HYDROXYMETHYLATED RESORCINOL COUPLING AGENT FOR ENHANCED DURABILITY OF BISPHENOL-A EPOXY BONDS TO SITKA SPRUCE

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ABSTRACT

Epoxy adhesives can develop bonds to wood that are as strong as the wood itself, but only if the bonds remain dry. Once exposed to repeated water soaking and severe stresses from drying, epoxy bonds delaminate and fail to meet requirements for structural wood adhesives intended for exterior exposure. A new hydroxymethylated resorcinol (HMR) coupling agent, applied to lumber surfaces before bonding, chemically couples both epoxy adhesive and lignocellulosics of wood to produce bonds to Sitka spruce that are extraordinarily resistant to delamination. In this report, we explain and demonstrate the nature of this coupling agent and the mechanism by which it enhances the durability of bonds of a bisphenol-A epoxy adhesive to wood. When diluted with benzyl alcohol, an epoxy adhesive developed structural bonds in HMR-primed lumber laminates that met the 5% maximum delamination requirement of ASTM Specification D 2559. The USDA Forest Service has applied for a patent for this invention.

Keywords: Hydroxymethylated resorcinol, coupling agent, bisphenol-A epoxy, polyethylenimine, primer, Sitka spruce, delamination resistance.

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INTRODUCTION

Using primers, coupling agents, and other surface treatments to enhance adhesion is now commonplace. Such treatments are essential to developing highly durable bonds to metals, advanced composites, ceramics, and plastics in aerospace, automotive, and plastics industries. However, these treatments are not common in the wood products industry. Water-based, polar wood adhesives such as phenolics, resorcinol, urea, and melamines perform quite well on wood whose polarity has not been chemically altered. Epoxy adhesives are an exception. Epoxies develop bonds to wood that are as strong as the wood itself as long as the bonds remain dry. Once they are exposed to the severe stresses of repeated soaking in water and drying, however, epoxy bonds fail to meet requirements for structural wood adhesives intended for exterior exposure.

Not long after the first epoxy adhesives were marketed in the United States (early 1950s), researchers Clarke and Nearn (1957) and Williamson and Nearn (1958) investigated formulations, assembly factors, temperature of cure, wood species, and wood densities as they affected the strength and durability of epoxy adhesives made from epichlorohydrin and bisphenol-A. Curing at 160°F (71°C) improved water resistance compared to that achievable with cure at room temperature. Lower density species produced bonds with higher wood failure and lower strength compared to higher density species, but none of the adhesives equalled the water resistance of a resorcinol adhesive. Then, Olson and Blomquist (1962) developed epoxy formulations, including Forest Products Laboratory (FPL) Formula 16, that appeared capable of withstanding rather severe exposure conditions, as determined from preliminary 120-h boil and soak-dry tests. Long-term exposure tests of these formulations were never reported. Improved durability of FPL Formula 16 was attributed to use of titanium dioxide as a filler and a specially blended lacquer thinner as a diluent. The epoxy resin was Epon 8282 with diethylenetri-amine hardener. This same formulation is used today by some builders of wood aircraft and aircraft components. Myal (1967) described FPL Formula 16 as “the ultimate glue” in Sport Aviation.

The Weyerhaeuser Company, cooperating with The Dow Chemical Company in the late 1960s, made significant progress in developing durable epoxy bonds to wood that could withstand exterior weathering. Caster (1980) demonstrated that wood specimens bonded with two epoxy adhesives performed comparably to solid-wood specimens. The epoxy-bonded specimens performed even better than specimens bonded with phenol-resorcinol-formaldehyde and phenol-formaldehyde adhesives during both accelerated aging in the automatic boil test and 11 years of exterior exposure in Mississippi, California, and Washington. The exceptional performance of both epoxy formulations was attributed to a primer of 2% aqueous solution of polyethylenimine. Apparently for business reasons, neither Weyerhaeuser nor Dow were in a position to perform follow-up work on these seemingly successful findings, so the work was discontinued and its promise forgotten.

In recent years, the FPL has received many inquiries from users of epoxy adhesives who were bonding wooden aircraft, boats, architectural posts and railings, and various specialty products. They often reported bond failures that were a consequence of exposure to water—usually an exterior exposure. No epoxy adhesives are known to meet the requirements of ASTM Specification D 2559 (ASTM 1992) for resistance to delamination in structural glued-laminated timbers. Epoxies are not approved for either laminating or repairing such timbers if the bonds are expected to withstand either shear or tension loading. The continuing need for structural epoxy adhesives with greater water resistance and the promise of a real solution based on the forgotten but credible research of Weyerhaeuser and The Dow Chemical Company (Caster 1980) led us to re-

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2 The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.
explore chemical primers as a means of improving the durability of epoxy bonds to wood. Our exploratory work led to the discovery of an hydroxymethylated resorcinol coupling agent that appears to bond chemically to both epoxy adhesive and lignocellulosics of wood to produce joints that are extraordinarily resistant to delamination. The USDA Forest Service has applied for a patent for this invention (Vick et al. 1994).

In this report, we describe the nature and mechanism of bonding of this new coupling agent, and demonstrate its ability to enhance the durability of bonds of epoxy adhesives to Sitka spruce.

EXPERIMENTAL MATERIALS AND METHODS

Hydroxymethylated resorcinol coupling agent

The hydroxymethylated resorcinol (HMR) coupling agent consists of mono-, di, and tri-hydroxymethylated resorcinol. At appropriate molar ratios of formaldehyde-to-resorcinol and reaction times, maximum hydroxymethylation occurs with limited further condensation of the hydroxymethylated species to higher oligomers.

The HMR coupling agent was prepared by reacting formaldehyde with resorcinol in a 1:5 mole ratio at mildly alkaline conditions. A 5% aqueous solution containing the following ingredients was reacted for 4 h at room temperature before application to the wood surfaces. The length of this reaction period is critical to the effectiveness of the coupling agent. Water from the coupling agent solution was evaporated before bonding with epoxy adhesives.

<table>
<thead>
<tr>
<th>HMR ingredient</th>
<th>percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, deionized</td>
<td>90.43</td>
</tr>
<tr>
<td>Resorcinol, crystalline</td>
<td>3.34</td>
</tr>
<tr>
<td>Formaldehyde (37 percent)</td>
<td>3.79</td>
</tr>
<tr>
<td>Sodium hydroxide, 3 Molar</td>
<td>2.44</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Polyethylenimine primer

A polyethylenimine (PEI) primer, similar to that used by Weyerhaeuser and The Dow Chemical companies to enhance adhesion of epoxy adhesives to wood (Caster 1980), was prepared for this study. The PEI was supplied by BASF Corporation (Parsippany, NJ) as a high molecular weight homopolymer in a 50% aqueous solution, identified as Polymin P. A 2% aqueous solution was selected as an appropriate concentration after preliminary experiments indicated that higher concentrations severely interfered with adhesion. As with the aqueous HMR primer, all water from the PEI primer was evaporated before bonding with epoxy adhesives.

Epoxy adhesives

The epoxy adhesive formulations were based on diglycidylether of bisphenol-A resin and triethylenetetramine curing agent, identified by their manufacturer, The Dow Chemical Company, as D.E.R. 331 epoxy resin and D.E.H. 24 epoxy hardener, respectively. The adhesives were mixed 88.5 parts (weight basis) of resin to 11.5 parts of curing agent. For diluting mixtures to enhance penetration of wood, 10% hydroxymethyl benzene (benzyl alcohol) was added. For thickening mixtures, 4% hydrophobic fumed silica, N70-TS grade Cab-O-Sil (Cabot Corporation, Tuscola, IL), was added.

Sitka spruce

Sitka spruce was selected for study because of its generally straight and uniform grain, gradual transition from springwood to summerwood, and moderately low specific gravity—near 0.42 (oven-dry weight and volume at 12% moisture content). Such a low-density wood can be penetrated more easily by high molecular weight epoxy adhesive. Sitka spruce is the preferred wood for aircraft construction because of its high strength-to-weight ratio.

The lumber was flat-sawn from flitches, then conditioned to 12% equilibrium moisture content (EMC) before bonding. The lumber was knife-planed to 3/4-in. (19-mm) thickness 24 h before either priming or bonding.

Experimental design

The experiment was designed to determine if surface primers of either a 5% aqueous HMR
coupling agent, a 2% aqueous PEI solution, or a combination of the two could improve the durability of adhesion of a typical bisphenol-A epoxy adhesive in Sitka spruce lumber laminates. The effectiveness of adhesion was evaluated by measuring the amount of delamination after laminated lumber joints were subjected to severe cyclic swelling and shrinking treatments of ASTM Specification D 2559 (ASTM 1992). This test is specified for qualifying adhesives for structural glued-laminated timbers in exterior (wet-use) exposures according to ANSI/AITC A190.1-1992 (AITC 1992). We did not conduct the required tests of shear strength and wood failure of dry bonds because most epoxy adhesives readily meet these requirements.

The experimental design with experimental factors and respective levels of treatment is shown in Table 1. The experiment was a completely randomized model with factorial arrangement of 4 epoxy adhesives and 4 surface primers to yield 16 treatment combinations. Each treatment combination was replicated three times. A replicate was a six-ply lumber laminate, from which three sections were cut. Delamination was measured from five bondlines on each end of each section in each replicate lumber laminate.

Analyses of variance were conducted for percentages of delamination. Because the percentages were not normally distributed, it was necessary to use the arcsine square-root transformation to fulfill the requirements for normality of the experimental model (Snedecor and Cochran 1967). The Ryan-Einot-Gabriel-Welsch multiple comparison F test was used to detect significant differences between treatment combinations (Welsch 1977).

**Preparation of test joint assemblies**

A test joint assembly (replicate) was prepared by laminating six pieces of lumber, each piece measuring 0.75 in. (19 mm) thick, 3 in. (76 mm) wide, and 12 in. (305 mm) long. If lumber surfaces were to be primed with either HMR coupling agent or PEI solution, aqueous solutions were spread on each bonding surface with a brush at a rate near 0.03 lb/ft² (0.15 kg/m²). Before bonding, the primed surfaces were dried 24 h in a conditioning room maintained at 80°F (26.7°C) and 65% relative humidity. The lumber was spread with adhesive on each bonding surface to total 0.07 lb/ft² (0.35 kg/m²) in each bondline. The adhesive was spread with a roller, and the accuracy of the spread was controlled by weighing the lumber as the adhesive was spread on each bonding surface.

Closed assembly time ranged from 70 min after the first bondline was spread with adhesive to 60 min after the last bondline was spread. Open assembly time was no more than 2 min for any bondline. The initial pressure for curing was about 20 lb/in.² (138 kPa), although pressure application was stopped once squeeze-out began from all bondlines. Test joint assemblies were kept under pressure about 15 h at room temperature. All bondlines were essentially cured to the same degree by heating the laminates at 150°F (65.5°C) for 5 h. To avoid stresses on bondlines from shrinkage of wood, EMC of the air was maintained at 12%—the same as the initial MC.

**Cyclic delamination test**

In its essentials, the ASTM Specification D 2559 (ASTM 1992) cyclic delamination test consists of three cycles of the following events:
Table 2. Delamination of epoxy adhesives on primed surfaces of Sitka spruce

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Mean delamination on primed surfaces (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R</td>
</tr>
<tr>
<td>K</td>
<td>15.3</td>
</tr>
<tr>
<td>KC</td>
<td>12.3</td>
</tr>
<tr>
<td>B</td>
<td>4.5</td>
</tr>
<tr>
<td>BC</td>
<td>12.1</td>
</tr>
</tbody>
</table>

*Maximum allowable delamination is 5% for softwood species when tested according to ASTM Specification D 2559-84 (ASTM 1992). * See Table 1 for description of adhesives and primers.

Cycle 1
(1) Vacuum-soak in water at 25 in.-Hg (635 mm) for 5 min
(2) Pressure-soak in water at 75 lb/in.² (5.27 kg/cm²) for 1 h
(3) Repeat events (1) and (2)
(4) Dry at 150 F (65.5 C) for 21–22 h

Cycle 2
(1) Steam at 212 F (100 C) for 1 h and 30 min
(2) Pressure-soak in water at 75 lb/in.² (5.27 kg/cm²) for 40 min
(3) Repeat event (4) in Cycle 1

Cycle 3
Repeat events in Cycle 1

The three 3-in.- (76-mm-) long sections cut from each test joint assembly were subjected to the cyclic delamination test. 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. Because of this more precise technique, delamination was no doubt higher than would have been measured with the unaided eye and a 0.005-in.- (0.13-mm-) thick feeler gauge, as recommended in the ASTM specification. A single delamination value expressed as a percentage of total bondline length was computed for each section. The statistical analyses were based on delamination measured after all three cycles were completed.

RESULTS AND DISCUSSION

HMR-primed surfaces

The maximum allowable delamination for softwood species is 5% in ASTM Specification D 2559-84 (ASTM 1992). Mean delamination percentages of the four epoxy formulations on four primed surfaces are shown in Table 2. The data clearly indicate that the HMR coupling agent (R) dramatically enhanced the resistance to delamination of all epoxies when compared with the unprimed (N), PEI-primed (P), and HMR/PEI-primed (RP) surfaces. It is also clear that only the epoxy adhesive diluted with benzyl alcohol (B) and bonded to the HMR-primed surface met the 5% delamination requirement; it delaminated 4.5%.

Tests for significant differences between mean percentages of delamination for all combinations of epoxy adhesives and primers are shown in Tables 3 and 4. In Table 3, comparisons for epoxy B show that the 4.5% delamination on the HMR-primed (R) surfaces was significantly lower than delamination on any other primed or unprimed surfaces. In comparisons of all adhesives on just the HMR-primed surfaces, the 4.5% delamination of the diluted epoxy B was significantly lower than that of any other epoxy formulation, i.e., epoxies BC, KC, and K (Table 4). The latter three epoxies did not differ significantly.

The HMR primer produced significantly lower delamination than any other primer regardless of epoxy formulation (Table 3), with the exception of one apparent statistical anomaly. That exception occurred with epoxy K where the 15% delamination by HMR primer was not significantly different from the 41% delamination by the PEI primer. Very large variances were associated with the unprimed surfaces and HMR/PEI primer, but the small variance associated with the HMR primer overlapped statistically and was not significantly different. However, the actual differences between means of the two primers were quite large and real.

PEI-primed surfaces

The PEI primer enhanced adhesion of two epoxy adhesives (B and BC) compared to that...
TABLE 3. Statistical comparison of ranked means of delamination of primers for epoxy adhesives.\(^a\)

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Mean delamination on primed surface (percent)(^a,c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>R 15 P 41 N 44 RP 47</td>
</tr>
<tr>
<td>KC</td>
<td>R 12 N 31 RP 53 P 59</td>
</tr>
<tr>
<td>B</td>
<td>R 4.5 P 22 RP 24 N 55</td>
</tr>
<tr>
<td>BC</td>
<td>R 12 P 22 RP 28 N 31</td>
</tr>
</tbody>
</table>

\(^a\) See Table 1 for description of adhesives and primers.
\(^b\) Mean percentages of delamination for primers are ranked left to right with lowest value first.
\(^c\) Ranked means are statistically compared; means underlined by the same line are not significantly different at the 0.05 level of probability.

TABLE 4. Statistical comparison of ranked means of delamination of epoxy adhesives for each primer.\(^a\)

<table>
<thead>
<tr>
<th>Primer</th>
<th>Mean delamination of adhesives (percent)(^b,c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>B 4.5 BC 12 KC 15 K 15</td>
</tr>
<tr>
<td>P</td>
<td>BC 22 B 24 K 41 KC 59</td>
</tr>
<tr>
<td>RP</td>
<td>B 22 BC 28 K 47 KC 53</td>
</tr>
<tr>
<td>N</td>
<td>KC 31 BC 31 K 44 B 55</td>
</tr>
</tbody>
</table>

\(^a\) See Table 1 for description of adhesives and primers.
\(^b\) Mean percentages of delamination for primers are ranked left to right with lowest value first.
\(^c\) Ranked means are statistically compared; means underlined by the same line are not significantly different at the 0.05 level of probability.

achievable on the unprimed lumber (Table 3). Epoxy B delaminated 24% on the PEI-primed surfaces, which was significantly lower than 55% delamination on the unprimed surfaces. Likewise, epoxy BC, which contained Cab-O-Sil, delaminated 22% on the PEI-primed surface. This mean was also significantly lower than the 31% delamination of epoxy BC on the unprimed surface.

The combined surface treatments of HMR primer applied first, followed by PEI primer, produced bonds by epoxies B and BC that were not significantly different from those of the PEI primer alone. Epoxies K (unmodified) and KC (thickened with Cab-O-Sil), which were of considerably higher viscosity than epoxies B and BC (diluted with benzyl alcohol), developed bonds of much lower delamination resistance (Tables 2 and 3). Table 4 shows that bonds of epoxies B and BC were not significantly more durable than those of either epoxies K or KC on the HMR/PEI-primed surfaces. Variations in delamination percentages were so great on the combined treatment surfaces that none of the epoxies had statistically distinguishable resistances to delamination. It seems evident that applying the HMR primer before PEI primer caused no improvement in adhesion over that achievable with the PEI primer alone.

Modes of delamination and stress fracture in laminates

Delaminations of epoxy B bonds in laminates with surfaces primed with HMR and PEI can be compared with that of unprimed surfaces in Fig. 1. Delamination averaged 55% on unprimed surfaces (Fig. 1A). When surfaces were primed with PEI, delamination was reduced to 24% (Fig. 1B). The effectiveness of the HMR primer is quite evident (Fig. 1C); average delamination was reduced to 4.5%. Note that stress fractures within the wood itself became greater in size and number as the epoxy bonds became more resistant to delamination (Fig. 1C). Two stress fractures extended almost completely across two laminates without entering a bondline. Potential stress fractures were relieved by delamination of weaker bonds on unprimed (Fig. 1A) and PEI-primed (Fig. 1B) surfaces.

As lumber laminates are subjected to severe stresses of soaking and drying, many stress fractures initiate and propagate within and adjacent to bondlines at the laminate edges. Typical examples of types of stress fractures are shown in Fig. 2. When surfaces were not primed, specimens delaminated for indefinite lengths along the bondline with little stress fracturing in the wood (Fig. 2A). With PEI primer, delamination was more limited in
Fig. 1. Delamination of epoxy adhesive bonds in lumber laminates with unprimed surfaces (A), surfaces primed with PEI (B), and surfaces primed with HMR coupling agent (C).
length as stronger bonds to the primed surfaces caused stresses along the bondline to eventually fracture the wood (Fig. 2B). With HMR primer, however, delamination never developed in or near the interface of the bondline. Wood fibers were always bonded to the epoxy. If only a few cells deep, such fracture was still considered delamination, although such strict interpretation is not required by the ASTM standard. If fracture extended to many cells deep, as shown in Fig. 2C, then no delamination was measured.

**Mechanism of adhesion enhancement**

*HMR coupling agent.* — By depositing a multi-molecular layer of hydroxymethylated resorcinol onto wood surfaces before bonding, bisphenol-A epoxy adhesives developed bonds that were dramatically more durable than bonds developed without the coupling agent. Statistical comparisons of delamination of four epoxies on HMR-primed and unprimed surfaces demonstrated this in Table 3. Thus, adhesion was enhanced primarily by what generally may be called physicochemical interactions. Without knowing how much any of these phenomena contributed to adhesion enhancement, it is assumed that covalent bonding, hydrogen bonding, and intermolecular dipole-dipole and London forces contributed variously under the term physicochemical interactions. In addition, mechanical interlocking of adhesive within the porous structure of wood was essential to developing the most durable bonds. This was demonstrated in the statistical comparisons of Table 4, where the benzyl alcohol-diluted epoxy (B) penetrated more effectively than the higher-viscosity epoxies to produce the most durable of bonds on the HMR primed surfaces.

At room temperature in dilute aqueous solutions, the chemicals of the HMR coupling agent are quite reactive. Although chemical structures have not been determined yet, particularly after specific reaction periods, HMR probably consists of mono-, di-, and trihydroxymethyl resorcinol, with a few dimers, trimers, or higher oligomers, which condense as
1. Bisphenol-A epoxy resin
2. Triethylenetetramine curing agent
3. Trihydroxymethyl resorcinol coupling agent
4. Cellulosics of wood
5. Ether linkage probable
6. Hydrogen bond
7. Ether linkage possible

**FIG. 3.** Mechanisms of covalent and hydrogen bonding of HMR coupling agent between bisphenol-A epoxy adhesive and cellulosics of wood.

The reaction period must be limited because its polymerization must be inhibited. The length of the reaction period is critical to the effectiveness of the coupling agent—whether too short or too long, adhesion can range from no improvement to drastically impaired.

The HMR coupling agent is believed to covalently bond with a bisphenol-A epoxy resin and the aliphatic amine curing agent as shown in Fig. 3. Functional hydroxyl groups formed along the epoxy chains at position (5) are capable of condensing with the hydroxymethyl groups of the HMR coupling agent to form covalent bonds.

Further condensation reactions can occur with these methylolated groups as reactive hydroxyl groups from molecules of other chemicals are presented. Three, and perhaps all five, of the hydroxyl groups can form hydrogen bonds. Hydrogen bonding, if numerous enough, is believed to be the primary contributor to adhesive bond durability and strength, even though a single hydrogen bond is relatively weak in comparison with a covalent bond.
ether linkages between the coupling agent and epoxy. Other available hydroxymethyl groups on the coupling agent are capable of forming ether linkages with the primary hydroxyl groups on cellulose of wood, as shown at position (7) (Fig. 3). If such is the case, then a completely cross-linked polymeric network is formed between epoxy resin and cellulosics of wood, made possible through the chemical linkages of the reactive HMR coupling agent. If conditions and cellulosic structures are not available for covalent bonding, then hydrogen bonding is more likely to take place, as shown at position (6) (Fig. 3). The surfaces of cellulosics and lignin of wood are relatively rich with secondary hydroxyl groups. With a multimolecular layer of HMR coupling agent thoroughly covering and penetrating cell walls, opportunities for high-density hydrogen-bonding between molecules are present. Spectrographic chemical analyses may reveal which chemical linkages are formed by the coupling agent with adhesives and wood cellulosics.

**PEI primer.**—Polyethylenimine adheres by strong attraction to electronegative substances, as well as its reactivity through its functional amino groups. It has been used as a "tie coat" in bonding dissimilar substrates. Adhesion of polyolefins and other resins to cellulosic fiber and paper is essentially poor, but it can be improved greatly by pretreatment with PEI. By far, the most important commercial application of PEI is as a primer for milk-carton board that is subsequently laminated with polyethylene (De Roo 1977).

Polyethylenimine is a highly branched polynamine produced by acid-catalyzed polymerization of ethylenimine monomer. The polymer segments, with two carbons per nitrogen, are randomly distributed in approximate ratios of one primary amino nitrogen, two secondary amino nitrogens, and one tertiary amino nitrogen. When PEI contacts water, the amino nitrogens react to form positively charged nitrogens in the same manner as simple amines, thereby yielding alkaline solutions. Since PEI is composed of many nitrogens per molecule, each molecule carries a high positive-charge density. Thus, PEI functions as a cationic polyelectrolyte and is attracted to the partial negative changes on hydroxyl oxygens on cellulosic surfaces. It can also undergo reactions with epichlorohydrin, which is one component of epoxy resins (De Roo 1977).

**CONCLUSIONS**

When used as a primer on lumber surfaces before adhesive application, a new hydroxymethylated resorcinol (HMR) coupling agent dramatically enhanced the durability of adhesion of a bisphenol-A epoxy adhesive to Sitka spruce. Epoxy adhesive diluted with benzyl alcohol developed structural bonds on the HMR-primed lumber that met the 5% delamination requirement of ASTM Specification D 2559. Enhanced adhesion occurred primarily by physicochemical interactions, although mechanical interlocking of the penetrating epoxy adhesive into the porous structure of wood was essential for the most durable of bonds. A dilute aqueous polyethylenimine primer also enhanced the delamination resistance of epoxy adhesive bonds to wood, but not nearly as effectively as did the HMR coupling agent.

**ACKNOWLEDGMENTS**

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