Improvements to hydroxymethylated resorcinol coupling agent for durable bonding to wood

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Abstract

Improving the exterior quality bonding of wood to epoxy adhesive resins is important for bonding glass-fiber-reinforced vinyl ester resin laminae to glulam structural members, as well as for repairing glulam members in exterior applications on site. The coupling agent for these applications, hydroxymethylated resorcinol (HMR), was recently improved by using a novolak version (n-HMR) to reduce reaction time. In this study, the chemical composition of HMR was changed to decrease the total amount of formaldehyde added to the system. The results showed that n-HMR can be applied to a wood surface and stored for up to 16 days without compromising its effectiveness as a coupling agent.

Several years ago, the coupling agent hydroxymethylated resorcinol (HMR) was developed and patented to improve bonding of adhesives to wood in situations where the bonds would not otherwise be durable for exterior conditions (Vick et al. 1996). Basically, HMR is a dilute, high formaldehyde-to-resorcinol (F/R) molar ratio resorcinol–formaldehyde polymer with active hydroxymethyl groups (Vick et al. 1996). The original system enhances the bonding of epoxy and one-part polyurethane adhesives to wood, greatly increasing the exterior durability of their bonds. HMR also helps phenol-resorcinol-formaldehyde adhesives bond more durably to chromated-copper-arsenate- (CCA) treated southern pine, the most commonly treated wood species (Vick 1995, 1996). Lopez-Anido et al. (2000) found that HMR also significantly improves the bond durability of wood laminates to vinyl ester resin used as a matrix resin for glass-reinforced composites. To improve the convenience ofmanufacturing HMR, a very low molecular weight novolak (a stable form for storage and shipping) was formed from resorcinol and a small amount of formaldehyde (Christiansen et al. 2001, 2003). When the coupling agent is to be used, additional formaldehyde is added to the novolak to activate the system, to build up the final molecular weight, and to produce the cross-linking necessary for the novolak-based HMR (n-HMR) to perform as a durable coupling agent. Novolak-based HMR has worked very well with epoxy resin. It can be applied to wood almost immediately after mixing in the final formaldehyde, and, as an unexpected benefit, it greatly increases the overall working time (pot life) to 7 hours (Christiansen et al. 2003).

Some phenomena observed during the development of n-HMR indicate that this modified coupling agent may yield some unexpected improvements or benefits. This paper presents the evaluation of two variables: 1) the effect of lowering the final F/R ratio for the complete system on delamination resistance; and 2) the duration of HMR effectiveness from the time the wood is primed with the coupling agent until the adhesive is applied.

Experimental

Resin and coupling agents

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

To prepare the novolak precursor to HMR, 3.34 percent (mass) resorcinol was mixed with 93.08 percent deionized

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Table 1.—Composition of test HMR formulations.

Total F/R	Novolak	Final formalin	Water
	(%)		
I.54	194.3 1	5.69	0
1.44	194.32	5.18	0.50
1.34	194.3 1	4.69	1.00
1.24	194.32	4.20	1.48

water, 2.5 1 percent 3 M aqueous sodium hydroxide, and 0.98 percent formalin (here, 37.1% formaldehyde). This resulted in a novolak with an F/R molar ratio of 0.39, which is the ratio used to make n-HMR that provided the best results in a previous study (Christiansen et al. 2001, 2003). To make the n-HMR coupling agent, more formaldehyde needs to be added.

For investigating the effect of various total FR ratios, the amount of final formaldehyde added to the novolak was varied. The novolak, various amounts of additional formalin, and additional water, as necessary, were mixed together **(Table 1).** The formulation with a total F/R of 1.54 was used for all trials on the use of different post-treatment times prior to adhesive application.

The n-HMR was applied to the wood surface 0.5 hours after the final formalin was mixed into the novolak. To aid wetting of the resinous wood surfaces, dodecyl sulfate sodium salt was added to n-HMR (at 0.5% by weight) just before applying the coupling agent to the wood.

Wood

Douglas-fir (*Psuedotsuga menziesii* (Mirb.) Franco) was used to evaluate the effect of total F/R molar ratio. Loblolly pine (*Pinus taeda* L.) was used to evaluate the effect of post-treatment time. 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 relative humidity (RH) to approximately 9.5 percent equilibrium moisture content (EMC). Twenty-four hours before bonding, laminates were knife-planed to a thickness of 16 mm. This thickness is slightly less than the 19 mm specified in ASTM D 2559, but we were primarily seeking to compare performance between members in a test series.

Because free water decreases the effective bonding of epoxy adhesives to wood, water must be removed from HMR-primed wood surfaces before the adhesive is spread. Water content at the surface was decreased by conditioning the primed wood overnight at 50 percent RH and 23°C.

Preparation and testing of delamination specimens

Laminated assemblies were prepared from six pieces of lumber, each 16 mm thick, 76 mm wide, and 305 mm long. Both wood surfaces for a bondline were spread by brush with 0.15 kg/m^2 HMR. Wood primed with HMR has generally been dried overnight before bonding with epoxy. In this study, we followed this procedure for samples used to evaluate the effect of total F/R molar ratio. However, for samples used to evaluate the effect of post-treatment time, drying/storage times were 1, 2, 4, 8, or 16 days at 50 percent RH and 23°C.

After drying the laminae for the designated time, the epoxy adhesive was spread on the surfaces by roller to a total of 0.34 kg/m^2. The laminae were quickly joined to build an assembly. Closed assembly time was 60 minutes for the first bondline and 50 minutes for the last bondline of an assembly. After placing the assembly in a cold press, pressure was increased until a small amount of adhesive squeezed out along the full length of each bondline. In a previous study, pressure was measured at about 69 kPa (Vick and Okkonen 1997). The assemblies were kept under pressure overnight. Then, to ensure that all bondlines were cured to the same degree, the laminates were heated at 71°C for 5 hours. The relative humidity of the oven was increased to maintain the EMC of the wood so that bondlines would not be stressed by shrinkage of the wood while the resin cured.

Three delamination specimens were cut as 76-mm-long cross sections from each six-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 (ASTM 1998). Industry standard ANSI/AITC A 190.1 (AITC 1992) specifies that all wet-use adhesives intended for exterior service in structural lumber laminates must be qualified according to this ASTM specification. Each treatment was replicated four times.

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

- First cycle: [Step 1] Vacuum-soak in 18° to 21°C water at 84 kPa for 5 minutes; [Step 2] pressure-soak in 18° 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 2] add water at 18° to 21°C and pressure-soak at 5 17 kPa for 40 minutes; repeat event [Step 4] in first cycle.
- Third cycle: Repeat events in 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 percentage of delamination.

Results and discussion

The effect of reducing the total F/R ratio of n-HMR (while using a constant novolak F/R of 0.39), from the normal F/R of 1.54 to 1.34, appeared to improve delamination resistance **(Fig. 1).** However, upon further decreasing total F/R to 1.24, average delamination increased markedly and variability of the results also increased substantially **(Fig. 1).** It is not known exactly why this lower ratio has a negative effect on delamination resistance, However, less formaldehyde would produce fewer hydroxymethyl groups in the molecules, which should reduce the number of crosslinks in n-HMR. Fewer hydroxymethyl groups might change interactions with, or bonds to, the wood or the adhesive that is subsequently applied. For example, fewer hydroxymethyl groups would make the coupling agent more hydrophobic and less likely to penetrate as deeply into

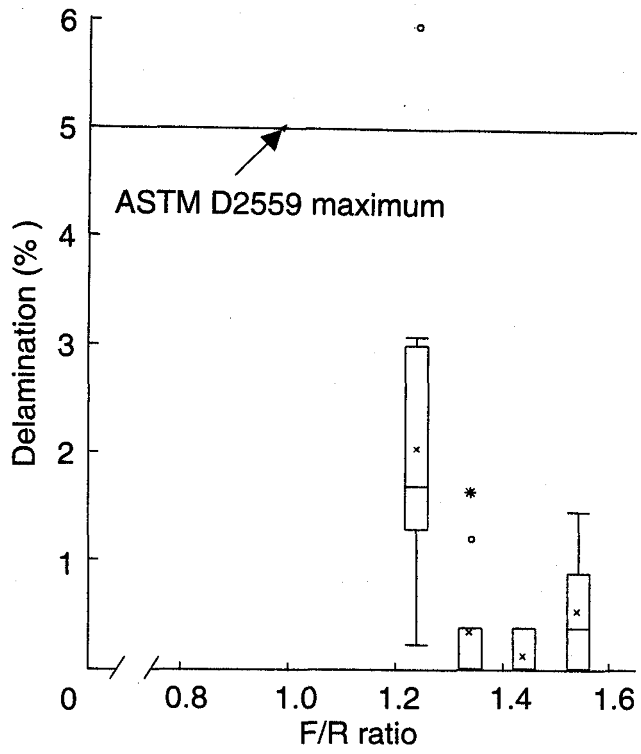

Figure 1.—Effect of total F/R molar ratio for novolak-based coupling agent on delamination resistance of Douglas-fir glulam assemblies. Top and bottom of box, 75th and 25th percentiles, respectively; line within box = median; x within box = mean; lines (whiskers) extending above and below box = highest and lowest connected data values (not including outliers); small circle outside box = outlying data; asterisk outside box = extreme outlying data.

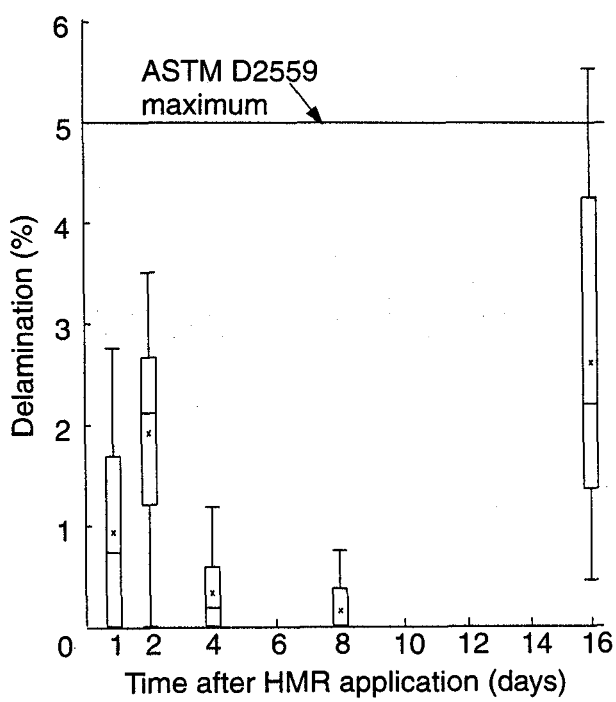

Figure 2.—Effect of post-treatment time between HMR and epoxy adhesive applications on delamination resistance of southern pine glulam assemblies. In all cases, novolak F/R = 0.39, total F/R = 1.54, and HMR was applied 0.5 hour after mixing.

the wood structure, or they would provide fewer sites for hydrogen or covalent bonds with wood or adhesive. Fewer crosslinks would make for a less rigid and weaker coupling agent, which could have an impact through less reinforcement of the wood or through lower maximum strength to resist swelling and shrinking stresses between the wood and epoxy adhesive.

The increase of delamination in reducing the F/R ratio from 1.34 to 1.24 shows a decrease in the coupling effect. For softwoods, delamination in one bondline is not allowed to constitute more than 20 percent of the overall 5 percent total permissible delamination; that is, no more than 1 percent of delamination should be observed in any one specimen from one of the assemblies made at one condition, in this case for one F/R value. None of the specimen bondlines in any of the tests in this study exceeded this limitation. Nevertheless, FIR ratios below 1.34 should be used with caution.

Extension of post-treatment time (between applications of n-HMR and adhesive) resulted in delamination resistance that initially improved with time, reaching a very low value after 8 days (Fig. 2). However, resistance subsequently degraded somewhat, so that after 16 days, mean delamination resistance was closer to the ASTM specified maximum-allowed mean value than at any previous time. This long tolerance (16 days) for the coupling agent to remain on the surface before adhesive bonding is very surprising. When the coupling agent is maintained as a solution before being spread onto wood, its effectiveness to meet the ASTM standard fades sometime after 7 hours (Vick et al. 1998, for original HMR; Christiansen et al. 2001, for n-HMR). But when n-HMR was applied to the wood, its effectiveness extended to at least 16 days under the conditions used in this study. This may mean that the loss of water from the coupling agent slows down chemical processes of n-HMR by removing the fluid environment in which HMR molecules can move about and react with each other. It does not appear that this slowed reaction lowered the eventual strength of the coupling action, because delamination remained low. However, an optimized usable shelf life must be determined for the system of wood, resin, and conditions expected during production.

This slowed reaction of n-HMR on wood could be commercially useful. If this reaction is generally true, it would mean that a manufacturer could prime wood 2 weeks prior to bonding, or that the plant could survive a 2-week shutdown of facilities without wasting preprimed wood. It also means that a wood mill could send primed wood to the manufacturer, who then only needs to apply adhesive to the wood before making the final bonded assembly. Shipping and storage times are included in the 16-day window of effectiveness.

This tolerance needs to be evaluated for other adhesive and wood combinations, different n-HMR formulations, and different storage or shipping environments.

Conclusions

The results of this study indicate that the level of formaldehyde added to the resorcinol–formaldehyde novolak to produce the n-HMR coupling agent can be reduced so that the total F/R molar ratio is lowered from 1.54 to 1.34. The consequent small reduction in solids level does not seem to adversely affect delamination resistance. Further reduction to F/R of 1.24 decreases delamination resistance, but not so much as to exceed specified delamination levels.

When a total F/R of 1.54 was used, n-HMR applied to wood surfaces remained active as a coupling agent for at least 16 days before an epoxy resin was finally applied to the surfaces for bonding. From this it can be inferred that wood surfaces could be primed with n-HMR of that F/R ratio and stored or shipped at 50 percent RH and 23°C for more than 16 days before the surfaces would need to be bonded. Different materials and procedures could affect acceptable storage time.

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