A Novolak-Based Hydroxymethylated Resorcinol Coupling Agent for Wood Bonding

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Abstract
A hydroxymethylated resorcinol (HMR) coupling agent was previously shown to enhance the exterior durability of epoxy and one-part polyurethane bonds to wood and of phenol-resorcinol-formaldehyde bonds to southern pine treated with chromated copper arsenate. In its original state of development, HMR is not user friendly. It has essentially no shelf life, and the resorcinol and formaldehyde components must be mixed and reacted for a few hours before being applied. By using less formaldehyde, we made a novolak-type pre-polymer that produces a liquid material stable in storage. Prior to applying this compound to wood, additional formaldehyde is added to the novolak to make the HMR usable immediately and up to 7 hours after formaldehyde addition. The new form of HMR is as good a coupling agent as the original HMR, producing epoxy bonds to wood that pass delamination requirements when exposed to the three accelerated aging cycles of ASTM D2559.

Introduction
Durable exterior-quality bonds to wood have been made for decades using hot-press phenolic resins and cold-setting resins based on resorcinol-formaldehyde (RF). However, these resins do not form bonds of adequate durability to certain materials, including
• chromated copper arsenate (CCA)-treated southern pine,
• composites of wood and nonwood materials such as plastics or metals that may require epoxies or polyurethane adhesives, and
• wood joints where significant pressures cannot be exerted to close gaps, for example, repairs to in-place structural members and structural joints of wood sport airplanes.

Although substantial research (summarized in reference 12) has shown that epoxies can provide strong bonds to wood in the dry state and on exposure to water, no epoxies are known to meet the requirements for resistance to delamination as specified in ASTM D2559 (2).

In 1995, researchers at the Forest Products Laboratory first published results on hydroxymethylated resorcinol (HMR) as a new coupling agent for wood products (4,12), and a patent was issued in 1996 (7). This coupling agent has the ability to enhance adhesive bonds to wood and other materials. HMR is effective in promoting durable bonding of phenol-resorcinol-formaldehyde (PRF) adhesives to CCA-treated southern pine (4). In the past, the American Institute of Timber Construction (AITC) did not certify southern pine lumber for glulam if the lumber had previously been treated with CCA (1). HMR was also used to make flakeboards from CCA-treated wood (7).

Epoxy and polyurethane adhesives that strongly adhere to many materials usually do not make bonds to wood that survive the most rigorous moisture cycling tests. However, HMR enables epoxy resin to make very durable bonds to wood (5,11,12), especially at low bonding pressures (8). After discovering that several one-part polyurethanes did not provide the quality of bonds needed for structural durability (9), researchers later found that pretreating the wood with HMR en-
abled these same one-part polyurethanes to produce highly durable bonds (10).

HMR also significantly improves bonding of wood to some plastics used in composites. Epoxy adhesives that bond well to fiber-reinforced vinyl ester or epoxy plastics (used for structural reinforcement matrices) do not make durable bonds to wood. Even RF adhesives do not form very durable bonds between wood and phenolic-matrix composites. Vick (5) demonstrated that highly durable composites could be made with epoxy adhesives if the wood surfaces were primed with HMR before bonding.

The original HMR coupling agent is prepared at the time of use by mixing resorcinol with formaldehyde (formaldehyde to resorcinol (F/R) molar ratio of 1.54) at pH 9 in a 5 percent solids aqueous solution at room temperature. The ingredients of the original HMR formulation (6) are shown in Table 1. This version of HMR becomes most effective 3 to 4 hours after mixing, and it can be used effectively for up to about 8 hours. The length of the reaction time between preparing the solution and applying it to the wood surface strongly affects the molecular size distribution and remaining reactivity of HMR, as well as the durability of adhesion (6). Reaction times either shorter or longer than the optimum range result in bonds to the HMR-primed wood that are less resistant to delamination. Fresh chemicals must be carefully prepared for each new batch of HMR.

To better understand the chemistry of HMR, research focused on the chemical and polymeric nature of HMR at its various stages of reaction (6). Differential scanning calorimetry (DSC) revealed that about a quarter of the total exothermic heat of reaction was given off between 3 and 4 hours; by 8 hours, about 50 percent of the heat was given off. Size exclusion chromatography showed that a series of products, varying from hydroxymethylated monomers to oligomers, was formed in the same period. After 8 hours, HMR liquid still contained at least 25 percent of monomeric material (resorcinol and its first derivative). This balance of reactive monomers and oligomers may be important for the effectiveness of the coupling agent. Finally, carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectroscopy showed that most of the original free formaldehyde was consumed quickly, but hydroxymethylated functional groups were still the most abundant product of formaldehyde after 8 hours. This means that polymerization to high molecular weight products had not generally occurred.

**Limitations to the Use of HMR**

Two main obstacles to the commercial use of HMR became apparent to us. First, HMR has no storage life. Thus, every batch has to be mixed on site from accu-

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcinol, crystalline</td>
<td>3.34</td>
</tr>
<tr>
<td>Water, deionized</td>
<td>90.43</td>
</tr>
<tr>
<td>Sodium hydroxide, 3 molar solution (10.8% by weight)</td>
<td>2.44</td>
</tr>
<tr>
<td>Formaldehyde solution (37.1% by weight, aqueous)</td>
<td>3.79</td>
</tr>
</tbody>
</table>

rately measured proportions of starting chemical, which is time consuming and prone to error. Each batch has only 3 to 4 hours of storage life. The second obstacle was another time constraints. There is a 3- to 4-hr. waiting period before the material can be used, and a mere 3- to 4-hr. pot life remains. These time constraints necessitate starting batches long before they could be used and require at least two batches per 8-hr. shift.

Normal resorcinol-based resins are sold as stable, aqueous novolak resins. Enough formaldehyde is added to increase molecular weight but not enough to induce gelation of the resin (F/R <0.8). When the adhesive is needed, additional formaldehyde is added to the novolak (for final F/R ≥1.1). These chemicals react to form reactive adhesive molecules that cure to a strong, hardened state. The novolak has an essentially infinite storage life.

We used this same approach to prepare HMR as a stable novolak system, with an infinite storage life, that could be activated simply by adding a premeasured quantity of formaldehyde. Previous NMR spectroscopy results (3) had indicated that formaldehyde put into alkaline resorcinolic solution reacts almost completely with resorcinol within 1.5 hours. What appeared to take the most time to bring HMR to an effective state as a coupling agent was to increase the molecular weight. This was observed by molecular size analysis. Rather than preparing HMR at the job site, it would be more convenient to synthesize an RF novolak at a resin company and then ship it to a wood-bonding plant. When ready for use, the novolak would simply be mixed with the final formaldehyde. The activated, novolak-based HMR (n-HMR) would quickly become an effective coupling agent. Thus, the novolak system could be stored indefinitely, measured proportioning of four starting chemicals would be unnecessary, and waiting time for reaction would be reduced.

However, because of the previously measured low degree of reaction of the original HMR at its earliest effectiveness (about 25% of total heat of reaction), we expected that the F/R molar ratio of the novolak would be
Table 2.—Ingredients of FPL 1A epoxy.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dglycidyl ether of bisphenol A (DGEBA) epoxy resin</td>
<td>100.0</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>12.5</td>
</tr>
<tr>
<td>Hydrophobic fumed silica</td>
<td>2.5</td>
</tr>
<tr>
<td>Triethylenetetramine hardener</td>
<td>11.1</td>
</tr>
</tbody>
</table>

DGEBA is D.E.R. 331 from Dow Chemical Company (Midland, MI); benzyl alcohol (99%), Aldrich Chemical Company (Milwaukee, WI); hydrophobic fumed silica, Cab-O-Sil N70-TS grade, Cabot Corp. (Tuscola, IL); triethylenetetramine hardener, D.E.H. 24, Dow Chemical Company.

Table 3.—Ingredients of n-HMR for exploratory and comprehensive tests.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Exploratory test</th>
<th>Comprehensive test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcinol, solid</td>
<td>0.23 (A)</td>
<td>0.31 (C)</td>
</tr>
<tr>
<td>Water, deionized</td>
<td>90.74</td>
<td>90.44</td>
</tr>
<tr>
<td>NaOH, solution</td>
<td>2.36</td>
<td>2.44</td>
</tr>
<tr>
<td>Formalin</td>
<td>3.12</td>
<td>3.03</td>
</tr>
<tr>
<td>For novolak</td>
<td>0.55</td>
<td>0.76</td>
</tr>
<tr>
<td>For final activation</td>
<td>0.92</td>
<td>0.95</td>
</tr>
</tbody>
</table>

considerably below the usual F/R of 0.7 to 0.8 for many resorcinolic novolak resins. One-quarter 1.54 F/R = 0.39.

Experiments with Novolak Versions of HMR

The chemicals for the original and novolak HMR compounds and for n-HMR were crystalline resorcinol, 37.1 percent aqueous formaldehyde solution, 3 M sodium hydroxide, and deionized water, as indicated in the previous text. The wood was Douglas-fir lumber at approximately 9.5 percent equilibrium moisture content (EMC), knife planed to 19 mm (3/4-in.) thickness the day before coupling agent was applied. The adhesive was FPL 1A epoxy. The ingredients of FPL 1A epoxy are shown in Table 2; they were mixed just before use.

In the present experiments, the final n-HMR was to have the same composition as that of the original HMR (F/R of 1.54). Thus, the novolaks were formed by leaving out a calculated amount of formaldehyde solution (formalin) to give one of the desired novolak F/R molar ratios. Later, the calculated amount of formaldehyde was added to produce active n-HMR.

The ingredients of n-HMR for the exploratory and comprehensive tests are shown in Table 3. For the exploratory tests, HMR was applied 0.5 or 2 hours after addition with mixing of the final formaldehyde solution. For the comprehensive tests, HMR was applied at intervals between 0 and 3 hours (up to 7 hr. for novolak D) after the final formaldehyde was incorporated. Dodecyl sulfate sodium salt [98% pure, Aldrich Chemical Company, Milwaukee, WI] was added to n-HMR (at 0.5% by weight), just prior to application to wood, to aid wetting of resinous wood surfaces. For effective bonding with epoxy adhesives, water must be evaporated from the primed wood surfaces before the adhesive is spread. Moisture was evaporated by drying the primed wood overnight at 50 percent relative humidity (RH). The coupling agents based on these novolaks were applied to wood assemblies before bonding with epoxy. A control set of epoxy-bonded assemblies was laminated without coupling agent.

Reaction times were determined by DSC for four novolaks with different F/R ratios. Reaction time was measured from the time the formaldehyde was added to the solution of resorcinol, water, and sodium hydroxide. The equipment and techniques used for DSC analysis of residual heat of reaction of the coupling agents are given in a previous paper (6), except that the temperature for each scan was 20°C (the original reference was incorrect). Before DSC measurements could begin, it was necessary to mix the novolak with formaldehyde to form the n-HMR solution outside the calorimeter. Within seconds after mixing, early reactions produced hydroxymethyl and hemiformal groups. Since some reactions occurred outside the calorimeter, this type of calorimeter could not give an exact measure of the total heat of reaction. Also, measuring very small residual heats of reaction at n-HMR reaction times after 8 hours became more difficult, particularly when dilute solutions were analyzed.

$^{13}$C-NMR was used to record resonance peaks for chemical groups derived from formaldehyde in the novolak. The equipment and basic techniques for $^{13}$C-NMR were described previously (6). In the present study, $^{13}$C formaldehyde was used to make a novolak at 0.38 F/R and 4.2 percent solids. Amounts of ingredients were adjusted to account for the 20 percent concentration of $^{13}$C-formaldehyde in its solution (compared
with normal 37%). Adjustment was also made for the slightly higher molecular weight of the $^{13}$C-formaldehyde compared with normal formaldehyde. Because $^{13}$C-formaldehyde is expensive, small masses and volumes were used, which produced less accurate additions of components. Deuterium oxide, used to provide a lock signal for the NMR experiment, replaced 11 percent of the water.

**Bonding and Delamination Tests of Specimens**

Laminate assemblies were prepared from six pieces of lumber, each 19 mm thick, 76 mm wide, and 305 mm long. Both surfaces intended for a bondline were spread by brush with 0.15 kg/m² of n-HMR on each surface. After the surfaces were dried overnight at 23°C and 50 percent RH, they were spread by roller with the epoxy adhesive to a total of 0.34 kg/m². After the last bondline was spread, closed assembly time ranged from 50 to 60 minutes. After the assembly was put in a cold press, the pressure was increased until a small amount of adhesive squeezed out along the full length of every bondline (pressure was measured at about 69 kPa in previous studies). The assemblies were kept under pressure overnight. Then, to ensure that all bondlines were cured to the same degree, the laminates were heated to 71°C for 5 hours. Relative humidity of the oven heating air was increased to maintain wood EMC (9.5%) so that bondlines would not be stressed by shrinkage of the wood while the resin cured.

Each treatment combination was replicated four times (four laminates) in the comprehensive tests and two times (two laminates) in the exploratory tests. The replicates were six-ply lumber laminates, each cut into three 76-mm-long sections. Delamination was measured along each bondline on both ends of each section. For the comprehensive tests (12 laminated sections), 9.14 lineal meters of bondline length were measured for each treatment combination.

The laminated sections representative of each treatment were subjected to the severe cyclic delamination procedure of ASTM D2559 (2). Industry standard ANSI/AITC A190.1-1992 (1) specifies that all wet-use adhesives intended for exterior service in structural lumber laminates must be qualified according to the ASTN specification. The ASTM D2559 cyclic procedure is as follows:

**First Cycle**
1. Vacuum-soak in 18° to 21°C water at 84 kPa for 5 minutes.
2. Pressure-soak in 18° to 21°C water at 517 kPa for 1 hour.
3. Repeat events 1 and 2.
4. Dry at 66°C for 21 to 22 hours.

**Second Cycle**
1. Steam at 100°C for 1 to 1.5 hours.
2. Admit 18° to 21°C water and pressure-soak at 517 kPa for 40 minutes; repeat event 4 of first cycle.

**Third Cycle**
Repeat events of first cycle.

Immediately after the final cycle, delamination was measured along all end-grain surfaces to the nearest 0.25 mm using a machinist's scale under a stereomicroscope. Delamination was expressed as a percentage of total bondline length for each section, for each laminate, and for each treatment. These delamination percentages were statistically analyzed by a generalized linear model procedure, and Tukey's studentized range test with a 0.05 level of probability was used to determine which treatments were significantly different.

**Results**

**DSC and NMR**

The DSC measurements of heats of reaction at hourly intervals are shown in Figure 1 for n-HMR mixes prepared at four novolak F/R molar ratios. Nearly all the potential reactivity of the novolak-forming reaction was consumed within the first 24 hours. Thus, it can reasonably be expected that within 2 days few, if any, hydroxymethyl groups would remain on the resorcinolic rings. Any subsequent reaction of the novolak must be initiated by introduction of more methylene donor, such as formaldehyde.

A 0.38 F/R novolak made with $^{13}$C-formaldehyde was synthesized at room temperature 17 days before NMR spectroscopic analysis. A spectrum of the novo-
Table 4.—Exploratory novolak-based-HMR delamination results.\(^a\)

<table>
<thead>
<tr>
<th>Novolak F/R ratio</th>
<th>Time after mixing (hr.)</th>
<th>Average delamination (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23 (A)</td>
<td>0.5</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.42</td>
</tr>
<tr>
<td>0.39 (B)</td>
<td>0.5</td>
<td>2.42</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.87</td>
</tr>
</tbody>
</table>

\(^a\) ASTM specification requires that average delamination allowed for softwoods be less than 5%.

Delamination

In an exploratory experiment to prove the concept of a novolak-based HMR, only two F/R mole ratios (0.23 and 0.39) were tested after reaction times of 0.5 and 2 hours, and only two assemblies were bonded for each of four treatment combinations. These novolaks were activated by addition of formaldehyde so that all solutions had a total F/R of 1.54. The low delamination values for the novolak- (0.39 F/R) based HMR (Table 4) were the most encouraging. The delamination values for the n-HMR based on a 0.23 molar ratio exceeded the maximum 5% ASTM limit for the 2-hr. reaction time. However, the values for the novolak- (0.39 F/R) based HMR were less than the 5 percent specification limit for both the 0.5- and 2-hr. reaction times. This encouraging result led to a more comprehensive test of several novolak molar ratios near 0.39.

For the comprehensive experiments, three F/R molar ratios of the HMR novolak were synthesized (0.31, 0.39, and 0.46). This comparison used reaction times of 0, 1, 2, and 3 hours between mixing novolak with final formaldehyde and application to wood. Assemblies without n-HMR suffered severe delamination (Table 5). However, those assemblies with n-HMR reacted between 1 and 3 hours showed very low delamination, well below the ASTM-specified 5 percent limit. In addition, the n-HMR made from the novolak with a F/R molar ratio of

Table 5.—Average delamination of primed epoxy-bonded lumber laminates after ASTM D2559 cyclic exposure.\(^a\)

<table>
<thead>
<tr>
<th>Reaction time(^a) (hr.)</th>
<th>Control(^b)</th>
<th>Delamination (%) for various F/R molar ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>49.5</td>
<td>0.31 0.39 0.46</td>
</tr>
<tr>
<td>0</td>
<td>7.6(^c)</td>
<td>3.8 11.8(^c)</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>0.8 1.1</td>
</tr>
<tr>
<td>2</td>
<td>2.7</td>
<td>0.9 2.1</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>1.1 0.6</td>
</tr>
</tbody>
</table>

\(^a\) Time between constituting n-HMR and applying it to wood.

\(^b\) Control specimens were not primed with n-HMR.

\(^c\) ASTM D2559 specified maximum allowable delamination for softwoods is 5%.
Figure 3.—Delamination of epoxy-bonded lumber laminates primed over 7-hr. reaction time with HMR coupling agent based on 0.39 F/R novolak. 0.39 passed the specification at 0 h reaction time (n-HMR applied to wood immediately after mixing).

Statistical analysis of percentage of delamination indicated that the control (unprimed) specimens constituted a distinctly separate Tukey group. These specimens badly failed to meet the 5 percent maximum specification. A second statistically separate group contained all F/R molar ratios at 0-hr. reaction time. A third group consisted of all other specimens and overlapped those at the 0-hr. reaction time for molar ratios of 0.31 and 0.39. This last group included all those specimens that passed the specification plus one specimen that averaged only 7.6 percent delamination.

These encouraging results prompted an extension of the experiment with the 0.39 F/R novolak to see whether delamination remains low at even longer reaction times. Consequently, specimens were primed after 5- and 7-hr. reaction times, but only two assemblies were laminated at each reaction time. For this small set, the averages of delamination were also below the 5 percent limits (Fig. 3). Thus, it appears that novolak-based HMR coupling agent with a novolak F/R molar ratio of 0.39 could be applied immediately and expected to last a whole 8-hr. shift.

Conclusions
A novolak version of the HMR coupling agent is as effective as the one-step HMR in providing exterior durable bonds of epoxy adhesive to Douglas-fir laminates. Most of the reactivity in forming the novolak is dissipated within 17 hours after the initial formaldehyde is added to the resorcinol, regardless of the molar ratio. The NMR measurements showed that essentially no hydroxymethyl groups are contained in the novolak after 17 days, at most. The lack of hydroxymethyl groups prevents the novolak from reacting further. Molecular weight increases during the novolak formation, as indicated by methylene bridge signals in the NMR spectrum. The F/R molar ratio affects the resistance of the bonded assemblies to delamination when the coupling agent is applied at different times after mixing. An n-HMR based on novolaks with molar ratios of 0.31 to 0.46 and reacted for 1 to 3 hours before being applied to wood suffered less delamination than the maximum specified by ASTM D2559. The best n-HMR tested, with a novolak molar ratio of 0.39, worked well after 0 to 7-hr. reaction time.

Acknowledgments
We wish to thank Kolby C. Hirth for obtaining NMR spectra on samples and Cherilyn A. Hatfield for statistically analyzing data from delamination tests.

References