

# THERMAL BEHAVIOR OF HYDROXYMETHYLATED RESORCINOL (HMR)-TREATED MAPLE VENEER

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## ABSTRACT

The objective of this research was to study the effect of hydroxymethylated resorcinol (HMR) treatment on the thermal and dynamic mechanical properties of maple veneer. The veneers were soaked in HMR solution for either 1, 15, or 30 min, and subsequently dried for either 1, 12, or 24 h at 20°C and 65% relative humidity. Dynamic mechanical thermal analysis (DMTA) tests were performed at a controlled heating rate of 5°C/min using a 3-point bending mode at an oscillatory frequency of 1Hz and an oscillating dynamic strain of 0.01%. Differential scanning calorimetry (DSC) was performed from -40 to 150°C at a heating rate of 10°C/min. Depending on the amount of drying, the storage moduli of wood can be unaltered or reduced as a response to HMR soaking time. Overall, there was no evidence that HMR treatments reinforce wood.

The lignin glass-transition temperature of HMR-treated maple veneer decreased with an increase in treatment time. The lowering of  $T_g$  by HMR treatments was confirmed by DSC results. Both DMTA and DSC data showed a glass-transition shift of wood hemicellulose that was subtle or none in responding to HMR treatments. HMR was theoretically determined to have a closer solubility parameter match (better compatibility) with lignin compared to the other wood cell-wall polymers (i.e., cellulose and hemicellulose). Based on these findings, HMR is postulated to act as a lignin plasticizer.

This study provides new insights into the interactions of HMR with wood and is expected to stimulate further investigations that lead to a better understanding of the wood bond durability enhancement of HMR treatment.

*Keywords:* Hydroxymethylated resorcinol, dynamic mechanical thermal analysis, storage modulus, loss modulus, damping ratio, glass-transition temperature, drying time, solubility parameter, differential scanning calorimetry.

## INTRODUCTION

Recent developments in the forest products industry indicate a trend to produce higher value-added products. This trend is apparent in the manufacture of engineered wood products, primarily beams and trusses for structural appli-

cations in housing, commercial buildings, and exterior structures. These products are seldom made out of a single log. Rather, lumber or veneer is layered to distribute natural defects and is bonded with very durable wood adhesives to attain the desirable dimensions. In composite materials manufacturing, it is commonplace to use primers, coupling agents, and other surface treatments to enhance adhesion. Such practices have

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been adopted by the aerospace, automotive, and plastics industries for the adhesion of metals, advanced composites, ceramics, and plastics. But, these treatments are not common in the wood products industry.

Hydroxymethylated resorcinol (HMR) is a coupling agent which is known to enhance wood adhesion. HMR has been demonstrated to physicochemically couple epoxy adhesive to lignocellulosics of wood, thereby yielding bonds that are extraordinarily high in structural durability (Vick et al. 1995). HMR also improves the adhesion of thermosetting adhesives to southern pine treated with chromated copper arsenate (CCA) preservative (Vick 1995), which is often detrimental to the formation of weather-resistant bonds. So far, thermosetting adhesives whose adhesion to CCA-treated wood is improved by HMR treatments are epoxy, emulsion polymer/isocyanate, polymeric methylene diphenyl diisocyanate (PMDI) (Vick 1996), and phenol-resorcinol formaldehyde resin (PRF) (Vick 1995, 1996). For bonding wood to fiber-reinforced plastics (FRP; e.g., glass-fiber/vinyl ester composites), HMR promotes the exterior durability of the joints bonded with adhesives such as epoxy, phenol-resorcinol formaldehyde resin (Vick 1996), and vinyl ester (Hensley et al. 2000).

The effectiveness of HMR at improving adhesion is dependent on reaction time, which is defined as the time between HMR solution preparation and application to the wood surface (Vick et al. 1998). The original HMR formulation, patented to the U.S. Department of Agriculture (Vick et al. 1994), has an optimum reaction time of 3–8 h (at room temperature) for attaining the highest level of weather resistance in the resulting adhesive bonds (Vick et al. 1998). Within this period, up to 42% of the formaldehyde reacted has been converted to a methylene bridge (Fig. 1) to cause an increase in molecular size. After this period, the molecules become too large to effectively interact with wood and adhesives, and a decrease in delamination resistance was observed (Vick et al. 1998). Therefore, the chemical reactivity of HMR influences the ability of the coupling agent in enhancing wood adhesion.

The chemical reaction of HMR after application to wood surfaces is also expected to influence the level of adhesion enhancement. With only 42% conversion rate prior to HMR application, the formation of methylene bridges and the resulting chemical reaction are expected to continue in the post-application stage. Most studies have been carried out to investigate the effect of HMR coupling agent on the performance of

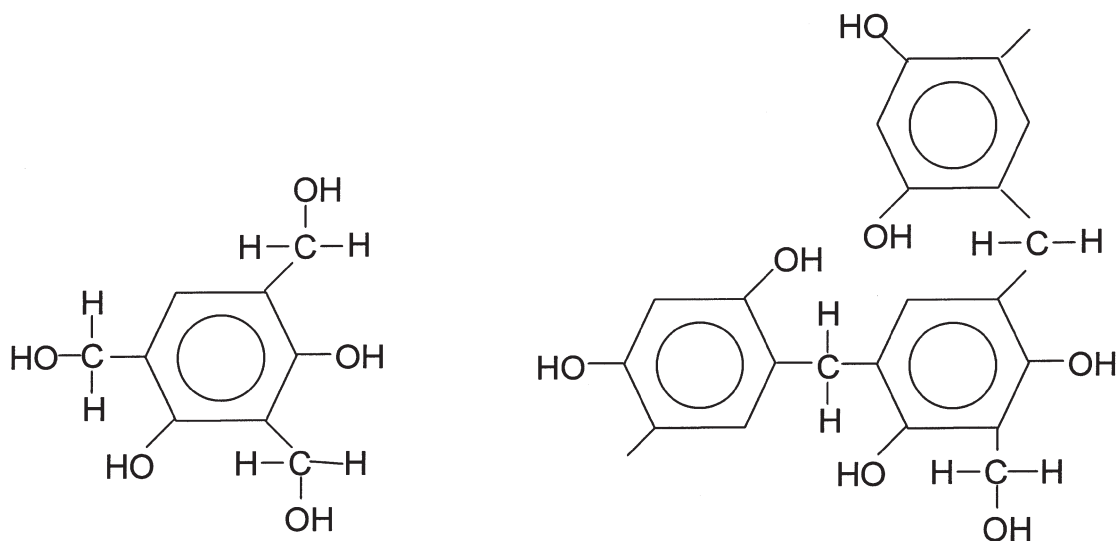


FIG. 1. Hydroxymethyl resorcinol (left) and its trimer (right). Figure adapted from Vick 1996.

wood composites in the presence of thermo-setting adhesives. Research about the behavior of wood after application of HMR to wood in the absence of adhesives is limited. Variables such as HMR spread rate determine the amount of HMR molecules available for further self-polymerization and for interaction with wood, both of which processes occur during standing (drying) time, presenting another variable that potentially can be manipulated. Investigation of such variables is expected to lead to a better understanding and an improved effectiveness of the bond enhancement of HMR treatment.

Thermal analyses are particularly useful for studying miscibility in polymer blends, an example of which is the association between wood and HMR. The dynamic mechanical thermal analysis (DMTA) technique is commonly used to evaluate polymeric materials, which include wood and adhesives, whose mechanical properties are frequency- (time) and temperature-dependent. The technique is widely used to investigate wood/thermosetting adhesive interaction (Marcinko et al. 1998), mechanical property development during curing, and phenomena such as glass transition (and secondary transitions) and cross-linking. A complementary technique is differential scanning calorimeter (DSC), which is often used to follow the process and degree of conversion in adhesive curing and (Park et al. 1999) for investigating glass-transition.

### *Objective:*

The objective of this research was to investigate the effect of HMR treatment and drying time on the thermal and dynamic mechanical properties of maple veneer.

## EXPERIMENTAL METHODS

### *Materials*

HMR coupling agent was prepared following the recipe of Vick (Vick 1995). The 5 weight-percent solution contained 3.34 weight-percent of resorcinol, 2.44 weight-percent of 3 molar sodium hydroxide solution, 90.43 percent of

deionized water, and 3.79 weight percent of a 37%-aqueous solution of formaldehyde. The mixture was reacted for 4 h at room temperature, after which dodecyl sulfate sodium salt (0.5% by weight) was added for promoting wetting of the wood substrate. The wood samples used for HMR treatment were hard maple (*Acer saccharum* Marsh.) veneers obtained from Northern Michigan Veneer (Gladstone, MI), a decorative veneer manufacturer.

### *Sample preparation for DMTA measurements*

Sample veneers with dimensions 6 mm tangential, 0.58 mm radial, and 34 mm longitudinal were prepared. Samples were selected from the earlywood veneer to minimize the effect of the natural variation of wood. Before the HMR treatments, all veneer samples were dried in an oven. In performing the treatment, a soaking procedure was employed as an alternative to spreading on single surfaces so that veneer distortion could be avoided upon drying of the treated samples. The veneers were soaked in HMR solution for either 1, 15, or 30 min. All samples were placed at the same depth from the surface of the HMR solution during treatment. Such treatments, according to previous study (Son and Gardner 2004), respectively result in average weight-percent gain (WPG) values of 1.68%, 2.3%, and 2.78% based on the oven-dried weight of the samples before soaking. Three replicates were investigated in this study for each of the soaking time levels.

The treated veneers were placed on a screen for drying in an environmental chamber (20°C, 65% relative humidity) for either 1, 12, or 24 h. At each drying time, three replications were performed. To observe the differences between HMR and water treatment, some veneers were also immersed in water at the same treatment and drying time levels.

### *DMTA measurements*

Dynamic mechanical thermal analysis was conducted using a model Mk IV DMTA instrument from Rheometrics Scientific. The analysis

was performed at a controlled heating rate of 5°C/min from 25°C to 180°C. The viscoelastic properties of HMR-treated maple veneer were characterized using a 3-point bending mode with the specimen aligned along the grain at an oscillatory frequency of 1 Hz and an oscillating dynamic strain of 0.01%. Data of storage modulus ( $E'$ ), loss modulus ( $E''$ ), and damping ratio ( $\tan \delta = E''/E'$ ) were calculated automatically by the instrument as a function of temperature. Some treated samples (24-h drying time) were also analyzed for a temperature range of -95° to 180°C under the same heating rate so that the glass-transition of hemicellulose could be investigated as a response to HMR treatment time.

#### Differential scanning calorimetry (DSC) measurements

A Perkin-Elmer Pyris-1 DSC with intracooler was used for the thermal analysis. Vented aluminum pans were filled with approximately 10 mg of ground (40-mesh) HMR-treated and untreated maple wood. The scans were made from -40 to 150°C at a heating rate of 10°C/min under a dry nitrogen atmosphere. Three sample replicates were run for DSC measurement.

#### Statistical analysis

Statistical analysis of the data included performing the pairwise multiple comparison procedure, Tukey's test ( $\alpha = 0.05$ ) between the storage modulus or glass-transition temperature of the treated samples for different soaking and drying time. The statistical analyses were performed using Sigma Stat software.

#### RESULTS AND DISCUSSION

##### Effects of treatment and drying time on the storage modulus of HMR-treated maple veneers

Figures 2a and 2b show samples of storage modulus as a function of treatment time for HMR- and water-treated maple veneers. An immediate observation could be made regarding the water-treated samples—the modulus was lower with a longer soaking time. The obvious explanation for this observation was that longer soaking resulted in a higher content of moisture at a designated drying time (Table 1), hence flexibility was increasingly induced in the water-treated samples. The moisture content levels prior to the DMTA experiments were higher in water-treated samples than the HMR-treated

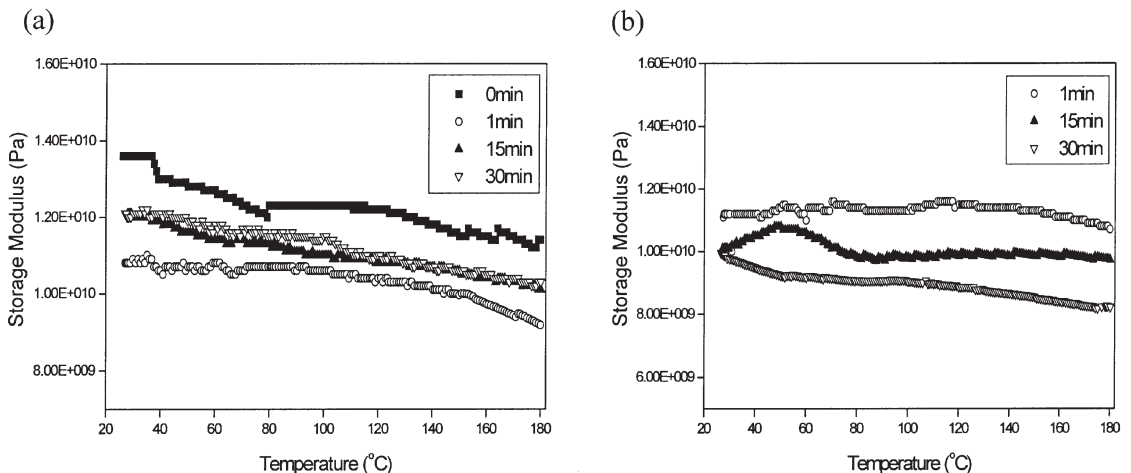


FIG. 2. Storage modulus of HMR (a) and water (b)-treated maple veneer as a function of treatment time after 12-h drying time.

samples (Tables 1 and 2). This observation seems to suggest that the HMR molecules (in aqueous solution of 5% solid content) either preferentially occupied the water-bonding sites of the cell walls or blocked water accessibility to the sites. More importantly, the observation implies that it is necessary to distinguish whether the modulus change in our samples is due to the treatment or the moisture alteration. Two approaches will be used to address the moisture issue. The first of these is to compare the modulus data with the expected values at the same moisture content level. The second approach is to compare the modulus data for the HMR-treated samples in the dry state.

To compare moduli at the same moisture content (MC) level, values of the storage modulus at 40°C were plotted as a function of the initial moisture content (Fig. 3). A predicted curve was made for the reference data points (the water-treated samples) by using the following relation (Haygreen and Bowyer 1989):

$$P = P_{12} \left( \frac{P_{12}}{P_s} \right)^{-\left( \frac{M-12}{M_s-12} \right)}, \quad (1)$$

where P refers to the property at M% moisture content,  $P_{12}$  stands for the property at 12% MC,  $M_s$  means the fiber saturation point, and  $P_s$  represents the property green. In this study, the  $P_{12}$  was given the average modulus value of the water-treated samples that were soaked for 1 min and dried for 24 h (MC 12%; Table 1) while the  $P_s$  value was from the water-treated samples that were soaked for 30 min and dried for 1 h (MC or  $M_s$  25%; Table 1). The justification of using such values for Eq. (1) was evidenced from Fig. 3, which shows that the predicted curve closely fits the experimental data points for the water-soaked samples. Figure 3, also shows that the data points of the HMR-treated samples were below the prediction curve, indicating that the moduli were generally lower than water-treated samples at the same moisture content level. Spe-

TABLE 1. Storage modulus of water-treated maple veneer at 180°C and moisture content (MC) of the samples before the DMA experiments

Soaking time (min)	Drying time (h)					
	1		12		24	
	MC (%)	Storage * modulus (GPa)	MC (%)	Storage * modulus (GPa)	MC (%)	Storage * modulus (GPa)
1	13.2	8.19 A (7.8)	13.1	8.86 A (18.5)	12.2	9.39 A (16.7)
15	15.5	7.80 AB (15.2)	14.0	8.49 A (19.5)	12.5	8.73 A (5.2)
30	24.8	5.80 B (11.7)	15.7	7.62 A (22.9)	12.9	9.89 A (9.9)

Note: \* Values in the brackets are coefficients of variation (COV) in percentage. Values assigned with the same letter in a column are not significantly different by Tukey's test ( $\alpha = 0.05$ ).

TABLE 2. Storage modulus of HMR-treated maple veneer at 180°C and moisture content (MC) of the samples before the DMA experiments.

Soaking time (min)	Drying time (h)					
	1		12		24	
	MC (%)	Storage * modulus (GPa)	MC (%)	Storage * modulus (GPa)	MC (%)	Storage * modulus (GPa)
1	8.1	10.8 AB (5.9)	7.1	9.17 B (8.9)	5.3	9.35 B (9.5)
15	8.6	10.2 AB (8.3)	7.5	10.2 AB (8.4)	6.0	9.81 B (3.8)
30	9.6	9.16 B (9.0)	7.5	10.6 AB (7.7)	6.0	10.4 AB (5.3)

Note: \* Values in the brackets are coefficients of variation (COV) in percentage. Values assigned with the same letter in a column are not significantly different by Tukey's test ( $\alpha = 0.05$ ). Each column of moduli comparisons includes the unsoaked samples (storage modulus = 11.7 GPa; COV = 5.9%), which is assigned a letter "A."

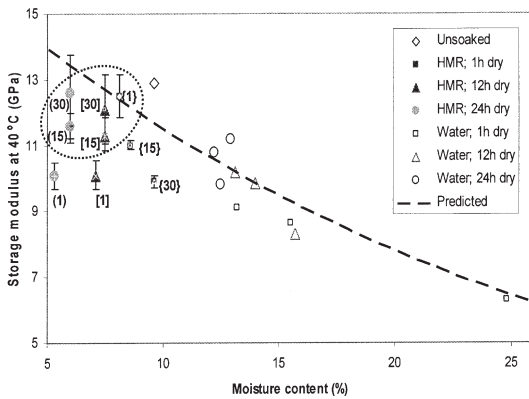


FIG. 3. The effects of pre-DMTA moisture on the storage moduli at 40°C Note: the figures in the brackets next to the data points refer to the HMR soaking time; the dotted circle is aimed at grouping those data points that are insignificantly different from the predicted values (reference curve).

cifically, HMR treatments at a low dosage (1-min drying time) did not alter the storage moduli at a short drying time (1 h), but a moduli reduction was observed upon longer drying (12 h and 24 h). On the other hand, the treatment at a longer soaking time (15 and 30 min) reduced storage moduli of wood initially (at 1 h drying), but the moduli were regained after a longer drying time (12 h and 24 h).

To compare moduli in the dry state, the modulus data at the end of the DMTA run (180°C) were examined. The use of such an approach was justified by the observation that the water-soaked samples at 180°C had storage moduli that were similar (no statistical differences; Table 1), suggesting that the moisture influences had been eliminated. One exception is the samples that had 25% MC, which exhibited a modulus value that was lower than the other samples. This exception seems reasonable because the highly moist samples might not have been dried to zero MC during the time frame of the DMTA run. In other words, if the sample MC prior to DMTA run did not exceed 16% (the next MC level lower than 25%; Table 1), it should be valid to assume that the samples would be in the dry state at the end of the experiment (180°C). Hence it follows that the

HMR-treated samples (5–10% MC before DMTA run; Table 2) should be in the dry state to allow moduli comparisons for examining the effects of HMR soaking and drying.

Values of storage moduli at 180°C (Table 2), at first glance, revealed similar trends that were described in the preceding paragraph, i.e., (1) progressive soaking (from 1 to 30 min) of wood in HMR softened the samples at 1-h drying, but (2) at a sufficient drying time (12 h and 24 h), the same soaking treatments (from 1 to 30 minutes) reversed the HMR softening. Such trends, though they may exist, were not very pronounced when the results of means comparison (Tukey's test) were examined. Samples subjected to different HMR soaking times did not statistically differ from one another at a particular drying time (they all bear the letter "B"; Table 2). Nevertheless, it suffices to conclude that the HMR-treated wood samples are not stiffer than the untreated (unsoaked) samples (which bear the letter "A"; Table 2). In other words, there was no evidence that HMR treatments reinforce wood.

#### *Effects of treatment and drying time on glass-transition temperature of HMR-treated maple veneers*

Table 3 shows the glass-transition temperature for HMR and water-treated maple veneer as a function of treatment and drying time, obtained by DMTA. Examples of  $\tan \delta$  curves of HMR-treated maple veneer as a function of drying time are also shown in Fig. 4. The  $T_g$  values of water-treated samples were first examined (Fig. 5). The effect of water-soaking is evidenced from the observation that a longer soaking time is associated with a lower glass-transition temperature at 1-h and 12-h drying. The effect of sample drying is demonstrated by the increase in  $T_g$  values when the water-soaked samples were progressively dried (from 1 h to 12 h and then to 24 h). The responses of  $T_g$  to both treatment and drying time could be traced to moisture differences – the longer treatment time resulted in a higher moisture uptake, while the longer drying time led to lower moisture content levels, as inferred from the MC data prior to DMTA experiments (Table 1). Moisture plasti-



TABLE 3. Glass-transition temperature and maximum value of  $\tan \delta$  for HMR and water-treated maple veneer as a function of treatment and drying time by DMTA.

Drying time (hr)	Treatment time (min)	$T_g$ (°C) / maximum value of $\tan \delta$		
		HMR		Water
		Peak 1 (Hemicellulose)	Peak 2 (Lignin)	
1	1	-	56.9/0.043	42.4/0.039
	15	-	43.8/0.031	40.5/0.043
	30	-	42.2/0.032	38.9/0.039
12	1	-	63.9/0.020	46.0/0.025
	15	-	54.3/0.022	42.9/0.025
	30	-	50.9/0.026	40.3/0.027
24	1	13.3/0.034	70.2/0.041	45.2/0.023
	15	9.9/0.025	62.5/0.037	45.4/0.028
	30	9.7/0.024	60.1/0.035	46.8/0.033
Unsoaked		14.2/0.034	55.6/0.042	

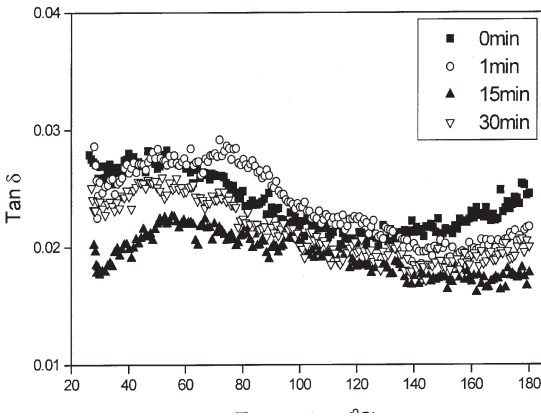


FIG. 4. The effect of treatment time on the damping ratio of HMR-treated maple veneer (drying time = 12 h).

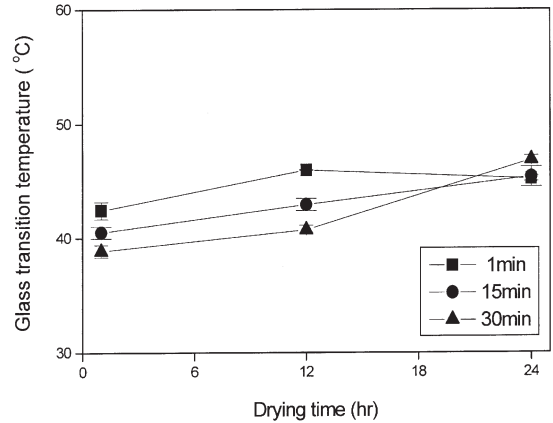


FIG. 5. The effect of treatment and drying time on the glass-transition temperature of water-treated maple veneer.

cizes wood, and this phenomenon is believed to result from the reversible replacement of intermolecular hydrogen bonds that have been restraining the mobility of the wood cell-wall polymer molecules (Irvine 1984). As the restraint is eased by the presence of water, molecular motions can be thermally activated more easily, hence the glass-transition temperature shifts to lower values. Indeed, when the moisture content levels of the samples were approximate in values (12–13%; Table 1) upon sufficient drying (24 h in this study), the samples exhibited  $T_g$  values (45–47°C; Table 3 and Fig. 5) that were very similar regardless of water-soaking time.

Figure 6 shows a plot of glass-transition temperature ( $T_g$ ) for HMR-treated veneers as a function of weight-percent gain (WPG) values, which were associated with different soaking times. To minimize the influence of moisture as discussed in the preceding paragraph, data points for the same drying time were grouped together because these samples had approximately similar moisture content levels (maximum difference of 1.5% MC; Table 2). From Fig. 5, it is observed that the  $T_g$  values of the HMR-treated veneers decreased as a function of WPG. Statistical comparisons performed for each drying time (Fig. 5) confirm that  $T_g$  values decreased with

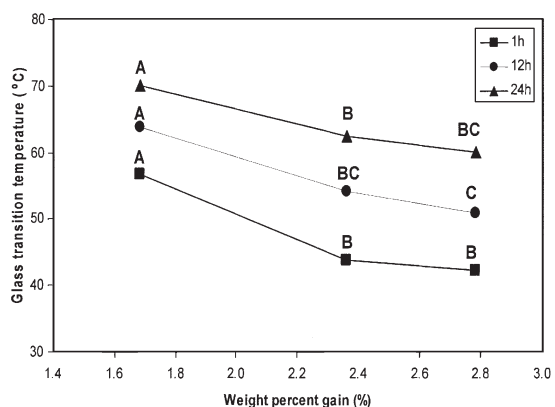


FIG. 6. The effect of weight percent gain and drying time on the glass-transition temperature of HMR-treated maple veneer. Note: Data points assigned with the same letter on a curve are not significantly different by Tukey's test ( $\alpha = 0.05$ ).

the increase of soaking time. To further verify the glass-transition responses to HMR treatments, differential scanning calorimetry (DSC) was performed for HMR-treated wood that had been dried for 24 h. Prior to grinding the samples for DSC experiments, the samples, including the unsoaked samples, were dried in an oven to 4–5% MC levels to allow subsequent  $T_g$  comparisons between treated and untreated wood. Compared to the unsoaked samples (Table 4), the glass-transition temperature of lignin was not altered at a brief soaking (1 min). However, the  $T_g$  value was reduced at a higher soaking time (or weight-percent gain). Such results were consistent for  $T_g$  values determined from either the mid-point or the onset of the temperature transition. Thus, the effects of HMR on the glass-

transition temperature are supported by both DMTA and DSC measurements.

The HMR-induced reduction of  $T_g$  can be attributed to the wood-HMR interaction. Low molecular weight phenolic compounds (290 number-average molecular weight), i.e., phenol-formaldehyde resin in 1% aqueous solution have been observed to penetrate wood cell wall at a weight-percent gain of 6% (Furuno et al. 2004). In the present study, the HMR in 5% aqueous solution should have also penetrated the wood cell wall, given that the resulting WPG values were 2–3%. The penetrated HMR molecules interacted with the wood cell wall to cause a shift in the glass-transition temperature. A shift (10°C) in the  $T_g$  value was also reported by Backman and Lindberg (2004) for the interaction of wood and a hydrophilic type acrylic resin. These researchers discovered that a strong wood/polymer interaction, as evidenced from the scanning electron microscopy (SEM) examination of the fractured bonded surfaces, was associated with a reduction of the glass-transition temperature of the polymer. Using the SEM fractography, Backman and Lindberg (2004) further demonstrated that no  $T_g$  shift was observed in the DMTA experiments when there was no adhesion at the cell-wall level, for example, in the bonding of wood to polyvinyl acetate or polymethylmethacrylate. The above-mentioned wood/polymer interaction study examined the transition temperature shift of the polymer instead of wood. However, it is believed that the tendency also holds true for wood, considering the finding of Oksman and Lindberg (1995) that the  $T_g$  value of one component would move closer to the  $T_g$

TABLE 4. Glass-transition temperature of HMR-treated maple veneer as a function of treatment time by DSC (moisture content of all samples = 4–5%).

Treatment time (min)	Hemicellulose		Lignin	
	$T_g$	$T_{onset}$	$T_g$	$T_{onset}$
0	-10.2 A	-12.4 A	71.9 AB	69.4 A
1	-10.5 A	-11.7 A	73.7 A	64.0 A
15	-14.8 A	-16.4 A	67.1 B	54.3 B
30	-15.4 A	-16.5 A	67.6 B	53.2 B

Note:  $T_g$  values were from the mid-point of the glass transition, while  $T_{onset}$  values were from the onset of the transition. Values assigned with the same letter in a column are not significantly different by Tukey's test ( $\alpha = 0.05$ ).



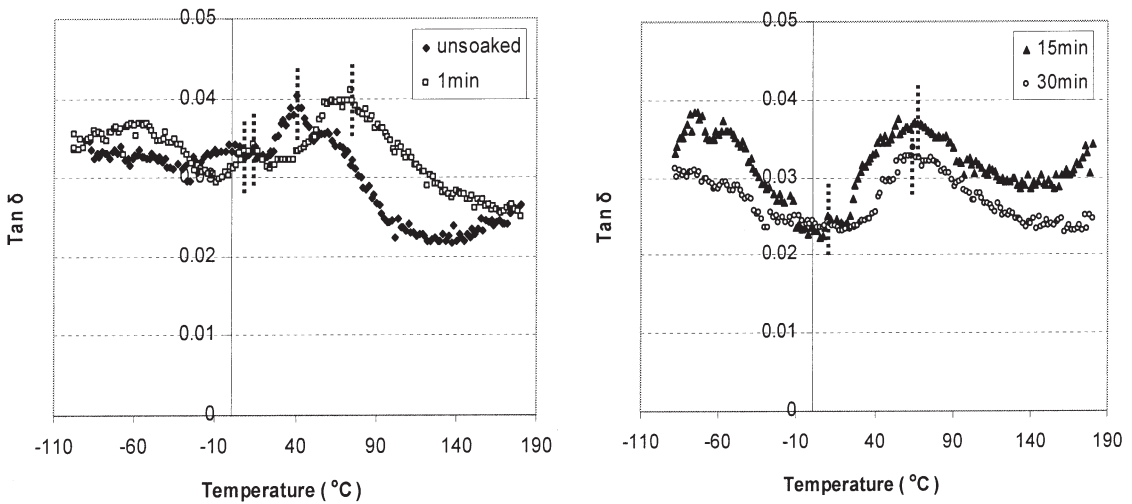


Fig. 7.  $\text{Tan } \delta$  curves of HMR-treated maple wood at 24-hr drying time

of another component in the presence of strong molecular interactions.

Having inferred from the above discussions that the shift in  $T_g$  was an indication of a favorable wood/HMR interaction, it is desirable to further investigate the interactions at the cell-wall polymer level. The changing of the  $T_g$  can be attributed to the HMR association with lignin, which, according to Kelley et al. (1987), exhibits a glass-transition temperature of 60°C at 30% MC. To examine possible associations of HMR molecules with hemicellulose, the thermo-mechanical properties of the veneer samples were determined. As shown in Table 3 and Fig. 7, the  $T_g$  values of hemicelluloses were distinctly different from those of lignin, implying the immiscibility of the two wood polymers. The glass-transition temperature of hemicelluloses decreased more subtly (from 13°C to 10°C) compared to lignin (from 70°C to 60°C) when HMR soaking time was increased from 1 min to 30 min, and the treated samples were dried at 24 h. The hemicellulose glass-transition temperature values (-16 to -11°C; Table 4), examined using DSC, did not show a significant difference among the soaking times although there appears to be a decreasing trend from a brief-soaking (1 min) to a longer-soaking (15 and 30 min) treatment. The subtle-to-none responses of hemicelluloses  $T_g$  to HMR

treatments can be either a consequence of (1) less preferential associations with HMR molecules, or (2) more orderly oriented molecules of hemicelluloses whose mobility was restrained.

To gain further insights into the difference in glass-transition temperature response of lignin and hemicellulose upon HMR treatment, the solubility parameter of the polymerized HMR was calculated. The calculation employed Hoy's method (Hoy 1985) where each of the different structural groups (e.g.,  $\text{CH}_2$ ,  $C_{\text{aromatic}}$ , primary, OH, phenolic OH, etc.) of a polymer repeating unit contributes a certain value of molar attraction and molar volume that are required to determine the solubility parameter value. A similar group contribution approach has been successfully used to produce solubility parameter values to describe different extents of silanol condensation of different silane coupling agents onto poly(vinyl acetate) (Suzuki and Ishida 2003). Such an approach provides a scenario for evaluating the interaction of HMR coupling agent with the wood cell-wall polymers.

In the calculation of the HMR solubility parameter, the HMR trimer in Fig. 1 (whose structure was proposed by Vick (1996), was treated as the repeating unit. This structure does not take into account any forms of hydroxyl group ionization, which may have been induced by the acidity or al-

kalinity of the reaction environment. Nevertheless, the calculated value can be considered an approximate measure for indicating the compatibility between HMR and wood polymer molecules. The calculated solubility parameter for HMR is  $27.5 \text{ J}^{1/2} \text{ cm}^{3/2}$  (Table 5). This value is closer to that of lignin ( $31.1 \text{ J}^{1/2} \text{ cm}^{3/2}$ ) than hemicellulose ( $36.3 \text{ J}^{1/2} \text{ cm}^{3/2}$ ) and cellulose ( $38.6 \text{ J}^{1/2} \text{ cm}^{3/2}$ ), suggesting a better molecular compatibility of HMR with lignin in the wood cell wall. This inference supports the earlier discussion of the preferential association of HMR with lignin.

*The effects of HMR on the wood cell wall—An implication to bond durability*

In the previous sections, it was discussed that HMR reduces glass-transition temperature. A reduction of lignin  $T_g$  values (from  $62\text{--}87^\circ\text{C}$  to  $54\text{--}78^\circ\text{C}$ ) was also observed for water-saturated hardwood species (*Eucalyptus regnans*) upon overnight soaking in dilute alkali (2% sodium hydroxide) at room temperature (Irvine 1984). The observation was attributed to either (1) the rupture of the lignin-carbohydrate bonds resulting in increased lignin mobility, or (2) the existence of alkaline-induced swelling leading to more plasticization by water (Irvine 1984). While the first possibility is likely to occur in HMR treatment which also involves alkali, the second possibility is unlikely because HMR-treated wood, as inferred from Tables 1 and 2, picked up less water compared to the untreated wood. Validating the first possibility would require another control experiment where veneer samples are soaked in a sodium hydroxide solu-

tion of about  $10^{-6} \text{ N}$ , whose pH ( $\sim 8$ ) is expected to resemble that of the HMR solution.

An alternative explanation for the reduction of the glass-transition temperature (and in some instances, the storage modulus) is that HMR acts as a diluent or plasticizer. Plasticizers are usually low-molecular-weight compounds, which exhibit a great ease of conformational rearrangement. When dispersed into the free volume of a polymer, these plasticizer molecules display a larger segmental motion than the host polymer and consequently result in an earlier onset of glass-transition (Sears and Darby 1982). Based on the aforementioned mechanism, HMR qualifies for the role of plasticizer because its molecular weight is expected to be lower than lignin (the host polymer), and according to solubility parameter values, it has a good compatibility with lignin to facilitate dispersion.

Having discussed the effects of HMR on wood cell wall, it is in order to address their implications on the enhanced bond durability commonly observed on HMR-treated surfaces. First, the postulated plasticization implies that the wood adjacent to the bond line becomes less rigid when the surfaces are pretreated with HMR. Although the implication of such a consequence is uncertain at this stage, the important roles of a flexible interphase (which includes the glueline and the adjacent region of the adherend) have been recognized in reducing the microscopic damage of thermosetting resin-based composites (Kobayashi et al. 2003). It was reported that the flexible interphase delayed the occurrence of resin (epoxy) cracking at debonding (Kobayashi et al. 2003). Hence the same effect could also contribute to reduce microscopic damage (and pre-mature failures) of wood joints when the products are subjected to hygrothermal stresses during weathering. Secondly, the calculated solubility parameters indicate a favorable compatibility of HMR ( $27.5 \text{ J}^{1/2} \text{ cm}^{3/2}$ ) to wood lignin ( $31.1 \text{ J}^{1/2} \text{ cm}^{3/2}$ ) and in a lesser extent to hemicellulose ( $36.3 \text{ J}^{1/2} \text{ cm}^{3/2}$ ). The favorable miscibility could reduce the ingress of water molecules (solubility parameter  $48.1 \text{ J}^{1/2} \text{ cm}^{3/2}$ ; Rodriguez 1982) to the bonded surfaces, thereby providing water resistance. Finally, based on the

TABLE 5. Solubility parameter value of HMR and wood components

Components	Solubility Parameter ( $\text{J}^{1/2} \text{ cm}^{3/2}$ )
HMR	27.5
Lignin	31.1
Hemicellulose	36.3
Cellulose	38.6

Note: Data from reference Hansen and Björkman (1998), where sucrose and dextran, respectively, were used as the model compounds for hemicellulose and cellulose.

high dimensional stability of the HMR-treated wood (Son and Gardner 2004), the internal stresses of the bond caused by the swelling of the intact wood can be minimized. These factors possibly combine to enhance bond durability in HMR pretreatment of wood.

#### CONCLUSIONS

This study was designed and performed to investigate the effects of HMR treatment and drying time on the thermal and dynamic mechanical properties of maple veneer.

The results obtained are summarized as follows:

1. Depending on the amount of drying, the storage moduli of wood can be unaltered or reduced as a response to HMR soaking time. Overall, there was no evidence that HMR treatments reinforce wood.
2. HMR lowers the glass-transition temperature of lignin and, to a lesser degree, hemicellulose. The T<sub>g</sub> value is reduced with the increase of treatment time.
3. HMR is postulated to act as a plasticizer, so that a flexible interphase (glueline and adjacent adherends) could exist upon adhesive bonding to delay damages induced by hygrothermal stresses in weathering.

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