

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

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## 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.

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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

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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.

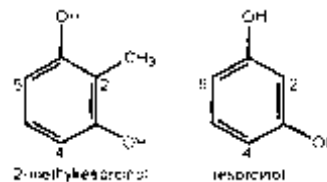
## Experimental

### 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 percentage 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-methylresorcinol (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-methylresorcinol (which cannot crosslink). Whereas resorcinol can form polymer chains, with branches, through the 2, 4, and 6 positions, 2-methylresorcinol 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



Structure 1.

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-methylresorcinol alone, the ratio would be 1.0. The 2-methylresorcinol [608-25.3] was obtained from Sigma-Aldrich (Milwaukee, WI) as 98 percent pure and was used as received. The relative reactivity of resorcinol and 2-methylresorcinol with formaldehyde was estimated from the disappearance of monomers from solution by high-performance liquid chromatography (HPLC). An essentially random incorporation of 2-methylresorcinol 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/m<sup>2</sup> 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/m<sup>2</sup>. 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 would not be stressed by shrinkage of the wood while the resin cured.

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 hour.
- Second cycle: [Step 1] Steam at 100°C for 1 to 1.5 hours; [Step 2] 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- $\mu$ L) 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- $\mu$ m particles). A 5-minute hold time was used, and then a linear solvent gradient from 10 to 40 percent acetonitrile 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.

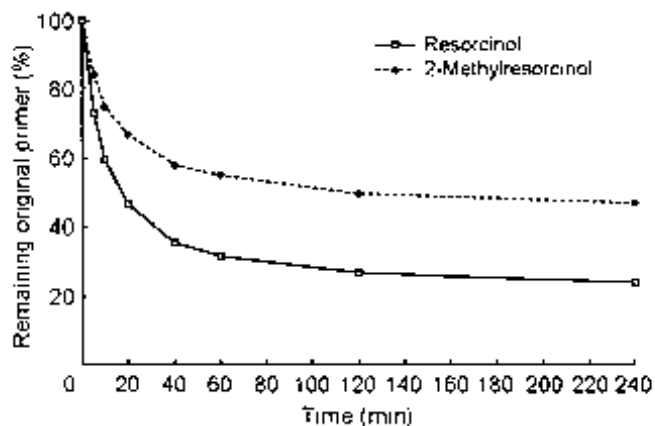


Figure 1. — Relative reactivity of resorcinol and 2-methylresorcinol with formaldehyde in the same solution at pH 8 and 25°C.

Table 1. — Relative reactivity of monomers in same solution.

Time (min)	Portion of original peak area lost		Ratio of resorcinol to 2-methyl resorcinol <sup>a</sup>	
	Resorcinol monomer	2-methyl-resorcinol	Molar ratio of disappearance	Ratio on per reactive site basis
0	0	0	--	--
5	27.2	16.0	1.70	1.13
10	40.5	25.2	1.61	1.07
20	53.6	33.1	1.62	1.08
40	64.3	41.9	1.53	1.02
60	68.4	45.0	1.52	1.01
120	73.2	50.5	1.45	0.97
240	75.8	53.1	1.43	0.95

<sup>a</sup>Overall ratio of resorcinol:2-methylresorcinol:formaldehyde was about 4:1.5; pH was 8 and temperature 25°C. Most possible reactions had occurred by 60 minutes.

## 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 area of each peak of the two starting monomer species relative to the size of the original peak for that monomer (100%) (Fig. 1). The quantity of each monomer decreased with time. If each were reacting with formaldehyde at the same rate to produce derivatives, then the percentages of residual monomer 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-

sitions). 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  $^{13}\text{C}$  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 resorcinolic 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  $30001^{-1}$  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,

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

Retention time (min)	Area (mAU·s)	Proportion of area (%)	Comment
Resorcinol + formaldehyde (F/R= 1:1)			
5.19	44.3	1.92	Unknown
5.73	25.5	1.11	Unknown
5.92	30.3	1.32	Unknown
6.47	43.8	1.90	Unknown
6.84	339.0	14.7	R-CH <sub>2</sub> OH
7.90	65.7	2.85	Unknown
10.41	46.1	2.00	Unknown
10.92 <sup>a</sup>	1,444.0	62.7	Resorcinol
13.19	211.0	9.15	R-CH <sub>2</sub> -R
2-Methylresorcinol + formaldehyde (F/2MeR= 1:1)			
9.02	27.5	1.91	Unknown
10.12	233.0	16.3	2MeR-CH <sub>2</sub> OH
12.25 <sup>b</sup>	1,013.0	70.6	2-Methylresorcinol
13.73	27.3	1.90	Unknown
16.57	99.8	6.96	2MeR-CH <sub>2</sub> -2MeR

<sup>a</sup>Position of peak for starting resorcinol (R).

<sup>b</sup>Position of peak for starting 2-methylresorcinol (2MeR)

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 an average 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.

Time and temperature of storage of HMR-primed lumber, before bonding with adhesive, seemed to have no effect on the eventual quality of the adhesive, as shown in **Figure 3**. **Figure 3** also shows the output of a statistical analysis by SAS. The upper and lower "hinges" of the box indicate the 75th and 25th percentiles of data, respectively; the horizontal line between the hinges indicates the median value; and the plus sign indicates the mean value. Up to 3 months of storage at 23°C and 50 percent RH had no adverse effects on delamination. Likewise, raising the storage temperature to 70°C for 24 hours (maintaining 9% MC) had no effect on delamination. For the intermediate condition (50°C for 4 days at 9% MC), the results were also below the 5 percent maximum delamination set by ASTM D 2559 for softwoods. For this intermediate

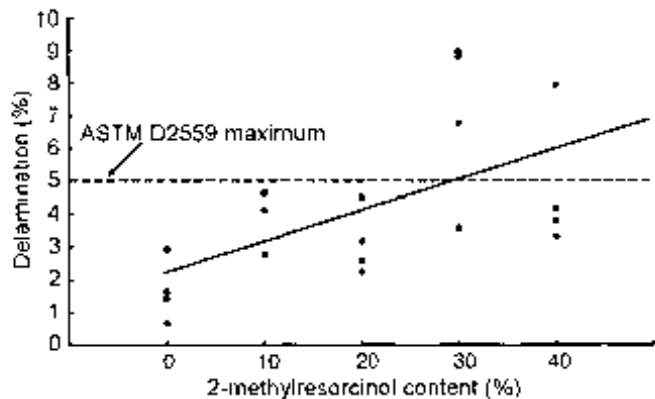


Figure 2. — Effect of substituting 2-methylresorcinol for proportion of resorcinol in HMR primer on subsequent delamination resistance of epoxy-bonded assemblies of southern yellow pine glulam.

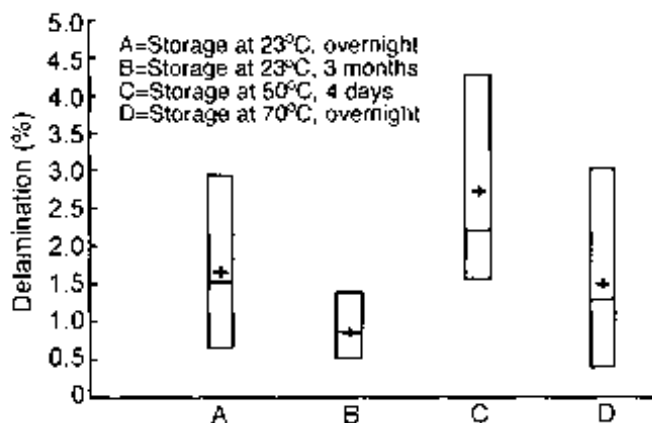


Figure 3. — Effects of storage conditions for HMR-primed southern yellow pine lumber on final delamination resistance of epoxy resin in glulam.

condition, the moisture source for one environmental chamber that held two assemblies was lost during the conditioning period, so those assemblies were drier than desired. Thus, our interpretation is conservative. Tests on the mean, at  $\alpha = 0.05$ , indicate that conditions A, C, and D (Fig. 3) constitute one Tukey group and that A, B, and D constitute another Tukey group. Under all these conditions, we expect that the HMR would have reacted to near its fullest extent within the wood, so it is unlikely that effective reactive sites remained to which the epoxy resin could bond.

The data support an interpretation that the durability of the adhesive bonds did not depend on the hypothesized residual reactivity of the HMR primer. Thus we can infer, again, that the mechanical restraint provided by the HMR to wood at the surface is important to increasing the durability of bonding in the presence of cyclic swelling and shrinking cycles. This is the likely reason why HMR improves the bonding to wood, and not only for epoxy resin. This also holds true for polyurethanes (Vick and Okkonen 2000), melamine-formaldehyde, and melamine-urea-formaldehyde resins for chromated copper arsenate treated wood (Vick 1997b), and phenol-resorcinol-formaldehyde, emulsion/polymer isocyanate (EPI), and polymeric methylenediphenyldiisocyanate (pMDI) resins (Vick 1996). Frihart (2003) proposed that ex-

pansion of nonstabilized wood cells results in large tensile strains on epoxy resins, resulting in epoxy fracture. Frihart also observed, using optical and fluorescence microscopy, that a thin film of epoxy adhesive remained on unprimed wood surfaces that by customary evaluation appeared to have interfacially separated. This failure mechanism had not been detected previously. The benefit bestowed by HMR may be to reduce the strain difference between the wood and adhesive by reducing wood expansion (improving its dimensional stability) in comparison to that of unprimed wood (Son and Gardner 2004), thereby reducing the likelihood of adhesive failure.

In a sense, this stabilization behavior seems to be a surface equivalent of the concept behind Impreg, developed by Stamm and Seborg (1936). The Impreg process involved soaking pieces of green lumber in a solution of a phenol-formaldehyde thermosetting resin and later curing the lumber at elevated temperature. The modified wood could be preservative treated without affecting the bonded joints, and it could be made into plywood with either a phenolic film or casein adhesive. In the present case, resorcinol enables cure at ambient temperatures. Also, because only a surface application is needed to stabilize the bondline, only a minimal amount of resorcinol is needed.

### Conclusions

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.

### Literature cited

- American National Standards Institute/American Institute of Timber Construction (ANSI/AITC). 1992. American national standard for wood products: Structural glued laminated timber, ANSI/AITC A 190.1-1992. AITC, Englewood, CO. 16 pp.
- American Society for Testing and Materials (ASTM). 1998. Standard specification for adhesives for structural laminated wood products for use under exterior (wet-use) exposure conditions. ASTM D 2559a. In: Annual Book of ASTM Standards. Vol. 15.06 Adhesives. ASTM, West Conshohocken, PA, pp. 157-161.
- Bolger, J.C. 1973. Structural adhesives for metal bonding. In: Treatise on adhesion and adhesives. Vol. 3. R.L. Patrick, ed. Marcel Dekker, New York. p. 70.
- Christiansen, A.W. 2000. Resorcinol-formaldehyde reactions in dilute

- solution observed by carbon-13 NMR spectroscopy. *J. Appl. Polym. Sci.* 75: 1760-1768.
- \_\_\_\_\_ and E.A. Okkonen. 2003. Improvements to hydroxymethylated resorcinol coupling agent for durable bonding to wood. *Forest Prod. J.* 53(4):81-84.
- \_\_\_\_\_, C.B. Vick, and E.A. Okkonen. 2001. A novolak-based hydroxymethylated resorcinol coupling agent for wood bonding. In: *Proc., Wood Adhesives 2000 Symposium*. Forest Prod. Soc., Madison, WI. pp. 245-250.
- \_\_\_\_\_, and \_\_\_\_\_, 2003. Development of a novolak-based hydroxymethylated resorcinol coupling agent for wood adhesives. *Forest Prod. J.* 53(2):32-38.
- Frihart, C.R. 2003. Wood structure and adhesive strength. In: *Characterization of the Cellulosic Cell Wall*. Proc. of SWST International Workshop on Assessment and Impact of Cellulosic Cell Wall. Blackwell Publishing Ltd., Oxford, UK.
- Gardner, D.J., W.T. Tze, and S.Q. Shi. 2001. Adhesive wettability of hydroxymethyl resorcinol (HMR) treated wood. In: *Proc., Wood Adhesives 2000 Symposium*. Forest Prod. Soc., Madison, WI. pp. 321-327.
- Grenier-Loustalot, M.-F., S. Larroque, P. Grenier, J.-P. Leca, and D. Bedel. 1994. Phenolic resins: I. Mechanisms and kinetics of phenol and of the first polycondensates towards formaldehyde in solution. *Polym.* 35:3046-3054.
- Lopez-Anido, R., D.J. Gardner, and J.L. Hensley. 2000. Adhesive bonding of eastern hemlock glulam panels with E-glass/vinyl ester reinforcement. *Forest Prod. J.* 50(11/12):43-47.
- Son, J. and D.J. Gardner. 2004. Dimensional stability measurements of thin wood veneers using the Wilhelmy plate technique. *Wood and Fiber Sci.* 36:98-106.
- Stamm, A.J. and R.M. Seborg. 1936. Minimizing wood shrinkage and swelling - treating with synthetic resin-forming materials. *Ind. & Eng. Chem. Res.* 28:1164-1169.
- Streitwieser, A., Jr. and C.H. Heathcock. 1981. *Introduction to Organic Chemistry*. 2nd ed. Macmillan Publishing Co., Inc., New York. 262 pp.
- Vick, C.B. 1996. Hydroxymethylated resorcinol coupling agent for enhanced adhesion of epoxy and other thermosetting adhesives to wood. In: *Proc., Wood Adhesives 1995 Symposium*. A.W. Christiansen and A.H. Conner, eds. Proc. 7296. Forest Products Soc., Madison, WI. pp. 47-55.
- \_\_\_\_\_. 1997a. More durable epoxy bonds to wood with hydroxymethylated resorcinol coupling agent. *Adhesives Age* 40(8):24-29.
- \_\_\_\_\_. 1997b. Enhanced adhesion of melamine-urea and melamine adhesives to CCA-treated southern pine lumber. *Forest Prod. J.* 47(7/8):83-87.
- \_\_\_\_\_ and E.A. Okkonen. 1997. Structurally durable epoxy bonds to aircraft woods. *Forest Prod. J.* 47(3):71-77.
- \_\_\_\_\_ and \_\_\_\_\_, 2000. Durability of one-part polyurethane bonds to wood improved by HMR coupling agent. *Forest Prod. J.* 50(10):69-75.
- \_\_\_\_\_, A.W. Christiansen, and E.A. Okkonen. 1998. Reactivity of hydroxymethylated resorcinol coupling agent as it affects durability of epoxy bonds to Douglas-fir. *Wood and Fiber Sci.* 30(3):312-322.
- \_\_\_\_\_, K.H. Richter, and B.H. River. 1996. Hydroxymethylated resorcinol coupling agent and method for bonding wood. U.S. patent 5 543 487. Aug. 6. 18 pp.
- \_\_\_\_\_, and A.R. Fried, Jr. 1995. Hydroxymethylated resorcinol coupling agent for enhanced durability of bisphenol-A-epoxy bonds to Sitka spruce. *Wood and Fiber Sci.* 27(1): 2-12.