Chemical and mechanical aspects of HMR primer in relationship to wood bonding

Alfred W. Christiansen*

Abstract

The mechanism by which hydroxymethylated resorcinol (HMR) primer improves the durability of various adhesives to wood has been hypothesized as covalent chemical links between the adhesive and primer and possibly between the primer and wood. The present work presents experiments to test this hypothesis. In the first test, some resorcinol was displaced by 2-methylresorcinol at various levels to decrease crosslinking but retain hydroxymethyl groups on the active primer for reaction with adhesive and possibly with wood. Increased substitution for resorcinol produced lower durability, which indicates that reduced crosslinking in the primer leads to performance loss. In the second test, HMR-primed wood was stored at elevated temperature and/or long times (up to 3 months) before being bonded with an epoxy adhesive. These extreme storage conditions were expected to allow any remaining hydroxymethyl groups to react and be consumed, if possible, before adhesive was applied. This treatment had no effect on bond durability. The results indicate that the mechanism for durability enhancement likely lies not in chemical reactions with the adhesive, but in some mechanical stabilization of the wood surface. In addition, the results demonstrated that HMR-primed wood has excellent bondability to epoxy resin and does not require that the surface be replaned, even after 3 months of storage.

Wood glued-laminated (glulam) beams are used for many structural applications, from buildings to bridges. Applications for bridges, piers, and other structures exposed to weather are very demanding on adhesives used to bond beams together. Testing is being done on glassfiber-reinforced composites attached to the bottom of beams, because these thin layers on the tension surface of a beam can greatly increase its bending stiffness. As a result, a beam with less top-to-bottom depth can be used to replace a deeper traditional glulam beam. A composite can be attached to a beam along its length in several ways. The attachment should be continuous so that stress is not concentrated along the bond. This generally means some sort of adhesive attachment. Unfortunately, often the adhesives that bond well to wood do not bond well enough to the matrix resin surrounding the glass fibers, which results in a poor bond or one that could fail during weather cycling.

A primer developed at the Forest Products Laboratory (Vick et al. 1996) has proven to be capable of providing a dependable way of enhancing the bonds of wood to fiber-reinforced composites such that the bonds will pass rigorous accelerated-aging cycles (Vick 1997a, Lopez-Anido et al. 2000). The original process for making the primer, hydroxymethylated resorcinol (HMR), required all the ingredients to be mixed on site at one time and the primer to be reacted for 3 hours before it could be used. This could be problematic if a production line were temporarily interrupted. Consequently, another form of HMR, a novolak-based system (n-HMR), was developed (Christiansen et al. 2001, 2003). This primer had the advantage of a shorter reaction time before it could be used and much longer usable pot life (Christiansen et al. 2001). The primed wood was found to have a storage life (at 23°C and 50 percent relative humidity [RH]) of at least 2 weeks (Christiansen and Okkonen 2003) in contrast to the same-day use required for the original HMR primer.

The mechanism of durability enhancement for HMR-primed wood was originally hypothesized to be the formation of covalent chemical bonds (ether links) between the wood and primer, and between the primer and adhesive; that is, the primer was thought to act as a coupling agent. However, the formation of ether bonds is usually done in solution under acidic conditions (Streitwieser and Heathcock 1981). Wood is usually slightly acidic but HMR is slightly alkaline. Bolger

The author is a Chemical Engineer, USDA Forest Serv., Forest Products Laboratory, Madison, WI (achristiansen@fs.fed.us). The author wishes to thank Matt Hansen, James Battaglia, Daniel Yelle, and Jermal Chandler for preparing and testing bonded wood samples; Cherylyn Hatfield for analyzing the data; and Linda Lorenz for HPLC analysis of resorcinol solutions. This study is based on work supported by the USDA Cooperative State Research Education and Extension Serv. under Agreement No. 2001-35103-11191. This paper was received for publication in July 2004. Article No. 9908. *Forest Products Society Member.

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(1973) stated that epoxies do not react with alcohols at room temperature. However, it is the alcohol groups of HMR that were hypothesized to react with the epoxy. These factors diminish the likelihood that reactions between alcohols could be linking the components via ether linkages. Research proved that HMR does not provide a more highly wettable surface than does normal wood for the spreading and penetration of adhesive (Gardner et al. 2001). Thus, the mechanism by which HMR primer works is still unknown, and other models needed to be developed.

Experiments were initiated to explore the importance of two aspects of the effectiveness of HMR. In one set of experiments, the mechanical integrity of HMR was altered by decreasing its maximum possible crosslink density, which should affect its strength and stiffness. The other set of experiments evaluated the ability of HMR to form covalent chemical bonds with an adhesive. In a previous study (Christiansen and Okkonen 2003), 16 days of exposure did not decrease the effectiveness of HMR primer. The conditions in the present study were meant to drive the reaction toward the formation of covalent chemical linkages of the primer before adhesive was applied. Increasing the severity of storage conditions (time and/or temperature) was expected to leave few, if any, reactive hydroxymethyl sites in the HMR primer that would be able to chemically react with the adhesive.

Experimental

Resin and primers

The chemicals used to prepare HMR and the adhesive components used to prepare the FPL 1A epoxy resin were described previously (Vick and Okkonen 1997); FPL 1A epoxy was used because it had formed more durable bonds with wood surfaces than had the other epoxy resins in that study.

In the n-HMR process, a novolak oligomer mixture is made from resorcinol and formaldehyde and then converted to the n-HMR formulation by adding more formaldehyde. For preparation of the novolak precursor to n-HMR, 3.34 mass percent of resorcinol was mixed with 93.08 percent of deionized water, 2.51 percent of 3 M aqueous sodium hydroxide, and 0.098 percent of formalin (37.1% formaldehyde). This resulted in a novolak with a formaldehyde/resorcinol (F/R) molar ratio of 0.38, the ratio used to make n-HMR that had provided the best results in previous studies (Christiansen et al. 2001, 2003). The n-HMR primer requires the addition of more formaldehyde. A formulation with a total F/R molar ratio of 1.50 was used for all trials evaluating the use of different post-treatment times and conditions before adhesive application. The PH of the novolak was adjusted with sodium hydroxide to 8.5 or above before the addition of formaldehyde as hardener.

A series of copolymers of resorcinol and 2-methylessorcinol (Structure 1) were synthesized with formaldehyde to produce a series of novolak primers that would have decreasing levels of resorcinol (which can crosslink into a three-dimensional network) and increasing levels of 2-methylessorcinol (which cannot crosslink). Whereas resorcinol can form polymer chains, with branches, through the 2, 4, and 6 positions, 2-methylessorcinol can only react at the 4 and 6 positions, resulting in a linear polymer. The amount of formaldehyde used to create these copolymers was adjusted to maintain its molar ratio to the two resorcinols at a level where the formaldehyde could theoretically link by cure every reactive position on the aromatic rings of the resorcinols. The 1.5 molar ratio used for the original HMR (Vick et al. 1995) did essentially that. For 2-methylessorcinol alone, the ratio would be 1.0. The 2-methylessorcinol [608-25.3] was obtained from Sigma-Aldrich (Milwaukee, WI) as 98% pure and was used as received. The relative reactivity of resorcinol and 2-methylessorcinol with formaldehyde was estimated from the disappearance of monomers from solution by high-performance liquid chromatography (HPLC). An essentially random incorporation of 2-methylessorcinol into the growing chains was desired, at about the same rate as its molar proportion to resorcinol.

The n-HMR was applied to the wood surface 0.5 hour after the final formalin was mixed into the novolak. Sodium dodecyl sulfate surfactant powder was added to n-HMR (at 0.5% by weight) just prior to application to wood, to aid wetting of the resinous wood surfaces.

Wood

The wood used was southern yellow pine ( *Pinus* spp.). In each case, the wood was straight-grained, free of defects, and flat- to quartersawn. The wood was conditioned at 23°C and 50 percent RH to approximately 9 percent equilibrium MC (EMC). Within 24 hours before bonding, laminates were knife-planed to the thickness of 19 mm specified in American Society for Testing and Materials (ASTM) D 2559 (ASTM 1998).

Because free water decreases the effective bonding of epoxy adhesives to wood, water must be removed from the surfaces of HMR-primed wood before the epoxy adhesive is spread. The water content at the surface was decreased by conditioning the primed wood for several hours, typically overnight. In the present study, the copolymer-primed samples were stored overnight at 50 percent RH and 23°C. For the storage experiments, the samples were stored to allow more chemical reactions to be completed in the applied primer. Samples were stored in three conditions, each at 9 percent MC: 1) 23°C for 3 months; 2) 50°C for 4 days; or 3) 70°C for 24 hours. For the latter two conditions, the assemblies were allowed to cool to room temperature at 50 percent RH before adhesive was applied.

Preparation and testing of delamination specimens

Laminated assemblies were prepared from six pieces of lumber, each 19 mm thick, 76 mm wide, and 305 mm long. The HMR primer was spread by brush on both wood surfaces at 0.15 kg/m² to form a bondline. Storage times for HMR-primed lumber to be bonded with epoxy resin were varied, as described in the previous text. After the laminae were stored for the designated time, the epoxy adhesive was spread on the surfaces by roller to a total of 0.34 kg/m². Laminae were quickly joined together to build an assembly, and the assembly was put into a cold press. The assembly was initially seated without pressure. Closed assembly time was 60 min-
utes for the first bondline and about 50 minutes for the last bondline. Four assemblies were made for each storage condition, each using a new, separate epoxy mix. After the closed assembly time, pressure was applied until a small amount of adhesive squeezed out along the full length of each bondline. In a previous study, such pressure was measured at about 70 kPa. The assemblies were kept under pressure overnight. After being removed from the press, the bonded assemblies were heated at 71°C for 5 hours to ensure that all bondlines were cured to the same degree. The RH of the oven was increased to maintain EMC of the wood to near 9 percent so that bondlines cured.

In a previous study, such pressure was measured at about 70 kPa for 40 minutes; [Step 3] dry at 66°C for 21 to 22 hours.

Three 76-mm-long cross sections were cut from each 6-ply assembly. Each set of three specimens from one assembly was considered one replicate. The specimens were subjected to the severe cyclic delamination procedure of ASTM D 2559. The industry standard for glulam beams (ANSI/AITC 1992) specifies that all wet-use adhesives intended for exterior service in structural lumber laminates must be qualified according to this ASTM specification.

The ASTM D 2559 cyclic delamination test procedure is as follows:

• First cycle: [Step 1] Vacuum-soak in 18°C to 21°C water at 84 kPa for 5 minutes; [Step 2] pressure-soak in 18°C to 21°C water at 517 kPa for 1 hour; [Step 3] repeat events [1] and [2]; [Step 4] dry at 66°C for 21 to 22 hours.

• Second cycle: [Step 1] Steam at 100°C for 1 to 1.5 hours; [Step 21 add water at 18°C to 21°C and pressure-soak at 517 kPa for 40 minutes; [Step 3] dry at 66°C for 21 to 22 hours.

• Third cycle: Repeat events in the first cycle.

Immediately after the final cycle, delamination was measured along all end-grain surfaces to the nearest 1.0 mm with a machinist’s scale under a stereomicroscope.

Delamination was measured from five bondlines on each end of the three cross-sectional specimens from each assembly. Delamination was expressed as a percentage of total bondline length for each specimen and assembly. Statistical analysis was based on these delamination percentages.

High-performance liquid chromatography

Resorcinol and 2-methyl resorcinol were mixed in aqueous solution at 25°C and pH 8, and formaldehyde was added in an amount that would only partially polymerize the solution. Samples (10-µL) were removed from the reaction mixture at 5, 10, 20, 40, 60, 120, and 240 minutes and diluted to 5.0 mL in methanol. The pH of the diluted samples was about 5. The methanolic samples were analyzed by HPLC on a Hewlett-Packard (Palo Alto, CA) 1050 Series HPLC instrument that used an Intersil (GL Sciences, Tokyo, Japan) ODs-3 column (25-cm long, 5-µm particles). A 5-minute hold time was used, and then a linear solvent gradient from 10 to 40 percent acetone in water was programmed over 12 minutes, at a flow rate of 1.0 mL/min. The eluted compounds were detected by ultraviolet (UV) light at 273 nm. Only one sample was analyzed per reaction time and type. The percentage of the area for the monomer peaks remaining, relative to the original (zero time) peaks, was plotted as a function of time. Because only the change in the peak area relative to its initial value was used, this process gave a reasonable approximation of the rates.

Results and discussion

Copolymer effects

In this first set of experiments, the maximum possible crosslink density of the HMR was decreased under the hypothesis that this would decrease its mechanical integrity. This change should affect the strength and stiffness of HMR, but still leave hydroxymethyl groups for possible linking reactions with wood or adhesive. HPLC was used to evaluate the relative reactivity of resorcinol and 2-methylresorcinol in a solution containing both molecules to which formaldehyde was added. The course of reaction was followed, plotting the amount that would only partially polymerize the solution. This change should affect the strength and stiffness of HMR, should remain equal for the two monomers over time, no matter how much of each monomer was originally in the mixture.

The amount of resorcinol decreased, relative to its initial level, at a faster rate than did the 2-hydroxymethylresorcinol. This is not surprising as resorcinol initially has three active sites (at the 2, 4, and 6 positions) for reaction, whereas 2-methylresorcinol has only two active sites (the 4 and 6 po-
tions). If all sites on resorcinol had equal reactivity, one would calculate that resorcinol monomer should react 1.5 times as fast as 2-methylresorcinol. In fact, the 2-position on resorcinol is a bit less reactive than the 4-(and identical 6-) position on the resorcinol ring. Results of 13C NMR experiments on solutions of resorcinol reacting with formaldehyde (Christiansen 2000) indicated that in the first 12 minutes, 2-hydroxymethylresorcinol constituted only 20 percent of the initial observed products (the only other product was 4-hydroxymethylresorcinol) as opposed to 33 percent expected if all three positions had equal reactivity. Therefore, the actual reactivity ratio for resorcinol to 2-methylresorcinol might be expected to be less than 1.5 but not as low as 1.0. (The methyl group in the 2-position of 2-methylresorcinol affects the absolute reactivity of the equivalent 4- and 6-positions in comparison with resorcinol.)

The values for an actual simultaneous test in Table 1 show that in the initial stages resorcinol evidenced more reactivity (was consumed more quickly) than did 2-methylresorcinol; but within 40 minutes, the rate of consumption of resorcinol and 2-methylresorcinol, on a per site basis, had equalized as a result of the relatively lower concentration of resorcinol at that point. Therefore, the likely initial products of such a reaction would be slightly more enriched in resorcinol than the proportion of its active sites would suggest; but after 40 minutes, the two resorcinol monomers would have been incorporating at equal molar ratios.

Derivatives of both resorcinol and 2-methylresorcinol formed quickly after formaldehyde was added to either compound. From both unreacted monomers, a hydroxymethylated species formed quickly, detected by HPLC at shorter retention times than was the unreacted monomer. A dimer (two resorcinols joined by a methylene bridge) formed soon afterward, detected at longer retention times than was unreacted monomer. This is seen in Table 2 for samples taken from analogous systems after 5 minutes of reaction with formaldehyde. Other derivatives also formed, but at this early reaction time they were present in much lower quantities than were the monohydroxymethylated monomer and dimer. This behavior is analogous to the pattern of hydroxymethylated phenol exiting the chromatographic column before phenol, and of phenol dimer exiting after phenol, that was observed in analogous solvent-gradient HPLC work by Grenier-Loustalot et al. (1994). Because species concentration is followed by means of UV absorbance, a dimer (two phenolic rings) will have approximately twice the absorption of a monomer (single phenolic ring), as illustrated by the molar absorption coefficients at 273 nm of phenol and 4,4′-dihydroxydiphenylmethane, 1700 and 30001·mol, respectively (Grenier-Loustalot et al. 1994).

Although 2-methylresorcinol had good reactivity, the important point here is its effectiveness as a primer in copolymers with resorcinol. In previous studies with n-HMR primer, the mean delamination values stayed below the 5 percent maximum level specified by ASTM, especially for primed specimens dried for only 1 day before adhesive was applied (Vick et al. 1998, Christiansen and Okkonen 2003). The incorporation of copolymer units into the resorcinol-formaldehyde primer did have effects on primer performance (Fig. 2). Whereas the four assemblies of normal n-HMR (0% 2-methylresorcinol) showed a mean delamination value of 1.65 percent, the level of delamination increased with addition of 2-methylresorcinol. Earlier trials of epoxy bonded to unprimed southern yellow pine in glulam specimens for control tests gave a mean delamination value of 50 percent (Christiansen et al. 2003). The results indicate that crosslinking, which provides the strength and stiffness of thermoset systems, may occur and is important to the effectiveness of n-HMR, and therefore HMR in general.

### Storage time and temperature effects

In the second set of experiments, the ability of HMR to form covalent chemical bonds with an adhesive was decreased by increasing the time and/or temperature conditions under which HMR-primed wood was reacted and stored before application of adhesive. These conditions were expected to drive the reaction of HMR before adhesive was applied.

Table 2.—Areas of HPLC peaks for reactants after 5 minutes.

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>Area (mAU·s)</th>
<th>Proportion of area (%)</th>
<th>Comment</th>
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</thead>
<tbody>
<tr>
<td><strong>Resorcinol + formaldehyde (F/R = 1:1)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.19</td>
<td>44.3</td>
<td>1.92</td>
<td>Unknown</td>
</tr>
<tr>
<td>5.73</td>
<td>25.5</td>
<td>1.11</td>
<td>Unknown</td>
</tr>
<tr>
<td>5.92</td>
<td>30.3</td>
<td>1.32</td>
<td>Unknown</td>
</tr>
<tr>
<td>6.47</td>
<td>43.8</td>
<td>1.90</td>
<td>Unknown</td>
</tr>
<tr>
<td>6.84</td>
<td>339.0</td>
<td>14.7</td>
<td>R-CHOH</td>
</tr>
<tr>
<td>7.90</td>
<td>65.7</td>
<td>2.85</td>
<td>Unknown</td>
</tr>
<tr>
<td>10.41</td>
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<td>2.00</td>
<td>Unknown</td>
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<tr>
<td>10.92</td>
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<td>62.7</td>
<td>Resorcinol</td>
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<tr>
<td>13.19</td>
<td>211.0</td>
<td>9.15</td>
<td>R-CH2-R</td>
</tr>
<tr>
<td><strong>2-Methylresorcinol + formaldehyde (F/2MeR = 1:1)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.02</td>
<td>27.5</td>
<td>1.91</td>
<td>Unknown</td>
</tr>
<tr>
<td>10.12</td>
<td>233.0</td>
<td>16.3</td>
<td>2MeR-CHOH</td>
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<td>12.25</td>
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<td>70.6</td>
<td>2-Methylresorcinol</td>
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<tr>
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<td>27.3</td>
<td>1.90</td>
<td>Unknown</td>
</tr>
<tr>
<td>16.57</td>
<td>99.8</td>
<td>6.96</td>
<td>2MeR-CH2-2MeR</td>
</tr>
</tbody>
</table>

*aPosition of peak for starting resorcinol (R).  
*bPosition of peak for starting 2-methylresorcinol (2MeR)
When resorcinol in an HMR-type primer is incrementally displaced by 2-methylresorcinol (which cannot form crosslinks), the ability of the primer to resist cyclic swelling and shrinking cycles is notably reduced. Bonds made to the more heavily modified primer-treated woods do not reach the 5 percent maximum delamination limit for softwoods set by ASTM D 2559. This chemical replacement affects the mechanical strength of the primer crosslink network.

The storage of a primed wood surface at either a substantially higher temperature or for a long time at room temperature, under conditions where accessible reactive sites in the chemical primer are expected to be as fully reacted as possible, does not seem to affect the ultimate durability-enhancing properties of the primer. Thus, covalent chemical bonding of primer to the subsequently applied adhesive seems unlikely to be a significant factor in bond durability.

These two results indicate that the likely mechanism of bond durability enhancement by the HMR primer is by dimensional stabilization of the wood surface. A surface that does not swell and shrink as much as a normal wood surface decreases the mechanical stresses on the bondline, leading to better bond strength and thus less delamination in cyclic shrink-swell cycles.

**Conclusions**

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