More Durable Epoxy Bonds to Wood With Hydroxymethylated Resorcinol Coupling Agent

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The lack of structural durability of epoxy bonds to wood has been a continuing frustration to fabricators of adhesive-bonded wood assemblies intended for service in exterior environments. Epoxy adhesives develop bonds to wood that are as strong as the wood itself, as long as the bonds remain dry. However, once exposed to the severe stresses from repeated water-soaking and drying, the bonds delaminate. As a result, epoxies fail to qualify as structural adhesives in laminated wood products intended for wet-use exposure, as required by industry standard ANSI/AITC A190.1-1992 *(2).* Furthermore, the American Institute of Timber Construction (AITC) does not recommend that epoxies be used in design or repair of structural timbers if the bonds are expected to withstand either shear or tension loading without steel reinforcement *(1).*

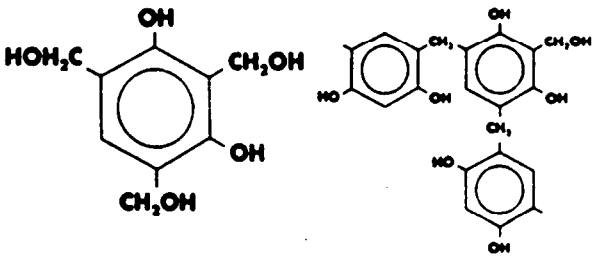
Table I

Composition of HMR Coupling Agent Solution

Ingredient	Parts by weight
Water, deionized	90.43
Resorcinol, crystalline	3.34
Formaldehyde, 37% solution	3.79
Sodium hydroxide solution, 3 M	2.44
Total	100.00
Dodecyl sulfate, sodium salt (added after reaction time)	0.50

Figure 1

Structure of Trihydroxymethylated Resorcinol and Its Trimer



Trihydroxymethyl resorcinol — **Hydroxymethylated resorcinol trimer**

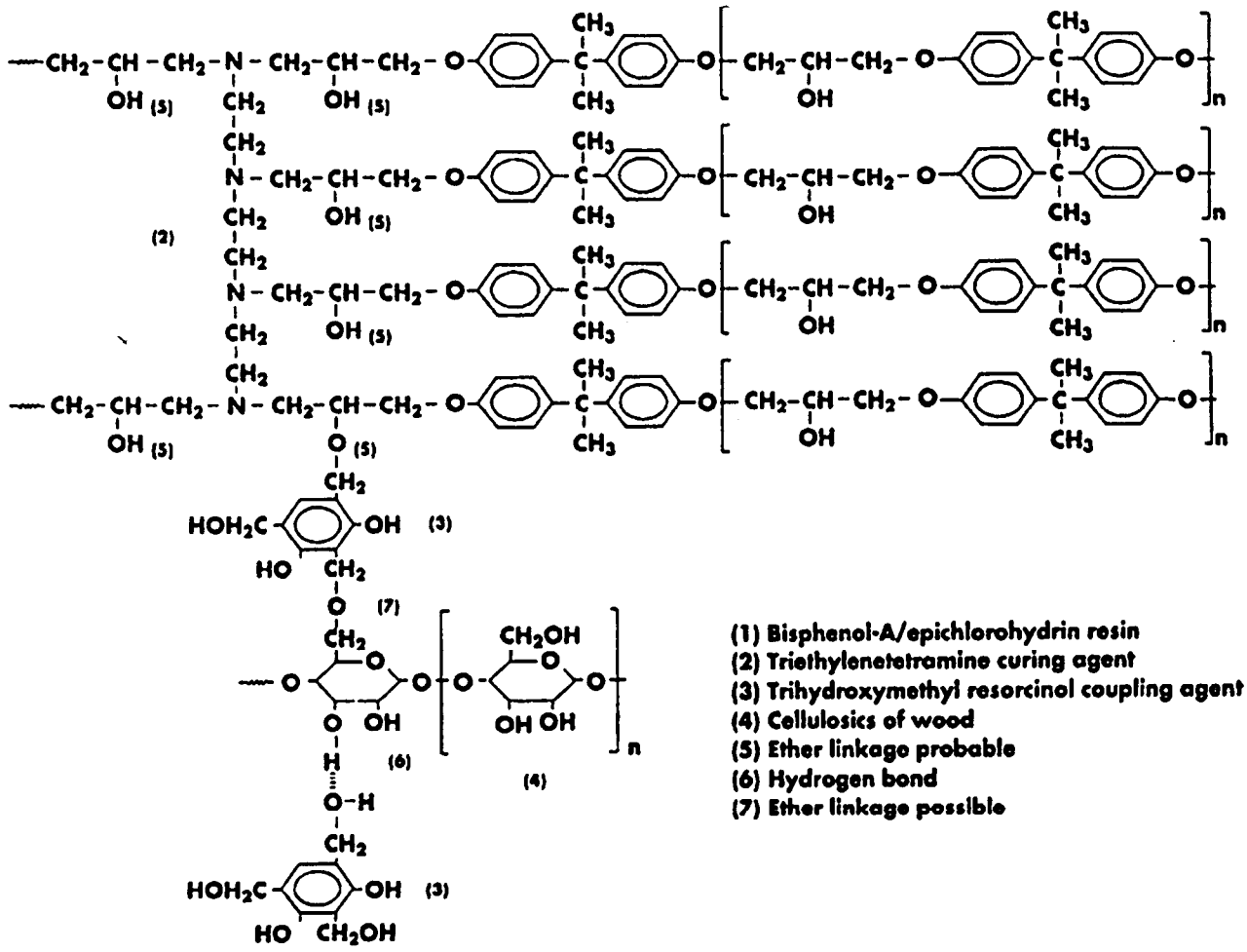
The unique combination of properties of epoxy adhesives — gap-filling, strong, durable, room-temperature curing — would make them ideal structural wood adhesives were it not for their lack of durability of adhesion to wood. Since epoxies were first marketed in the United States in the early 1950s, investigators have searched for ways to make epoxy bonds to wood as durable as resorcinol-formaldehyde adhesive bonds. One of the most notable achievements in the early 1960s was work by Olson and Blomquist *(6),* who formulated epoxy adhesive FPL 16. This adhesive was capable of exposure to 120 hr boil-dry tests, but it still did not equal the durability of resorcinol. FPL 16 epoxy was modified, marketed privately as FPL 16A and is now more popular than ever before with builders of wood aircraft. In *Sport Aviution* magazine, Myal *(5)* described FPL 16A as the "ultimate glue." Caster *(4)* of the Weyerhaeuser Co., in cooperation with the Dow Chemical Co., made further progress toward more durable epoxy bonds by priming wood surfaces with a 2% aqueous solution of polyethylenimine. In small lap-shear specimens, this primer enabled two epoxy adhesives to perform comparably to small solid-wood specimens in accelerated and exterior aging tests.

A continuing need for epoxy adhesives with greater resistance to delamination, particularly for bonded joints in wooden aircraft, boats, architectural posts and railings, led the Forest Products Laboratory (FPL) to explore chemical primers es a means of improving bond durability. The FPL work led to discovery of an hydroxymethylated resorcinol (HMR) coupling agent that physiochemically bonds to both epoxy and lignocellulosics of wood to produce bonds that are extraordinarily resistant to delamination *(10).* HMR is equally effective at enhancing adhesion of other thermosetting wood adhesives, including phenol-resorcinol-fomaldehyde, emulsion polymer/isocyanate, polymeric isocyanate, melamine-formaldehyde, melamine-urea-formaldehyde end urea-formaldehyde resin adhesives *(8).* A U.S. patent covering this invention has been assigned to the U.S. Department of Agriculture *(11).*

This report describes the nature and mechanism of bonding of the HMR coupling agent. Furthermore, it demonstrates HMR's ability to enhance the durability of epoxy bonds to softwood and hardwood species commonly used to construct structural components in wood aircraft. Also reported are dramatic increases in adhesion of epoxy to preservative-treated wood, despite the well-known adhesion-inhibiting effects of chromium-containing preservatives. Preliminary tests of epoxy bonds

Figure 2

Covalent and Hydrogen Bonding of HMR Coupling Agent Between DGEBA Epoxy Adhesive and Cellulosics of Wood



in composites of fiber-reinforced plastics and HMR-primed wood indicate an opportunity to make stronger and stiffer engineered composites. Even though industry-accepted test methods and requirements were used in these experiments, it should be recognized that conformance to these standards does not mean that HMR-enhanced epoxy bonds have been tested or approved by any code, agency, corporation or trade association.

Nature of HMR and Bonding Mechanisms

The HMR coupling agent is prepared in aqueous solution by reacting formaldehyde with resorcinol in a 1.5 mole ratio under mildly alkaline conditions at room temperature. The components of the 5% solids solution are shown in Table L Dodecyl sulfate sodium salt (0.5% by weight) was added to the mixture at the end of the reaction time to aid wetting of the wood surface.

HMR is quite reactive at room temperature. Therefore, the reaction time (the time between preparing the solution and applying it to the wood surface) determines the molecular-size distribution and reactivity of HMR. Experiments have shown that reaction time has a strong influence on the durability of adhesion. For all thermosetting wood adhesives, a 4 hr reaction time has proven effective. For epoxy adhesive, the optimum range is 4-6 hr; however, the range may be expanded to 3-7 hr for some lower density wood species. Reaction times either shorter or longer than the optimum range will result in bonds being less resistant to delamination.

Reaction of HMR slows and essentially stops when water from the HMR solution is evaporated and absorbed by the wood surface. The reaction resumes on application of adhesive. Since water interferes with adhesion of epoxy to wood. water from the HMR solution must be evaporated and absorbed so that wood surfaces are dry before the adhesive is applied. Heat must not be used to accelerate evaporation of water. otherwise reaction of HMR will be accelerated. thereby rendering the coupling agent useless.

Molecular structures of HMR may range from trihydroxymethylated resorcinol to its trimeric forms, and perhaps higher oligomers, as suggested in Figure 1. Molecular-size distributions are being determined for the optimum reaction time.

Possible coupling reactions of HMR with the cellulosics of wood and epoxy are suggested in Figure 2. Functional hydroxyl groups formed along the epoxy chains at position (5) are believed to condense with hydroxymethyl groups on the coupling agent to form ether linkages. Other available hydroxymethyl groups on the coupling agent are capable of forming ether linkages with the primary alcohols of cellulose. as shown at position (7). If conditions favor HMR coupling,

Table II

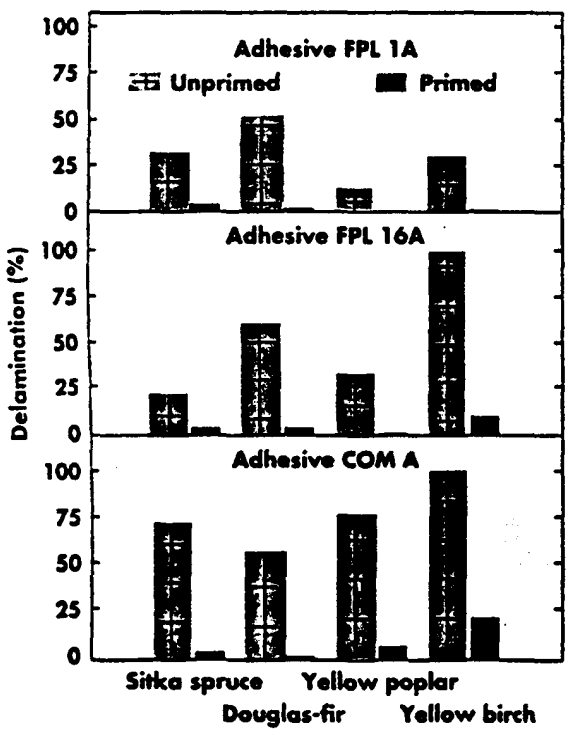
Composition of FPL 1A, FPL 16A and COM A Epoxy Adhesives

Formulation	Parts by weight
FPL 1A	
D.E.R. 331* epoxy resin	100.0
Benzyl alcohol	12.5
Hydrophobic fumed silica (N70-TS Cab-O-Sil**)	2.5
D.E.H. 24* hardener (triethylenetetramine)	11.1
FPL 16A	
EPON 828*** epoxy resin	100.0
Blended lacquer thinner	18.0
Titanium dioxide	30.0
Diethylenetriamine hardener	13.0
COM A	
DGEBA epoxy resin	100.0
Blended hardeners	20.0

* Dow Chemical Co.
** Cabot Corp.
*** Shell Chemical Co.

Figure 3

Effects of Epoxy Adhesive, HMR Priming and Wood Species on Delamination of Lumber Joints After Cyclic Delamination Test*



*ASTM D 2559 (3) requirements: softwoods ≥5%; hardwoods ≥8%

then a cross-linked network could form between epoxy resin and cellulosics of wood. If conditions and cellulosic structures are not conducive to covalent bonding, then hydrogen bonding is more likely to take place, as shown at position (6). The surfaces of wood lignocellulosics are rich with secondary hydroxyl groups. With a multimolecular layer of HMR thoroughly covering and penetrating cell walls, opportunities for high-density hydrogen bonding abound. Even though a single hydrogen bond is weak relative to a covalent bond, if numerous enough, hydrogen bonds could be the major contributor to epoxy bond durability to wood.

Materials and General Procedures

Three epoxy formulations were prepared from diglycidylether of bisphenol-A (DGEBA) resin (Table II). Fomulations FPL 16A and COM A are commercial products.* For proprietary reasons, ingredients in COM A could not be shown.

Two softwood speck (Sitka spruce and Douglas-fir) and two hardwood species (yellow-poplar and yellow birch) were used in adhesion tests. They are representative of wood species and density ranges commonly used in adhesive-bonded structural components in wood aircraft. Generally, all pieces of lumber were heartwood, straight grain of defects and flat-sawn.

Southern pine lumber was defect-free untreated and treated sapwood. Lumber was pressure-treated at FPL with commercial Type-C chromated copper arsenate (CCA) to a retention of 9.6 kg/m^3(0.6 lb/ft^2).

All wood materials were conditioned to approximately 10% equilibrium moisture content (EMC), then knife-planed 24 hr before bonding.

Fiber-reinforced plastics (FRPs) consisted of fiberglass strands embedded in matrices of vinylester and phenolic resins. For best adhesion with epoxy, vinylester surfaces were either smooth and cleaned with an acetone wipe or textured by peeling away a factory-laminated woven fabric (peel-ply). It was necessary to sand the phenolic FRP for most effective bonding.

The effectiveness of adhesion was evaluated by subjecting laminated lumber specimens to the cyclic delamination test, shear strength and wood failure tests, and deformation test under static loading at elevated temperature and humidity, in accordance with ASTM D 2559 *(3)*. This specification is used to qualify adhesives for structural glued-laminated timbers intended for wet-use exposures, as required in industry standard ANSI/AITC A190.L1992 *(2)*. The laminated FRP/lumber composites were subjected to the cyclic delamination test only.

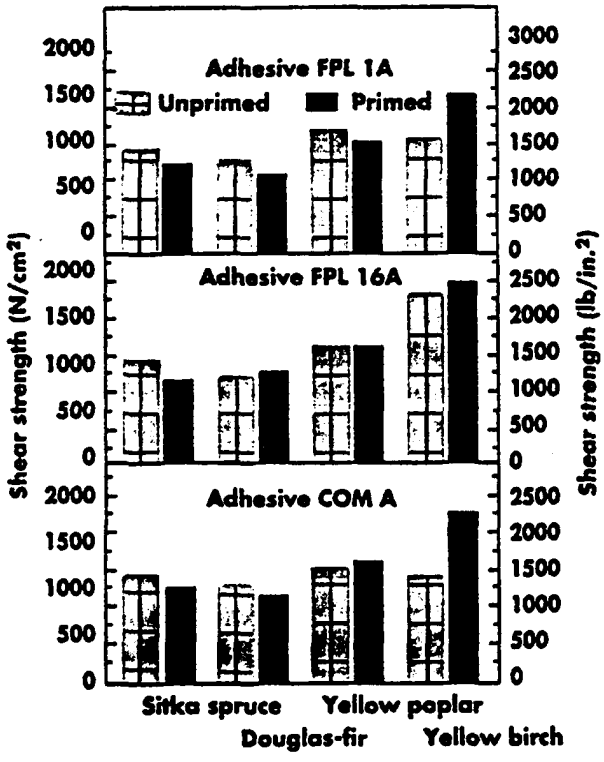
Delamination specimens were 7.6-cm (3-in.)-long cross-sections cut from lumber laminates. Laminates were prepared by bonding six pieces of lumber with a test adhesive each piece was 1.9 cm (3/4 in.) thick 7.6 cm (3 in.) wide, and 30.5 cm (12 in.) long. The sections were cut from each of four lumber laminates for a total of 12 delamination specimens. Delamination was measured along the end-grain surfaces, then expressed as a percentage of total bondline length.

Shear strength and wood failure were determined from compression-loaded, block-shear specimens with 19.4-cm^2 (3.0-in.^{2}) shear area Specimens were cut from lumber laminates prepared by bonding two pieces of lumber with a test adhesive; each piece was 1.9 cm (3/4 in.) thick, 6.4 cm (2.5 in.) wide, and 30.5 cm (12 in.) long. Five shear specimens were cut from each of four lumber laminates for a total of 20 specimens. Shear strength at failure was based on a 19.4-cm^2(3.0-in.^{2}) shear area. Wood failure in the shear areas was estimated to the nearest 5%

The use of trade or firm names in report is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Figure 4

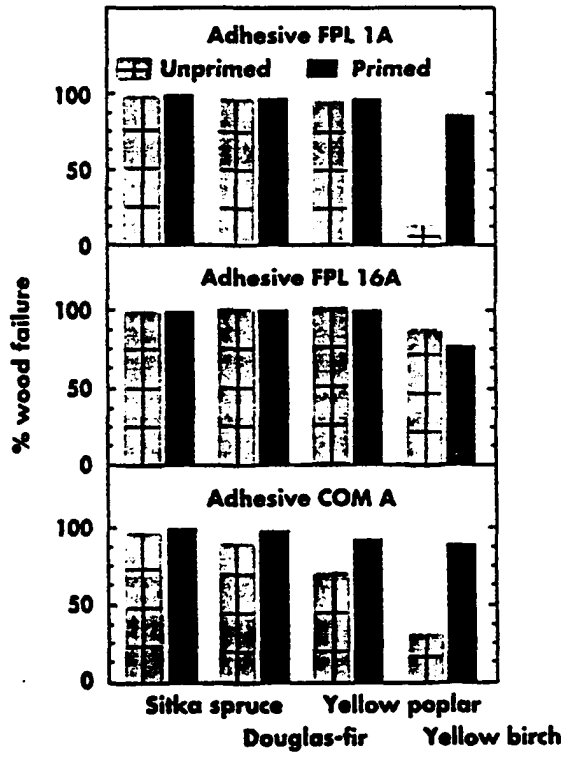
Effects of Epoxy Adhesive, HMR Priming and Wood Species on Shear Strength of Lumber Joints in Dry Condition*



*ASTM D 2559 *(3)* requirements: Sitka spruce ≥841 N/cm² (≥1,219 lb/in.²); Douglas-fir ≥776 N/cm² (≥1,125 lb/in.²); yellow-poplar ≥879 N/cm² (≥1,261 lb/in.²); yellow birch ≥1,374 N/cm² (≥1,993 lb/in.²)

Figure 5

Effects of Epoxy Adhesive, HMR Priming and Wood Species on Wood Failure After Shear of Lumber Joints in Dry Condition*



*ASTM D 2559 *(3)* requirements: ≥75%

Delamination specimens from the FRP/lumber composites were prepared, cut and treated in a manner similar to the all-lumber laminates. Vinylester FRP 9.5 mm (3/8 in.) thick and phenolic FRP 4.8 mm (3/16 in.) thick were substituted for the top and bottom members in the six-ply laminates. Three sections were cut from each composite laminate and used to measure delamination resistance.

Lumber laminates and FRP/lumber composites were assembled in essentially the same manner. Planed lumber surfaces were brushed with a 5% HMR solution at a spread rate near 0.15 kg/m^2 (0.03 lb/ft^2). The primed surfaces were dried 24 hr at 22.8°C (73°F) and 10% EMC before bonding. Adhesive was spread with a roller on both bonding surfaces to total near 0.39 kg/m^2 (0.08 lb/ft^2). The closed assembly time was 50-60 min and initial pressure approached 70 kPa (10 lb/in.^{2}). Laminates were cured in a press for 15 hr at room temperature. Epoxies in all specimens were cured to the same degree by heating laminates at 65.5°C (150°F) for 5 hr. To avoid stresses on bondlines from shrinkage of wood. the moisture of the air was maintained at the same EMC as that of the wood.

Results

Aircraft Woods. Priming wood surfaces with HMR produced sharp, consistent and statistically significant increases in delamination resistance by all three epoxy adhesives on all four species of wood *(9)* as shown in Figure 3. Without HMR, however, none of the epoxies had sufficient delamination resistance to meet the 5% and 8% maximums required for softwoods and hardwoods, respectively, by ASTM D 2559 *(3)*. Priming with HMR allowed FPL 1A to meet delamination requirements on all four species and FPL 16A to meet requirements on all except yellow birch. COM A performed well on Douglas-fir and yellow-poplar, lightly exceeded 5% delamination on Sitka spruce, but did not perform well on high-density yellow birch

Only FPL 16A exceeded dry shear strength and wood failure requirements on the unprimed woods, as well as the HMR-primed woods (Figures 4 and 5). FPL 16A owes its popularity — particularly among builders of wood aircraft — to its ease of use, minimum clamping pressures and ability to produce high shear strength and wood failure on a wide variety of wood species. This epoxy is highly diluted with a blended lacquer thinner so that it penetrates deeply and mechanically interlocks into the wood's cellular structure — even into a high-density species such as yellow birch. Yet, despite deep mechanical interlocking. FPL 16A delaminated severely when surfaces were not primed with HMR (Figure 3).

The viscosity of FPL 1A is much higher than that of FPL 16A, yet without priming, its shear strength and wood failure exceeded requirements on all species except yellow birch, where wood failure was very low. With HMR primmg, however, wood failure met requirements (see Figures 4 and 5).

The viscosity of COM A is between that of FPL 1A and FPL 16A. When the wood was not primed. COM A met shear strength and wood failure requirements

on both softwood species, but not hardwoods. When the wood was primed, however, COM A met strength and wood failure requirments on all four species (see Figures 4 and 5).

EPOXY adhesive FPL 1A in yellow birch lumber joints was loaded under static shear of 166 N/cm^2 (240 lb/in.^{2}) for 60 weeks without any deformation. The required time of exposure by ASTM D 2559 *(3)* is only 1 week at 71°C (160°F), ambient RH, and at 26.7°C (80°F), 90% RH.

CCA-Treated Wood. Since 1945, scientists have known that chromium-containing preservatives seriously interfere with adhesion of thermosetting resins to the treated wood. Research conducted over many years indicates that chemically fixed CCA deposits on the treated wood are so pervasive, as shown in Figure 6, that most opportunities for physiochemical interaction between normally polar wood and adhesive are physically blocked. The cellular structures of wood are essentially covered with microscopic-size deposits of mixtures of mostly chromium copper and arsenic oxides. These metallic deposits are insoluble in water, are chemically bound to lignocellulosics of the cell wall and do not appear to be chemically active enough to interfere with the cure of phenolic wood adhesives *(2,8)*.

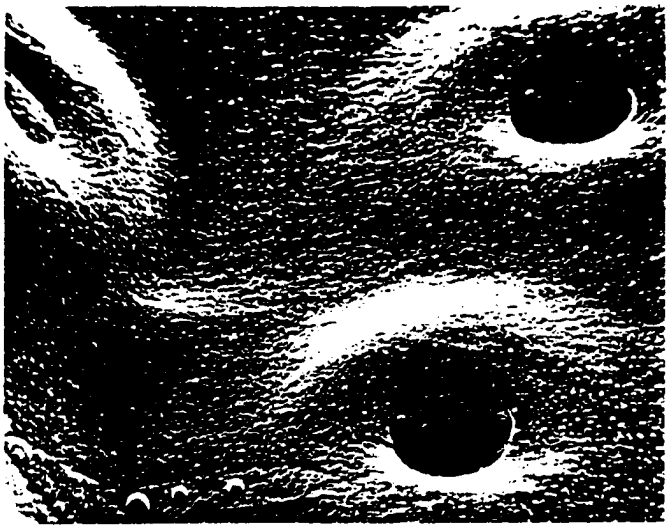


Figure 6. Surface of cell lumen of CCA-treated Southern pine covered with chemically fixed deposits of mixtures of chromium, copper and arsenic oxides.

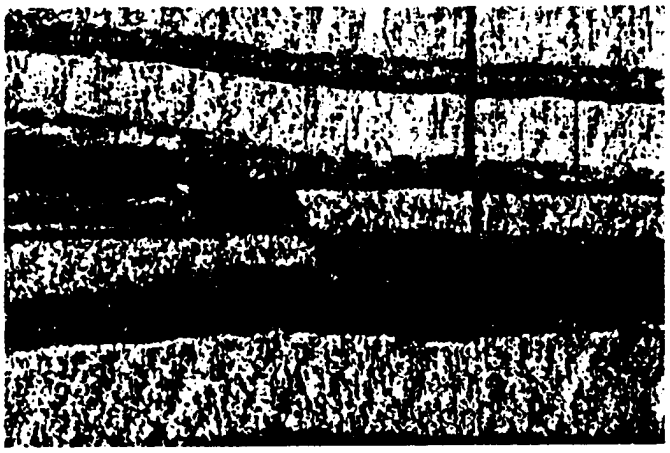


Figure 7. Stress fracture through CCA-treated lumber laminate as epoxy bond resisted delamination stresses.

In view of the drastic physical and chemical changes to CCA-treated wood surfaces, it is remarkable, and indeed not clear, how HMR developed bonds to CCA oxides strong enough to dramatically increase adhesion of epoxies to CCA-treated wood *(8)*. Resistances to delamination and shear of COM A epoxy bonds to CCA-treated Southern pine are shown in Table III for unprimed and HMR-primed surfaces. Delamination was almost complete (89%) on unprimed wood, but only 3% (well below the 5% allowable) after priming with HMR. Epoxies are known to develop bonds to wood as strong as the wood itself. However, bonds to CCA-treated wood are Weaker than that required by ASTM D 2559 *(3)*. Wood failure was 46%, well below the required 75%. Shear strength was slightly below the required 948 N/cm^2 (1,375 lb/in.^{2}). By priming the wood with HMR, shear strength and wood failure were raised above the standard to 1,154 N/cm^2 (1,673 lb/in.^{2}) and 83% respectivley.

The extraordinary delamination resistance of COM A epoxy bonds to HMR-primed CCA-treated wood is demonstrated in Figure 7. Fracture initiated at the specimen edge and propagated through the high-density summerwood. If the bondline had been weaker at the edge or along the interface of adhesive and summerwood, or even in the low-density springwood, then high stresses would have produced rupture there, rather than through bands of summerwood.

FRP/Lumber Composites. Resorcinolic adhesives develop highly durable structural bonds to wood, but they have limited adhesion to moat plastics. On the other hand, epoxy adhesives develop durable bonds to certain plastics, but they fail as durable structural adhesives on wood. However, epoxy adhesives may equal the structural durability of resorcinolic adhesives on wood if the wood surfaces are primed with HMR, as the previous experiments have demonstrated. Excellent adhesion to both materials by epoxies presents an opportunity to make durable structural composites from FRPs and wood. Engineering composites that are stronger and stiffer in bending, and of less cross-sectional dimension and cost, should have significant potential for development in the structural products market-

The durability of epoxy adhesion to HMR-primed Southern pine lumber and to vinylester and phenolic FRPs was demonstrated in preliminary delamination tests of FRP/lumber composites *(8)*. When these composites were subjected to the ASTM D 2559 *(3)* cyclic delamination test, neither vinylester nor phenolic FRPs delaminated from the lumber, as shown in Figure 8. Recall that lumber surfaces were prepared for epoxy bonding by priming with HMR. Vinylester FRP surfaces were prepared by either cleaning smooth surfaces with an acetone wipe or texturing by peeling away a factory-laminated woven fabric. It was necessary to sand the phenolic FRP prior to bonding.

Table III

Delamination and Shear Resistance of Epoxy Bonds to CCA-Treated Southern Pine Compared to ASTM Requirement

Surface primer	Delamination (%)	Shear strength N/cm^2 (lb/in.^{2})	Wood failure (%)
None	88 8	935 (1.356)	46
HMR	3 0	1.154 (1.673)	83
ASTM (3)	·. 5 0	·. 948 (· 1 375)	· 75

However, with these simple surface preparations, delamination-free bonds to these materials were possible with epoxy adhesives.

Conclusion

Research at the Forest Products Laboratory demonstrated that an hydroxymethylated resorcinol (HMR) coupling agent enables bisphenol-A epoxy adhesives to develop bonds of extraordinary structural durability to two softwood and two hardwood species, as well as to CCA-treated wood. When used to prime wood surfaces before bonding, HMR increased delamination resistance, shear strength, wood failure and deformation resistance so that epoxy bonds met requirements of ASTM D 2559. Epoxy bonds in laminated composites of HMR-primed lumber, vinylester and phenolic fiber-reinforced plastics (FRPs) were equally resistant to delamination. The capability of epoxies to bond to both wood and plastics presents an opportunity for making strong and durable composites from FRP and wood.

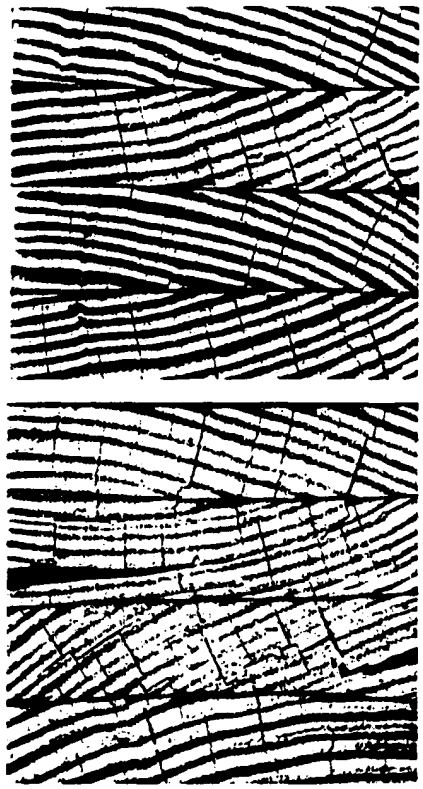


Figure 8. Cross-sections of FRP/lumber composites (vinylester, top; phenolic, bottom) free of delamination after ASTM D 2559 (3) delamination test.

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