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# Hydroxymethylated resorcinol coupling agent for wood surfaces to produce exterior durable bonds

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Abstract-A recently discovered surface treatment enhances the durability of bonding of several polymeric adhesives to wood. The treatment material, hydroxymethylated resorcinol (HMR), is a dilute, alkaline mixture of resorcinol and formaldehyde which continues to react. It forms a resorcinol-formaldehyde polymer in time but provides a coupling action between the wood and other resins that a common resorcinol-formaldehyde adhesive cannot. When wood was properly treated with this material, bonds formed using epoxy, polyurethane, urea-formaldehyde resin, or emulsified polymer/isocyanate adhesives were much more durable to exterior exposure than were bonds formed without prior HMR treatment. In addition, HMR application to wood treated with chromated copper arsenate (CCA) preservative resulted in phenol-resorcinol-formaldehyde and melamine-formaldehyde resin bonds that were durable to accelerated outdoor exposure, an outcome that previously was not possible. The critical factor for successful treatment was the extent of reaction in the mixture when it was applied to the wood, which determines the blend of molecular sizes and the extent of hydroxymethylation of the resorcinol molecules and oligomers. The effect of preapplication reaction time on bond quality was determined by bond delamination measurements. Chemical reactivity was followed by a series of differential scanning calorimetry measurements. The continuously changing molecular and chemical nature of the material was followed by size exclusion chromatography and by $^{13}$C-NMR spectroscopy using $^{13}$C-enriched formaldehyde.

*Keywords:* Hydroxymethylated resorcinol; glass-fiber-reinforced plastic; epoxy adhesive; bonding; CCA-treated wood; delamination.

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## 1. INTRODUCTION

The repair of wood structures exposed to outdoor weathering or high moisture conditions is hampered by the lack of a gap-filling, low-temperature-curing structural adhesive that is effective in these severe exposure conditions. Some adhesives develop a strong bond to wood under dry conditions, but with wetting and drying and resultant wood swelling and shrinking, they progressively debond from the wood. Under industry standard ANSI/AITC A190.1-1992 [1], epoxies fail to qualify as structural adhesives in laminated wood products intended for wet-use exposure. Furthermore, the American Institute of Timber Construction (AITC) does not recommend the use of epoxies in design or repair of structural timbers if the bonds are expected to withstand either shear or tension stresses without steel reinforcement [2]. Alternative formulations of epoxies [3] and a polyethyleneimine coupling agent [4] were developed to improve bonding, though not with sufficient success. The polyethyleneimine coupling agent did not enhance durability of epoxies in large, thick laminates [5].

Another polar material, a resorcinol-formaldehyde resin used for bonding cotton tire cord to rubber [6], maintains adhesion over long periods of hard use. It has a chemical structure like that used for traditional wood adhesive, but the tire cord binding resin is much more reactive and is used at an earlier stage of condensation. For the tire cord application, it was combined with rubber latex to help it bond to the rubber. Could this form of resorcinol-formaldehyde resin (without the latex) serve as a coupling agent to durably bond wood to a reactive, gap-filling adhesive such as epoxy? It has been used here in this way and has proven to be much more versatile than anticipated.

## 2. MATERIALS AND METHODS

### *2.1. Materials and preparation*

Hydroxymethylated resorcinol (HMR) coupling agent consists of mono-, di-. and trihydroxymethylated resorcinol and oligomers of such molecules. The HMR was prepared by reacting formaldehyde with resorcinol in a 1.5 molar ratio at mildly alkaline conditions. The ingredients were as follows:

| HMR ingredient | Percentage by mass |
|---|---|
| Water, deionized | 90.43 |
| Resorcinol, crystalline | 3.34 |
| Formaldehyde (aq., 37%) | 3.79 |
| Sodium hydroxide, 3 molar | 2.44 |
| Total | 100.00 |

The 5% aqueous solution was reacted a minimum of 3 to 4 h, but not more than 8 h, at room temperature before use. The length of this reaction period is critical to

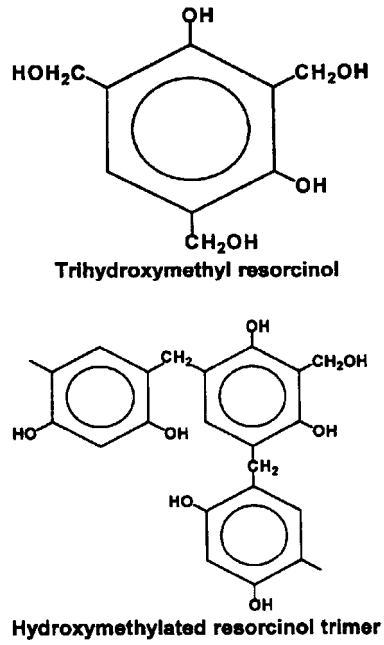


**Figure 1.** Trihydroxymethyl resorcinol (top) and hydroxymethylated resorcinol trimer (bottom).

the effectiveness of the coupling agent. The solution was spread on wood surfaces at 0.15 kg/m$^2$. Before bonding with epoxy adhesives, water from the applied HMR must be evaporated or be absorbed by wood. The method of enhancing adhesion with this composition was patented [7]. Some typical structures of molecules expected from this reaction are shown in Fig. 1.

### *2.2. Delamination test*

For wood-adhesive bonds, the most critical bond stress usually comes not from temperature but from swelling and shrinking of the wood in response to moisture changes, especially full soaking and drying cycles. The test specimens consisted of six pieces of lumber (each 19 mm thick, 76 mm wide, and 305 mm long) bonded together along their flat faces under 138 kPa pressure until some adhesive squeezed from the bondline. This resulted in gluelines that were predominately in the range of 0.06 to 0.20 mm. The adhesives were cured for about 15 h at room temperature and then for another 5 h at 65.5°C to assure uniform cure in all bondlines. Three sections 76 mm long were cut from the middle portion of an assembly and then exposed to an accelerated aging test. The primary test for these experiments was based on the severe cyclic delamination for timber laminates, ASTM D 2559 [8]. The test consisted of three cycles:

- Cycle 1 Vacuum-water soak for 5 min, pressure-water soak for 1 h, repeat these two steps, dry at 66°C for 21-22 h
- Cycle 2 Steam at 100°C for 1.5 h, pressure-water soak for 40 min, dry as before
- Cycle 3 Repeat cycle 1

After testing, delaminations were measured along the end-grain of the sections. A single delamination value expressed as a percentage of total bondline length was computed for each section.

## 3. RESULTS

### *3.1. Bonding to wood*

The efficacy of HMR as a coupling agent was shown by a study in which Sitka spruce lumber was bonded with epoxy resins [5]. Epoxy resin, D.E.R. 331 with hardener D.E.H. 24 (Dow Chemical Company, Midland, Michigan), was modified with a thickener (Cab-O-Sil, a hydrophobic fumed silica, Cabot Corp., Tuscola,

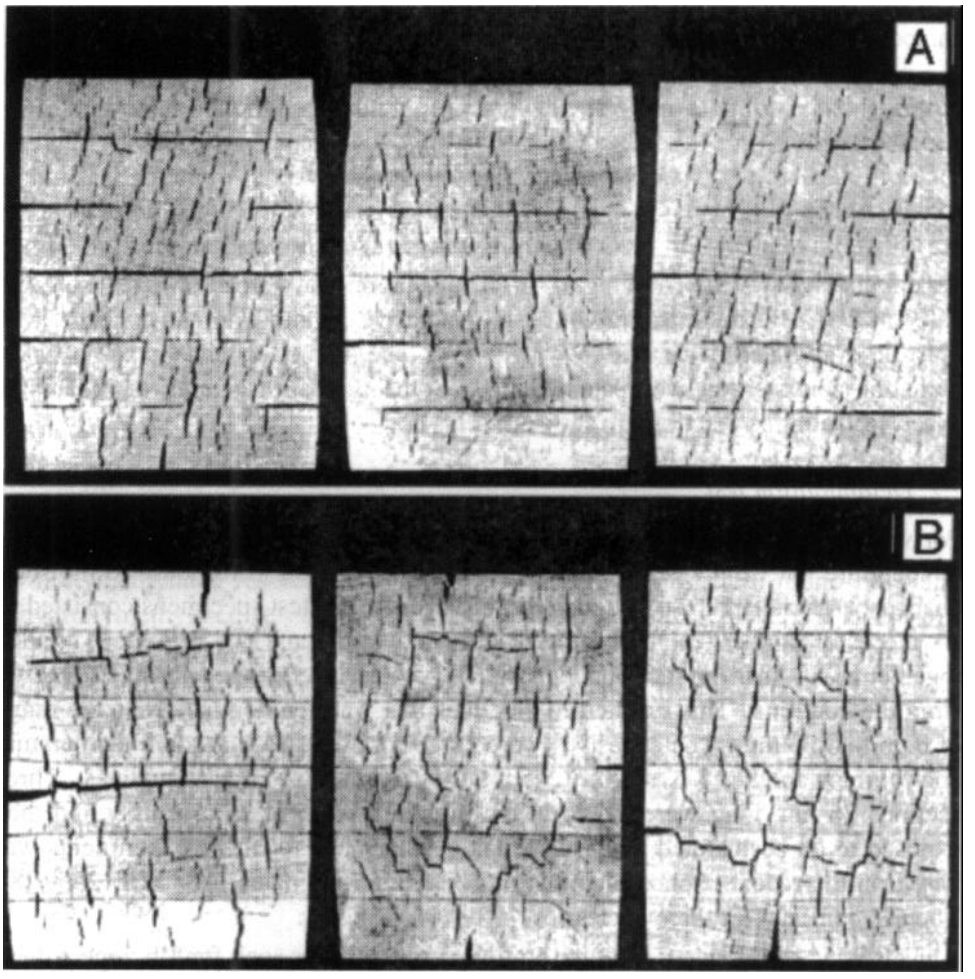


**Figure 2.** Optical photograph showing delamination of epoxy adhesive bonds in lumber laminates with (A) unprimed surfaces and (B) surfaces primed with HMR coupling agent. The lumber lamina are 19 mm thick.

Illinois) or a thinning agent (benzyl alcohol, Aldrich Chemical Co., Milwaukee, Wisconsin), or both:

| Epoxy formulations |
|---|
| D.E.R. 331 + D.E.H. 24 |
| D.E.R. 331 + D.E.H. 24 + Cab-O-Si1(4%) |
| D.E.R. 331 + D.E.H. 24 + Benzyl alcohol (10%) |
| D.E.R. 331 + D.E.H. 24 + Benzyl alcohol (10%) + Cab-O-Sil(4%) |

On unprimed laminates, the best epoxy formulation (top of Fig. 2) delaminated substantially within the bondlines, averaging 55%, whereas the same epoxy on the HMR-primed surface (bottom of Fig. 2) delaminated only 4.5%, which is within the ASTM specification. In the HMR-primed assemblies where very little delamination occurred, cracks developed in the wood to relieve stresses from shrinking of the wood.

The efficacy of this primer on two softwood species (Sitka spruce and Douglas-fir) and two hardwood species (yellow poplar and yellow birch) is shown in Fig. 3. Three epoxies, two of them formulated at the Forest Products Laboratory, used both with and without primer were tested for delamination. The adhesion of all the

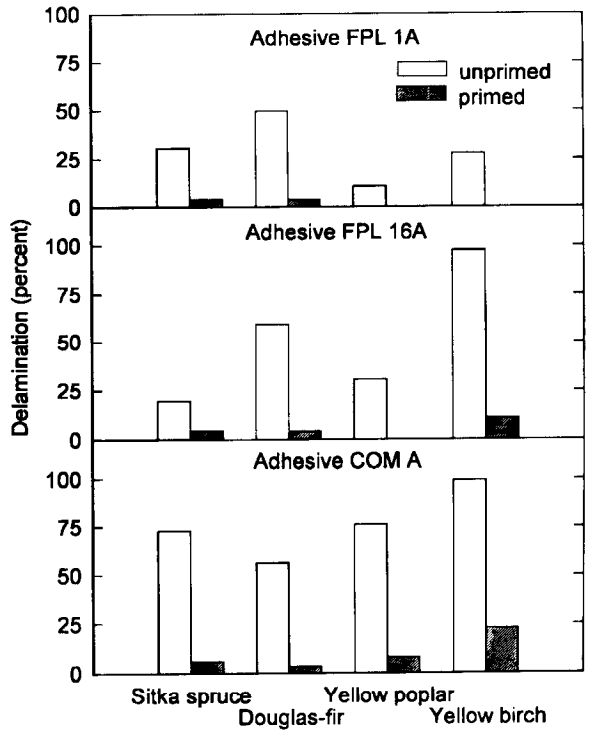


**Figure 3.** Effects of epoxy adhesive, HMR priming, and wood species on delamination of lumber joints after the ASTM D 2559 cyclic delamination test.

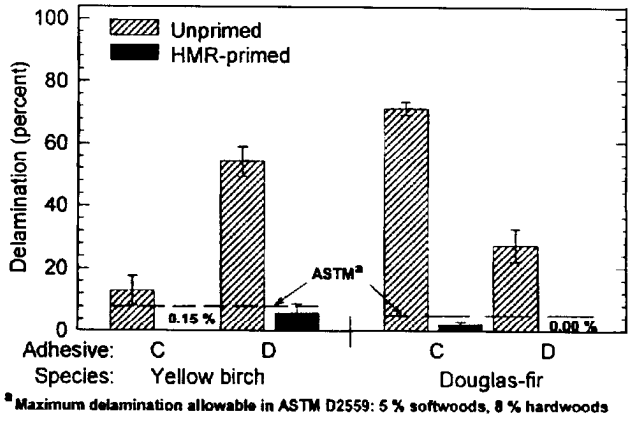


**Figure 4.** Delamination of polyurethane bonds in unprimed and HMR-primed yellow birch and Douglas-fir lumber joints after the ASTM D 2559 cyclic delamination test.

epoxies to wood was increased remarkably by the HMR coupling agent: All but one epoxy on yellow birch fell within delamination requirements of ASTM D 2559 [9]. Yellow birch, the densest of these four woods, is often used to determine the ultimate bond strength of an adhesive because its wood is very strong and more difficult to penetrate by the adhesive.

One-part polyurethanes are promoted in the consumer market as a waterproof alternative to traditional poly(vinyl acetate) adhesives. Even wooden airplane builders are interested in bonding structural components with one-part polyurethanes. Recent work [10] has shown that four different commercial one-part polyurethanes did not provide durability to meet the delamination requirements of ASTM D 2559, whereas resorcinol-formaldehyde (RF) adhesive, a standard of durability, did meet those requirements. Recent unpublished work shows that HMR-primed wood bonded with one of the more durable one-part polyurethanes will pass the delamination requirements of ASTM D 2559 (Fig. 4). Figure 5 shows 71% delamination in assembly cross sections that were not primed, whereas Fig. 6 shows only 2.1% delamination in assemblies primed with HMR.

### *3.2. Bonding fiberglass-reinforced plastics to wood*

In recent years, wood is sometimes used in structures where the surface layers of expensive wood can be replaced with a thinner layer of fiber-reinforced plastic (FRP) composite. Lamination with FRP gives a higher strength, defect-free surface to the tension side of assemblies, such as architectural beams and bridge members. Lamination of an FRP to the tension side of truck body flooring significantly reduces the cost resulting from use of expensive hardwoods and provides a chemically resistant surface to protect the wood floor. The wood-FRP composite requires bonding high-polarity wood to fairly low-polarity thermoset “plastic”. In this application HMR has proven to be very useful [11]. Though phenol-resorcinol-formaldehyde (PRF) adhesive bonds well to the wood, it cannot maintain a durable bond to vinylester FRP. However, epoxy bonds well to HMR-primed wood and to

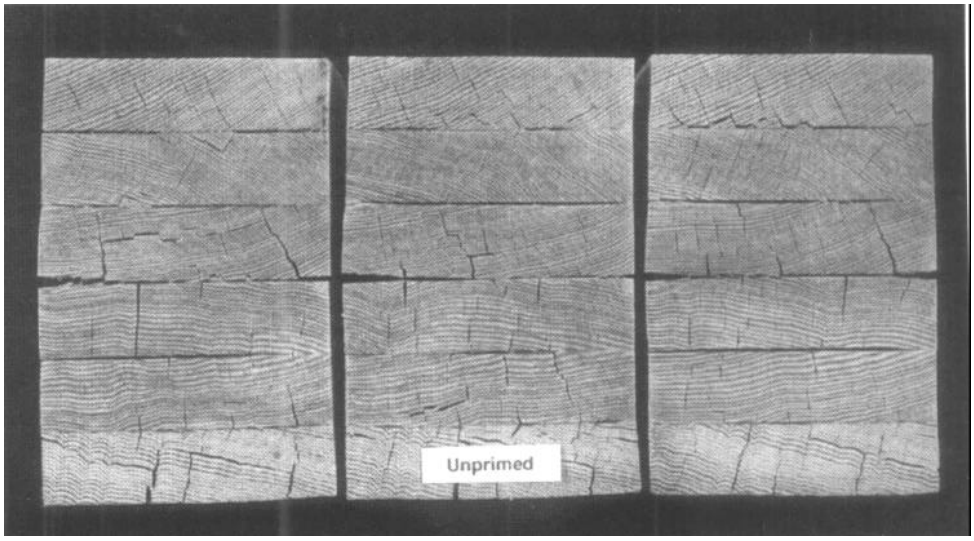


**Figure 5.** Optical photograph of cross sections of Douglas-fir lumber laminate showing 71.1 % delamination of polyurethane adhesive C in unprimed joints. The lumber lamina are 19 mm thick.

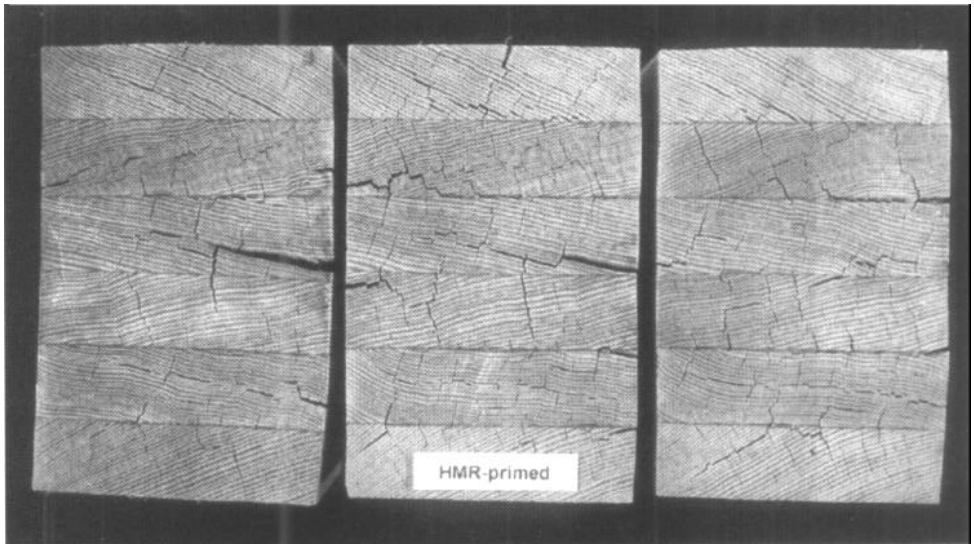


**Figure 6.** Optical photographs of cross sections of Douglas-fir lumber laminate showing 2.1% delamination of polyurethane adhesive C in HMR-primed joints. The lumber lamina are 19 mm thick.

vinylester FRP (Table 1). A section of a composite assembly of vinylester FRP bonded to the compression and tension sides of Southern Pine is shown in Fig. 7 after exposure to the delamination test. All wood laminates were primed with HMR and bonded with an epoxy adhesive. The wood checked (cracked) while the bondlines held together under the high shrinking stresses as the soaked wood

**Table 1.**
Delamination resistance of epoxy and PRF adhesives in vinylester FRP/lumber composites

| Treatment combination | | | | Delamination (%) | |
|---|---|---|---|---|---|
| Adhesive | Wood species | Wood primed | FRP surface[a] | Wood to wood | FRP to wood |
| Epoxy-FPL 1A | Yellow poplar | Yes | Peel-ply | 0 | 0 |
| | | Yes | Solvent wipe | 0 | 0 |
| | Southern Pine | Yes | Peel-ply | 9.1 | 0 |
| | | Yes | Solvent wipe | 9.1 | 0 |
| PRF | Yellow poplar | No | Peel-ply | 0 | 100 |
| | | No | Solvent wipe | 0 | 100 |
| | Southern Pine | No | Peel-ply | 0 | 100 |
| | | No | Solvent wipe | 0 | 100 |

[a]Peel-ply cleaned and textured by peeling away woven fabric that had been laminated to the vinylester in the manufacturing process.

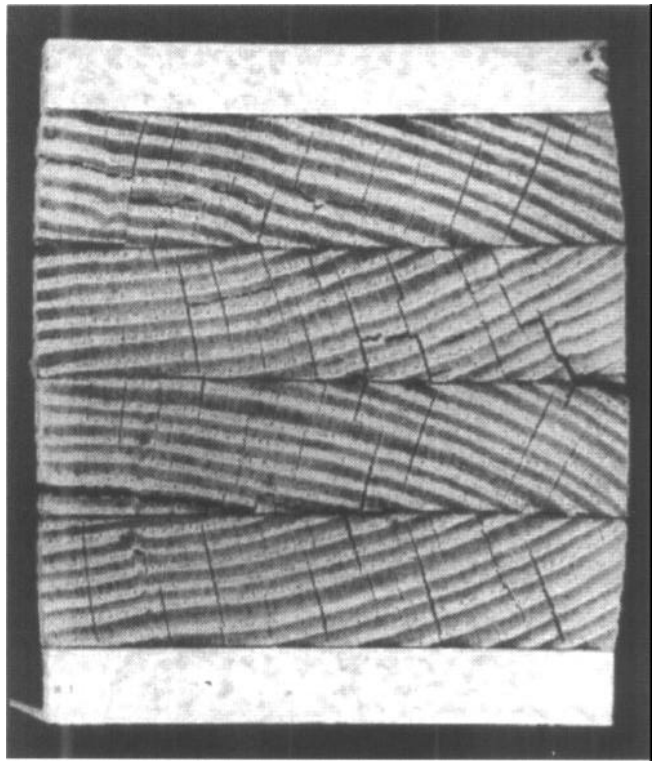

**Figure 7.** Optical photograph of cross section of vinylester FRP composite laminated to HMR-primed Southern Pine lumber with FPL IA epoxy adhesive, following ASTM D 2559 delamination test. The lumber lamina are 19 mm thick.

dried. The same effects are seen for epoxy-bonded assembly of phenolic FRP composite with HMR-primed Southern Pine lumber (Fig. 8). Finally, Fig. 9 shows an epoxy FRP bonded with epoxy to red oak truck body flooring that was primed with HMR. The original flooring section was 140 mm (5.5 in.) wide. The epoxy FRP maintained that size, but after swelling and drying the width of wood at the

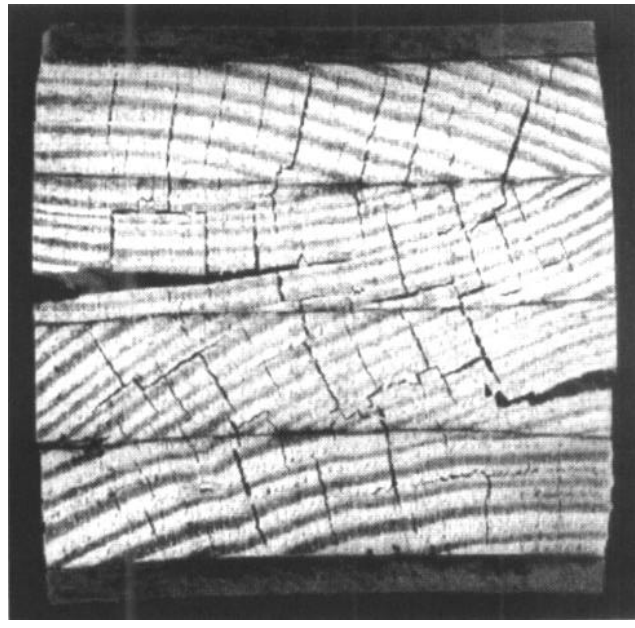

**Figure 8.** Optical photograph of cross section of phenolic FRP composite laminated to HMR-primed Southern Pine lumber with FPL 1A epoxy adhesive, following ASTM D 2559 delamination test. The lumber lamina are 19 mm thick.

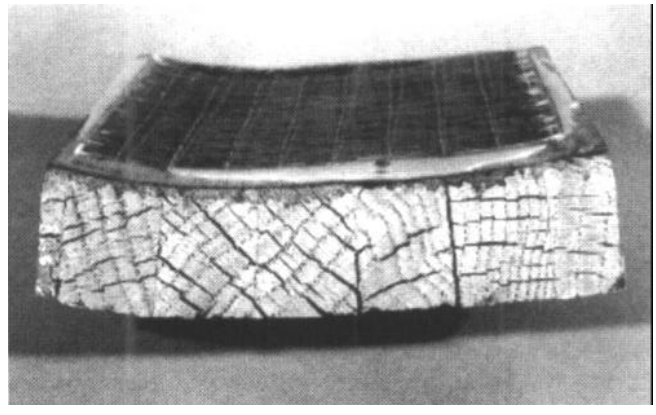

**Figure 9.** Optical photograph of cross section of epoxy FRP composite laminated to HMR-primed red oak truck body flooring with FPL 1A epoxy adhesive, following ASTM D 2559 delamination test. Total thickness is 24 mm.

bottom edge was 13 mm (0.5 in.) greater. The bond held so well that only the unrestrained wood away from the FRP could swell in response to the soaking.

### *3.3. Bonding to preservative-treated wood*

Wood should be treated with preservatives for applications where it contacts moisture and where it is subject to attack by insects and decay fungi. The main preservative used in the United States is chromated copper arsenate (CCA). By the late 1980s almost 40% of Southern Pine lumber was treated with CCA. In the past it was essentially impossible to both treat Southern Pine lumber and then adhesively bond it to make bigger assemblies, even with durable PRF adhesives. Tiny deposits of the CCA oxides and hydroxides cover the cell walls of wood (Fig. 10), physically blocking direct access of an adhesive to the wood. Vick and Christiansen [12] showed that the problem was not caused by a chemical reaction between the adhesive and the metallic oxides of CCA preservative. If CCA-treated Southern Pine was primed with HMR, two commonly used PRF adhesives could produce durable bonds that would meet the requirements of the ASTM D 2559 delamination test [13]. Without the primer neither PRF adhesive could meet the requirements (Table 2). Photographs of assembly sections after the three-cycle ASTM test (Fig. 11) show the difference in bondline durability between the HMR-primed wood on the left and the unprimed wood on the right. Cracks in the

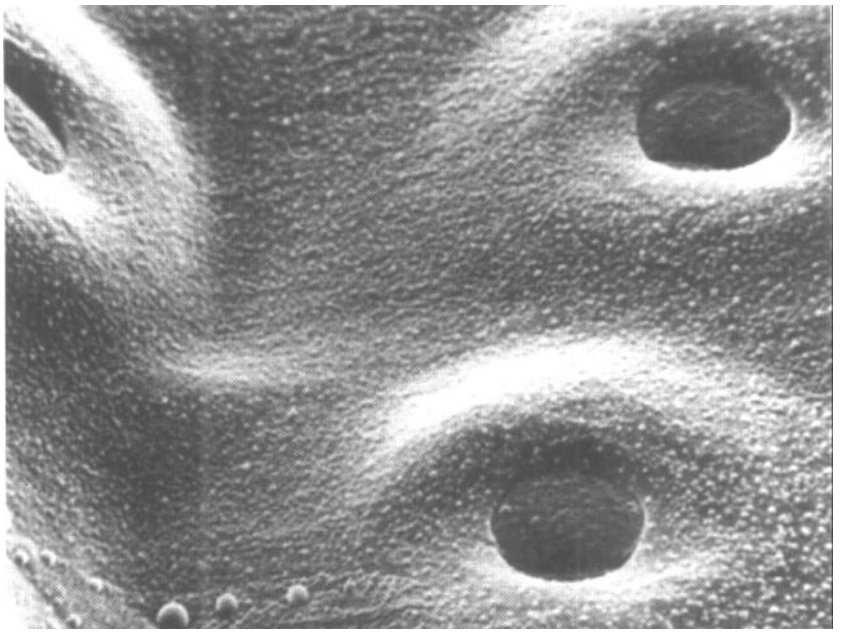

**Figure 10.** Electron microscope photograph of surface of cell lumen of CCA-treated Southern Pine covered with chemically fixed deposits of mixtures of chromium, copper. and arsenic oxides (7,000 ×).

**Table 2.**
Enhanced durability of PRF bonds to CCA-treated Southern Pine with HMR primer

| Adhesive | CCA retention ($lb/ft^3$)[a] | Delamination (%) | | |
|---|---|---|---|---|
| | | Unprimed | HMR primed 1 h | HMR primed dried 24 h |
| PRF A | 0 | 3.4 | 1.4 | 2.3 |
| | 0.4 | 17.3 | 4.8 | 5.0 |
| | 0.6 | 17.6 | 4.4 | 4.1 |
| PRF B | 0 | 2.1 | 1.7 | 2.2 |
| | 0.4 | 10.4 | 3.9 | 3.7 |
| | 0.6 | 12.4 | 5.1 | 2.6 |

[a] Multiply $lb/ft^3$ by 16.01 to convert to $kg/m^3$.

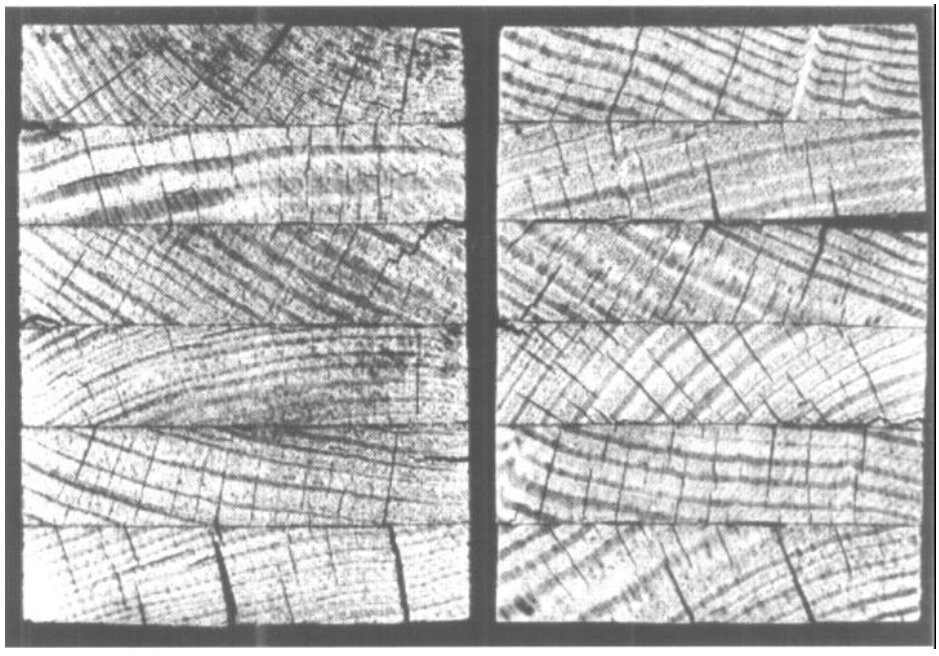

**Figure 11.** Optical photographs of cross sections of lumber laminates after three cycles of ASTM D 2559 delamination test. Lumber surfaces in laminates on the left were primed with HMR coupling agent, and those on the right were not primed. The lumber lamina are 19 mm thick.

primed wood (Fig. 12) actually propagated across the bondline without following it, showing the durability of the HMR-primed bondlines.

Similarly durable bonds resulted from bonding to HMR-primed, CCA-treated Southern Pine lumber with emulsion/polymer isocyanate or epoxy adhesives [11]. Without the primer neither adhesive produced durable bonds.

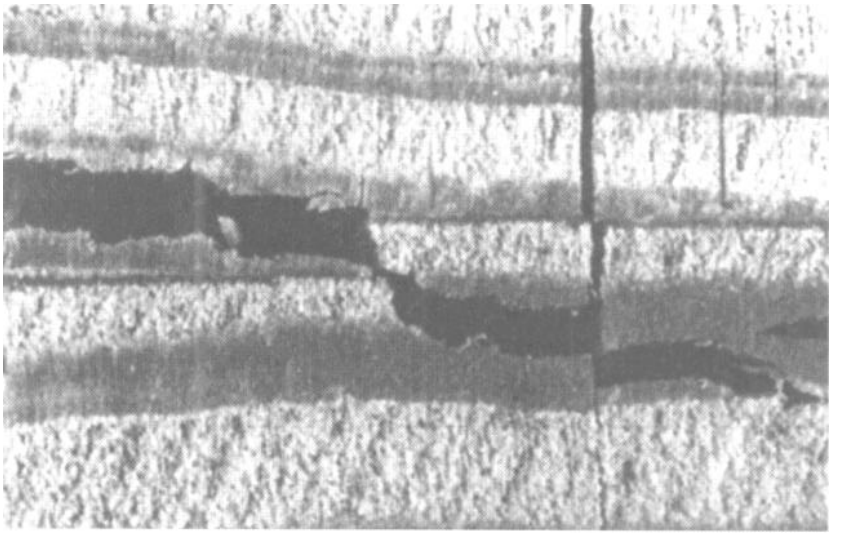

**Figure 12.** Optical photograph of typical pattern of stress fracturing that occurred around bondlines when they effectively resisted delamination during ASTM D 2559 cyclic delamination test. Thickness shown (top to bottom) is 9.5 mm.

### *3.4. Analysis of HMR*

The remarkable improvement in adhesion of all thermosetting wood adhesives was the most important aspect of the HMR coupling agent. However, we wanted to learn more about its chemistry so that HMR could be modified to make it more user-friendly by overcoming a few troublesome characteristics: the material needs to pre-react for 3 to 4 h before it is applied, depending on wood species; a batch of HMR is usable for only about 4 h after it becomes sufficiently effective; and it has no shelf life. Having such a long pre-reaction time and short use life can be costly for a production line if a disruption shuts down the line for several hours. Hoping to find a way to decrease the pre-reaction time and increase its shelf life, we analyzed the reactions by various techniques to understand the important aspects of the reactions as a function of reaction time before application to surfaces.

Differential scanning calorimetry was used to follow the decrease in the heat of reaction of HMR after the addition of the final ingredient, formaldehyde [14]. HMR becomes effective at producing durable epoxy bonds to Douglas-fir in about 3 h (Fig. 13). The heat of reaction from mixing to the 3-h period declined about 20% from the first measurement, to 19.8 J/g; and up to the maximum usable time of 8 h the heat of reaction declined to about 50% of its initial level, to 11.4 J/g.

Although calorimetry gave us a quick estimate of the range of optimum reaction time and reactivity, we also needed to get an idea of what chemical structures were occurring at the optimum reaction times. Molecular size of oligomeric molecules in solution can be estimated by gel permeation (or size exclusion) chromatography (GPC). After experiments with a number of solvent systems for both early and late stages of the reaction, we decided the best eluent was a dimethylformamide (DMF)

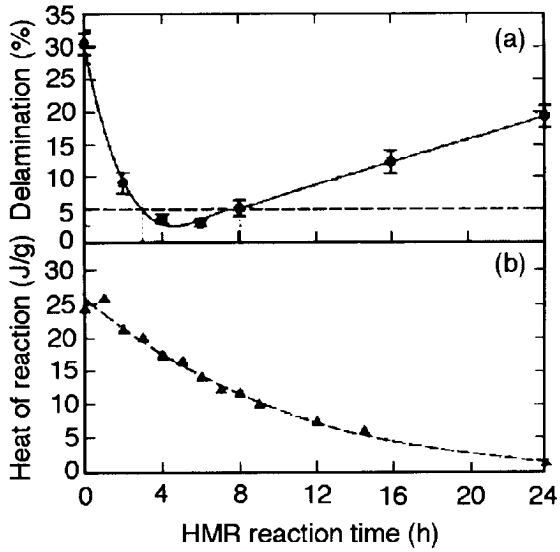


**Figure 13.** Effect of HMR reaction time between initial mixing and either application or analysis: (a) epoxy-to-Douglas-fir bond durability by delamination test and (b) residual primer reactivity as measured by DSC. The error bars in plot (a) indicate the standard error of the mean.

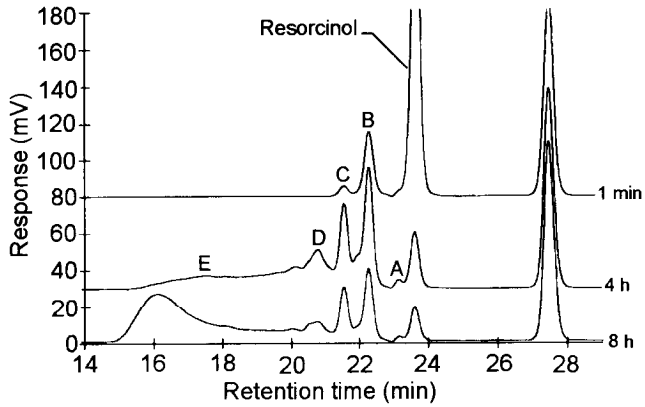


**Figure 14.** Gel permeation chromatograms of HMR after reaction times of 1 min. 4 h. and 8 h

solution containing 5% by volume of water and 2% of acetic acid. Samples from the reaction mixture were essentially stable for 24 h when quickly diluted 1 : 70 in this solvent. This stability allowed us to take samples frequently at early stages of the reaction and analyze them later. A small amount of phenol was added to the dilution solvent as a retention time reference (peak near 27.5 min) and as an approximate reference for concentration. Both a 50-nm-pore-size column and a 5-nm-pore-size column were used in series, and detection was by ultraviolet absorption at 233 nm. Within the first minute of reaction, two derivatives of resorcinol (its peak is near 23.5 min) were formed (Fig. 14). The more prominent peak was assumed to be produced by 4-methylresorcinol, based on the high reactivity of the 4-resorcinol

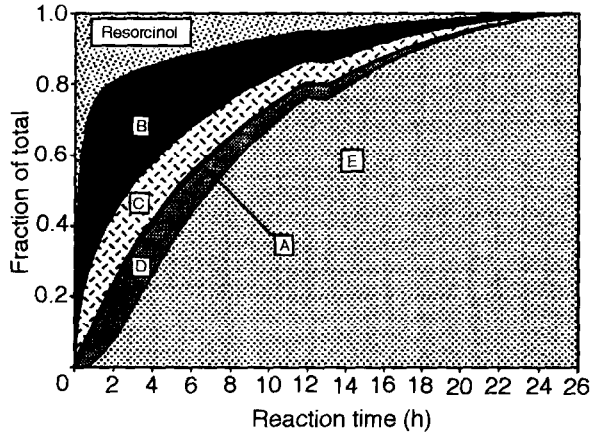


**Figure 15.** Progress of peaks in the gel permeation chromatograms of HMR over 26 h of reaction time. The letters on the area portions refer to the peaks labeled in Fig. 14. (The apparent discontinuity between 12 and 14 h is due to the use of two runs to establish the full curve.)

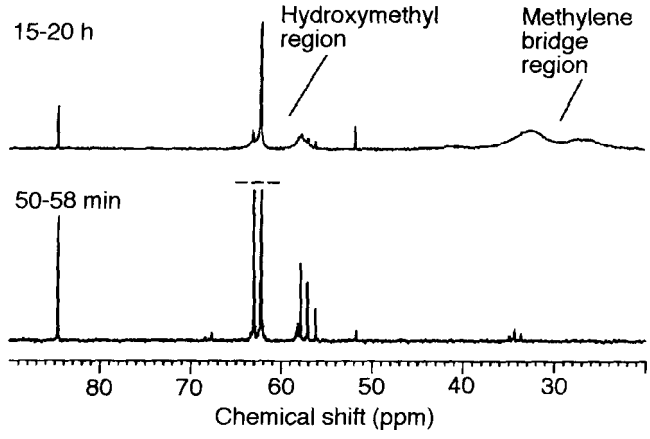


**Figure 16.** $^{13}C$ nuclear magnetic resonance spectra of HMR primer acquired during periods after mixing in $^{13}C$-enriched formaldehyde: (bottom) during 50-58 min reaction time: (top) during 15-20 h reaction time.

position. After 4 h reaction time (Fig. 14) several definite peaks and a high-molecular-weight tail appeared at the shortest retention times. After 8 h reaction time (Fig. 14) the tail developed into a major portion of the mass. Over 24 h the proportion of the mass, divided into regions according to the GPC peak shapes, followed the course shown in Fig. 1.5.

The polar functionality of the HMR molecules is another important chemical aspect that needed study. With so much formaldehyde available, resorcinol quickly garnered one to three hydroxymethyl groups on its ring, making it much more reactive. It was expected that the epoxy resins might react with the hydroxyl groups of the hydroxymethyl groups to form covalent links. To find what functionalities, on average, were in the HMR solution at various times, carbon-13 nuclear magnetic

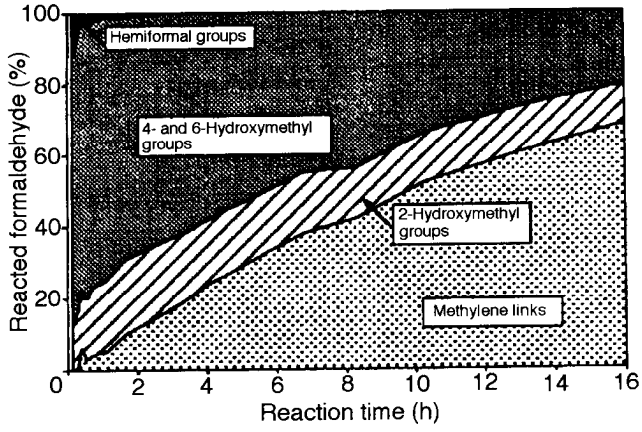


**Figure 17.** Summary plot of changes in the distribution of formaldehyde-derived species in HMR with time (acquisition of data started several minutes after the reaction began).

resonance spectroscopy was performed on HMR solutions using formaldehyde enriched to 99% carbon-13. High carbon-13 levels allowed quick, quantitative runs (4-min minimum in the earliest stages) to follow the fate of the formaldehyde [14, 15]. A scan taken between 50 and 58 min (Fig. 16) shows evidence that the HMR contains many hydroxymethyl groups at the 2-, 4-, and 6-positions (53-63 ppm), some residual hydrated formaldehyde (85 ppm), and some methylene bridges between rings (around 35 ppm). A scan taken between 15 and 20 h reaction time shows (Fig. 16) some residual hydroxymethyl groups, but the major proportion of formaldehyde carbon has been incorporated into the various forms of methylene bridges (20-45 ppm). This transformation of reacted formaldehyde is summarized in Fig. 17, which shows hydroxymethyl groups dominant at first but transforming to methylene bridges with time.

## 4. CONCLUDING REMARKS

The HMR is capable of promoting durable bonds to wood with epoxy or one-part polyurethane adhesives that otherwise would not meet the delamination requirements of ASTM D 2559 for exterior-durable or wet-exposure bonds. Durable bonding to CCA-treated Southern Pine lumber with PRF adhesive was also sufficiently improved to pass requirements for ASTM D 2559, and similarly beneficial results were obtained for bonding CCA-treated pine lumber to emulsion/polymer isocyanate and epoxy adhesives. HMR priming of wood makes possible the durable epoxy linking of several types of fiberglass-reinforced thermoset plastic composites to wood, which was not possible without the HMR. Information on the chemical structure of HMR was obtained to further its development to commercial acceptance.

We are now working on creating a novolak HMR that can be stored prior to use. When used, because of its advanced molecular weight, it will significantly decrease

the amount of time necessary to pre-react the coupling agent before it can be applied to wood. Preliminary experiments have been encouraging.

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