THE EFFECT OF SEQUENTIAL AMMONIA AND METHYL FORMATE INJECTION ON THE STRENGTH DEVELOPMENT OF PHENOL-FORMALDEHYDE BONDS TO WOOD

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ABSTRACT

It has been reported in a companion paper that gaseous anhydrous ammonia may readily penetrate compressed wood fiber mats and that subsequent cell-wall softening is very rapid. Literature also shows that alkaline catalyzed phenol-formaldehyde (PF) resins of the resole type are stable at pH levels above nine. Methyl formate has, however, been shown to accelerate the rate of PF cross-linking, and its volatility (sea level boiling temperature 33°C) makes it well suited to vapor phase injection into resinated mats at near ambient temperatures. It was hypothesized at the outset of the reported investigation that mats may be treated with gaseous ammonia to affect softening without stimulation of resin cure, and that the PF could be subsequently catalyzed with methyl formate in the vapor phase. Before adopting this strategy in a sealed pressing system, the strength development characteristics of miniature PF-to-wood bonds exposed first to ammonia and then to methyl formate were explored. Bond formation and testing were conducted with an Automated Bonding Evaluation System (ABES) equipped with a computer-controlled fluid injection accessory. Results, in the form of room-temperature strength development plots, show that ammonia does not greatly stimulate PF cure (1.65 MPa after 600 s), but application of methyl formate significantly hastens strength development (3.5 MPa after 150 s). These results are aiding in the development of techniques for the rapid room-temperature formation of strong and dimensionally stable fiber composites using sealed pressing with sequential chemical injection.

Keywords: ABES, chemical injection, phenol-formaldehyde.

INTRODUCTION

High performance engineering components of the future may be formed from natural fibers by controlling the spatial distributions of chemical and thermodynamic environments within preformed mats during their consolidation. Much may be gained by taking proactive control of the sequencing of rheological mechanisms (densification and stress relaxation) and adhesion during such consolidation processes. Ideally, only when the microstructure of composite objects has been

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fully established and stresses largely relaxed should adhesion between the natural fiber elements be triggered. A sealed pressing system to affect such control has been developed (Chowdhury and Humphrey 2005; Chowdhury 1999). The pressing system has provision for: (1) dynamic control of uniaxial compressive stress, (2) sequential injection and removal of chemical reactants in the vapor phase, (3) full peripheral sealing, (4) controlled heating, and (5) internal sensing of material conditions. The development of adhesion under the sequence of chemical conditions that occur at bonding sites in the composite is an important factor in affecting transitional and final bonding, and this is the subject of the present report.

LITERATURE

Davidson (1968) reported that plasticization of wood is possible by treating it with anhydrous ammonia at room temperature and partial pressure of 0.99 MPa. Bariska et al. (1969) and Davidson and Baumgardt (1970) also reported that plasticization of wood was possible by treating it with gaseous ammonia when the relative vapor pressure of the gaseous ammonia was close to saturation. Most studies have been conducted on solid wood, and rates of plasticization were found to be rather low. Results of tests conducted by Chowdhury and Humphrey (2005) do, however, suggest that softening speeds for fiber networks may be much faster. For this purpose, circular air-formed mats (Douglas-fir medium density fiberboard furnish) of 97-mm diameter, 20-mm thickness, and 10% moisture content (MC) were compressed in a sealed pressing system under a range of loading conditions and ammonia treatment cycles.

A typical response of a mat to the injection of ammonia is shown as Fig. 1. The sample was prepressed to 18-mm thickness, and then the pressing chamber was evacuated. The mat was then compressed to a thickness of 5.00 mm (corresponding to a target density of 525 kg/m^3 on an oven-dry weight basis) at a closing rate of 1 mm/s. After a delay of 76 s (to allow natural stress relaxation to stabilize partially), ammonia
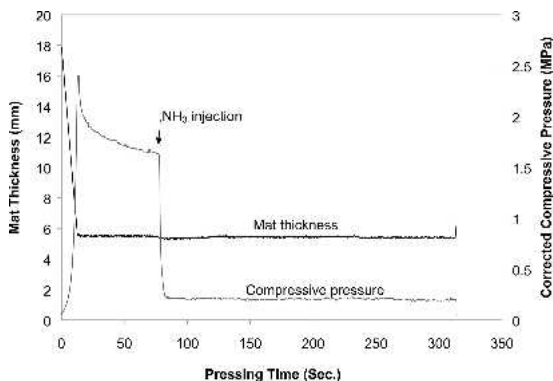

FIG. 1. Compressive pressure versus time during sealed pressing of a fiber mat to constant density of 525 kg/m^3 with ammonia injection after 76 s of press closure (from Chowdhury and Humphrey 2004).

gas was injected at a pressure of 0.42 MPa. Evident in Fig. 1 is an almost instantaneous drop in compressive pressure necessary to maintain press position. The sequencing of ammonia pressure and associated compressive pressure reduction is also shown in Fig. 2. This result suggests both that the ammonia gas easily penetrates the compressed fiber mat and that softening of the fiber walls is very rapid. A range of similar experiments were conducted to explore the effects of ammonia concentration and treatment time on softening of compressed fiber mats.

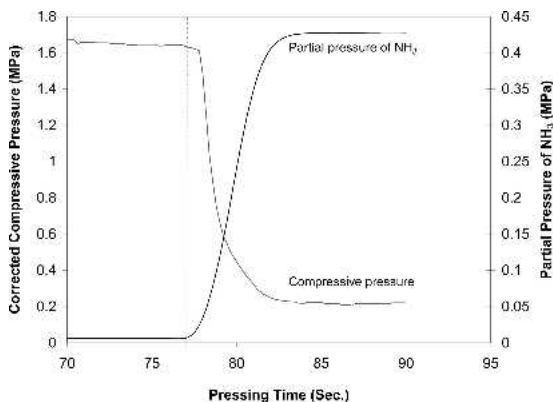In the absence of a convenient means of trans-

FIG. 2. The variation of mat counter-pressure and internal gas pressure during ammonia gas injection (corresponding to the data of Fig. 1).

porting an adhesive system into the fiber mat in the vapor phase during pressing in the sealed pressing system, and considering that NH_3 may be used as a softening agent, adhesive was added before mat formation. The following discussion explores the use of alkaline catalyzed PF adhesives in such an application.

It is well accepted that the curing rate of alkaline catalyzed PF resins increases with pH (Pizzi 1983; Skeist 1977). This is due to an increase in the functionality of phenolic nuclei as nucleophiles, which is a consequence of the ionization of the phenol to the phenate ions as shown in Fig. 3. Pizzi and Stephanou (1994a) found, however, that under very high pH conditions, the reaction and curing behavior of alkaline catalyzed PF resin markedly slows instead of accelerating as previously assumed. In the foundry industries, very alkaline PF resins are used to bind sand. Esters such as propylene carbonate, methyl formate, and glycerol triacetate are added in the liquid (called α-set) or vapor (called β-set) phases to accelerate the rate of curing of the resin at room temperature (Lemon 1990). Pizzi and Stephanou (1994b) measured gel times of alkaline catalyzed PF resins at 94°C after addition of methyl formate, propylene carbonate, glycerol triacetate, and phenyl acetate at pH 11.26. It was found that with increasing addition of an ester, curing speed increased correspondingly.
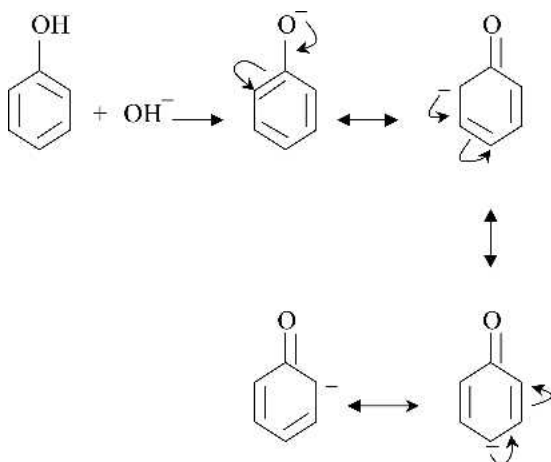

FIG. 3.   Ionization of phenol to form phenate ions.

Propylene carbonate (boiling point 87°C) stimulates very fast curing at relatively low concentrations, but at higher concentrations the effect decreases. Methyl formate (another ester, boiling point 33°C) also shows very good curing acceleration, and its higher volatility makes it better suited to vapor phase injection into porous fiber mats at near ambient temperatures. From the above discussion, it is clear that alkaline catalyzed PF resins are stable at high pH. It may therefore be possible to treat PF pre-dosed fibers with gaseous ammonia for softening while avoiding the stimulation of resin cure, and subsequently catalyze the resin with methyl formate in the vapor phase.

The objective of the present study was to evaluate the effect of gaseous NH_3 and methyl formate (MeF) on the strength development of miniature standardized test bonds formed at room temperature. The study was carried out with a view to predicting the response of bonds between PF-resinated fibers in the sealed pressing system under development.

MATERIALS AND METHODS

Materials

Wood strips.—Sliced maple (*Acer macrophyllum* Pursh) veneers (0.7 mm thick) were cut into strips 25.0 × 120.0 mm with the aid of a pneumatically driven sample cutter. Care was taken to maximize uniformity among them, though no attempt was made to control growth ring orientation on the surfaces of the pieces; longitudinal cells ran lengthways (in the 120.0-mm direction). The pieces were conditioned at 40% RH and 21°C to a moisture content of 7.5% (± 0.5%).

Adhesive.—A commercially available alkaline catalyzed phenol-formaldehyde (PF) adhesive of the resole type (pH 12) kindly donated by Borden Chemical, Inc. of Springfield, Oregon, was used in this research. This has a solids content of 60%, a viscosity of 2,200 centipoise at 21°C, and was not extended.

Bond formation and testing

An Automated Bonding Evaluation System (ABES) equipped with a gas injection accessory (Humphrey 1993, 1999) was used to evaluate the effect of the sequential application of NH_3 and MeF on wood-PF resin bond strength development. This system is summarized below.

The automated bonding evaluation system.— The principal parts of the ABES are shown as Fig. 4. The instrument enables the strength development characteristics of a variety of adhesive and adherend combinations to be explored. In its standard format, it enables the effect of temperature on the strength development rate of thermosetting adhesives to be characterized at temperatures ranging from ambient to 200°C.

Small adhesive bonds are formed in the ABES under highly controlled conditions of temperature, pressing load, and time. Almost immediately after each bond is cured to the required level, it is tested to destruction in shear mode. Tensile load and gripping head movement (sample elongation) are monitored digitally during bond pulling, and shear-stress-to-failure (area-corrected peak load) is calculated (Humphrey 1999). Repetition of the bond forming and testing procedure for a range of pressing times (while holding temperature constant) enables isothermal bond strength accumulation with time to be plotted. Each point on such a plot therefore corresponds to a similar glue bond that has been cured under controlled conditions of temperature, time, and pressure and immediately thereafter pulled to measure its accumulated shear strength. The ABES has provision for computer-controlled cooling of bonds immediately prior to their being pulled. This is achieved with a pneumatically driven and spring-loaded PTFE cooling head.

Fluid injection.—An automated fluid injection accessory was added to the ABES, shown schematically in Figs. 5 and 6. The cooling air supply connections to the PTFE blocks were disconnected: one was connected to a temperature-controlled miniature chemical (MeF liquid) reservoir, and the other PTFE block was connected to a small NH_3 gas container (volume 62.0 cm^3) as shown in Fig. 6. The supply of NH_3 to the bond was controlled with a 2-way valve, while MeF application was affected with computer-control by air pressurization of the reservoir. About 62 cm^3 of NH_3 at 0.41 MPa was applied to each of the selected bonds.

The penetration of NH_3 through the wood was sensed in some supplementary trials by interposing red litmus paper at the bond-line between the wood strips. Equal quantities of chemical were applied to each of the selected bonds. Approximately 0.25 cc of MeF was supplied to each of the selected bonds. Ammonia was seen to readily penetrate the wood. The penetration of MeF was also explored. This was done by putting a drop of the liquid on one surface of a wood strip and observing that penetration through to the other surface was very rapid.
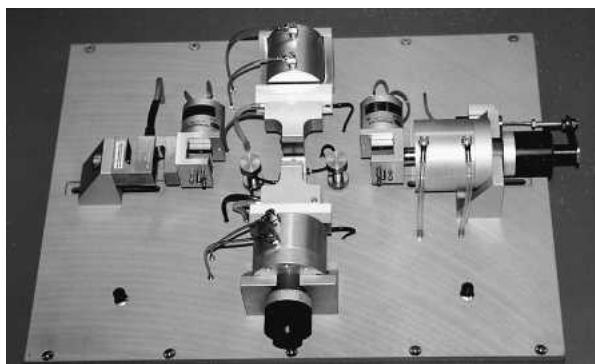

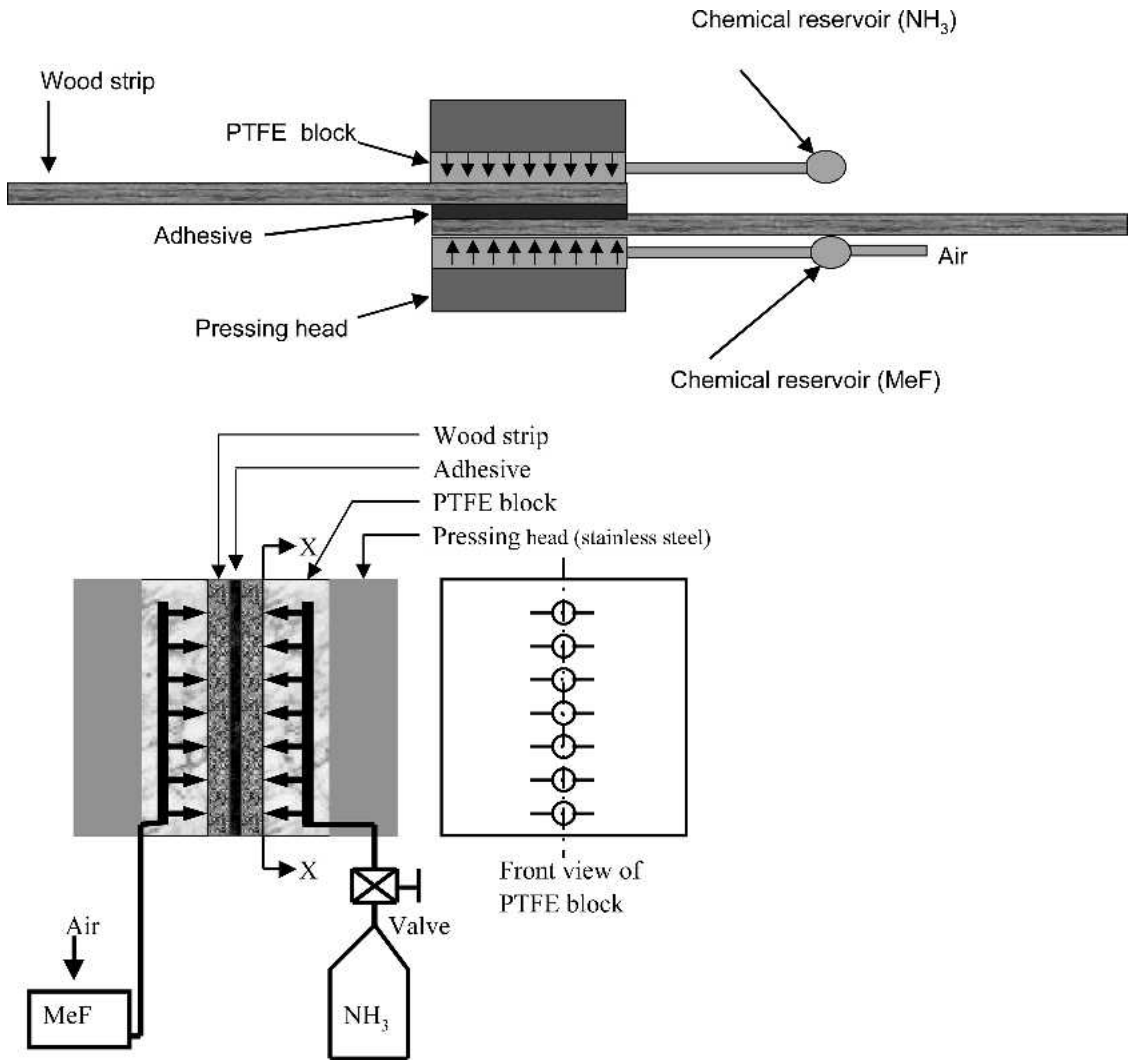FIG. 4.   Principal parts of the Automated Bonding Evaluation System (ABES.)

FIG. 5.   Schematics showing the basic principle of bond formation with chemical injection, and a vertical cross-section of the ABES pressing heads.

Clearly, the chemical is highly polar and also of low viscosity.

Bond pressing and testing sequences.—To form each bond, one end of one surface of one wood strip was coated with adhesive over a 25- × 8-mm area. A pair of strips (one without adhesive coating) were lapped together and placed in the ABES with an 8-mm overlap. A bonding pressure of 1.1 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 8 g/m^2). All tests were conducted at a temperature of 40°C.

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. For each treatment type, at least 17 bonds were tested (except tests where the application of MeF was delayed; here, 11 bonds were
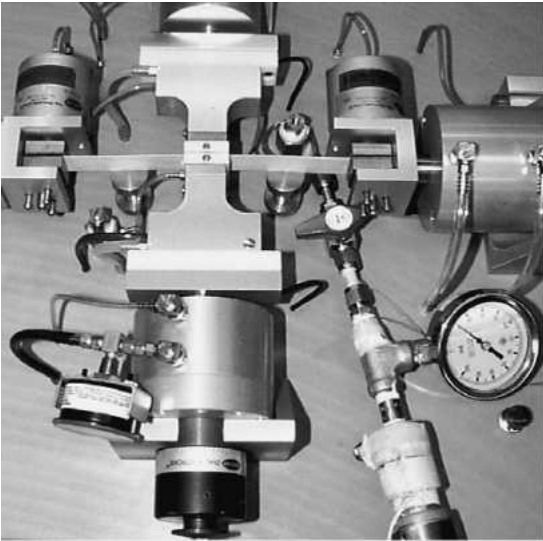
FIG. 6. A close-up of the bond pressing zone of ABES with a sample being injected with chemicals.

tested.) Pressing times ranged between 10 and 604 s. Table 1 shows the number of bonds formed and tested for each of the different treatment types. Bonds were formed with five different types of treatment as shown below:

1. control (without NH_3 or MeF),
2. NH_3 gas was injected into bonds 4 s after press closure to explore the effect of NH_3 on bond strength development rate. The delay in press closure was necessary to allow the press pressure to reach the target value (1.1 MPa). Application of gas prior to the attainment of full press force would have led to gas escape at the PTFE-wood interface.
3. MeF was injected in the liquid phase 8 s after press closure. The 8-s delay was employed

TABLE 1. *Bonds formed and tested using a range of treatment types.*

Treatment	Range of pressing time (Sec.)	Number of bonds formed & tested
Control	0–604	20
NH_3	0–604	19
MeF	0–604	20
NH_3 + MeF	0–604	17
MeF (delay)	0–604	11

for consistency with sequential treatment No. 4 described below.

4. NH_3 and MeF were injected sequentially into the bond 4 s and 8 s after the press closure, respectively. This was in order to explore the combined effects of NH_3 and MeF on bond strength development rate.
5. MeF was injected 400 s after press closure in order to explore the action of methyl formate on partially cured bonds.

In addition to conducting time-based bond strength development studies, five bonds of each type (control, injection of NH_3, injection of MeF, and injection of both NH_3 and MeF) were formed at 308 s of pressing time and then tested in shear mode. This was done to gauge the statistical variability in bonding behavior.

RESULTS AND DISCUSSION

Bond strength development studies

A set of control strength development data for which PF bonds were formed in the absence of any injected chemicals is shown as Fig. 7. Each point represents the bond strength developed at that particular pressing time; pressing times ranged between 20 and 600 s. It is evident from Fig. 7 that at the early stages of bond formation (the first 250 s), bond strength development rate was almost linear (4.7 kPa/s). The rate subsequently declined to near zero and strengths
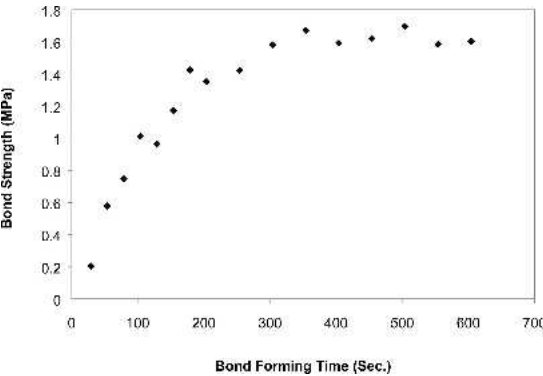

FIG. 7. A set of strength development control data for PF-to-maple wood bonds formed at room temperature in the absence of any injected chemicals.

stabilized at 1.55–1.65 MPa between 300 and 600 s. It is unclear whether strengths would attain higher values if bonds were to be cured for times well in excess of 600 s. Although maximum strengths are only modest and the rate is low, the data show that the adhesive had some reactivity at such a low temperature. The data of Fig. 7 will be used as a control with which to compare the individual and combined effects of NH_3 and MeF injection on strength development of PF adhesive-to-maple bonds.

Figure 8 represents the accumulated shear strength values for bonds formed for a range of times and with various combinations of chemical treatments. These data suggest the following:

1. Bond strength development with the application of methyl formate alone, and with the application of ammonia followed by methyl formate were much higher than those developed with no chemical injection and with ammonia alone.
2. The differences in bond strength between samples formed with only PF and PF + NH_3 are not noticeable, though the PF + NH_3 series shows slightly higher values.
3. Similarly, the strength differences between PF + MeF and PF + NH_3 + MeF are not large, though the latter series shows slightly higher values.

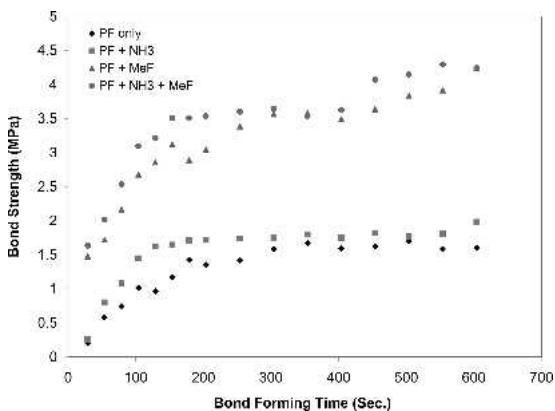Replicated bonds of each treatment type that

FIG. 8.   Strength values for bonds formed at room temperature at various bond forming times and with various chemical treatments.

were formed for 308 s of pressing time show the following P values:

- Only PF and PF + MeF
$$P \text{ value} = 7.28 \times 10^{-7}$$
- Only PF and PF + NH_3 + MeF
$$P \text{ value} = 1.47 \times 10^{-8}$$
- PF + NH_3 and PF + MeF
$$P \text{ value} = 9.66 \times 10^{-7}$$
- PF + NH_3 and PF + NH_3 + MeF
$$P \text{ value} = 1.75 \times 10^{-8}$$

Differences between PF and PF + NH_3 and between PF + MeF and PF + NH_3 + MeF are not significant (P values = 0.31 and 0.36, respectively.)

From the above results and discussion, it is clear that the influence of ammonia on the bond strength development of PF adhesive at room temperature is small or negligible. However, the influence of methyl formate under similar conditions is very significant. According to Pizzi and Stephanou (1994b), the probable cause of the significant positive influence of methyl formate is an increase in the number of cross-linking sites in the PF resin. Fragments from the dissociation of formate ester provide different and additional cross-linking sites than methylene linkages in unaltered PF resins.

To examine the action of methyl formate following partial pressing of bonds, methyl formate was applied to bonds after 400 s of pressing (i.e. delayed injection of methyl formate), and the results of that experiment are presented in Fig. 9. This figure indicates that delayed injection of methyl formate has a similar positive influence on bond strength development. The findings will be helpful for the industrial application of methyl formate for low temperature curing of PF resin in wood-based composite manufacturing.

CONCLUSIONS

This study investigated the individual and combined effects of gaseous ammonia and methyl formate on the shear strength development of alkaline catalyzed phenol-formaldehyde resin-to-wood bonds using a specially modified Automated Bond Evaluation System (ABES)
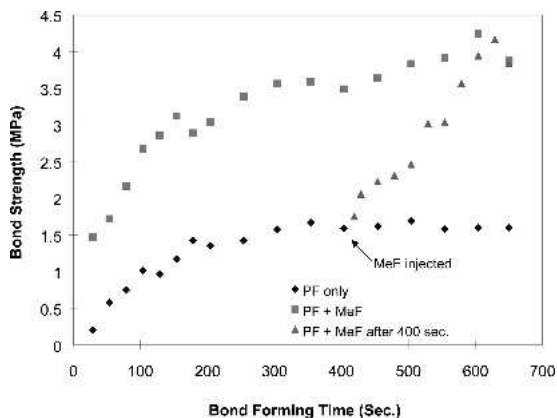
FIG. 9.   Bond strength data for delayed (after 400 s) injection of methyl formate.

operated at near-ambient temperature. Bonding studies showed that methyl formate has a significant positive influence on PF curing speed. The influence of gaseous ammonia is small or negligible. This information helped in the establishment of sequential treatment schedules of gaseous ammonia and methyl formate during formation trials of PF-resinated wood fiber composites at near-ambient temperature.

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