01)	1.500	1.17 (0.03)	2.26 (0.30)
Control	1.26 (0.07)			

[a] Data in parentheses indicate standard deviation. I is arithmetic mean of MOE of each treatment and II is adjusted MOE with MOE of untreated wood as covariate at 1.259 $\times 10^4$ MPa.
[b] Ratio is equal to MOE of WPC divided by MOE of end-matched control.
[c] Difference is equal to MOE of WPC minus MOE of end-matched control.

References

1. Tabil, L. G., Jr.; Sokhansanj, S.; Crerar, W. J.; Patil, R. T.; Khoshtaghaza, M. H.; Opoku, A. Can Biosystems Eng 2002, 44, 55.
2. Briscoe, B. J.; Sinha, S. K. Mat- wiss U Werkstofftech 2003, 34, 989.
3. Baltá Calleja, F. J.; Boneva, D.; Krumova, M.; Fakirov, S. Macromol Chem Phys 1998, 199, 2217.
4. Zamfirova, G.; Lorenzo, V.; Benavente, R.; Perena, J. M. J Appl Polym Sci 2003, 88, 1794.
5. Mina, M. F.; Ania, F.; Baltá Calleja, F. J.; Asano, T. J Appl Polym Sci 2004, 91, 205.

6. Doyle, J.; Walker, J. C. F. Wood Fiber Sci 1985, 17, 369.
7. Holbery, J. D.; Eden, V. L. J Micromech Microeng 2000, 10, 85.
8. Martinez, E.; Esteve, J. Appl Phys A 2001, 72, 319.
9. Alcalà, G.; Skeldon, P.; Thompson, G. E.; Mann, A. B.; Habazaki, H. Nanotechnology 2002, 13, 451.
10. Gong, J. H.; Miao, H. Z.; Peng, Z. J. J Mater Sci Lett 2003, 22, 267.
11. Fu, G. H. J Mater Sci 2004, 39, 745.
12. Gómez-del Río, T.; Poza, P.; Rodriguez, J. J Mater Sci 2005, 40, 1513.
13. Liu, C.; Zhao, Y.; Sun, Q.; Yu, T.; Cao, Z. J Mater Sci 2005, 40, 1501.
14. Wimmer, R.; Lucas, B. N.; Tsui, T. Y.; Oliver, W. C. Wood Sci Technol 1997, 31, 131.
15. Wimmer, R.; Lucas, B. N. IAWA J 1997, 18, 77.
16. Gindl, W.; Gupta, H. S.; Grünwald, C. Can J Bot 2002, 80, 1029.
17. Gindl, W.; Gupta, H. S.; Schöberl, T.; Lichtenegger, H. C.; Fratzl, P. Appl Phys A 2004, 79, 2069.
18. Lewis, J. U.S. Pat. 5,461,108 (1995).
19. Lewis, J. U.S. Pat. 5,612,142 (1995).
20. Rowell, R. M.; Konkol, P. Gen Tech Rep FPL-GTR-55; Forest Products Laboratory, U.S. Department of Agriculture Forest Service: Madison, WI, 1987; p 12.
21. Wright, J. R.; Mathias, L. J. J Appl Polym Sci 1993, 48, 2241.
22. Elvy, S. B.; Dennis, G. R.; Ng, L.-T. J Mater Process Technol 1995, 48, 365.
23. Şolpan, D.; Güven, O. Angew Makromol Chem 1998, 257, 12.
24. Dale Ellis, W.; O'Dell, J. L. J Appl Polym Sci 1999, 73, 2493.
25. Doss, N. L.; Elawady, M. M.; Elawady, N. I.; Mansour, S. H. J Appl Polym Sci 1991, 42, 2589.
26. Magalhães, W. I. E.; da Silva, R. R. J Appl Polym Sci 2004, 91, 1763.
27. Thomas, R. J. In Wood Structure and Composition; Lewin, M.; Goldstein, I. S., Eds.; Marcel Dekker: New York, 1999.
28. Holmberg, H. Holz als Roh- und Werkstoff 2000, 58, 91.
29. Hirata, S.; Ohta, M.; Honma, Y. J Wood Sci 2001, 47, 1.
30. Lewis, W. C. U.S. Forest Service Research Note FPL-0189; Forest Products Laboratory, U.S. Department of Agriculture Forest Service: Madison, WI, 1968.
31. Zhang, Y.; Wan, H.; Zhang, S. Y. Holzforschung 2005, 59, 322.
32. Moore, G. R.; Kline, D. E.; Blankenhorn, P. R. Wood Fiber Sci 1983, 15, 223.
33. Littell, R. C.; Milliken, G. A.; Stroup, W. W.; Wolfinger, R. D. SAS System for Mixed Models; SAS Institute: Cary, NC, 1996.
34. Zhang, Y.; Zhang, S. Y.; Wan, H. J Appl Polym Sci, to appear.
35. Wright, J. R.; Mathias, L. J. J Appl Polym Sci 1993, 48, 2225.
36. Gibson, L. J.; Ashby, M. F. Cellular Solids: Structure and Properties 2nd ed.; Cambridge University Press: Cambridge, 1997.