Adhesive bonding of wood treated with ACQ and copper azole preservatives

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Abstract

Treated wood has generally been more difficult to bond than untreated wood for a variety of reasons. Alkaline copper quat (ACQ) and copper azole (CA-B), the most prominent substitutes for chromated copper arsenate (CCA), are difficult to bond consistently. Using a phenol-resorcinol-formaldehyde (PRF) adhesive formulated for bonding to CCA-treated wood, we examined the bonding of southern yellow pine treated with CCA, ACQ, or CA-B. In durability tests, bonds were not as durable in the ACQ- or CA-B-treated southern yellow pine as in the CCA-treated or untreated pine as measured by delamination. Using differential scanning calorimetry (DSC), we determined that the adhesive tends to react more quickly with ACQ- or CA-B-treated southern yellow pine than with untreated or CCA-treated southern yellow pine. A hydroxymethylated resorcinol primer (HMR) did not penetrate as well into ACQ- or CA-B-treated southern yellow pine as into untreated wood, suggesting that PRF penetration is not as effective in treated wood. However, the HMR primer was able to reduce the extent of bond delamination of treated southern yellow pine bonded with PRF.

Treated wood is generally more difficult to bond than untreated wood (Vick et al. 1990, Vick 1994). The poorer bondability of treated wood has been attributed to multiple causes (Frihart 2004). Among the potential causes are chemical interference of the preservative with the curing of the adhesive, reduction of the wettability of the wood, and physical blockage of the surface where the adhesive attaches to the wood. Thus, preservatives have to be considered separately because they can interfere in one or more ways with bonding wood. Creosote, one of the first preservatives used for wood, made wood difficult to bond, especially if it resulted in an oily surface, which caused a chemically weak boundary layer (Selbo 1975). Even the solvents used to treat wood with preservatives can sometimes cause bonding problems (Herzog et al. 2004).

The transition from the use of creosote to heavy-metal chemicals gave rise to different problems. Research on a number of options led to chromated copper arsenate (CCA) being selected as the best-performing preservative. Initially difficult to bond, CCA-treated wood bonding was improved through various methods, such as reformulating phenol-resorcinol-formaldehyde (PRF) adhesives or using hydroxymethylated resorcinol (HMR) primer (Vick 1995). The problem of bonding CCA-treated wood was attributed to the presence of CCA nodules on the wood surface, which limited access of the adhesive to the wood, rather than to inhibition of the curing of the adhesive (Vick and Kuster 1992). However, this model is inconsistent with later data that showed that southern yellow pine (SYP) treated with a low level of CCA had less bond strength than did red pine, white spruce, balsam fir, and jack pine with higher levels of CCA adsorption (Wang et al. 2001). Because the surface of CCA-treated wood is harder to wet than that of untreated wood, lower bond strength may be better explained by chemical interference upon wetting as opposed to physical blockage (Maldas and Kamdem 1998), but this hypothesis does not explain the species effect (Wang et al. 2001). Although metals such as copper are catalysts for the curing of phenol-formaldehyde resins (Pizzi 1983), a prior study using differential scanning calorimetry (DSC) showed that CCA-treated wood does not accelerate the cure of a phenol-formaldehyde resin (Vick and Christiansen 1993).

Currently, significant volumes of CCA-treated wood are laminated for applications such as bridge construction. Recent

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concern about the release of arsenic from CCA has accelerated the search for alternative preservatives. All borates are suitable for interior application, but they are too easily extracted by water for any exterior application. Among the preservatives most commonly considered for replacing CCA are alkaline copper quat (ACQ) and copper azole (CA-B) (Smith and Wu 2005).

We felt it was important to evaluate the bonding of wood treated with ACQ or CA-B because the chemistry of these preservatives is different (Frihart 2003). The copper in wood treated with ACQ or CA-B is not as firmly bound as that in CCA-treated wood. Some ACQ and CA-B formulations contain boric acid, which can increase the viscosity of phenolic adhesives (Vick et al. 1990).

Few studies have examined the bonding of wood treated with ACQ or CA-B. Studies on Japanese larch concluded that the preservatives did not adversely affect wettability or cure of a PRF as measured by infrared spectroscopy, but they accelerated cure as measured by torsional braid dynamical mechanical testing (Miyazaki et al. 1999). In a related study, these preservatives did not affect bond strength and delamination (Miyazaki and Nakano 2003). However, industrial laboratories have reported that bonding to ACQ- and CA-B-treated wood is more difficult than bonding to CCA-treated wood (R. Kline, personal communication, 2002). Additional surface treatment, such as using low levels of citric acid and drying before applying the adhesive has been used with treated wood (R. Kline, personal communication, 2002). Thus, we initiated a study to examine the bonding of ACQ- or CA-B-treated SYP in comparison to CCA-treated SYP using a PRF adhesive formulated for bonding to CCA-treated wood.

Adhesives have to pass a variety of performance standards, but given that the selected PRF is already used commercially, we concentrated on durability tests. The conditions that generally are hardest on bonded wood assemblies are soaking and drying cycles. Expansion and contraction of the wood requires the adhesive to withstand significant internal tensile and compressive forces. The American Society for Testing and Materials test method ASTM D 2559 (ASTM 2000) is usually considered the most severe test because it subjects the samples to rapid swelling using a vacuum-pressure water soak followed by rapid drying, and it does not allow for stress relaxation of the wood. The standard requires a minimal amount of bondline delamination in blocks bonded together with the tangential surfaces alternating between pith-to-pith and bark-to-bark sides. The forces within the tests are both lateral forces on the bondline from swelling and normal forces resulting from rapid drying, which cause the wood to bow.

Materials and methods

Materials

Treated and control SYP were supplied by the manufacturers of the preservatives. In all cases, the SYP was treated to a level satisfactory for in-ground use: 6.4 kg/m^3 (0.40 pcf) for ACQ (Type C), 3.4 kg/m^3 (0.21 pcf) for CA-B, and 9.3 kg/m^3 (0.58 pcf) for CCA. We assumed that the effect of the preservatives on the adhesive would be greatest for in-ground treatment levels since the treated wood contains more preservative than that for aboveground use. The wood was 19 mm (0.75 inch) thick and planed to 16 mm (0.63 inch) thick within 24 hours of bonding.

The SYP sawdust used to obtain DSC data had a particle size of approximately 1 by 0.5 mm (0.04 by 0.02 in) and was treated with the following preservative chemical formulations: 1.83 percent CCA (9.3 kg/m^3, 0.58 pcf), 0.66 percent CA-B (3.4 kg/m^3, 0.21 pcf), 1.26 percent ACQ (6.4 kg/m^3, 0.40 pcf), 0.88 percent CuO with boric acid (4.5 kg/m^3, 0.28 pcf), 0.85 percent CuO without boric acid (4.4 kg/m^3, 0.27 pcf), or 0.42 percent quat (quaternary ammonium compounds) (2.2 kg/m^3, 0.13 pcf). The pH of treated and untreated SYP sawdust was determined by adding 5 mL of water to 1 g of sawdust and measuring the pH after about an hour.

Two components for a commercial PRF currently being used in bonding CCA-treated wood were mixed and applied according to the manufacturer's instructions. One part hardener (containing paraformaldehyde plus filler) was mixed with 2 parts water by weight. After the mixture had stood for 20 minutes, 1 part of the hardener slurry was mixed with 2.5 parts resin by weight.

Bonding

The spread rate was 0.17 kg/m^2 (0.035 psf) on each surface of each adhesive joint. The open and closed assembly times were 0 and 30 minutes, respectively. The 305- by 76-mm (12- by 3-in), 5-ply SYP assembly was bonded in a cold press at 1034 kPa (150 psi) for at least 8 hours as recommended by the adhesive manufacturer. After bonding, the assemblies were cut into 76- by 76-mm (3- by 3-in) test specimens, which were tested according to specifications in ASTM D 2559-00 (ASTM 2000). In the first cycle, specimens were submerged in water in a pressure vessel. A vacuum of 85 kPa (25 in) Hg was drawn for 5 minutes; 517 kPa (75 psi) pressure was then applied for 1 hour. This vacuum-pressure cycle was repeated once more and specimens were then dried in an oven at 65.5°C (150°F) for 21 hours. In the second cycle, specimens were returned to the pressure vessel and steamed at 100°C (212°F) for 90 minutes, after which they were submerged in water at 18° to 27°C (65° to 80°F) and 517 kPa (75 psi) pressure was applied for 40 minutes Specimens were dried in the oven as described in the first cycle. The first cycle was repeated, and delamination was measured immediately after the final drying period.

The data presented here are not acceptable as proof of passage of ASTM D 2559 since we did not study the variation in assembly times as required by this method and because we bonded 305- by 76-mm (12- by 3-inch) 5-ply wood members instead of the 1-m by 140-mm (40- by 5.5-inch) 6-ply wood members required by the standard. In past experience we had learned that soaking and heat drying tend to have the greatest effects on bonded assemblies, so we concentrated on the delamination part of ASTM D 2559.

Primers

For the cases in which an HMR primer was used, the SYP was brushed with a 5 percent solution of HMR at a rate of 0.15 kg/m^2 (0.031 psf) and dried overnight at 50 percent relative humidity and 27°C (80°F) before the adhesive was applied. The novolak HMR solution contained 3.34 g resorcinol, 2.51 g 3M sodium hydroxide, and 0.98 g formaldehyde (37% solution) in 93.18 g water and was mixed at least 24 hours before use. This solution is stable for several weeks because the balance of the required formaldehyde (2.84 g of 37% solution) is added immediately before the solution is used. The citric acid primer was applied as a 5 percent solution at a rate of 0.01

kg/m^2 (0.002 psf) and dried for 1 to 2 hours before the adhesive was applied.

Differential scanning calorimetry and gel time

The DSC data were obtained on a Perkin-Elmer DSC 7 (Norwalk, CT) using sealed stainless steel capsules (LVCs). The adhesive samples (50 to 75 mg) were mixed just prior to putting them in the capsules and weighed. The capsules were then sealed. The samples were heated at 10°C/min (18°F/min) from 30° to 200°C (86° to 392°F).

Gel time was obtained with a Sunshine Gel Time Meter (SSI, Philadelphia, PA) using a water bath at 40°C (104°F). A test tube containing approximately 5 g of adhesive, with a glass stirring rod connected to the instrument in the center of the adhesive, was placed in the water bath. The stirring rod rotated slowly and eventually stopped as the adhesive cured and increased in viscosity. Gel time was the time required for the stirring rod to stop rotating.

Results and discussion

Delamination

Since previous work showed that the HMR primer was effective in improving bonding (Vick 1995), we tested the HMR with the ACQ and CA-B wood preservatives. In bonding treated and untreated SYP, we noticed some interesting effects when the HMR was applied. The HMR can be considered a dilute resorcinol-formaldehyde type of adhesive, which allowed us to better understand adhesive penetration. Although we did not establish a test procedure to measure the rate of wood penetration, we observed that the HMR solution was absorbed much slower into some of the treated SYP compared to the untreated SYP. There seemed to be some correlation between poor penetration by the HMR solution and very high delamination rates.

Many studies have looked at the wetting of wood using water, but in general, there has not been a good correlation to bond performance. Water is not a good representation of an adhesive formulation because adhesives are usually basic or acidic and contain organics that can help solubilize surface extractives. Also, it has not been demonstrated that contact angles correlate to penetration rates. An optimum amount of penetration is generally considered important for good bond formation. Thus, HMR solution might be better than water to model wetting of wood by phenolic adhesives.

The delamination results show that the adhesive formulation, which was optimized for bonding to CCA-treated wood, indeed gave very good results on CCA-treated wood, as shown in **Table 1**. The bonding of CA-B- and ACQ-treated SYP was not as good, with ACQ-treated SYP being the hardest to bond. The pH of the treated wood did not seem to be a factor in the bonding since the ACQ- and CA-B-treated SYP were at pH 5.5 and 5.4, respectively, whereas the CCA-treated SYP was slightly more acidic at pH 4.6, compared to untreated SYP at pH 5.8. The citric acid primer actually increased delamination of the ACQ-treated SYP. We expected that citric acid would tend to neutralize and chelate the metals and improve bonding. However, it may have done the opposite and "unfixed" the copper so that it was more available to react with the adhesive and/or lowered the wood surface pH to disrupt the cure of the adhesive.

The HMR primer reduced delamination of CCA- and CA-B-treated SYP compared to the corresponding unprimed treated wood. However, the ACQ-treated SYP did not pass the ASTM D 2559 standard of 5 percent delamination, even with the HMR primer.

Table 1. — Delamination of SYP bonded with PRF adhesive after three cycles of ASTM D 2559.

Wood treatment	Primer concentration	Delamination
		(%)
None	None	1.7 to 3.0
CCA	None	0.4 to 1.2
CA-B	None	2.0 to 8.9
ACQ	None	6.5 to 15
CCA	HMR, 5%	0.2 to 0.4
CA-B	HMR, 5%	0.8 to 1.5
ACQ	HMR, 5%	5.4 to 12
ACQ	Citric acid, 5%	74 to 94

Differential scanning calorimetry

An important aspect in looking at the interaction of the adhesive with the treated SYP was to measure the reaction temperature using the exothermic peak in the DSC data. In these experiments, the reaction temperature was determined as the peak of the exotherm and the heat evolved (ΔH) was the area under the exothermic peak. These values were measured for the adhesive by itself and with additives such as the preservative chemicals or treated SYP sawdust, as given in **Table 2**. Reconfirming earlier results (Vick and Christiansen 1993), CCA-treated sawdust did not affect the reaction temperature. The interaction of the adhesive with the wood did lower the heat evolved per gram of sample for all the samples containing wood, because the amount of wood diluted the reactants. On the other hand, CA-B- or ACQ- treated sawdust significantly lowered the peak temperature 4°C to 10°C.

The monoethanolamine (MEA), used for solubilizing the copper salt in ACQ-treated wood, also accelerated the reaction process, but copper carbonate solid, which is not soluble, did not catalyze the reaction process. This could indicate that it is soluble copper that catalyzes the reaction by itself or in combination with the MEA. The quaternary compounds (quat), which contain no copper, had no effect on the peak exothermic temperature (**Table 2**). Some borates can cause phenolic resins to gel (Vick et al. 1990). In our study, we did not see any difference between samples with and without boric acid.

For CCA-treated wood, copper may be firmly bound and therefore not go into solution to catalyze the reaction of the PRF adhesive. However, SYP treated with ACQ and CA-B did catalyze the reaction, suggesting that the copper in these preservatives is more extractable. This has been supported by measurements of leached copper from ACQ-treated wood (Lebow 1996). We therefore conclude that the solubilization of copper, whether with quaternary compounds or azole, tends to accelerate the reaction of the PRF adhesive.

Gel time

Measurement of gel time was also used to study the reaction of the PRF adhesive. Gel time is a measurement of when adhesive viscosity has increased enough to trip the timer as a result of viscous drag. We found a fairly consistent gel time of about 18 minutes with the PRF adhesive. As shown in **Table 3**, the combination of copper salt and MEA caused a substan-

Table 2. — DSC data for PRF adhesive mixed with preservative chemicals or preservative-treated SYP (sawdust).[a]

Additive	Peak temp	Δ H
	(°C ± 0.4)	(J/g)
None	81.0	79.6
MEA (0.2% of PRF, w/w)	71.2	64.9
$CuCO_3$ (solid) (3% of PRF, w/w)	80.3	77.2
Wood	82.1	43.2
CCA wood	81.8	46.8
CA-B wood	77.8	42.7
ACQ wood	75.6	32.6
CuO wood, with boric acid	75.7	44.9
CuO wood, without boric acid	73.9	30.0
Quat wood	81.6	39.8

[a]PRF:wood = 2:1, w/w.

Table 3. — Gel time data at 40°C (104°F) for PRF adhesive mixed with preservative chemicals or preservative-treated SYP (sawdust).[a]

Additive	Gel time (min)
None	18
CuO + MEA (0.6%)	14
MEA (0.25%)	10
Wood	11
CuO wood	12 to 14
Quat wood	8 to 15

[a]PRF:wood = 8:1, w/w.

tial reduction in gel time. In addition, MEA alone caused a very substantial reduction of gel time by accelerating the reaction. As in the DSC tests, we tried these experiments with SYP sawdust. The results showed considerable variability, partly due to the uneven particle size and/or distribution of the sawdust in the adhesive. Gel times were similar for untreated and treated wood. Therefore, no conclusion could be made about the effect of preservative-treated wood on gel time.

Conclusions

Our laboratory data indicated that the commercial PRF adhesive was very effective in bonding untreated and CCA-treated SYP. However, the bonding of SYP treated with ACQ or CA-B was not as good as that of untreated and CCA-treated SYP as determined by the ASTM D 2559 delamination test. Our data revealed important differences among these preservatives pertaining to bonding. One area of variability was the penetration of HMR primer into the wood; in general, penetration could be ranked as untreated > CCA-treated > CA-B-treated > ACQ-treated wood. This information about the penetration of HMR primer could be used to determine which kind of treated wood would be more difficult to bond. Another area of difference between CCA- and ACQ- or CA-B-treated SYP is the fact that CCA did not interfere with the reaction of the adhesive. In contrast, ACQ- or CA-B-treated SYP tended to accelerate the reaction, which lessened penetration of the adhesive into the wood. The presence of soluble copper in ACQ and CA-B accelerates the reaction of the PRF adhesive. Acceleration of reaction by the copper component in ACQ may also be enhanced by MEA, which is used to solubilize the copper. The acceleration of reaction was indicated by both a lowering of the reaction temperature in DSC and a decrease in gel time. A slower reacting PRF may be useful in addressing both the acceleration of reaction and slower penetration rate when bonding to ACQ- or CA-B-treated wood.

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