Hydroxymethylated Resorcinol Coupling Agent for Enhanced Adhesion of Epoxy and Other Thermosetting Adhesives to Wood

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Abstract

The durability of adhesive bonds poses a continuing problem for the wood products industry Priming wood surfaces with the coupling agent hydroxymethylated resorcinol (HMR) holds promise for increasing the delamination resistance and shear strength of adhesive bonds. The purpose of this study was to determine if HMR could enhance structural adhesion of various epoxy formulations to softwood and hardwood species, as well as to wood in fiber-reinforced plastic composites. The effectiveness of adhesion was evaluated by measuring delamination of lumber joints as they were subjected to the severe cyclic delamination test of ASTM D2559. Epoxy adhesives in laminated composites of HMR-primed lumber and fiber-reinforced plastics were extraordinarily resistant to delamination. Epoxy, as well as phenol-resorcinol, emulsion polymer/isocyanate, and polymeric isocyanate adhesives, also met the ASTM standard on HMR-primed Southern Pine lumber treated with chromated copper arsenate preservative. The capability of epoxies to adhere to both wood and plastics presents an opportunity for making highly durable composites from fiber-reinforced plastics and wood.

Introduction

The coupling agent is one of several surface modifications that have become essential to the durability of adhesive bonds to metals, plastics, and advanced composites in aerospace and automotive industries. Such treatments are virtually nonexistent in the wood products industry Surface modification could solve important adhesion problems in wood products. The bonds formed by epoxy adhesives are not durable enough for structural exterior applications where they must withstand severe stresses from water soaking and drying. Thermosetting wood adhesives do not adhere to wood treated with chromated copper arsenate (CCA) preservative well enough to consistently meet rigorous industrial standards for resistance to delamination.

The Terminology Subcommittee of ASTM Committee D-14 on Adhesives is proposing a new definition for coupling agent: A *coupling agent is a molecule, having different or like functional groups, that is capable of reacting with surfice molecules of two different substances, thereby chemically bridging the substances.* Previous definitions have described only silane coupling agents that have dual functional groups. Vinylethoxysilane, for example, has a vinyl functional group capable of reacting with organic polymers such as polyester resin. This coupling agent also has three ethoxy groups that hydrolyze to silanols, which can react with inorganic materials such as fiberglass. The proposed ASTM definition is broader in scope and includes not only silanes with their dual functional groups, but also molecules with like functional groups that may also react with different surface molecules of different materials. Hydroxymethylated resorcinol (HMR) is such a coupling agent, and its ability to couple epoxy and other thermosetting adhesives to wood is the subject of this paper.

Recent studies at the Forest Products Laboratory led to a discovery that trihydroxymethyl resorcinol and its dimers, trimers, and perhaps higher oligomers, similar in chemical structure to that shown in Figure 1, are capable of physiochemically coupling bisphenol-A epoxy adhesives to the lignocellulosics of wood (12,13). Although the molecular structures and size distributions are still being determined, the coupling reactions of HMR with epoxy resin and wood are suggested in Figure 2. The HMR coupling agent is believed to covalently bond with the epoxy resin by forming ether linkages through condensation reactions between hydroxyls of the epoxy and hydroxymethyl groups of HMR (position 5, Figure 2). Other available hydroxymethyl groups of the coupling agent are capable of forming ether linkages with the primary alcohols of wood cellulosics, as shown at position 7 in Figure 2. If conditions and sites are not conducive to covalent bonding, then hydrogen bonding is more likely to occur, as shown at position 6 in Figure 2. When cell

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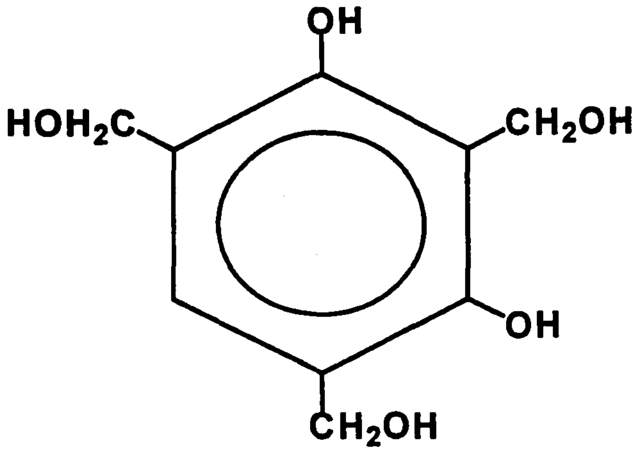
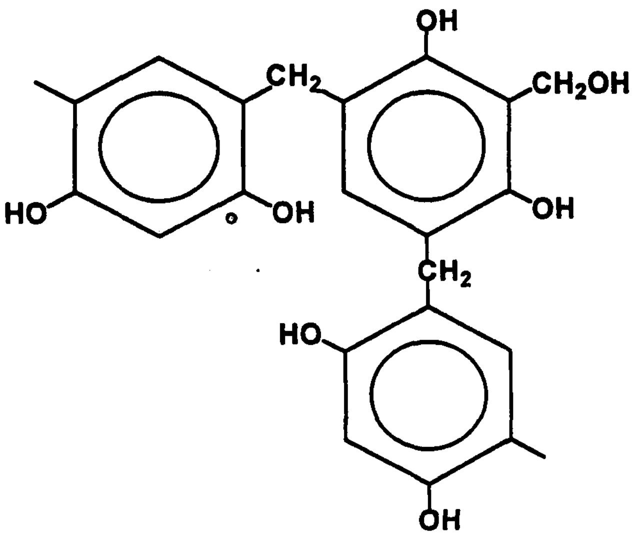
Keywords: hydroxymethytated resorcinol, coupling agent, adhesive, epoxy, phenol-resorcinol, emulsion polymer/isocyanate, polymeric isocyanate, delamination resistance.

walls are thoroughly covered and penetrated by a multimolecular layer of highly reactive HMR of relatively small molecular size, opportunities abound for high-density hydrogen bonding with primary and secondary hydroxyls of wood lignocellulosics.

The purpose of this report is to demonstrate that HMR has the versatility and effectiveness to enhance structural adhesion of various epoxy formulations to softwood and hardwood species, as well as to wood in fiber-reinforced plastic (FRP) composites. The versatility of HMR is further demonstrated in its reactions with thermosetting adhesives of differing functional groups to solve adhesion problems to CCA-treated Southern Pine. The effectiveness of adhesion was evaluated by measuring delamination of lumber joints as they were subjected to the severe cyclic delamination test of ASTM D 2559 (3). This test is used to qualify adhesives for structural glued-laminated timbers intended for wet-use exposures under industry standard ANSI/AITC A190.1-1992 (l).



Trihydroxymethyl resorcinol



Hydroxymethylated resorcinol trimer

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

Experimental Materials and Methods

The HMR coupling agent was prepared as a 5-percent-solids aqueous solution by reacting formaldehyde with resorcinol in a 1.5 mole ratio at mildly alkaline conditions. The ingredients were reacted for 4 h at room temperature before application to the wood surfaces. The length of this reaction time is critical to the effectiveness of adhesion.

HMR coupling agent

Composition of HMR coupling agent

Ingredient	Parts by weight
Water, deionized	90.43
Resorcinol, crystalline	3.34
Formaldehyde, 37 percent	3.79
Sodium hydroxide, 3 molar	2.44
Total	100.00

Dodecyl sulfate sodium salt (0.5% by weight) was added to HMR after its reaction period to aid wetting of resinous wood surfaces. For most effective bonding with epoxy adhesives, water must be evaporated from the primed wood surfaces before the adhesive is spread.

Adhesives

Three epoxy formulations were used in the experiments, but all resins were based on diglycidylether of bisphenol-A (DGEBA). Other ingredients in each adhesive varied. Formulations for FPL 16A (6) and FPL 1A are shown in Table 1. For proprietary reasons, the formulation for the commercial adhesive, identified as COMA, is not shown.

Two commercial phenol-resorcinol-formaldehyde (PRF) adhesives were used to laminate CCA-treated Southern Pine lumber. Both adhesives meet the structural durability requirements of ANSI/AITC A190.1-1992 (1) on untreated Southern Pine, according to the manufacturer's technical literature.

A commercial phenol-modified resorcinol-formaldehyde adhesive was used to laminate the vinylester FRP to wood. The phenolic FRP was laminated to wood with a commercial resorcinol-formaldehyde (RF) adhesive. Both adhesives meet the referenced ANSI/AITC standards.

The emulsion polymer/isocyanate (EPI) was a two-part thermosetting adhesive. The resin component was an aqueous synthetic rubber latex emulsion, and the hardener, a polymeric diphenylmethane-type diisocy-

Table 1. *Formulations of FPL 16A and FPL 1A adhesives.*

Ingredient	Parts by weight
FPL 16A	
DGEBA epoxy resin	100.0
Blended lacquer thinner	18.0
Titanium dioxide	30.0
Diethylenetriamine hardener	13.0
FPL 1A	
DGEBA epoxy resin	100.0
Benzyl alcohol	12.5
Hydrophobic fumed silica	2.5
Triethylenetetramine hardener	11.1

anate (MDI). This adhesive also meets the structural durability requirements of ANSI/AITC A190.1-1992 (1) on untreated Southern Pine, according to the manufacturer's technical literature.

A proprietary experimental polymeric MDI (pMDI) was used as a laminating adhesive.

Wood Species

Two softwood species (Sitka spruce and Douglas-fir) and two hardwood species (yellow poplar and yellow birch) were selected from a range of medium- to high-density wood species commonly used as structural components in wood aircraft. Generally, specimen material was cut from flat-sawn boards, nominal 1- × 8-in. (stand-

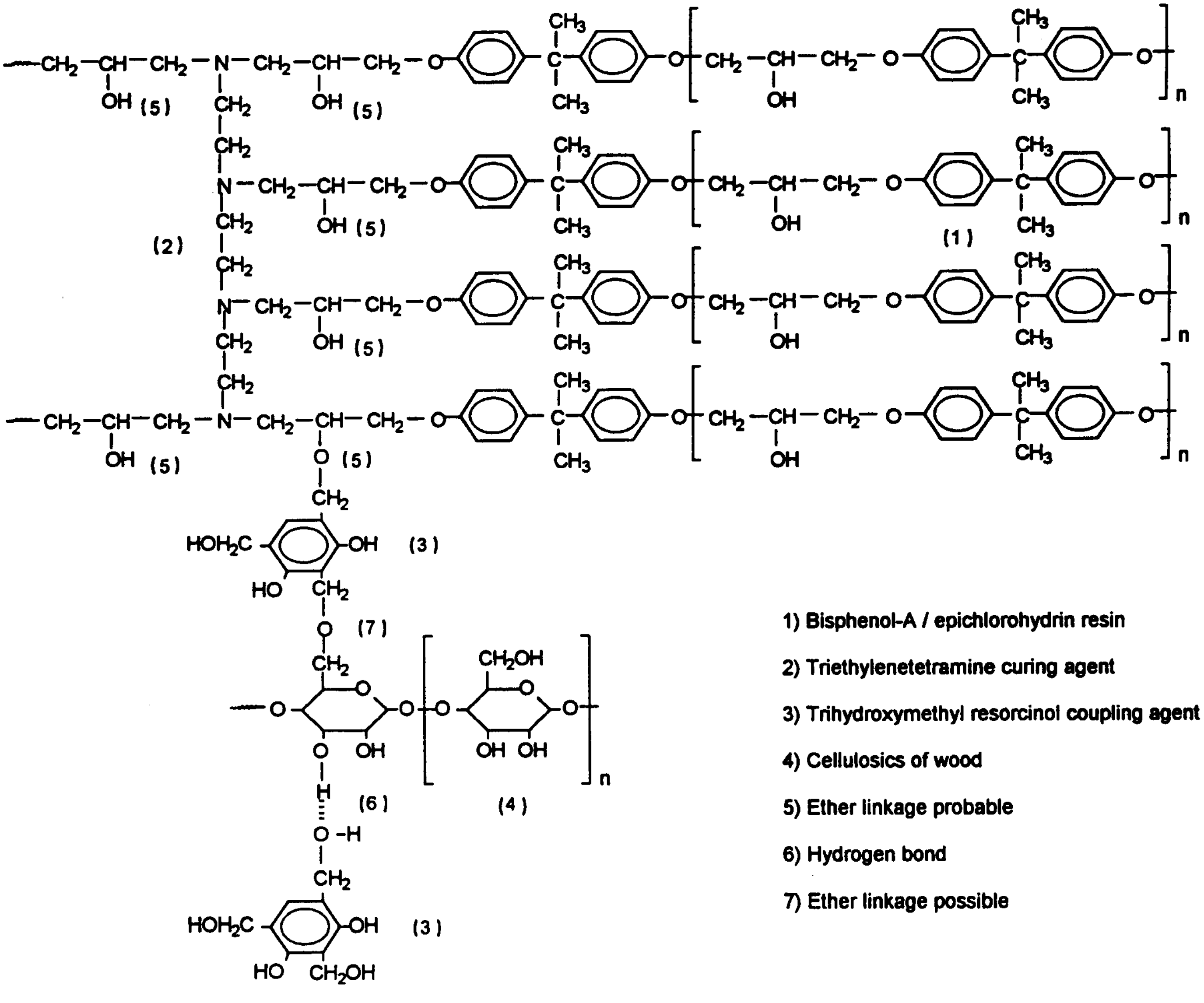


Figure 2. *Covalent and hydrogen bonding of HMR coupling agent between bisphenol-A epoxy adhesive and cellulosic components of wood.*

ard 2.5- × 20-cm), near the average density for the species. The boards were heartwood, straight-grained, and free of defects.

Southern Pine boards were flat-sawn, nominal 1- × 8-in. (standard 2.5- × 20-cm), near average density for the species. The boards were sapwood, straight-grained, and free of defects. The CCA-treated boards were pressure-treated at the Forest Products Laboratory with a commercial preservative of Type C to retentions of 0.4 and 0.6 lb/ft^3 (6.4 and 9.6 kg/m^3).

All boards were conditioned to equilibrium moisture content (EMC) near 10 percent. Twenty-four hours before bonding, lumber laminates were jointed and knife-planed to ensure that they would lie flat and be free of surface contamination at the time of bonding.

Fiber-Reinforced Plastics

Fiber-reinforced plastic (FRP) sheets consisting of fiberglass strands embedded in matrices of vinylester and phenolic resins were supplied by their manufacturers. The FRP surfaces were prepared in several ways for bonding smooth-surface, peel-ply, sanded, solvent-wiped, and primed with HMR. The specific surface preparations used in each bonding test are shown with the test results.

Preparation of Specimens

Delamination specimens were 3-in. - (7.6-cm-) long cross-sections cut from lumber laminates. Laminates were prepared by bonding six pieces of lumber with a test adhesive; each piece was 3/4 in. (1.9 cm) thick, 3 in. (7.6 cm) wide, and 12 in. (30.5 cm) long. Three sections were cut from each of four lumber laminates for a total of 12 delamination specimens for each treatment combination. For the pMDI adhesive, one lumber laminate was prepared for each treatment combination.

Shear strength and wood failure were determined from compression-loaded, block-shear specimens with 3.0 in^2 (19.4 cm^2) shear area. Specimens were cut from lumber laminates prepared by bonding two pieces of lumber with a test adhesive; each piece was 3/4 in. (1.9 cm) thick, 2.5 in. (6.4 cm) wide, and 12 in. (30.5 cm) long. Five shear specimens were cut from each of four lumber laminates for a total of 20 specimens for each treatment combination.

Delamination specimens from the FRP/lumber composites were prepared and cut in a manner similar to the lumber laminates just described. Vinylester and phenolic FRPs were substituted for the top and bottom lumber laminates in the six-ply laminates. Three sections were cut from each lumber laminate and used to measure delamination for each treatment combination.

Lumber laminates and FRP/lumber composites were prepared in essentially the same manner. If lumber or FRP surfaces were to be primed before bonding, a 5-percent HMR solution was spread with a brush at approximately 0.03 lb/ft^2 (0.15 kg/m^2). The primed surfaces were dried for 24 h at 73°F (22.8°C) and 10 percent EMC before bonding. Regardless of adhesive type, adhesive was spread with a roller on both bonding surfaces to total approximately 0.08 lb/ft^2 (O.39 kg/m^2). The closed assembly time (CAT) and initial pressure for the adhesives were as follows:

Adhesive	CAT (min)	Initial pressure	
		lb/in²	(kPa)
Epoxy	50-60	10	69
PRF	40-50	100	690
RF	40-50	100	690
EPI	20-30	100	690
pMDI	≤ 10	100	690

Generally, the above pressures produced small amounts of squeeze-out, full-length of all joints. As indicated above, far less pressure was required to produce squeeze-out of epoxies than of wood adhesives. All laminates were cured in a press for 15 h at room temperature. The PRT EPI, and pMDI adhesives were cured an additional 7 days at 73°F (22.8°C) and 10 percent EMC before testing. The epoxies were cured to the same degree by heating laminates at 150°F (65.5°C) for 5 h. To avoid stresses on bondlines from shrinkage of wood, the EMC of the air was maintained at 10 percent—the same as the initial EMC of the wood.

Delamination and Shear Tests

Delamination specimens cut from lumber laminates and FRP/lumber composites were subjected to the cyclic delamination test of ASTM D2559 (3). Essentially, the test consists of three cycles of vacuum-pressure soaking in water followed by oven drying. The second cycle also includes steaming followed by vacuum-pressure soaking. The test produces severe stresses on bondlines, and it is the most challenging to adhesive bond durability of any industry-accepted standard. Immediately after specimens were dried in the last cycle, delamination was measured along all end-grain surfaces to the nearest 0.01 in. (0.25 mm) with a machinist's scale under a stereomicroscope. Delamination was expressed as a percentage of total bondline length for each specimen.

Block-shear specimens were tested for shear strength and wood failure in a dry condition according to ASTM Method D905 (2). Shear strength at failure was calculated as pounds per square inch (Newtons per square centimeter), based on 3.0 in^2 (19.4 cm^2) shear area. Wood failure in the shear area was estimated to the nearest 5 percent.

Results and Discussion

Epoxy Bonds to Softwoods and Hardwoods

The delamination resistance values of FPL 16A and FPL 1A epoxy formulations in lumber laminates of two softwood and two hardwood species, with and without priming with HMR coupling agent, are shown in Table 2. Maximum delamination allowed by ASTM D2559 (3) is 5 percent for softwoods and 8 percent for hardwoods. The data show that HMR was highly effective in enhancing the durability of adhesion of both epoxies. Without the HMR primer, neither epoxy had the delamination resistance to meet ASTM requirements on any species. By priming with HMR, delamination percentages were lowered below requirements for the species group, with the exception of FPL 16A on yellow birch.

FPL 16A was highly diluted with lacquer thinner, so it penetrated and mechanically interlocked deeply within the wood structure. This epoxy owes its popularity particularly among builders of wood aircraft, to its ease of use, minimum clamping pressures, and ability to produce high, dry shear strength and wood failure on a wide variety of wood species. Yet, despite deep mechanical interlocking, FPL 16A delaminated severely when wood surfaces were not primed with HMR, as shown in Table 2. The ability of the coupling agent to greatly enhance the resistance of FPL 16A to delamination is quite evident.

Table 2. *Delamination resistance of FPL 16A and FPL 1A epoxy adhesives.*

Adhesive and lumber species	Delamination (percent)	
	Unprimed	HMR-primed
FPL 16A		
Sitka spruce	19.7	4.3
Douglas-fir	59.3	4.2
Yellow poplar	30.9	0.5
Yellow birch	97.5	10.8
FPL 1A		
Sitka spruce	30.5	4.0
Douglas-fir	49.6	3.7
Yellow poplar	10.5	0
Yellow birch	27.7	0.7

FPL 1A had better resistance to delamination than did FPL 16A on the unprimed wood, particularly on yellow birch and yellow poplar, despite its thixotropy and much higher viscosity With the coupling agent, delamination of FPL 1A was essentially nonexistent on the hardwoods and below ASTM requirements on the softwoods.

Epoxy and Resorcinolic Bonds in FRP/Wood Composites

As the results of the preceding experiments demonstrated, epoxy adhesives are capable of developing highly durable bonds to wood, if the wood surfaces are primed with HMR before bonding. Epoxy adhesives also develop durable bonds to certain plastics; only simple cleaning and abrading are needed to ensure adhesion to the plastic surfaces. Thus, the capability of excellent adhesion of epoxies to both wood and plastics presents an opportunity to make highly durable composites from FRPs and wood. The potential advantage of a properly engineered composite is a stronger and stiffer bending member of less cross-sectional dimension at lower cost.

The delamination resistance of epoxy and PRF adhesives in laminated composites of vinylester FRP and lumber, along with treatment conditions, is shown in Table 3. The FRP surfaces were either wiped with acetone or cleaned and textured by peeling away woven fabric that had been laminated to the vinylester in the manufacturing process. For the epoxy adhesive, both yellow poplar and Southern Pine were primed with HMR. The wood was not primed for PRF The FRP surfaces were not primed because preliminary tests had indicated that HMR does not adhere well to vinylester.

After the ASTM delamination test, none of the epoxy bonds between vinylester and HMR-primed lumber failed, regardless of wood species or surface preparation of vinylester (Table 3). Epoxy FPL 1A delaminated 9.1

Table 3. *Delamination resistance of epoxy and PRF adhesives in vinylester FRP/lumber composites.*

Treatment combination				Delamination (percent)	
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	100.0
		No	Solvent wipe	0	100.0
	Southern Pine	No	Peel-ply	0	100.0
		No	Solvent wipe	0	100.0

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

percent in the wood-to-wood joints of Southern Pine, but no delamination occurred in the yellow poplar joints. Figure 3 shows an epoxy-bonded vinylester/Southern Pine composite after the cyclic delamination test.

In sharp contrast to the results for the epoxy-bonded composite, PRF bonds to vinylester failed completely, regardless of surface preparation on the FRP As expected, PRF bonds to both wood species were delamination free. These results were not unexpected because phenolic and resorcinolic adhesives make excellent bonds to polar wood, but not to nonpolar vinylester.

Phenolic FRP has higher strength and stiffness than does vinylester and would make a more efficient reinforcer in a FRP/lumber composite. To evaluate this alternative, epoxy and RF adhesives were used to laminate phenolic FRPs to Southern Pine lumber, with material surfaces prepared as described in Table 4.

The epoxy adhesive between wood and the sanded phenolic FRP resisted delamination whether or not the phenolic surface was primed with HMR (Figure 4). Sanding was the critical surface preparation. Without it, the epoxy bond to phenolic FRP failed completely. The HMR-primed, wood-to-wood bonds made with FPL 1A delaminated approximately 9 percent.

The RF adhesive did not develop as durable a bond to the phenolic FRP as did the epoxy adhesive. As with the epoxy, the RF bond failed completely on the unsanded phenolic surface whether or not it was primed with HMR. Again, sanding was the critical surface preparation. However, priming of the sanded surface with HMR caused a significant decrease in delamination-from 45 percent on the unprimed surface to 12 percent on the primed surface

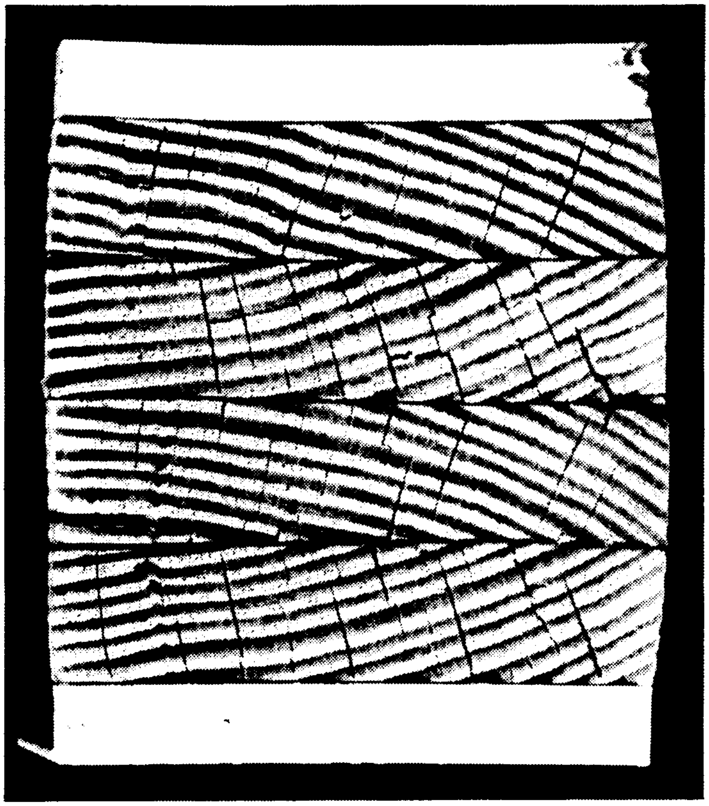


Figure 3. *Cross section of vinylester FRP composite laminated to HMR-primed Southern Pine lumber with FPL IA epoxy adhesive, following ASTM D2559 delamination test.*

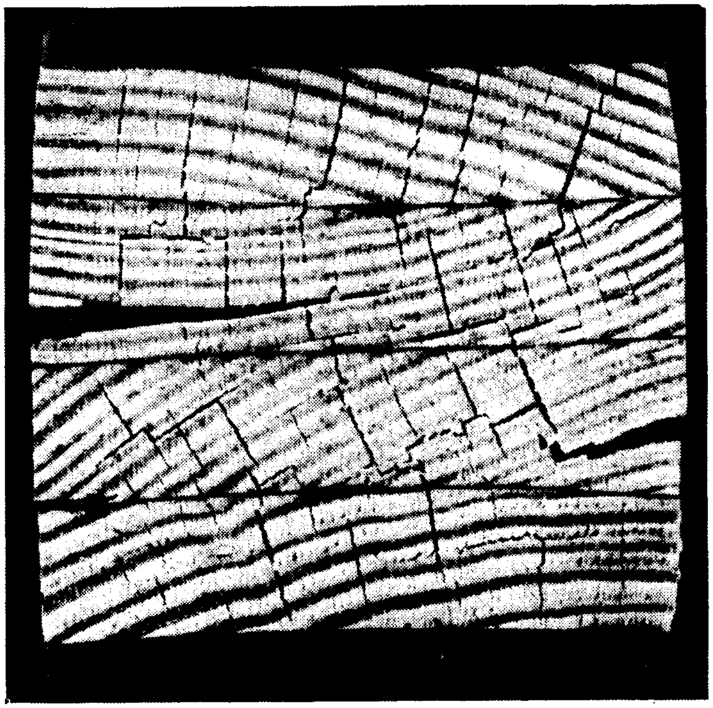


Figure 4. *Cross section of phenolic FRP composite laminated to HMR-primed Southern Pine lumber with FPL 1A epoxy adhesive, following ASTM D2559 delamination test.*

Table 4. *Delamination resistance of epoxy and RF adhesives in phenolic FRP/lumber composites.*

Treatment combination					Delamination (percent)	
Adhesive	Wood species	Wood primed	FRP surface	FRP primed	Wood to wood	FRP to wood
Epoxy-FPL 1A	Southern Pine	Yes	Unsanded	Yes	8.9	100.0
		Yes	Unsanded	No	8.9	100.0
		Yes	Sanded	Yes	9.5	0
		Yes	Sanded	No	9.5	0
RF	Southern Pine	No	Unsanded	Yes	1.3	97.5
		No	Unsanded	No	1.3	95.1
		No	Sanded	Yes	2.4	12.3
		No	Sanded	No	2.4	45.1

(Table 4). The RF adhesive made excellent bonds in the wood-to-wood joints.

Bonds to CCA-Treated Wood

Since 1945, scientists have known that chromium-containing preservatives seriously interfere with adhesion of commonly-used thermosetting adhesives to the treated wood. Researchers worldwide have searched for causes for poor adhesion, developed new adhesive formulations, and investigated special techniques that might help to remove this obstacle to better adhesion, Considerable information accumulated over many years has shed light on how CCA preservatives interfere with adhesion. The surfaces of the cellular structures of wood are essentially covered with microscopic-size deposits of mixtures of primarily chromium, copper, and arsenic oxides that are chemically bound to lignocellulosic constituents of the cell walls (4,5,7,8,11). These metallic deposits are insoluble in water and do not appear to be chemically active enough to interfere with the cure of phenolic-type wood adhesives (10). Wood is normally polar and molecular forces of attraction exist between wood and polar adhesives; however, chemically fixed CCA deposits are so pervasive, as shown in Figure 5, that most opportunities for physiochemical interaction between normally polar wood and adhesive are physically blocked (11).

PRF Bonds

Despite the interference with adhesion by chemically fixed deposits of CCA oxides, recent studies showed that HMR coupling agent significantly enhanced the durability of adhesion of commercial PRF adhesives to CCA-treated Southern Pine (9). Delamination percentages of two PRF adhesives in laminates of HMR-primed and unprimed CCA-treated and untreated Southern Pine are shown in Table 5. The data show that both adhesives delaminated ≤ 5 percent at CCA retentions of either 0.4 and 0.6 lb/ft^3 (6.4 or 9.6 kg/m^3), if the lumber was primed with HMR. The delamination requirement was met whether the primed surfaces were dried 1 or 24 h before the adhesive was spread. When the lumber was not primed, delamination percentages of both adhesives were unacceptable. Both adhesives met the delamination requirements on the untreated wood. Priming with the HMR coupling agent was essential for the PRF adhesives to meet ASTM delamination requirements in CCA-treated lumber laminates of Southern Pine.

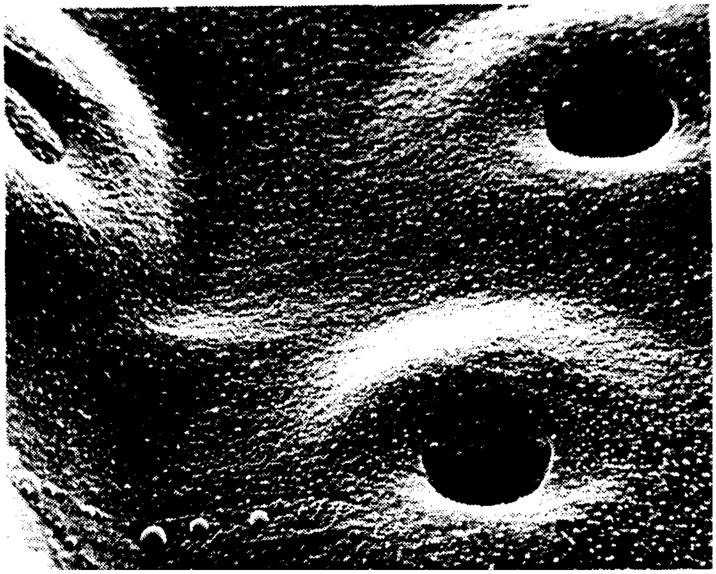


Figure 5. *Surface of cell lumen of CCA-treated Southern Pine covered with chemically fixed deposits of mixtures of chromium, copper, and arsenic oxides.*

Epoxy Bonds

Adhesion of epoxies to softwood and hardwood species was enhanced by the HMR coupling agent, as was demonstrated in the previous discussion. However, in view of the drastic physical and chemical changes to wood surfaces caused by fixation of CCA preservative (Figure 5), it is even more remarkable how effectively HMR enhanced adhesion of epoxies to CCA-treated wood. Resistance of COMA epoxy bonds to stress fracturing is demonstrated in Figure 6, where fracture initiated at a specimen edge in summerwood near a bondline, then propagated across the bondline and into summerwood of the adjacent laminate without any fracture in the HMR-primed bondline. Resistance to delamination and shear values of COMA epoxy adhesive on unprimed and HMR-primed CCA-treated Southern Pine are compared in Table 6. Delamination was almost complete at 88.8 percent on unprimed wood, but reduced to only 3.0 percent after priming with HMR. Even though epoxy adhesives are generally known to produce above-standard dry shear strength and wood failure on untreated woods, shear strength on the CCA-treated wood was slightly substandard, and wood failure was 46 percent, well below the required 75 percent. By priming with HMR, shear strength and wood failure were raised above standards to 1,673 lb/in^2 (1,154 N/cm^2) and 83 percent, respectively.

Table 5. *Enhanced durability of PRF bonds to CCA-treated Southern Pine with HMR primer.*

Adhesive	CCA retention (lb/ft^3)[a]	Delamination (percent) Unprimed	HMR primed dried 1h	HMR primed dried 24h
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 × 16.01 to convert to kg/m^3.

At least from a conceptual approach, it seems plausible that functional hydroxyls of the epoxy resin might form covalent or at least hydrogen bonds with reactive hydroxymethyl groups of HMR. However, it is not clear what types of linkages might develop between HMR and the insoluble chromium, copper, and arsenic oxides that are deposited and chemically bound to the cellular structures of CCA-treated wood. Strong adsorption of HMR to CCA deposits is clear, given the durability of the resultant bonds. We observed that aqueous-based thermosetting adhesives, and even epoxy adhesives, wet and spread more readily over CCA-treated wood that had been primed with HMR than over wood that had not been primed.

EPI Bonds

Even though the EPI adhesive meets all requirements of ANSI/AITC A190.1-1992 (1) on untreated Southern Pine, it failed to meet delamination requirements on Southern Pine treated with CCA to 0.6 lb/ft^3 (9.6 kg/m^3) (Table 6). Delamination was 10.6 percent when the lumber surfaces were not primed; when primed with HMR, delamination dropped to 1.7 percent, well below the 5 percent allowable.

The EPI adhesive developed acceptable levels of shear strength and wood failure on CCA-treated wood when the bonds were tested in the dry condition. Such was also true for PRF and epoxy adhesives. High and acceptable levels of both properties are shown in Table 6 for the unprimed and HMR-primed CCA-treated lumber. Note that all delamination and shear specimens primed with HMR were prepared with flat-grain lumber. The unprimed shear specimens contained large proportions of edge-grain lumber, which results in higher shear strength and lower wood failure than that of flat-grain lumber.

Hydroxymethylated resorcinol adsorbs strongly to the metallic deposits on the surfaces of CCA-treated wood. Thus, an enriched surface of reactive hydroxymethyl groups is presented for possible chemical linkage with adhesive. pMDI was used as the cross-linker for the synthetic rubber latex system of EPI. It seems plausible that some isocyanate groups of pMDI might react with hydroxymethyl groups of HMR to form urethane linkages and contribute to enhanced adhesion of EPI to HMR-primed CCA-treated wood.

Figure 6. *Pattern of stress fracturing around epoxy bond to HMR-primed CCA-treated lumber when it resisted delamination during ASTM D2559 delamination test.*

pMDI Bonds

The experimental pMDI laminating adhesive bonded very well to HMR-primed CCA-treated Southern Pine, as well as to the untreated wood (Table 7). Without the primer, delamination was extremely severe. Poor adhesion to both treated and untreated unprimed wood appears suspect in view of the well-known and excellent adhesion of pMDI to wood. This adhesive had short gel and cure times, and perhaps it did not have time to wet and penetrate Southern Pine effectively. On the other hand, HMR enriched the wood surface with functional hydroxymethyl groups that were capable of reacting with isocyanate groups to perhaps form urethane linkages. Whatever the chemical mechanism, the data in Table 7 show quite clearly that HMR was highly effective in increasing the delamination resistance of pMDI bonds to untreated and CCA-treated Southern Pine lumber.

Table 6. *Delamination and shear resistance of epoxy and EPI bonds to unprimed and HMR-primed CCA-treated Southern Pine compared to ASTM requirement.*

Adhesive and surface primer	Delamination (percent)	Shear strength (lb/in^2)[a]	Wood failure (percent)
COMA epoxy			
Unprimed	88.8	1,356	46
HMR primed	3.0	1,673	83
EPI			
Unprimed	10.6	2,107[b]	92
HMR primed	1.7	1,708[c]	96
ASTM D2559	≤ 5.0	≥ 1,375	≥ 75

[a] Multiply lb/in^2 × 0.6895 to convert to N/cm^2.

[b] Edge grain.

[c] Flat grain.

Table 7. *Enhanced durability of pMDI bonds to untreated and CCA-treated Southern Pine with HMR primer*

	Delamination (percent)	
Southern Pine lumber[a]	Unprimed	HMR-primed
Untreated	73.7	3.7
CCA-treated, 0.6 lb/ft^3	78.7	3.5

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

Conclusions

Hydroxymethylated resorcinol (HMR) can physiochemically couple bisphenol-A epoxy adhesives to softwoods and hardwoods to produce highly durable bonds that meet the delamination requirements of ASTM D2559. When this adhesive was used to laminate vinylester and phenolic fiber-reinforced plastics to HMR-primed lumber, the composites were extraordinarily resistant to delamination. When CCA-treated Southern Pine laminates were bonded with epoxy phenol-resorcinol, emulsion polymer/isocyanate, and polymeric diisocyanate adhesives, the bonds met the delamination requirements of ASTM D2559.

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