

THE EFFECTS OF CHROMATED COPPER ARSENATE AND AMMONIACAL COPPER ZINC ARSENATE ON SHEAR STRENGTH DEVELOPMENT OF PHENOLIC RESIN TO SITKA SPRUCE BONDS¹

T. R. Narayana Prasad

Visiting Scientist

Philip E. Humphrey

Associate Professor

and

Jeffrey J. Morrell

Associate Professor

Department of Forest Products

Oregon State University

Corvallis, OR 97331

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ABSTRACT

Preservative treatment of whole, wood-based composite products (mainly panels) has disadvantages; problems largely stem from swelling, strength loss, and incomplete or inappropriate penetration during treatment, and distortion during redrying. Pretreatment of comminuted wood prior to mat lay-up is one alternative, though the addition of chemicals may affect bonding during subsequent pressing. With this possibility in mind, the strength accumulation of small test bonds (15 × 4 mm) between variously treated thin wood pieces was investigated. Pieces of Sitka spruce (sliced 0.8 × 15 × 150 mm) were treated with one of four concentrations (0.25 to 1.50% oxide basis) of either chromated copper arsenate or ammoniacal copper zinc arsenate. An automated device was used to form and test lap-shear specimens from matched pairs of variously treated wood and a phenol-formaldehyde adhesive. Each specimen was pulled immediately after pressing to measure the accumulated shear strength of the bond. Pressing times ranged from 10 to 300 sec at 95 C and 1.5 MPa, and this enabled near-isothermal strength-development plots to be constructed for each level of pretreatment. The plots suggested that preservative pretreatment did not significantly affect shear strength development rates at the chemical retention levels and pressing and testing conditions employed.

Keywords: Wood-based composites, preservative pretreatment, hot-pressing, bond-strength development, chromated copper arsenate, ammoniacal copper zinc arsenate, phenol-formaldehyde.

INTRODUCTION

As wood-based panel products are more widely used, it is inevitable that some will be found in environments conducive to decay. Panel products will require some type of preservative treatment in order to perform sat-

isfactorily under more severe conditions. Assembled panels can be treated with preservative by using conventional pressure processes; the preservative may not completely penetrate the panel, however, and the process can induce strength loss, excessive swelling, and delamination.

As an alternative to pressure treatment of completed panels, constituent veneers, flakes,

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or wafers may be treated with preservative prior to lay-up. Uniformly treated products can thereby be produced with very low-cost technologies such as dipping or soaking. Conventional chemicals such as waterborne inorganic chromated copper arsenate (CCA) and ammoniacal copper zinc arsenate (ACZA) may be useful for pretreatment of wood. These formulations strongly bind to the wood and leave a clean, paintable surface.

One drawback of pretreatment is the possibility of chemical interference with gluing processes and associated bond-strength development during the hot-pressing stage of manufacture. Bivalent metallic ions such as copper are known to catalyze the polymerization of phenol-formaldehyde (PF) adhesives (presently the predominant adhesives used in North America), which may produce much faster interaction of the aldehyde with the phenol (Pizzi 1983). Copper in CCA and ACZA might thus affect adhesive penetration and the subsequent strength development of bonds between treated wood surfaces. In the present study, the effect of chemical pretreatment on the isothermal shear-strength development of small (15 mm wide \times 4 mm overlap) PF adhesive-to-wood bonds was investigated.

It is important to realize from the outset that the bonds formed and tested in this study do not directly correspond to those that occur during the manufacture of any specific product type. This is neither in terms of adherend surface texture and fiber juxtaposition nor the physical conditions to which they are exposed during bond formation. To reliably reproduce such complex conditions experimentally would be very difficult. Indeed, the fluctuations in localized stress intensity and strain that occur during the pressing of composite products—whether fiber-, particle-, or veneer-based—differ greatly within the product. Furthermore, the very nature of such variations depends upon the type of product being pressed. This complexity is in part a consequence of the diverse rheological behavior sustained by the wood components (Bolton et al. 1989; Suchsland 1962) which is, in turn, dependent upon the

unsteady-state migration of heat and moisture (Humphrey and Bolton 1989).

In the absence of any reliable means of reproducing the above complexity of bond formation, a standardized set of bond-forming and testing conditions was established for this and related (Kreber et al. 1993) studies. These standards enable the relative impact of selected variables associated with a particular adhesive-adherend combination to be explored while all other variables are held constant. In the present study, for example, the chemical treatment of adherends varied, but a pressing temperature of 95 C and pressure of 1.5 MPa were employed throughout, and all lap-shear bonds were formed with fibers running parallel to one another in each of the adherends. The rationale for these choices is considered in sections to follow.

MATERIALS AND METHODS

One thousand pieces of Sitka spruce [*Picea sitchensis* (Bong.) Carr.], each 0.8 \times 15 \times 150 mm, were conditioned to 12% moisture content (MC), then pressure-treated with CCA Type C or ACZA prepared according to the standards of the American Wood-Preservers' Association (1992). Solutions were prepared at concentrations of 0.25, 0.50, 1.00, and 1.50% (oxide basis). Each solution was applied to 100 pieces, and an additional 200 pieces received no treatment. The wood was submerged in the appropriate solution and treated through a modified Bethell process, wherein a vacuum (12 KPa absolute pressure) was drawn for 30 min, followed by a 1-h pressure period at 880 KPa. The treated wood specimens were blotted dry to touch and stored under cover for 24 h to retard drying and permit fixation reactions to proceed. They were then stacked and conditioned in an atmosphere of 65% relative humidity and 21 C until they equilibrated to a constant weight.

Phenol-formaldehyde resin (Type BB-005, Reichhold Ltd., Tacoma, WA) was prepared in accordance with the manufacturer's guidelines. Test specimens were placed in matched

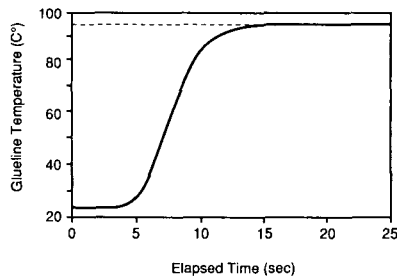


FIG. 1. A typical glue-line heating curve (measured by inserting a miniature thermocouple probe into a bond that was formed but not tested).

pairs according to chemical type and concentration level (50 pairs of each chemical at each of four concentrations and 100 untreated pairs). A technique developed by Humphrey and Zavala (1989) and modified by Humphrey (1993) was followed to form and test bonds. Each specimen was coated with adhesive on one surface of one end over a 15- \times 4-mm area. Each pair of specimens was lapped together and placed in a testing device that simultaneously applied heat (95 C) and pressure (1.5 MPa) to the overlapping region via heated steel blocks (Humphrey 1993). The use of a slight excess of adhesive and a constant loading pressure during bond pressing resulted in a near-constant 100 g of adhesive-per-square meter in the glue-line; any surfeit adhesive tended to be squeezed out. Because the wood specimens were thin (0.8 mm), heat was rapidly transferred to the glue-line, which created near-isothermal conditions for much of the bond-pressing period. A glue-line heating curve (Fig. 1) shows that the target temperature (within 1 C) was reached in 20 sec.

After a selected curing time, bond pressure was reduced, the free ends of the specimens were gripped, and the bond was loaded (at a rate of approximately 1.2 MPa/sec) to failure in shear mode. Forming time and shear strength were automatically recorded for each bond. For each chemical treatment and target retention level, at least 10 bonds were tested over a range of pressing times (10 to 300 sec); this enabled a near-isothermal strength-development plot to be constructed for each sample type.

In this technique, the transition from bond-forming (press fully closed) to bond-testing (press released and bond pulled) was intentionally short (< 1 sec); the bonds were, therefore, tested at the pressing temperature. Cooling prior to testing would have introduced unacceptable inaccuracies since polymerization could not be halted instantaneously and stresses could have been introduced into the bond. In any event, it was the possible impact of chemical pretreatment on composite manufacturing efficiency (hot-pressing) that was a primary concern in the investigation, rather than final product properties (although there assuredly is a link between the two). Minimum press time in industry is in part determined by the ability of partially cured bonds in the composite to withstand stresses transferred to them upon press opening—when the adhesive is hot (Humphrey and Ren 1989). This rationale is discussed further by Humphrey and Zavala (1989).

After testing, 15-mm-long sections were removed from the non-bond ends of 10 selected specimens from each treatment. There were ground to pass an 800-mesh/m screen. The ground wood was analyzed for preservative content with an ASOMA 8620 X-ray fluorescence analyzer (ASOMA Instruments, Austin, TX).

RESULTS AND DISCUSSION

Chemical retentions (dry chemical per unit volume of oven-dry wood) ranged from 2.62 to 14.03 kg/m³ for CCA-treated veneers and 4.10 to 15.71 kg/m³ for the ACZA-treated veneers (Table 1). The American Wood-Preservers' Association standards (1992) require 6.4 kg/m³ for plywood in ground contact and 9.6 kg/m³ for plywood panels used in permanent wood foundations. Thus, the treatment levels provide a range of retentions that encompass those commonly used commercially.

Families of bond strength versus pressing time data curves for the two types of chemical treatments at the range of treatment levels are shown in Fig. 2a, b (CCA and ACZA, respectively). Taking bond-strength development

TABLE 1. Average preservative retention of Sitka spruce pieces treated with selected concentrations of ACZA or CCA as determined by X-ray fluorescence spectroscopy.

Solution concentration (%) (oxide basis)	Retention (kg/m ³)				Total
	CrO ₃	CuO	As ₂ O ₅	ZnO	
CCA					
0.25	1.37	0.44	0.81	—	2.62
0.50	2.68	0.89	1.79	—	5.35
1.00	4.85	1.60	3.67	—	10.20
1.50	6.68	2.30	5.06	—	14.03
ACZA					
0.25	—	2.56	0.53	1.01	4.10
0.50	—	4.16	0.99	1.57	6.72
1.00	—	6.98	1.79	2.53	11.30
1.50	—	9.47	2.77	3.47	15.71

data for all treatment levels together, a well-defined increase in shear strength with time was evident when isothermal conditions were approached. Strength development that was apparent within the first 15 sec of pressing was attributable to tack of the adhesive and to some

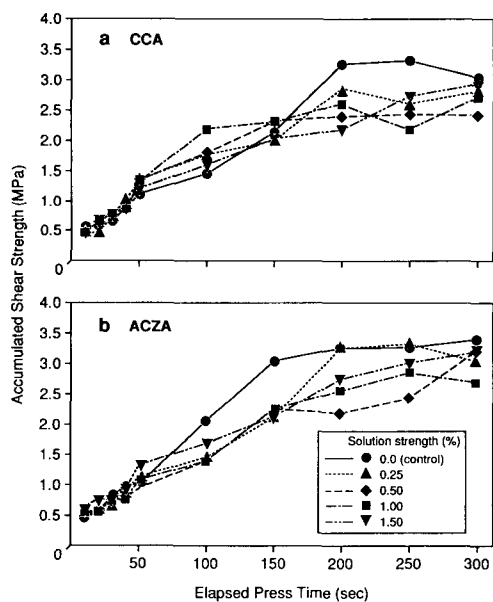


FIG. 2. Shear-strength development of Sitka spruce to phenol-formaldehyde test bonds in wood pretreated with (a) chromated copper arsenate and (b) ammoniacal copper zinc arsenate for varying time periods at 95 C and a pressure of 1.5 MPa.

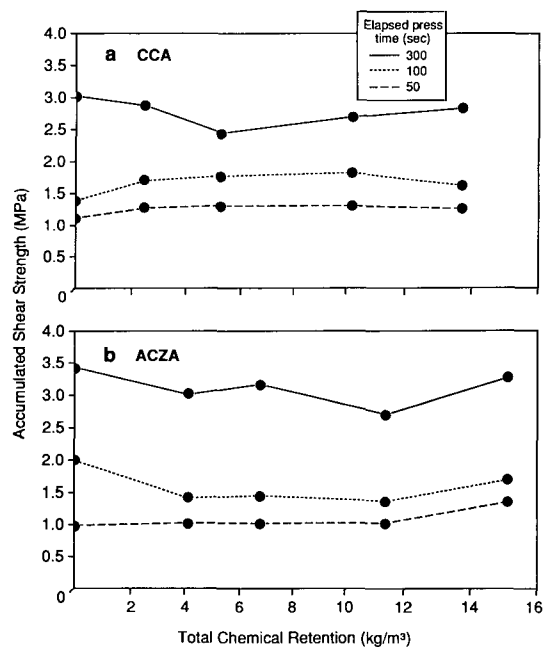


FIG. 3. The effect of chemical retention on bond strength at three stages (50, 100, and 300 sec) during the pressing of test bonds between adherends pretreated with (a) chromated copper arsenate and (b) ammoniacal copper zinc arsenate.

mechanical interlocking of the adherends. Conversely, beyond about 250 sec of pressing, strength development showed a marked decrease, and by 300 sec it had all but ceased.

Shear-strength development of bonds formed between both ACZA- and CCA-treated pieces differed little from those found when untreated control pieces were used. This was clear when chemical retention was plotted against bond strength for three arbitrarily selected pressing times (50, 100, and 300 sec) (Fig. 3a, b). No significant correlation was found to exist between strength and chemical retention at any stage in the bond-pressing process.

Using a similar apparatus, Kreber et al. (1993) found that borate pretreatment significantly increased the rate of shear-strength development between pieces of Sitka spruce. Other studies have suggested that increasing the concentrations of CCA in pretreated veneers adversely affects shear strength of ply-

wood made from that material (Thompson 1962; Bryant 1968; Choong and Attarzedah 1970; Hutchinson et al. 1977); however, no such effect on the rate of shear-strength development was found in the present study. Chromium and copper in the treated wood were expected to accelerate the rate of adhesive curing in comparison to untreated controls; both of these chemicals, however, undergo a series of fixation reactions that may reduce their accessibility to the adhesive.

Although the approach of Humphrey and Zavala (1989) is best suited to exploring the early stages of adhesive cure, the present tests were conducted with a bonding overlap sufficiently small (4 mm) to enable ultimate strengths at elevated temperature to be explored (large overlaps result in bonds that have tensile strength greater than that of the adherends themselves, which were only 0.8 mm thick). The results also suggest, therefore, that neither CCA nor ACZA treatment produced any clearly detectable effect on this strength property.

Previous studies have shown that modest retentions of ACZA have little effect on the shear strength of panels made with aspen veneers, although the percentage of wood failure was seen to decrease (Boggio and Gertjeansen 1982; Vick et al. 1990). Our results, at much higher chemical loadings, indicated that this trend in strength properties also occurs with conifers. It did not, however, prove practicable to assess bonding quality in terms of "percentage wood failure" since adherends were overlapped, with fiber directions in each adherend running parallel to one another. Mechanisms of wood failure for well-cured bonds proved difficult to interpret reliably. This precluded comparison of wood failures with those from other studies (where adherends are normally juxtaposed at right angles).

Core temperatures in commercial pressing operations exceed 95 C in the later stages of the pressing cycle. Our use of a lower temperature did, however, enable well-defined bonding rates to be detected after the test-bond warm-up period (up to 20 sec) had lapsed. The

effect of a range of curing temperatures on strength development rate may be the subject of a future study. A comparison of rates at one moderate temperature, however, provides a useful indication of chemical compatibility, although it cannot be assumed that the chemicals' influence is entirely independent of curing temperature.

Bond shear-strength development appears unaffected by moderate loadings of CCA or ACZA (such as the concentrations used in this experiment). This lends weight to the assertion that it is technically feasible to fabricate composite panels and the like from wood elements treated with either of these chemicals.

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