ENHANCED ADHESION OF MELAMINE-UREA AND MELAMINE ADHESIVES TO CCA-TREATED SOUTHERN PINE LUMBER

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ABSTRACT

Thermosetting wood adhesives do not adhere well enough to wood treated with chromated copper arsenate (CCA) preservatives to consistently meet rigorous standards for resistance to delamination in structural laminated timbers. Melamine-urea-formaldehyde (MUF) and melamine-formaldehyde (MF) are two such adhesives. Furthermore, MUF combinations are not acceptable for bonding to CCA-treated wood under the commercial standard ANSI/AITC A 190.1-1992. However, this study demonstrated that a hydroxymethylated resorcinol (HMR) coupling agent greatly enhances the durability of adhesion, particularly resistance to delamination, of both types of adhesives in radio-frequency-cured lumber laminates of CCA-treated southern pine. Although neither adhesive quite met delamination requirements in these tests, it appears that properly formulated MUF and MF adhesives could meet requirements of the qualifying standard ASTM D 2559 on HMR-primed CCA-treated wood.

Recent studies at the USDA Forest Service, Forest Products Laboratory (FPL), led to the discovery that hydroxymethylated resorcinol (HMR) coupling agent enhanced adhesion of epoxy, phenol-resorcinol-formaldehyde, isocyanate, emulsion-polymer/isocyanate, and phenol-formaldehyde wood adhesives on untreated and CCA-treated wood surfaces, so that bonds were extraordinarily resistant to delamination (5,6,8,9). When HMR was used as a dilute aqueous primer on lumber surfaces before bonding, these adhesives met the 5 percent maximum delamination requirement of ASTM D 2559 (3) on southern pine lumber treated with CCA at a retention of 9.6 kg/m^3 (0.6 pcf). This test procedure is used to qualify adhesives for wet-use (exterior) structural laminated timbers under ANSI/AITC A190.1-1992 (1).

It is generally known that CCA-treated wood causes adhesion problems, particularly for thermosetting wood adhesives that are expected to produce highly durable bonds for rigorous exterior service. The causes for poor adhesion can be explained, in part, by the fact that cellular structures of CCA-treated wood are thoroughly covered with hemispherically shaped deposits of mixtures of chromium, copper, and arsenic. The very presence of these insoluble metallic oxides, which are physiochemically bound to the wood, physically blocks virtually all opportunities for intermolecular forces of attraction between normally polar lignocellulosics of wood and adhesive (7). Despite the radically changed physical and chemical nature of CCA-treated wood surfaces, HMR has a remarkable ability to physiochemically adsorb onto the insoluble metallic oxides and enhance adhesion of several thermosetting adhesives to CCA-treated wood (5,6,8,9).

According to ANSI/AITC A190.1-1992 (1), melamine-urea-formaldehyde (MUF) combinations in which melamine resin solids are at least 60 percent by weight of total resin solids, and meet the requirements of ASTM D 2559 (3), may be considered wet-use adhesives. An exception is that MUF adhesives cannot be used on woods chemically treated before or after bonding. Also, MUF combinations are not to be used when service conditions result in exposure to the combined effects of moisture content (MC) of wood in excess of 16 percent and a temperature of 48.9°C (120°F). Poor adhesion to CCA-treated wood notwithstanding, other reasons for not accepting MUF combinations on CCA-treated wood are not specifically known.

HMR has demonstrated the ability to enhance the durability of adhesion of thermosetting adhesives to CCA-treated wood. Hydroxymethylated groups on HMR can condense, theoretically at least, with similar reactive groups on urea- and melamine-formaldehyde (MF) resins. Therefore, an opportunity exists for HMR to couple these types of adhesives to treated wood to form durable structural bonds. Perhaps improved per-

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formance of MUF adhesive could initiate the process for its acceptance in wet-use applications. The purpose of this study was to assess these possibilities. MUF and MF adhesives are well suited for radiofrequency (RF) curing, and high-speed processing is an important consideration in some of today's cost-sensitive operations; therefore, RF curing was made apart of the adhesive bonding system.

EXPERIMENTAL MATERIALS

HMR COUPLING AGENT

The HMR coupling agent was prepared by reacting formaldehyde with resorcinol in a 1.5 mole ratio at mildly alkaline conditions. The mixture was reacted 4 hours at room temperature before application to the wood surfaces. The length of reaction time determines the reactivity and molecular-weight distribution of HMR; therefore, the reaction time has a strong effect on adhesion. Research is underway to determine the optimum range of reaction times for best adhesion. The following proportions of ingredients yield 5.0 percent dry solids in aqueous solution:

HMR ingredient	Percentage by weight
Water (deionized)	90.43
Resorcinol (crystalline)	3.34
Formaldehyde (37%)	3.79
Sodium hydroxide (3 molar)	2.44
Total	100.00

Dodecyl sulfate sodium salt (0.5% by weight) was added to this mixture at the end of the reaction time to aid wetting of the wood surfaces.

ADHESIVES

Commercial MUF and MF adhesives, both of which meet structural durability requirements of ASTM D 2559 (3) and ANSI/AITC A 190.1-1992(1) according to the manufacturer's technical literature, were used in these experiments. Both were supplied as one-component powders mixed with filler and hardener. It was necessary to increase viscosity of the MF adhesive by adding 4 percent walnut shell flour and 2 percent birch wood flour to approximately equal the viscosity of the MUF adhesive. Both adhesives were mixed with water in 100:45 ratio of parts by weight.

LUMBER AND PRESERVATIVE TREATMENTS

Southern pine lumber, 25 by 52 mm, (nominal 1 by 6 in.), flat-sawn with minimum specific gravity of 0.51 (based on ovendry weight and volume at 12% MC) was purchased from a lumber wholesaler. Randomly selected boards were pressure treated with a commercial CCA preservative of Type C to a target retention of 9.6 kg/m^3. Preservative treatments were conducted at the FPL where retention levels of each board were monitored by automatic weighing. Amounts of active metals in treating solutions and treated boards were determined by chemical analysis.

After treating, the lumber was air-dried, then kiln-dried to 10 percent MC. Lumber was conditioned to an equilibrium moisture content (EMC) of approximately 10 percent at 26.7°C (80°F) and 50 percent relative humidity (RH). The untreated lumber, which was used as the control, was dried and conditioned to the same EMC. All specimen materials were jointed on one side, then knife-planed on the other so that pieces would lie flat without pressure. The surfaces were planed approximately 24 hours before assemblies were laminated.

EXPERIMENTAL METHODS

EXPERIMENTAL DESIGN

The experiment was designed to determine the effectiveness of the HMR coupling agent in enhancing the durability of adhesion of MUF and MF adhesives in lumber laminates of CCA-treated southern pine, in comparison with the untreated wood. Adhesives were cured by RF heating. The durability of bonding was evaluated by measuring delamination as lumber joints were subjected to a severe cyclic delamination test, and testing for shear strength and wood failure in a dry condition, as required in ASTM D 2559 (3).

Statistical experiments were conducted for delamination resistance, dry shear strength, and wood failure. Each experiment was a completely randomized model with factorial arrangement (4) of two adhesives (MUF and MF), two wood treatments (CCA-treated and untreated), and two surface primers (HMR-primed and unprimed), yielding eight treatment combinations. Each treatment combination was replicated four times. For the delamination test, a replicate was a six-ply lumber laminate from which three sections were cut. Delamination was measured from five bondlines on each end of three sections in each laminate. For the dry shear strength and wood failure tests, a replicate was a two-ply lumber laminate. A total of 5 block-shear specimens were cut from each of 4 replicates, yielding 20 specimens for determining dry shear strength and wood failure for each treatment.

Parametric and nonparametric analyses of variance were conducted for each tested property. The Ryan-Einot-Gabriel-Welch multiple comparison F-test was used to detect significant differences between treatment combinations (10).

PREPARATION OF SPECIMENS

The delamination specimens were 7.6-cm- (3-in.-) long cross sections cut from a six-ply lumber laminate (replicate). The laminate was prepared by bonding six pieces of lumber, each measuring 1.9 cm (.75 in.) thick, 7.6 cm wide, and 30.5 cm (12 in.) long.

Shear strength and wood failure specimens were compression-loading block-shear specimens with 19.4-cm^2 (3.0-in.^{2}) shear areas, prepared and cut from two-ply laminates, as described in ASTM D 905 (2). Each piece of lumber measured 1.9 cm thick, 6.4 cm (2-1/2 in.) wide, and 30.5 cm long.

Two- and six-ply laminates were prepared in the same manner. If lumber surfaces were to be primed before bonding, a 5 percent HMR solution was spread on both surfaces with a brush at approximately 0.15 kg/m^2 (0.03 lb/ft^2). The primed surfaces were dried 24 hours at 22.8°C (73°F) and 50 percent RH before bonding. Adhesive was spread with a roller on both bonding surfaces to total 0.35 kg/m^2 (0.07 psi). Closed assembly time ranged from 20 minutes after the first bondline was spread to 15 minutes after the last bondline was spread. The adhesive was cured with a Mann-Russell Model 200 12KVA RF generator operating at 27.12 MHz. The laminates were placed between electrodes so that the current of the RF field flowed parallel to the plane of the bondlines. The bonds were cured under pressure of 689 kPa (100 psi), with a plate current of 0.65A with 4.5 kW RF output for 3 minutes.

DELAMINATION TEST

Delamination specimens were subjected to the following three cycles of the delamination test in ASTM D 2559 (3).

Cycle 1

1. Vacuum soak in water at 84.4 kPa (25 in.-Hg) for 5 minutes.

2. Pressure soak in water at 517 kPa (75 psi) for 1 hour.

3. Repeat events 1 and 2.

4. Dry at 65.5°C (150°F) for 21 to 22 hours.

cycle 2

1. Steam at 100°C (212°F) for 1-1/2 hours.

2. Pressure soak in water at 517 kPa for 40 minutes.

3. Repeat event 4 from Cycle 1.

Cycle 3

Repeat events in Cycle 1.

Immediately after the final cycle, delamination was measured along all end-grain surfaces to the nearest 0.25 mm (0.01 in.) with a machinist's scale under a stereomicroscope. This technique is more accurate than using the unaided eye and a 0.127-mm- (0.005 -in.-) thick feeler gauge, as recommended in the ASTM specification. Delamination was expressed as a percentage of total bondline length for each specimen. Statistical analyses were based on delamination measured after all three cycles were completed.

Shear strength and wood failure tests

Block-shear specimens were tested for dry strength and wood failure according to ASTM D 905 (2). At the time of testing, specimens were conditioned to 10 percent EMC — the same EMC used during specimen preparation and adhesive curing. Shear strength at failure was calculated as Newtons per square centimeter and pounds per square inch based on 19.4-cm^2 shear area. Wood failure in the shear area was estimated to the nearest 5 percent.

Results and discussion

Effects of coupling agent

Resistance to delamination, as determined by ASTM D 2559 (3), is the most rigorous of tests used to specify durability of adhesives in structural laminated wood products. Without the HMR coupling agent, however, neither of the melamine-based adhesives could meet the 5 percent maximum delamination requirement on either untreated or CCA-treated southern pine **(Table 1, Fig. 1).** By priming with HMR, both MF and MUF adhesives delaminated only 3.6 and 2.7 percent, respectively, on the untreated wood. On the CCA-treated wood, respective delaminations were 7.0 and 6.6 percent, which is just above the required 5 percent maximum. The effectiveness of the coupling agent in reducing delamination of both adhesives on both woods is clearly evident in **Table 1** and **Figure 1.** These reductions proved to be highly significant in the statistical analyses.

TABLE 1. — Resistance to delamination and shear of MF and MUF bonds to HMR-primed untreated and CCA-treated southern pine lumber.[a]

Adhesive	Wood treatment	Surface primer	Delamination	Shear strength	Wood failure
			(%)	(N/cm^2 (psi))	(%)
MUF	None	None	8.0	1335 (1,936)	90
		HMR	2.7	1480 (2,146)	85
	CCA	None	21.3	1387 (2,012)	68
		HMR	6.6	1403 (2,035)	86
MF	None	None	21.0	1417 (2,055)	79
		HMR	3.6	1330 (1,929)	56
	CCA	None	35.3	982 (1,424)	20
		HMR	7.0	1380 (2,001)	32

[a] Requirements of ASTM D 2559: delamination, maximum 5 percent; wood failure, minimum 75 percent; and shear strength, minimum 948 N/cm^2 (1,375 psi).

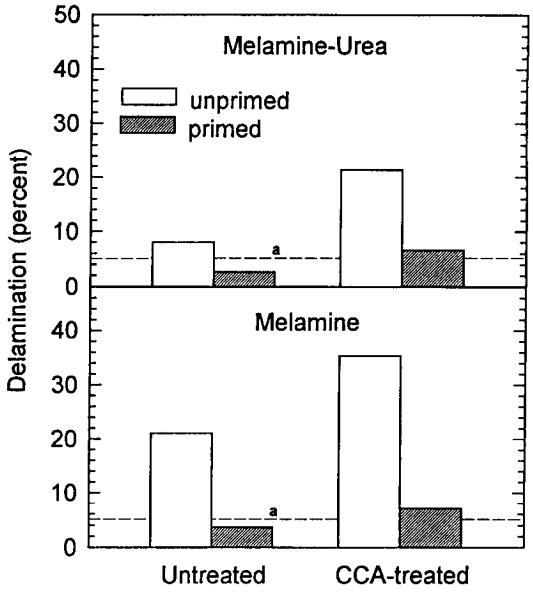

Figure 1. — Delamination of MF and MUF adhesives on HMR-primed, untreated, and CCA-treated southern pine.

It is generally recognized that tests of shear strength and wood failure of bonds in a dry condition, as required by ASTM D 2559 (3), are not effective indicators of the durability of adhesive bonds to wood. The shear strength values shown in **Table 1** confirm this in that all values exceeded the 948 N/cm^2 (1,375 psi) minimum requirement for untreated southern pine. With the exception of the significantly lower 982 N/cm^2 (1,424 psi) for the MF adhesive on unprimed CCA-treated wood (explained later), none of the other comparisons of shear strength showed significant differences. Thus, priming wood surfaces with HMR coupling agent did not increase the level of dry shear strength of any adhesive bonds, as expected.

Table 1 shows that wood failure on HMR-primed surfaces was well above the acceptable 75 percent level on both CCA-treated and untreated wood, but only with the MUF adhesive. Even without the coupling agent, MUF produced

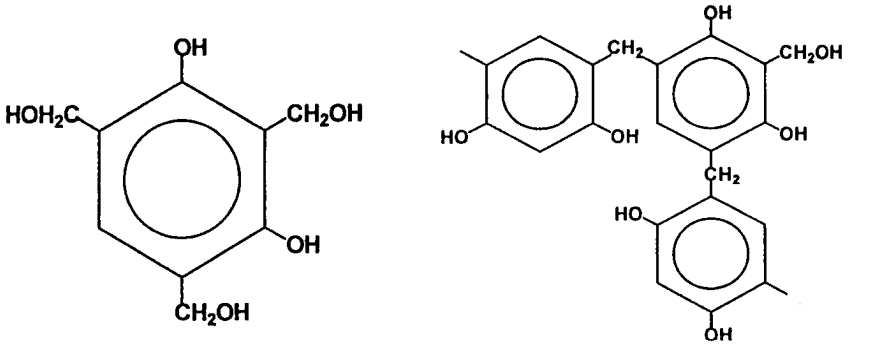

Figure 2. — Trihydroxymethyl resorcinol and its trimer.

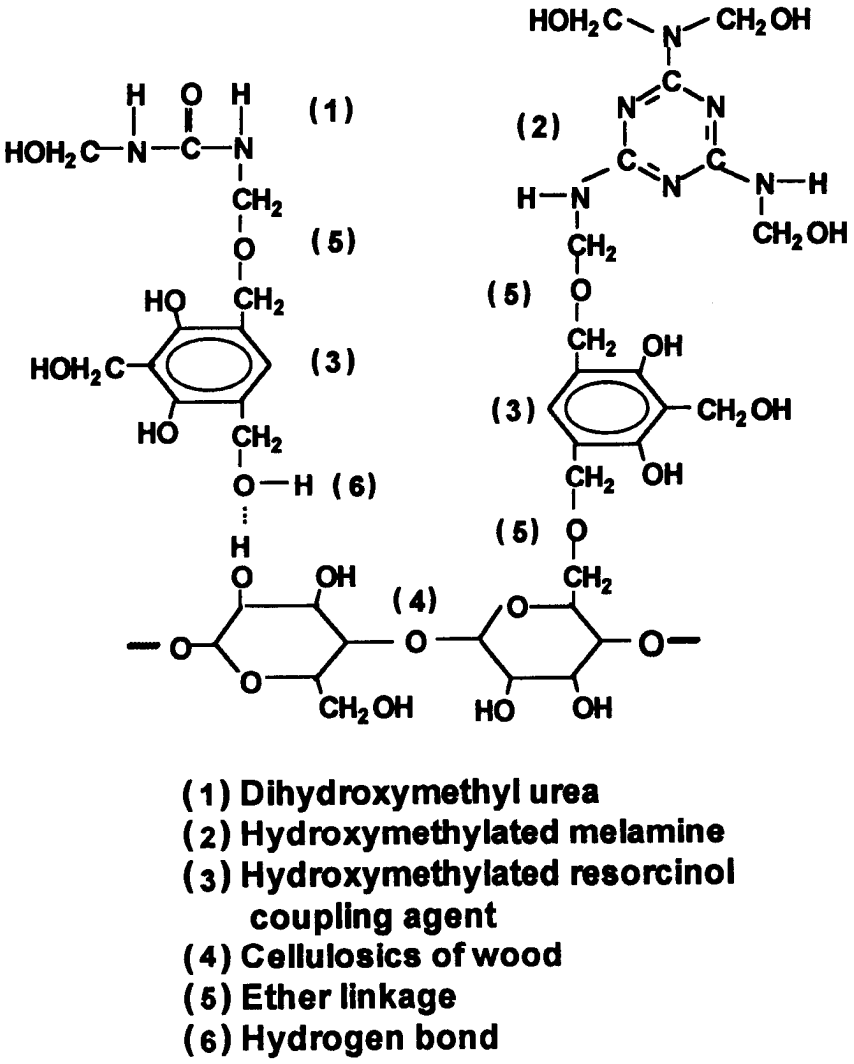

Figure 3. — Possible mechanisms of covalent and hydrogen bonding of HMR coupling agent between cellulosics of wood and dihydroxymethyl urea and hydroxymethylated melamine.

high wood failure on untreated wood. On CCA-treated wood though, the coupling agent significantly increased wood failure, which was essential for acceptable performance. However, the coupling agent did not enhance adhesion of MF on either treated or untreated wood to levels that would meet standards. This poor performance of the MF adhesive, relative to the MUF, will be explained.

HMR coupling agent clearly enhanced adhesion of an MUF adhesive, and even the excessively filled MF adhesive, so that laminates of untreated and CCA-treated southern pine very closely approached the 5 percent maximum allowed in the critical delamination test of ASTM D 2559. Shear strength values generally exceeded species requirements, even without the coupling agent. However, HMR priming was essential for meeting standards of wood failure on treated wood with the better performing MUF adhesive. It appears that HMR priming might be the key to gaining acceptance of MUF (60% melamine solids) as a wet-use adhesive for CCA-treated lumber under ANSI/AITC A190.1 - 1992 (l).

MECHANISM OF ADHESION ENHANCEMENT

HMR is considered a coupling agent because it has functional groups that are theoretically capable of chemical bonding to two dissimilar materials by reacting with the surface molecules of both substances. Resorcinol and formaldehyde, when proportioned and reacted in dilute aqueous solution at mildly alkaline conditions, are quite reactive at room temperature. Thus, HMR must be mixed at the bonding site, then allowed to react for an appropriate time before application to the wood surface. During this reaction time, HMR polymerizes to molecular structures that may be approximated by the HMR monomer and trimer shown in **Figure 2.** Recent experiments have indicated a limited and optimum reaction time during which HMR can make a maximum contribution to increased resistance to delamination. That range of reaction time appears to be 4 to 6 hours, but may be expanded to 4 to 8 hours, depending on the temperature of the reacting mixture and especially the species of wood being bonded. Chemical analyses will more clearly define the state of reactivity and molecular structures at the time of maximum enhancement of adhesion.

Hydroxymethylated functional groups on HMR species can react with certain functional groups of other polymers, including hydroxymethylated groups on urea- and melamine-formaldehyde resins, as suggested in **Figure 3.** The HMR coupling agent is believed to covalently bond through condensation reactions to form ether linkages with urea and melamine resins. Other available hy - droxymethyl groups on HMR are capable of forming ether linkages with primary hydroxyl groups on the cellulosics of wood. If such is the case, then HMR would couple adhesive and wood to form a cross-linked polymeric network. It is not clear what types of linkages develop between HMR and the insoluble chromium, copper, and arsenic oxides that are deposited on the cellular surfaces of CCA-treated wood. It is clear, however, that highly durable bonds arc formed on CCA-treated wood when these surfaces are primed with the HMR coupling agent (5,6,8,9).

If conditions and reactive lignocellulosic structures are not available for covalent bonding, then hydrogen bonding is a more likely explanation for enhanced adhesion. The surfaces of cellulosics and lignin are rich with secondary hydroxyl groups. Perhaps the metallic oxides on the surfaces of CCA-treated wood offer sufficient attraction forces for hydrogen bonding with HMR. With a multimolecular layer of HMR coupling agent thoroughly covering and penetrating cell walls, opportunities for high density hydrogen bonding are present. Even though a hydrogen bond is relatively weak compared with a covalent bond, hydrogen bonding, if numerous enough, could be a primary contributor to adhesive bond durability.

ADHESIVES

The MF adhesive did not perform as might be expected, probably because an excess of fillers was added to the adhesive during this experiment. As supplied, the MF adhesive was of much lower viscosity than the MUF, and the MF tended to squeeze out excessively, even after 15 minutes of closed assembly time. To achieve approximate equivalency in viscosity with the MUF, 2 percent (by weight) wood flour and 4 percent walnut shell flour were added to the MF mixture. Adhesive mobility was controlled but, unfortunately, structural integrity of the adhesive film was compromised, and perhaps penetration was limited by an excess of fillers. Thus, on loading in shear, the adhesive film fractured and crumbled at the wood-adhesive interface, This generally resulted in low wood failure, particularly on the CCA-treated wood where adhesive penetration appeared to be less than on the untreated wood, Low adhesive film structural integrity appeared not to be a limiting factor in the resistance of the adhesive bonds to delamination, especially when the HMR coupling agent was used to prime untreated and CCA-treated wood surfaces.

The MUF adhesive performed quite well in terms of its working properties. As shown in **Table 1,** MUF produced nearly acceptable levels of resistance to delamination (slightly above the maximum allowable) shear strength and wood failure, when wood surfaces were primed with the coupling agent. MUF adhesives, even those with 60 percent melamine solids, are not acceptable for bonding to CCA-treated wood under ANSI/AITC Al 90.1-1992 (l). Neither are MUF adhesives allowable when service conditions would create a combination of 16 percent wood MC and a temperature of 48.9°C or greater. Perhaps the coupling agent is a means of achieving acceptable levels of bond durability for MUF adhesives in wet-use applications.

CONCLUSIONS

In this study, the HMR coupling agent greatly enhanced the durability of adhesion of MUF and MF adhesives in southern pine lumber laminates treated with CCA preservatives to 9.6 kg/m^3. Although the need for additional work to improve adhesion is indicated, priming lumber surfaces with HMR might be the key to gaining acceptance of MUF (60% melamine solids) as a wet-use structural adhesive for CCA-treated lumber under ANSI/AITC Al90.1 (1992).

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