THE EFFECT OF ACETYLATION ON THE SHEAR STRENGTH DEVELOPMENT KINETICS OF PHENOLIC RESIN-TO-WOOD BONDS[1]

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ABSTRACT

Chemical pretreatment of materials used in wood-based composite products before lay-up and pressing has some advantages over the post-treatment of panels. However, pretreatment may affect the relationship between temperature and strength development rate of adhesive bonds (as well as final strengths). Such relationships affect minimum pressing times and the consequent economic viability of panel production. Acetylation is a possible chemical pretreatment. The effect of acetylation level on the strength development rates of small phenol-formaldehyde-to-wood test bonds was therefore investigated. Pieces of maple (*Acer macrophyllum* Pursh) measuring 0.8 × 20 × 106 mm were acetylated with acetic anhydride at 120°C to achieve weight percentage gains of 8.17, 11.62, and 14.49. Bonds were formed at pressing temperatures of 86°C, 97°C, 107°C, and 113°C for a variety of times and were immediately thereafter tested in shear mode. An automated bond formation and evaluation system (ABES) was used for this purpose. Four near-isothermal bond strength development curves were constructed for each acetylation level. The curves suggest differences in shear strength development rates at the early stages of bond development. Linearly regressed early rates were affected by both temperature and acetylation level, although the effect of acetylation level was small. Cold and fully cured bond strengths were impaired by acetylation; this is consistent with others' findings.

Keywords: Acetylation, bond strength development, pressing temperature and pressing time, phenol formaldehyde.

INTRODUCTION

Dimensional instability and susceptibility to biodegradation are critical limitations of wood-based composite materials exposed to weather. It is, however, well known that these limitations may be partially overcome by chemically modifying the walls of the wood cells. Acetylation decreases the hygroscopicity of wood cell-wall material and increases its dimensional stability and bioresistance. When assembled panel products are so treated, op-timal penetration by the active chemical may not be achieved, and the process can induce strength loss, excessive swelling, delamination, and distortion during redrying after the treatment. As an alternative to treatment of whole panels, veneers, flakes, particles, or fiber bundles may be chemically treated prior to being layed-up, thus allowing quite uniformly treated composite products to be produced.

Acetylation is widely acknowledged as a candidate chemical treatment method. Stamm and Tarkow (1947) were among the first to acetylate whole wood pieces with acetic an-

hydride. Wood acetylated to weight gains of around 17% was found to be highly resistant to fungal and termite attack (Goldstein et al. 1961). Furthermore, antishrink efficiency of about 70% has been achieved with wood weight gains of 20–25% (Tarkow et al. 1950). A number of workers have subsequently explored the applicability of acetylation (Rowell et al. 1986; Sheen 1992).

Acetylation has the generally advantageous effect of decreasing the hygroscopicity of wood cell-wall material (Rowell 1982); one hydroxyl group is blocked for each acetyl group with which it reacts. Acetylation may consequently, however, also decrease the number of hydrogen bonds formed between wood and adhesives and thereby interfere with the adhesion process which is all-important in wood-based composites manufacturing. Indeed, it is reasonable to expect that reduced availability of hydroxyl groups may decrease bond strength development *rates* as well as final bond strengths. Acetylation may impair the hydrophilic nature of the wood substrate, reduce its wettability, and thus lead to poor adhesive penetration and bonding (Humphrey 1997; Rowell and Banks 1987; Gollob and Wellons 1990). Chow et al. (1996) observed that the mechanical properties (including internal bond strength) of hardboard produced from acetylated fibers with resol phenol-formaldehyde adhesive were lower than those of panels produced from normal fibers with it.

On the other hand, it is known that small esters accelerate the curing of phenol-formaldehyde adhesives of the resol type (Pizzi 1994). Wood acetate created by acetylation may hydrolyze during pressing to produce acetate. This, in turn, can accelerate the polymerization of resol PF adhesives and may therefore enhance cohesive strength development. Furthermore, Gomez-bueso et al. (1996) observed that the mechanical properties (including internal bond strength) of fiberboards made from acetylated fibers with PF adhesive of the novolak type were higher than those produced from normal fibers with novolak PF adhesive.

Bearing in mind the possible localized effect of acetyl groups on wood-adhesive bond formation as discussed above, it is reasonable to expect that such modification may affect the *rates* of strength development of bonds within a composite during their formation, as well as their ultimate strengths. The former (bonding rates) are of primary concern in the present work. The effect of temperature on the strength development rates of bonds influences the interaction of mechanisms during the pressing of composites (particularly rheological mechanisms and stress relaxation). This, in turn, is likely to influence minimum pressing times. During pressing, the press may be opened only when bonds have accumulated sufficient strength to counter destructive stresses such as those resulting from internal vapor pressure and residual elasticity of the deformed wood elements (Bolton and Humphrey 1988). If a chemical pretreatment is to be viable, therefore, it is important that strength development rates, which affect intermediate levels of bonding, are not greatly decreased. Alternatively, if rates are affected, then it may be feasible to tailor the pressing operation to such characteristics. In either case, it is important to quantify the effect.

The present work therefore explores bonding characteristics for the candidate pretreatment of acetylation. An aim is to evaluate the effect of acetylation level (various weight percentage gains) on subsequent strength development rates of small, standardized test bonds formed under a range of near-isothermal conditions. This study was carried out in light of the above discussion with a view to qualitatively predicting the likely response of bonds between particles, flakes, or veneers under the range of temperature conditions that typically occur locally within core layers of panels during the hot pressing operation. Such evaluation may increase our understanding of the mechanisms affected by acetylation and point to ways of tailoring adhesives for use with acetylated wood elements. Of primary concern here is the effect of acetylation on the pressing operation rather than on the strength properties

of finished products. For this reason, the strength of partially cured bonds has been investigated; the strength of fully cured panel products made with resol PF adhesive is already known to be somewhat reduced by acetylation (Youngquist and Rowell 1986; Chow et al. 1996).

MATERIALS AND METHODS

Wood samples

Sliced maple (*Acer macrophyllum* Pursh) veneers (0.8 mm thick) were cut into strips 20.0 × 106.0 mm. These pieces were conditioned at 25% relative humidity (RH) and 44.5°C to a moisture content of 2.6%. No attempt was made to control growth ring orientation on the surfaces of the pieces, although longitudinal cells ran lengthways (in the 106.0-mm direction).

Acetylation

Acetylation was carried out in closed stainless-steel reaction vessels (245.0 mm high by 53.0 mm diameter internally). The vessels were each loaded with acetic anhydride (99.4% purity level) and 12 conditioned and preweighed wood samples (supported and separated in a specially designed polytetrafluoroethylene frame). The prepared vessels were placed in a preheated oil bath (120°C) for 1, 2, or 4 h, this temperature was a compromise between optimizing reaction speed and avoiding the danger of thermo-chemical degradation of the wood samples. The reaction vessels were agitated (sinusoidally oscillated at a frequency of 1 Hz) in order to hasten heat transfer and also to maximize chemical interaction with the wood surfaces. Figure 1 shows a typical heating curve for the treatment solutions (initially at room temperature) upon immersion in the oil bath.

Following treatment, the acetylated samples were washed twice at room temperature with xylene and then washed twice with water at room temperature to remove excess reagent and by-products of the reaction. The weight percentage gain (WPG) (oven-dry basis) due
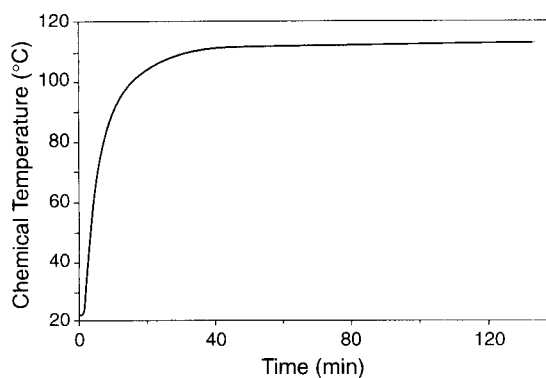

FIG. 1. The relationship between immersion time in oil bath (120°C) and temperature of solution in treatment vessels.

to acetylation was calculated for premarked samples that were assumed representative of all pieces. Weight percentage gains of 8.17 (SD 0.36), 11.62 (SD 0.43), and 14.49 (SD 0.56) were found after 1, 2, and 4 h of acetylation, respectively. Totals of 150 control and 450 acetylated samples were dried at 25% RH and 44.5°C and then conditioned to constant weight in an environment of 45% RH and 21°C.

Bond pressing and testing sequence

The variously treated and conditioned strips were used to assess the effect of acetylation on the shear strength development characteristics and final strengths of bonds of PF adhesive to wood. For this purpose, an automated device developed by Humphrey and Zavala (1989) and subsequently refined by Humphrey (1993, 1996) was used to form test bonds for several times and temperatures and to measure their strength in shear mode. The principal functions of the device are schematically represented in Fig. 2. The approach allows determination of the shear strength accumulation of small lap-shear bonds formed under controlled pressure and a range of almost isothermal conditions (between ambient temperature and 150°C).

A commercially available precatalyzed and filled PF adhesive of the resol type formulated for use in laminated veneer lumber production
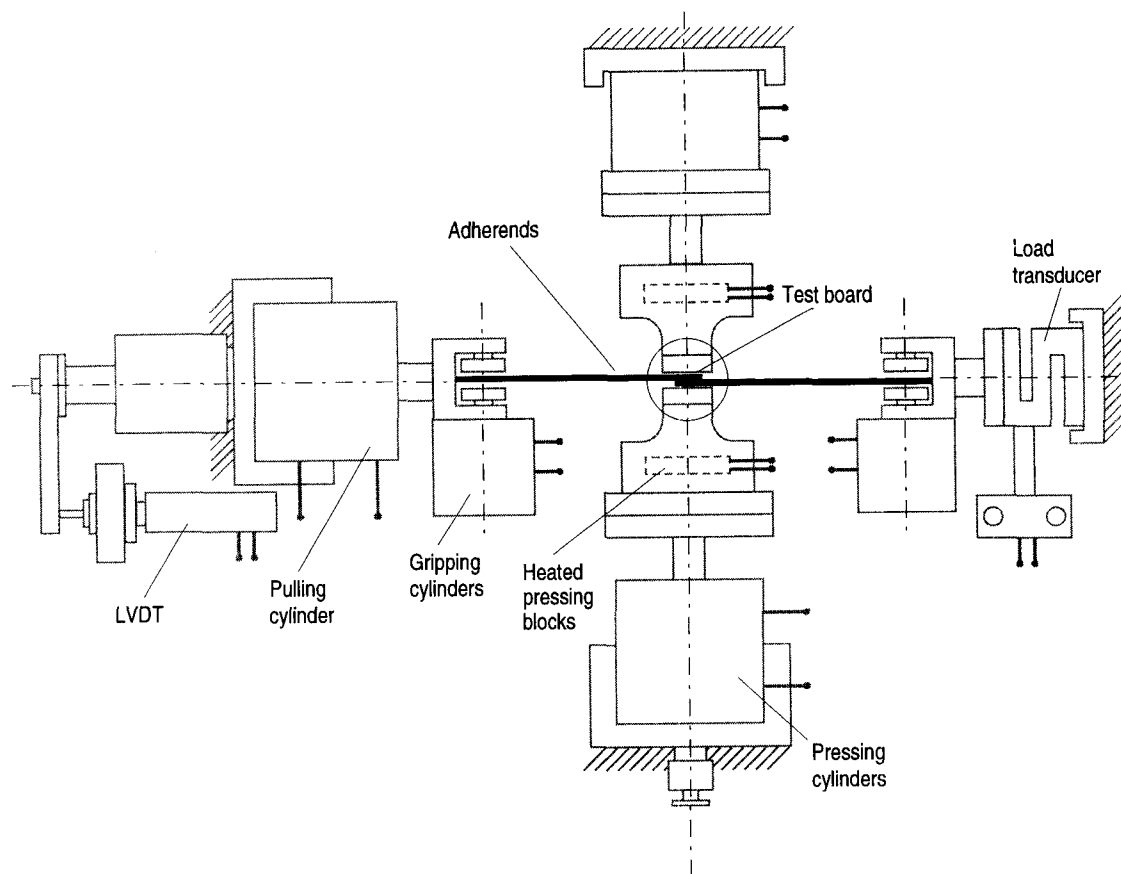
FIG. 2.   Schematic showing principal functions of a system used to form and, immediately thereafter, test adhesive bonds between thin wood samples.

(kindly donated by Georgia-Pacific Resins, Inc.) was used throughout the tests.

To form each bond, one surface of one end of each wood strip was coated with adhesive over a 20 × 3-mm area. A pair of strips were lapped together and placed in the testing device (3-mm overlap), which simultaneously applied heat and pressure to the overlapping region via heated steel blocks. A bonding pressure of 1.4 MPa was used for all tests. The use of a very slight excess of adhesive and a constant pressure during bond pressing meant that a small amount of "squeeze-out" occurred, and the remaining adhesive was almost constant among bonds (approximately 0.1 kg/m²). Furthermore, heat transfer into the glue-lines was rapid because the wood samples

were thin; this created near-isothermal conditions throughout most of the bond pressing period. To quantify the variation in temperature at the gluelines, miniature thermocouple junctions were placed in supplementary bonds that were formed (pressed) but not tested (pulled). A family of typical glueline heating curves is shown as Fig. 3; this demonstrates that target temperatures (± 1°C) were reached after approximately 8 s.

After a preselected curing time, bond forming pressure was reduced, the free ends of the specimens were gripped pneumatically, and the bond was pulled to effect failure in shear mode. Forming time and shear strength (corrected for bonding area) were automatically recorded for each bond.
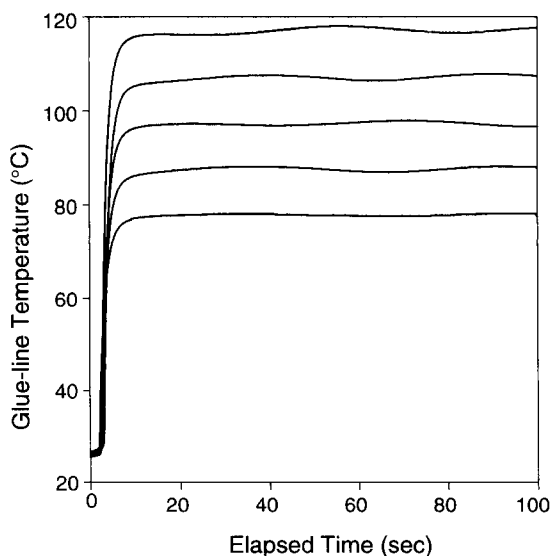
FIG. 3. Glueline heating curves for five bond pressing temperatures (measured by inserting miniature thermocouple probes into bonds that were formed but not tested).
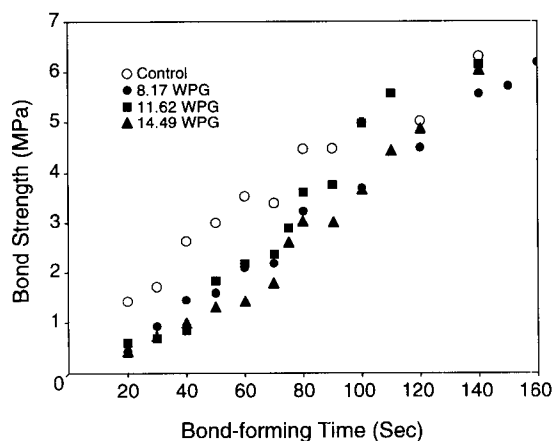

FIG. 4. A typical set of data for isothermal bond strength development versus forming time. Untreated maple samples and those treated with acetic anhydrate long enough to cause three levels of weight percentage gain (WPG) were bonded with phenol-formaldehyde resin at 107°C and a pressure of 1.4 MPa. The scatter and form of data for bonds formed at other temperatures were similar.

Bonds were formed at four pressing temperatures. For each WPG and temperature, at least 12 bonds were tested over a range of pressing times (20 to 650 s at 86°C, 20 to 350 s at 97°C, 20 to 160 s at 107°C, and 20 to 100 s at 113°C).

In a supplementary experiment conducted to verify the effect of WPG level on the ultimate (fully cured) cold strength of bonds, four bonds were formed for each WPG level (including a control with no acetylation treatment). These bonds were pressed at a glueline temperature of 113°C for 200 s. It was assumed that such bonds were fully cured but that thermal degradation was unlikely to have begun. Following conditioning at 45% RH and 21°C, the strength of these bonds was also tested.

RESULTS AND DISCUSSION

Figure 4 shows a typical set of accumulated shear strength values for bonds formed at 107°C and at various treatment levels. The scatter of data for other temperatures and treatment levels is similar to that implicit in Fig.

4; therefore, not all graphs are included. It is evident that at the early stages of cure, bonds formed between acetylated pieces were always weaker than those formed between untreated control pieces. Figure 4 also shows, however, that although the differences are difficult to described numerically, they do decrease with further pressing. This result suggests that even modest levels of acetylation affect the earliest stages of bonding, but that these effects decrease when bonds attain higher strengths.

Regression of data for bond strength versus time for specific combinations of temperature and WPG allows isothermal bond strength development rates to be calculated. Figure 5 shows the variation of such rates with temperature for a range of WPG values. These regressed rates are based on data for the early stages of bonding. It is evident from Fig. 5 that pretreatment with acetic anhydride decreased the rates of bond strength development at all temperatures. However, the effect of the level of treatment on development rate is negligible. This finding is consistent with the hypothesis that adhesion depends only on surface modifi-
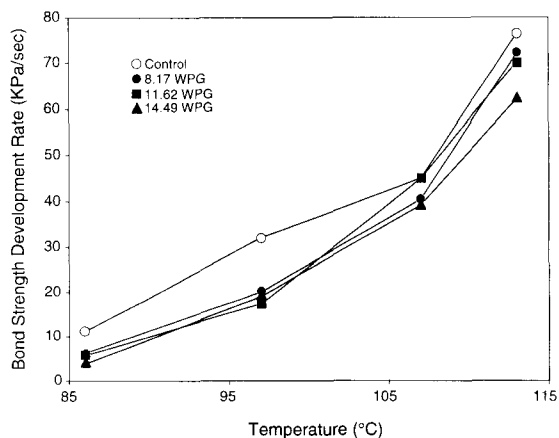
Fig. 5. Regressed bond strength development rate versus forming temperature for the four acetylation treatment levels (based on weight percentage gain (WPG)). Regressed rates are for the early stages of curing (20 to 300 s at 86°C, 20 to 170 s at 97°C, 20 to 80 s at 107°C, and 20 to 50 s at 113°C).
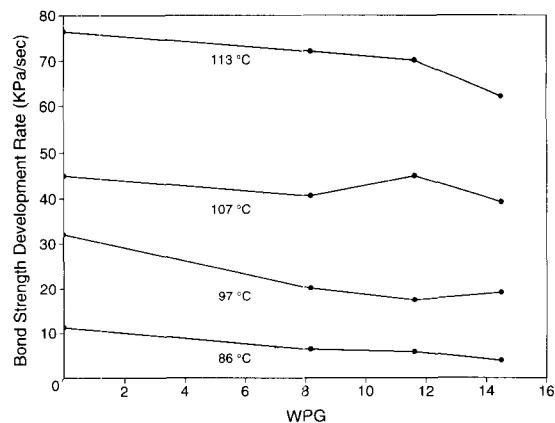

Fig. 6. Acetylation treatment level (WPG) versus regressed bond strength development rate for the four pressing temperatures. (Regressed rates are the same as those in Fig. 5).

cation; surface modification may not vary with higher bulk treatment levels.

The effect of treatment level (WPG) on bond strength development rate at different temperatures is shown in Fig. 6. This family of curves suggests that acetic anhydride pretreatment has a small negative effect on isothermal bond strength development rate at all four temperatures. This may be due to a reduction in the wettability of the wood substrate. Here, we assume that there is no residual acetic acid by-product that could effect adhesion rates; the acetylated samples were washed twice with xylene and then washed twice with water. If, however, after such washing some acetic acid *did* remain, this may also be a cause of the reduced adhesion rate that has been detected.

Bonds in the main study were formed (pressed) and tested (pulled) while at the same temperature in order to explore rate effects. However, Fig. 7 shows the effect of acetic anhydride treatment level on the cold (21°C) strength of fully cured bonds. At 8.17 and 14.49 WPG, the mean strengths of such bonds were 18 and 25% lower than the control, respectively. In previous studies, Youngquist

and Rowell (1986) observed impairment of internal bond strength and other strength properties in acetylated aspen flakeboard, and they assumed that this was due to lack of wetting and penetration of the glue in the acetylated flakes. Vick and Rowell (1990) also found lower levels of shear strength in acetylated than in nonacetylated strips of yellow-poplar (*Liriodendron tulipifera* L.) sapwood bonded with PF adhesive. The finding of this research agrees with these works.
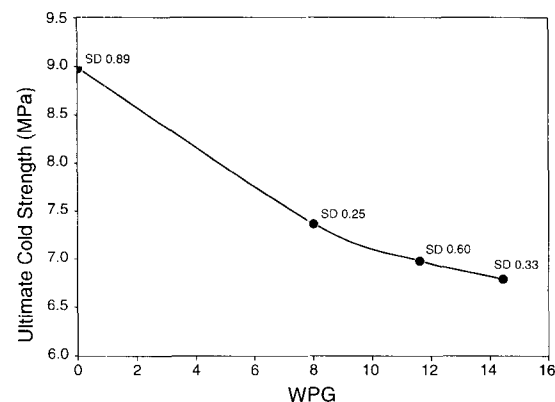

Fig. 7. Acetylation treatment level (WPG) versus cold strength of fully cured bonds.

CONCLUSIONS

This study investigated the effect of acetylation and its level on subsequent strength development of PF-resin-to-wood bonds formed under a range of nearly isothermal conditions. The bond strength development plots show considerable scatter (variability); this is probably due to wood surface treatment variability. In spite of this scatter in the data, the bond strength development plots show differences between acetylated and untreated adherends. These differences are most evident at the early stages of bond development and are all but negated at higher pressing times. Linearly regressed early rates of strength development are affected by temperature, but the effect of the level of acetylation is small.

The strength of cold and fully cured bonds is affected significantly by acetylation and its level; this is consistent with the findings of others. However, the results of the main part of this study suggest that acetylation has relatively small effects on the curing rates of adhesives at the early and intermediate stages. Therefore, industrial pressing processes for pretreated material may not be greatly limited or hindered. Although acetylation does have some effects on the curing rates of adhesives and their final strengths, it may well prove useful to acetylate materials used in wood-based composites in order to reduce the hygroscopicity and improve dimensional stability and bioresistance of finished panels.

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