Wood Sci Technol (2006) 40: 228–236
DOI 10.1007/s00226-005-0036-7

ORIGINAL

**Dong-heub Lee · Myung Jae Lee · Dong-Won Son
Byung-Dae Park**

Adhesive performance of woods treated with alternative preservatives

Received: 23 March 2005 / Published online: 5 October 2005

Abstract The extended use of woods treated with traditional or alternative preservatives for exterior applications requires an assessment of wood adhesive performance. This study attempts to evaluate the performance of wood adhesives for woods treated with various waterborne preservatives. Two softwood species, i.e. Korean pine (*Pinus koraiensis* Sieb. et Zucc.) and Japanese Larch (*Larix leptolepis* [Sieb. et Zucc.] Gordon) were treated with copper–chrome–arsenic (CCA), CB-HDO, or copper azole (CY), and then bonded with four different wood adhesives such as urea–melamine–formaldehyde (UMF) resin, melamine–formaldehyde (MF) resin, phenol–formaldehyde (PF) resin, and resorcinol–formaldehyde (RF) resin. The performance of these adhesives was evaluated by measuring the dry shear strength of adhesive-bonded wood block on compression. Both UMF and MF resins produced a relatively strong adhesive strength for CY-treated pine and larch woods. The PF resin also produced good bond strength when bonded with either larch wood treated with CY or pinewood treated with CB-HDO. The best result was obtained when the CB-HDO-treated woods were bonded with RF resin. For a better bond strength development, a proper combination of adhesive, preservative, and wood species should be selected by taking into consideration of the characteristics of these three parameters as well as their interactions.

Introduction

With increasing use of lumber for exterior applications the concerns about insect attack, fungal degradation, or weathering lead to treatment of lumber with various wood preservatives. Thus, woods treated with waterborne preservatives are being used for various exterior applications such as structural and non-structural assemblies. An enhanced adhesion of treated woods to bond

D.-h Lee · M. J. Lee · D.-W. Son · B.-D. Park (✉)
Department of Forest Products, Korea Forest Research Institute (KFRI), 130-712, Seoul, Republic of Korea
E-mail: byungdae@foa.go.kr

treated lumber and their greater durability obviously increase the use of treated woods for exterior applications.

In general, glued wood products for structural applications include laminated veneer lumber (LVL), laminated strand lumber (LSL), parallel strand lumber (PSL), and glulams. The manufacture of these products essentially requires the use of wood adhesives. Exterior grade wood adhesives such as phenol–formaldehyde (PF) resin, resorcinol–formaldehyde (RF) resin, or melamine–formaldehyde (MF) resins are mainly used due to their high moisture resistance in outdoor environment. In particular, the use of woods treated with preservatives for the manufacture of these products requires assessment of the performance of wood adhesives.

Most of the research on adhesive performance of treated woods concern copper–chrome–arsenic (CCA) treated woods (Calusen et al. 2001; Li et al. 2004; Mengeloglu and Gardner 2000; Munson and Kamdem 1998; Hong et al. 1997) and reported inferior strength of CCA-treated woods (Sellers and Miller 1997; Vick 1980, 1994, 1995, 1997; Vick and Kuster 1992; Vick et al. 1996). Many factors contribute to the development of insufficient adhesive strength of treated woods. The presence of contaminants such as waxy, oily, and inorganic materials hinders the development of cohesive adhesion bonds between wood substrate and adhesive (Pizzi 1994). The insoluble metallic components of wood preservatives, for example, impede the formation of interfacial adhesion between wood and adhesives leading to a poor adhesive strength in products (Vick 1997). The effects of CCA treatment on the curing behavior of PF resin in the presence of CCA-treated wood have been investigated using differential scanning calorimetry (DSC) (Vick and Christiansen 1993). Treated wood often contains many defects such as twist, checks, or splits on its surfaces after its drying and curing processes. Furthermore, the formation of effective adhesive bonds in treated woods is interfered by the preservative compounds present on the surface of treated woods (Vick 1994). Using a scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDXA), Vick and Kuster (1992) showed that the inside of cell lumen of CCA-treated southern pine was completely covered with a mixture of chrome, copper, and arsenic, which prevented bond formation between wood and adhesives. In addition, one attempt to improve adhesion of CCA-treated wood was to use hydroxymethylated resorcinol (HMR), which led to an increase in adhesive strength (Hong et al. 1997; Munson and Kamdem 1998; Vick 1997).

However, there were positive results regarding the adhesive performance of treated woods. It was reported, for example, that bivalent metallic ions present in CCA could accelerate the reaction of formaldehyde to phenol while trivalent metallic ions retarded the same reaction (Pizzi 1979). Trivalent chrome ions present in CCA could form stable chelates with RF or PF resins, which retarded the reaction of formaldehyde to phenolic nucleus. In addition, the ions of chrome, copper, and arsenic present in CCA could play a catalytic role in accelerating its curing reaction while no acceleration reaction occurred after the ingredients of CCA were chemically fixed in the wood cell wall (Vick and Christiansen 1993). When bonded with phenolic adhesives, CCA-treated woods could have strong internal bond (IB) strength providing good durability, which was proportional to the depth of adhesive penetration into the wood (Vick and Kuster 1992).

The use of alternative preservatives to replace CCA as wood treatment has increased in recent years. For example, the production of laminated lumber treated with alternative preservatives such as ammoniacal copper quat (ACQ), copper azole (CuAz; CY), and alkyl ammonium compound (AAC) was feasible to obtain sufficient bond strength (Junko et al. 1999; Junko and Takato 2002a, b, 2003). The authors showed that the surface properties of treated woods depend to a great extent on the preservatives used, and further processing like surface planing, incising, etc. heavily affected the adhesive wetting and strength.

Therefore, this study attempts to evaluate the adhesion performance of four wood adhesives such as urea–melamine–formaldehyde (UMF) resin, MF resin, PF resin, and RF resin for two softwoods treated with three preservatives such as CCA, CB-HDO, and CY.

Materials and methods

Materials

Logs of two softwood species, Korean pine (*Pinus koraiensis* Sieb) and Japanese larch (*Larix leptolepis*), were sawn to obtain lumber with quarter-sawn surfaces, following air-drying for 6 months. Small wood strips of 30 cm×200 cm and 5 cm thickness were planed for specimen preparation. About 1,000 specimens of 15 mm×25 mm×30 mm were prepared for preservative treatments and gluing with adhesives.

Preservative treatment and determination of its retention levels

In this study, four wood preservatives, including CCA, copper azole (Tanalith CY), and CB-HDO were used. Both CCA and copper azole (Tanalith CY) were obtained from the Koppers Arch (North Sydney, Australia) and CB-HDO (trade name CX-10) from Dr Wolman GmbH, Sinzheim, Germany. Specimens with a density of about 450–500 kg/m^3 without visible defects were selected for pressure impregnation (full-cell method) of preservatives at a level of 3% (w/v). Treated specimens were cured at 25°C and 75% relative humidity for at least 3 weeks. Characteristics of these preservatives are shown in Table 1.

In order to avoid the destruction of wood blocks, the gauge retention of each specimen treated with a preservative prior to adhesive bonding was determined by measuring the weight gain of treated wood blocks after drying at 60°C for 48 h following preservative treatment, which was a similar procedure to the one used by Lebow et al.(1999).

Adhesives and gluing of treated woods

Wood adhesives used were UMF resin, MF resin, PF resin, and RF resin. These commercial grade adhesives were supplied from a local resin company in the Republic of Korea. The properties of these adhesives are shown in Table 2. About 3 g of the adhesives were dried for 3 h at 105°C to obtain non-volatile solid contents. The viscosity was measured with a Brookfield viscosity meter using spindle #2 at 60 rpm.

Table 1 Ingredient compositions of the preservatives used in this study

Preservatives	Active ingredient	Composition (wt%)	pH
CCA	CrO_3	47.5	2.4
	CuO	18.5	
	AS_2O_5	34.0	
CB-HDO	Bis-(*N*-cyclohexyldiazenium dioxy)-copper	14.1	10.2
	Copper (?) hydroxide carbonate	65.7	
	Boric acid	20.2	
CY	Copper carbonate	23.2	10.1
	Monoethanolamine	50.0	
	Cyproconazole	0.4	
	Polyethyleneamine	26.4	

The information is based on the MSDS of each preservative and AWPA standards (2002)

Prior to gluing, the specimens were further dried in a drying oven at 60°C for 2 days to obtain a moisture content (MC) of about 4–6%. The prepared specimen blocks were glued with adhesives at a loading of 100 g/m^2 for both surfaces and then clamped in a steel jig under a pressure of 785 kPa at room temperature for 24 h.

Dry shear strength determination

In order to compare the adhesion strength of wood adhesives used, a compressive dry shear test was done according to the procedure specified in the American Standard (ASTM D 905 1994). For the compressive shear test 25 specimens were used for each combination of adhesive and preservative. These samples were tested in compression using an universal testing machine (Model H50K-S, Hounsfield, UK) with the crosshead speed of 2 mm/min. An average dry shear strength with 25 replications for each experimental unit was reported.

Results and discussions

The determined preservative retentions are summarized in Table 3. The retention levels are greater for CCA-treated pinewood. Lower retention of the CCA in larch wood could be attributed to inherent characteristics of larch wood. This result is compatible with another report (Kang et al. 1995), but the retention levels of CY and CB-HDO were not significantly different between the two wood species.

Table 2 Characteristics of wood adhesives used in this study

Resin type	pH	Solids content (%)	Viscosity (mPas)
UMF	8.6	44.9	144.0
MF	8.4	41.7	137.0
PF	12.2	39.2	144.0
RF	9.2	59.5	973.3[a]

[a]Viscosity was measured with a spindle #3 at 60 rpm

In order to compare the performance of adhesives used, dry shear strengths of preservative-treated and adhesive-bonded samples are shown in Fig. 1. Average values of shear strength for the combinations of wood species, preservatives, and adhesives are also summarized in Table 4. Figure 1a shows dry shear strengths of both untreated and treated woods when they were bonded with UMF resin. When the untreated wood blocks were bonded with the UMF resin, dry shear strengths of both pine and larch samples were 1.8 and 1.63 MPa, respectively. For pinewood specimens, the dry shear strengths of the untreated, CY-treated, and CB-HDO-treated samples were not statistically different from each other. While that of the CCA-treated sample was lower than that of the untreated sample.

Statistical analysis was done to compare adhesive strengths of each group of wood species for each wood adhesive type. Dry shear strengths of larch wood specimens were not statistically different for CCA- and CB-HDO-treated woods when they were bonded with the UMF resin. When the UMF resin was used as samples of both species, the maximum dry shear strength was obtained for the CY-treated wood. This might be due to the amine groups in CY, which accelerate the curing rate of amino resins (i.e. UMF and MF resins) in their polymerization for adhesive bond formation. In fact, the addition of amines into UF resin accelerates a cross-linking reaction (Meyer 1979).

When treated with CCA, the specimens of the two species showed a decrease in their dry shear strengths. This result is compatible with other results reported (Vick 1980, 1994; Vick and Kuster 1992). As shown in Table 3, a greater strength of a larch specimen treated with CCA than the counterpart of pinewood could be attributed to lower CCA retention for this species (Kang et al. 1995). As two possible reasons for lower preservative retention large heartwood percentage and smaller radius of pit-pore in the cell wall were reported (Wang and DeGroot 1996).

Figure 1b shows dry shear strengths of treated wood blocks when they were bonded with MF resin. A greater strength was found for all treated samples than those of untreated samples for both wood species. All dry shear strengths of treated pinewood were greater than those of treated larch wood. The CY-treated samples showed relatively greater strength than those of other preservatives for both wood species. This result can also be explained in an enhanced curing rate of amino resins (i.e. UMF and MF resins) due to the large amount of amines in the CY (Meyer 1979).

Figure 1c shows dry shear strengths of treated woods when they were bonded with PF resin. For pinewood, the greatest shear strength was found when treated with CB-HDO while the CCA-treated samples showed the smallest shear strength. In general, the PF resin requires high temperature and low moisture content for its cure. The greatest shear strength of CB-HDO-treated samples could be attributed to the cure acceleration of carbonates present in the CB-HDO (Table 1). It was already shown that the addition of carbonates into

Table 3 Preservative retentions (kg/m^3) of treated wood samples prepared

Wood species	CCA	CB-HDO	CY
Pine	14.2 ± 1.4[a]	5.3 ± 1.3	6.5 ± 1.0
Larch	9.7 ± 2.1	6.2 ± 2.4	5.5 ± 1.6

[a]Standard deviation of preservative retention

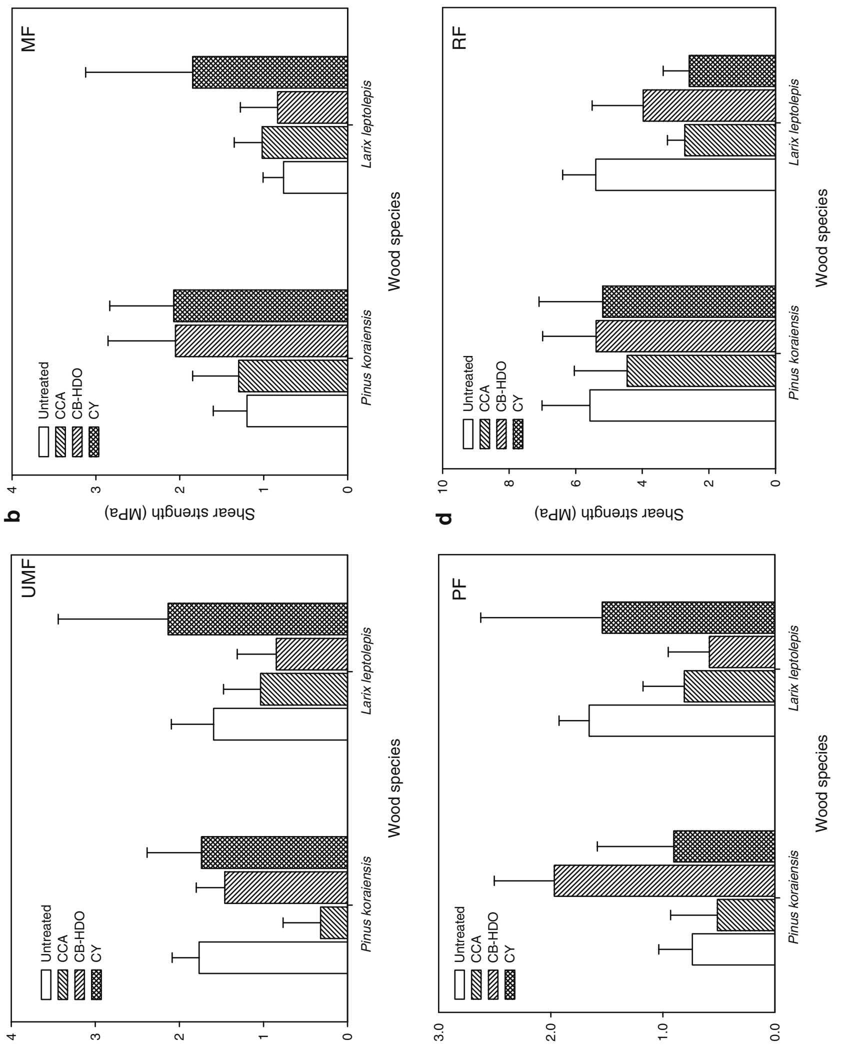

Fig. 1 Dry shear strength of treated woods bonded with different wood adhesives

PF resin accelerated the cure of PF resin under alkaline condition (Park and Riedl 2000). However, lower shear strength of CCA-treated pinewood could be attributed to copper, which interfered the curing by reacting with methylol groups (CH_2OH). In addition, a strong acid level of CCA could retard the cure of PF resin when bonded with CCA-treated pinewood. When the larch wood samples were bonded with PF resin, the shear strength of the untreated samples was greater than those of all treated samples. The shear strength of CY-treated samples was comparable with that of untreated ones.

Figure 1d shows shear strengths of treated wood samples when they were bonded with RF resin. The shear strengths of samples bonded with RF resin were much greater than those of other adhesives. The pinewood samples treated with CB-HDO showed the greatest shear strength, followed by CY-treated and

Table 4 Dry shear strengths of untreated and treated woods depending on types of preservatives and adhesives used

Adhesive type	Wood species	Preservative type and dry shear strength (MPa)*			
		Untreated	CCA	CB-HDO	CY
UMF resin	Pine	1.80a	0.86c	1.49 b	1.77a
	Larch	1.63b	1.06c	0.86a	2.18c
MF resin	Pine	1.22b	1.33b	2.09a	2.11a
	Larch	0.78b	1.04b	0.85b	1.89a
PF resin	Pine	0.75b,c	0.52c	2.01a	0.92b
	Larch	1.69a	0.83b	0.60b	1.57a
RF resin	Pine	5.69a	4.55a	5.50a	5.30a
	Larch	5.51a	2.78c	4.05b	2.64c

*Means with the same letters are not statistically different at a *P* value of 0.05 using Duncan's multiple range test

CCA-treated samples in descending order. As for PF resin, the presence of a relatively large amount of carbonate in the CB-HDO could be a possible cause for this result. In other words, the carbonate present in the CB-HDO played a role in accelerating the cure of RF resin used for treated pinewood samples.

The shear strengths of treated pinewood samples were lower than that of untreated ones. This might be due to the presence of copper in all preservatives used in this study. It was reported that the copper present in copper-based preservatives had an influence in retarding the cure of RF resin, resulting in lower adhesive strength (Sellers and Miller 1997). However, all dry strengths of treated pinewood samples were not statistically significant for the different preservatives.

All dry shear strengths of treated larch wood were lower than those of treated pinewood and also lower than that of the untreated larch wood. This result indicated that the copper present in all preservatives influenced the shear strength of treated larch wood. The CB-HDO used for the treatment of larch wood showed the best shear strength among the preservatives although its shear strength was relatively small. It was believed that the carbonate present in the CB-HDO played the same role for treated larch wood.

The greatest shear strength of treated woods bonded with RF resin among four adhesive types could be attributed to greater reactivity of the RF resin (i.e. cold setting adhesive). Differences in shear strengths could be ascribed to various factors such as types of preservatives, their chemical composition, pH levels of preservative and wood species, surface properties, extractive content of each wood species, etc. The presence of extractives dissoluble in ethanol and water, for example, accelerated the cure of UF resin used for preparing particleboards (Chen and Paulitsch 1974).

The shear strength of treated wood showed differences depending on wood species as well as adhesives types, although the samples were treated with the same preservatives. This result suggests that other factors rather than the ingredients of preservatives affect adhesion strength of treated wood. For example, lower pH of CCA could have an impact on the curing of all adhesives except MF resin. Also, greater pH levels of CB-HDO and CY could accelerate the curing of MF resin, PF resin, and RF resin except UMF resin that cured under acidic condition.

In summary, the results obtained from this study show that both UMF and MF resins produce relatively strong adhesive strength for CY-treated pine and larch woods. When larch wood was treated with CY, PF resin also produced good bond strength. In addition, the combination of CB-HDO and PF resin was good for developing bond strength of pinewood. RF resin gave the best result when CB-HDO was used for the treatment of both wood species. However, to use the treated woods for exterior applications, their water resistance should be evaluated by measuring wet strength. The above results also indicate that many factors as well as interactions of the factors impact the development of adhesive bond strength in treated woods.

Conclusions

In order to extend the use of treated woods for exterior applications, this study attempts to evaluate the performance of wood adhesives for two softwood species, pine and larch lumber, treated with traditional and alternative preservatives such as CCA, CY, or CB-HDO using UMF resin, MF resin, PF resin, and RF resin. The following results are obtained from this study:

1. Both UMF and MF resins produced relatively strong adhesive strength for CY-treated pine and larch woods.
2. The PF resin was also good for developing bond strength of pinewood treated with CB-HDO or CY. RF resin gave the best result when CB-HDO was used for the treatment of both wood species. These results indicated that alternative wood preservatives could be replaced with traditional CCA.
3. A proper combination of adhesive, preservative, and wood species should be selected for the best bond strength development, which was affected by the characteristics of these three parameters as well as their interactions.

References

ASTM D 905 (1994) Standard test method for strength properties of adhesive bonds in shear by compression loading. ASTM, Philadelphia

Chen TY, Paulitsch M (1974) The extractives of needles, bark and wood of pine and spruce and their effect on particleboard made thereof. Holz Roh- Werkst 32(10):397–401

Clausen CA, Kartal SN, Muehl J (2001) Strength and durability of phenol-resorcinol joints of CCA-treated and untreated southern pine. For Prod J 51(7/8):61–64

Hong JZ, Gardner DJ, Wang JZ, Shi Q (1997) Surface tension, adhesive wettability, and bondability of artificially weathered CCA-treated southern pine. For Prod J 47(10):69–72

Johns WE, Niazi KA (1981) Effect of pH and buffering capacity of wood on the gelation time of urea–formaldehyde resin. Wood Fiber Sci 2(4):255–263

Junko M, Takato N, Yasushi H, Masanori K (1999) Effects of wood preservatives on adhesive properties of phenol–resorcinol–formaldehyde resin. Mokuzai Gakkaishi 45(1):34–41

Junko M, Takato N (2002a) Effects of wood preservatives on adhesive properties II; curing reaction of resorcinol–formaldehyde resin with Cu. Mokuzai Gakkaishi 48(3):178–183

Junko M, Takato N (2002b) Effects of wood preservatives on adhesive properties III; curing of aqueous vinyl polymer solution-isocyanate adhesive with preservatives. Mokuzai Gakkaishi 48(3):184–190

Junko M, Takato N (2003) Effects of wood preservatives on adhesive properties IV; effects of preservation and incising on shear strength and delamination. Mokuzai Gakkaishi 49(3):212–219

Kang SM, Kim GH, Paik KH (1995) Treatment characteristics of Japanese larch heartwood with CCA or CCFZ and improving its CCA treatability by incising techniques. J Korean Wood Sci Technol 23(4):60–66
Lebow ST, Foster DO, Lebow PK (1999) Release of copper, chromium, and arsenic from treated southern pine exposed in seawater and freshwater. For Prod J 49(7/8):80–89
Li W, Shupe TF, Hse CY (2004) Physical and mechanical properties of flakeboard produced from recycled CCA-treated wood. For Prod J 54(2):89–94
Mcnamara WS, Sullivan CE, Higgins JC (1970) pH measurements on northeastern woods. Wood Sci 3(1):48–51
Mengeloglu F, Gardner DJ (2000) Recycled CCA-treated lumber in flakeboards: evaluation of adhesives and flakes. For Prod J 50(2):41–45
Meyer B (1979) Urea–formaldehyde resins. Addison-Wesley, London, pp 22–96
Munson JM, Kamdem DP (1998) Reconstituted particleboards from CCA-treated red pine utility poles. For Prod J 48(3):55–62
Park BD, Riedl B (2000) ^{13}C-NMR study on cure-accelerated phenol–formaldehyde resins with carbonates. J Appl Polym Sci 77(4):841–851
Pizzi A (1979) Phenolic and tannin-based adhesive resins by reactions of coordinated metal ligands. I. Phenolic chelates. J Appl Polym Sci 24:1247–1255
Pizzi A (1994) Advanced wood adhesive technology. Marcel Dekker, New York, pp 1–18
Sellers T, Miller GD (1997) Evaluations of three adhesive systems for CCA-treated lumber. For Prod J 47(10):73–76
Subramanian RV, Somasekharan KN, Johns WE (1983) Acidity of wood. Holzforschung 37:117–120
Vick CB (1980) Structural bonding of CCA-treated wood for foundation systems. For Prod J 30(9):25–32
Vick CB (1995) Coupling agent improves durability of PRF bonds to CCA-treated southern pine. For Prod J 45(3):78–84
Vick CB, Geimer RL, Wood JE (1996) Flakeboards from recycled CCA-treated southern pine lumber. For Prod J 46(11/12):89–91
Vick CB (1997) Enhanced adhesion of melamine-urea and melamine adhesives to CCA-treated southern pine lumber. For Prod J 47(7/8):83–87
Vick CB (1994) Preliminary finding on adhesive bonding of CCA-treated southern pine. Adhesive and Bonded Wood Prod, pp 158–176
Vick CB, Christiansen AW (1993) Cure of phenol–formaldehyde adhesive in the presence of CCA-treated wood by differential scanning calorimetry. For Prod J 25(1):77–86
Vick CB, Kuster TA (1992) Mechanical interlocking of adhesive bonds to CCA-treated southern pine: a scanning electron microscopic study. Wood Fiber Sci 24(1):36–46
Wang JZ, DeGroot R (1996) Treatability and durability of heartwood, Gen. Tech. Report FPL-GTR-94. Forest Products Lab., Madison, WI, USA. pp 252–260
Zhang HJ, Gardner DJ, Wang JZ, Shi Q (1997) Surface tension, adhesive, wettability, and bondability of artificially weathered CCA-treated southern pine. For Prod J 47(10):69–72