Progress in using hydroxymethylated resorcinol coupling agent to improve bond durability to wood

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Introduction

Durable exterior-quality bonds to wood have been made for decades using hot-press phenolic resins (PF) and cold-setting resorcinol-based resins (RF). However, these resins usually do not form bonds of adequate durability to certain materials including

- CCA-treated wood from 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 complex structural joints, as in wooden sport airplanes).

Although substantial research (Vick and others 1995) has shown that epoxies can provide strong bonds to wood in the dry state and on exposure to water, no epoxies were known to meet the requirements for resistance to delamination as specified in ASTM D 2559 (ASTM 1998).

In the mid-1990s, researchers at the Forest Products Laboratory developed a coupling agent, hydroxymethylated resorcinol (HMR), that has the ability to enhance adhesive bonds between wood and nontraditional adhesives (Vick and others 1995, 1996). HMR is also effective in promoting durable bonding of phenol-resorcinol- formaldehyde (PRF) adhesives to CCA-treated Southern Pine (Vick 1995). This presentation reviews progress in development of HMR for use with nontraditional adhesives and for treated wood.

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 (Vick 1996; Vick and others 1995, 1996), especially at low bonding pressures (Vick and Okkonen 1997). After discovering that several one-part polyurethanes did not provide the bond quality needed for structural durability (Vick and Okkonen 1998), the reseachers later found that pretreating the wood with HMR enabled two of these one-part polyurethanes to produce highly durable bonds (Vick and Okkonen 2000).

Bonding fiberglass-reinforced plastics to wood

The inherent large strength-to-weight ratio of wood sometimes is used in structures where the surface layers can be reinforced with a fiber-reinforced plastic (FRP) composite. Wood members may be laminated with FRP to give much higher stiffness and strength to a tension side of the assembly (such as in building beams and bridge members) or to provide a chemically resistant and less easily damaged surface (such as for truck flooring). The wood-FRP

combination requires bonding high-polarity wood to fairly low-polarity plastic surfaces that were already thermoset. HMR has proven to be very useful in this application (Vick 1996). Although PRF adhesive bonds well to the wood, it cannot maintain a durable bond to the vinyl ester FRP. But an epoxy bonds to the HMR-primed wood as well as to the vinyl ester FRP (Table 1). Assemblies of Southern Pine lumber primed with HMR, bonded on both top and bottom surface layers with vinyl ester FRP composite plies, using an epoxy as the only adhesive, were put through cycles of ASTM D 2559 to induce delaminations. The swelling and shrinking strains caused the wood itself to crack in places, but the bondlines held together. Similar results were seen for epoxy-bonded assemblies of phenolic FRP composite with HMR-primed Southern Pine lumber.

Vinyl ester has also been used as an adhesive to bond directly to wood surfaces, with or without priming of the wood with HMR (Lopez-Anido et al. 2000). PRF adhesive was used as a control in adhesive shear block tests. All samples were clamped and then cured at room temperature. The PRF adhesive had good strength and excellent wood failure results, both in a dry state and after vapor pressure saturation for 12 hours. The vinyl ester adhesive by itself had unacceptably low strength and very poor wood failure results, especially when tested wet. Vinyl ester used in conjunction with HMR priming of the wood resulted in strength results that were approximately equal to those from PRF, and the wood failure values were excellent. Also, bonding of vinyl ester in a wet lay-up of FRP fabrics onto HMR-primed wood resulted in very low delamination values, whereas bonding unprimed wood resulted in high delamination values.

Preservative-treated wood

Wood is treated with CCA preservative for uses where it will contact moist environments or is accessible to termites or other degrading mechanisms. CCA-treated wood is harder to bond than is untreated wood. HMR-primed Southern pine provided surfaces with which PRF adhesives usually produce durable bonds, even under the stringent ASTM D 2559 cyclic tests. In contrast, without HMR, delamination values for CCA-treated Southern Pine were much higher than the ASTM specified 5% maximum level (Vick 1995).

Improvement in HMR formulation

The original HMR was prepared by mixing resorcinol with sodium hydroxide, water, and formaldehyde solution at least three hours before it was to be used. It was effective until 8 hours after being mixed. Recently, the formulation of HMR was made more convenient for commercial use (Christiansen et al. 2001). Most of the ingredients, except for a portion of the formaldehyde, are mixed together and allowed to react for a day. The product can be shipped in this form and stored for an indefinitely long time. This novolak form is analogous to those for PRF and RF adhesives. The major difference for HMR is that the formaldehyde-to-resorcinol ratio is much lower, which provides the molecular sizes needed to be an effective coupling agent, rather than an adhesive. To activate the material, the rest of the formaldehyde (hardener) is added and reacts very quickly with the novolak to form a usable coupling agent. This material is effective almost immediately and for over 7 hours after mixing, and so one batch should supply material for an 8-hour shift.

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Table 1. Delamination resistance of epoxy and PRF adhesives in vinyl ester FRP/lumber composites

Treatment combination				Delamination, %	
Adhesive	Wood species	Primed?	FRP surface[a]	Wood-to-wood	FRP-to-wood
Epoxy	Yellow-poplar	Yes	Peel-ply	0	0
		Yes	Solvent wipe	0	0
	Southern Pine	Yes	Peel-ply	9	0
		Yes	Solvent wipe	9	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 vinyl ester in the manufacturing process. Solvent wipe: wiped with acetone.

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