# The effects of temperature and humidity on phenol-formaldehyde resin bonding

X.-M. Wang; B. Riedl; A. W. Christiansen; R. L. Geimer

**Summary** The effects of temperature and relative humidity on phenol-formaldehyde resin bonding were evaluated. Two flakes in a lap-shear configuration were bonded under an environment of controlled temperature (110°C, 120°C, 130°C, 140°C) and relative humidity (41%, 75%, 90%) for a series of time periods (0.25 to 16 min). The lap-shear specimens were then shear-tested on a mechanical testing machine and the results were used to establish a family of bond strength development curves at each temperature and level of relative humidity. At 110°C, the higher relative humidity appeared to retard resin bonding. The effects of relative humidity diminished as temperature increased to 140°C. Bond strength development was chemical rate-controlled. The rate of bond strength development at each relative humidity follows a first order reaction mechanism. The activation energy of resin-wood bonding, determined by bonding kinetics, was higher than that of resin alone, determined by differential scanning calorimetry. This comparison indicates that to form a strong resin-wood bond, a higher energy level might be required.

#### Introduction

Phenol-formaldehyde (PF) resin is a widely used thermosetting adhesive for exterior-grade wood composites. During the wood-composite manufacturing process, the resin undergoes polymerization reaction with itself and chemical reaction with

Received 9 May, 1994

Xiang-Ming Wang (Graduate Student)
Bernard Riedl (Associate Professor)
Departement des Sciences du Bois
Centre de Recherche en Sciences et Ingénierie des Macromolécules
Faculté de Foresterie et de Géomatique
Université Laval, Québec, Canada G1K 7P4

Alfred W. Christiansen (Chemical Engineer) Robert L. Geimer (Research Technologist) USDA Forest Service, Forest Products Laboratory One Gifford Pinchot Drive, Madison, Wisconsin, 53705-2398 USA

Correspondence to: Prof. Bernard Riedl

This material is based on work supported by the Ministry of International Affairs, Quebec Government, the Natural Sciences and Engineering Research Council of Canada, and Laval University (Quebec City). The work was also supported by the U.S. Department of Agriculture under research joint venture agreement FP-92-1835

wood under various environmental conditions, which comprise temperature, relative humidity (RH), moisture content (MC), and water vapor pressure. These variables may significantly affect the resin curing and bonding behavior and consequently affect the final performance of wood composites. In addition, the resin bonding is also influenced by some wood-related factors, such as density and porosity, shrinking and swelling, surface texture and chemistry, and wettability. Therefore PF resin bonding to wood is a complex process. Economic considerations require both resin suppliers and composite manufacturers to understand the basic interaction of the resin and wood under certain manufacturing conditions in order to provide the most appropriate resin or to optimize process variables to produce the best quality boards.

The cure process of PF resin can be described as the conversion of small molecules to large molecules through the processes of chain extension, chain branching and crosslinking, which finally result in a three-dimensional network of infinite molecular weight (Provder 1989). A number of indirect analytical techniques have been used to characterize the cure of PF resins by responding to either the chemistry or physics of the curing process. Such techniques include: (1) nuclear magnetic resonance (NMR) (Woodbrey et al. 1965; Maciel et al. 1984); (2) Fourier transform infrared (FTIR) spectroscopy (Myers et al. 1991); (3) ultraviolet spectroscopy (Chow 1969; Chow and Hancock 1969; Chow and Mukai 1972); (4) differential thermal analysis (DTA) or differential scanning calorimetry (DSC) (White and Rust 1965; Burns and Orrell 1967; Kurachenkov and Igonin 1971; Chow 1972; Chow et al. 1975; Kay and Westwood 1975; Christiansen and Gollob 1985); (5) torsional braid analysis (TBA) (Steiner and Warren 1981; Kelley et al. 1986); and (6) dynamic mechanical analysis (DMA) (Young et al. 1981; Young 1986a; Young 1986b; Follensbee 1990; Geimer et al. 1990; Kim et al. 1991; Follensbee et al. 1993; Christiansen et al. 1993). The resin samples measured by these indirect methods are usually in the forms of pure liquid or solids, mixtures with various portions of wood powders, and resin-impregnated glass cloth or wood

Optimum conditions for resin curing determined by these methods may not be suitable for optimum resin bonding, because of the interaction between the resin and wood. To address this concern, a direct method to evaluate resin-wood bonding is required. Humphrey and Ren (1989) and Geimer et al. (1990) separately developed techniques to follow the strength development of a resin-bonded joint under controlled isothermal and isohydro conditions. These studies showed that an optimum environmental condition exist for resin bonding. Humphrey and Ren (1989) studied the effects of temperature and equilibrium moisture content (EMC) of wood on bond strength development of powdered PF resin between two wood disks. They observed that at 100°C or 115°C, 10% EMC appeared to be optimal for the resin bonding, whereas a lower EMC (4%) significantly retarded resin bonding and a higher EMC (16%) caused relatively low bond strength by reducing the chemical reactivity of the resin. Geimer and Christiansen (1994) investigated liquid PF resin bond development between aspen flakes at 0%, 41%, or 91% RH at 115°C bonding temperature. They found that bond strength increased with increased bonding relative humidity from 0% to 41%, but the lowest bond strength was obtained at 91% RH.

In this study, lap-shear joints were bonded in an environment of controlled temperature and relative humidity for a preselected range of pressing times. The PF bonded specimens were tested in tensile shear at room temperature and the results were then used to construct bond strength development curves. In addition, the rate of bond strength development at each relative humidity was used for the evaluation of bonding kinetics.

## Experimental

### Resin and substrate preparation

The resin synthesis procedure, which has been reported in detail in a separate paper (Wang et al. 1994), is briefly described here.

The PF resin used in this study is a 2-part laboratory-synthesized phenol-formaldehyde resin. Part 1 is a low molecular weight, methylolated phenol oligomer. Part 2 is a more condensed phenol-formaldehyde resin. The two parts of the resin were prepared separately and then mixed together in a 1:1 ratio by volume. The mixed PF resin is henceforth referred to as PF resin. The initial resin properties are shown in Table 1. Gelation time was measured by heating a 2-ml resin sample in a 19.5-mm I.D. test tube at  $125^{\circ}$ C ( $\pm$  5°C) and is quoted in minutes between the start of the test and the point at which bubbles ceased moving upwards.

Aspen (Populus spp.) flakes, with dimensions 15 mm wide by 0.89 mm thick by 76 (or 70) mm long, were used as adherends in the adhesion study. The wood grain direction was paralleled to the length. To reduce the influence of the surface texture of wood (variation of springwood-summerwood) on the bond strength (Marian et al. 1958), all flakes were prepared from ambiently conditioned quarter-sawn blocks. First, the  $15 \times 55 \times 76$  mm (or  $15 \times 55 \times 70$  mm) blocks were put into a pressure vessel, which was then filled with hot water (100°C or less), and a vacuum of 760 mm-Hg was applied for 30 min to draw air out of the wood. Next, the wood was soaked by applying a pressure of 3100-3600 mm-Hg in the vessel for one and a half hours. After this vacuum-pressure soak (VPS) cycle, the wetted wood blocks were cut into flakes by using a small, manual microtome. During cutting (knife edge parallel to the grain), it was found that there were some visible lathe checks on the flake surfaces, even when a newly sharpened knife was used. To eliminate these lathe checks, a very thin layer of wood was sliced away from the top of wood block after each flake cut. This procedure guaranteed that each flake had at least one very smooth surface, to which the resin was to be glued. After being cut, the wet flakes were restrained between glass plates to keep them flat and straight. These flakes held by the glass plates were then dried in an oven at 105°C for 2-3 hours, until their moisture content reached nearly zero. All flakes were conditioned to 50% RH (22°C) for at least 24 hours before being used.

## Methods

Two flakes to be bonded were both coated with liquid PF resin on their smooth surfaces. The amount of resin, 17-21 mg, applied on a  $15 \times 15$  mm area at one end of each flake, was controlled to give a thin, uniform and continuous resin film. After an open assembly time of 20 min, the two specimens were lapped over the length of their coated ends.

Table 1. Initial resin properties

Resin type	Gelation time at 125 C ( $\pm$ 5 C) (min-sec)	Viscosity (mPa·s)	pН	Solids content (%)	
Part 1	14'54"	51	10.1	50.1	
Part 2	10'05"	583	10.6	39.8	
Mixed PF	13'40"	79	10.2	45.8	

The over-lapped flake assembly was prepared for bonding in a steam treatment chamber (Geimer et al. 1990), which is an especially designed environmental treatment chamber that can provide a wide variety of constant relative humidity environments at various temperatures. The chamber allows curing or bonding to be carried out at a relative humidity of up to 100% at any temperature below 180°C, or up to 62% RH at the maximum temperature of 200°C. The procedure for bonding a lap-shear specimen we followed is outlined here. First, a desired bonding condition, i.e., a controlled temperature and relative humidity, was established in the treatment chamber. Before opening the chamber port for introducing the specimen, the vapor pump which was used to circulate the humidified air or superheated steam through the chamber was turned off. After quickly inserting the specimen into the chamber, a bonding pressure of 2.05 MPa was applied to a lap-bonded specimen (on its bonding area of  $15 \times 15$  mm) by a pair of 6.5-cm diameter stainless steel piston heads. Following that, the chamber was immediately closed and the vapor pump was turned on. The bonding time is defined as the period between the moment of turning on the vapor pump and the moment prior to reopening the chamber port for removing the specimen. It took about 10 seconds to

Table 2. Bonding conditions vs. failure patterns of lap-shear tension specimens<sup>a</sup>

Bonding conditions	Bonding time (min)												
	0.25	0.5	1.0	1.5	2.0	3.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0
110 °C, 41% RH 110 °C, 75% RH							BF <sup>b</sup> NB°	BF BF	PFF° BF	PFF BF	FF <sup>d</sup> BF (BF)	BF	FF PFF (BF
110 °C, 90% RH					NB	NB	BF	BF	BF	BF	BF		BF
120 °C, 41% RH			BF (BF)		BF (BF)	BF (PFF)	FF (FF)	FF (PFF)	GF <sup>f</sup> (FF)		FF		
120 °C, 75% RH			BF	PFF	(/	BF (BF)	BF	PFF	FF		PFF		
120 °C, 90% RH			BF		BF	PFF (BF)	BF	BF	BF		BF		
130 °C, 41% RH		BF	PFF	BF	PFF		FF	FF (FF)		FF			
130 °C, 75% RH		BF	BF	PFF	PFF		PFF	FF (FF)		FF			
130 °C, 90% RH		BF	PFF	PFF	PFF (PFF)		FF	PF (PFF)		FF			
140 °C,41% RH	BF	PFF	PFF (FF)		PFF (FF)		FF (FF)		FF (FF)				
140 °C,75% RH	BF	BF	FF		FF		FF (FF)		FF				
140 °C, 90% RH	PFF	PFF	PFF		PFF		PFF (FF)		FF				

<sup>&</sup>lt;sup>a</sup> Symbols in parentheses are the results of replicates

<sup>&</sup>lt;sup>b</sup> BF = bond failure

<sup>°</sup> PFF = partial flake failure

d FF = flake failure

<sup>&#</sup>x27;NB = no bond

<sup>&</sup>lt;sup>1</sup>GF = grip failure (at the position of a specimen clamped during tensile tests)

place the specimen in the chamber, from the port opening to closing, or to retrieve the specimen. A thermocouple attached to one piston head indicated the exact temperature in the vicinity of the bonding area. The bonding conditions are given in Table 2.

After bonding, all specimens were reconditioned at 50% RH (22°C) for at least 24 hr prior to testing. The tensile lap-shear bond strength tests were performed on an Instron mechanical testing machine at a strain rate set at 10 mm/min. The specimen was vertically clamped between two serrated grips. The length between the grips was 73 mm. This configuration has been shown to be most suitable for a flake bonding study with a 15-mm lap length of specimen (Geimer and Christiansen 1994). For each test, maximum tensile load and extension were recorded, from which curves of bond strength development were obtained as a function of bonding temperature and relative humidity. Under some bonding conditions, the experiment was repeated, while the data were presented on the plots as individual points instead of averages. Although curves of bond strength development made were based on computer fitting of data, some man-made changes have been made to show the trends as we thought to be more representative. The rate of bond strength development at each relative humidity was then used to calculate an activation energy for flake bonding.

Heats of curing of the pure liquid PF resin were measured in a Mettler DSC 20 with Mettler TA4000 Thermal Analysis System. About 10 mg of liquid resin was hermetically sealed in a large capsule and scanned from 30°C to 250°C at a heating rate of 5°C/min. The values of activation energy were calculated on the basis of solid resin weight and a simple kinetic model. Comparisons of activation energies determined by DSC and by the rate of bond strength development were used to explain the resin curing and bonding behavior in the presence of wood.

## Results and discussion

Bond strength development at 110°C

The relationship between the bond strength of the partially cured or bonded specimens and press time (which we will henceforth referred to as a bonding curve), as a function of relative humidity in the steam treatment chamber at 110°C, is shown in Fig. 1. The result indicates that the extent of bond strength development was highly dependent on the environmental relative humidity. Bond strength of PF resin built up faster and achieved finally higher bonding at 41% RH than it did at 75% RH or 90% RH. Bond strengths developed in the early stages of cure were higher at 90% RH than at 75% RH. However with cures extended beyond 10 min. those bond strengths developed at 75% RH were stronger. Retardation of resin bonding at the higher relative humidities can be attributed to excess moisture present in the bondline, which likely dilutes the reactive components of the resin and causes excessive resin penetration into wood. Although bond strength development at relative humidities below 41% RH was not measured in this study, it could be estimated by comparison with a similar study by Geimer and Christiansen (1994), which showed that an optimal resin bonding condition was 41% RH when cured at 115°C. In our case, the bonding temperature is 110°C, which is close to the 115°C they used. It is possible to state that a certain level of relative humidity (around 41%) is necessary for optimal resin bonding at a temperature around 110°C. So if an optimum relative humidity or moisture content exists for PF resin bonding, it would favor the interaction between resin and wood, improving resin hydrodynamic flow while allowing maximum resin chemical reactivity.

The effect of environmental relative humidity at 105°C on the cure of the same PF resin as used in this study was measured by DSC in our previous study (Wang



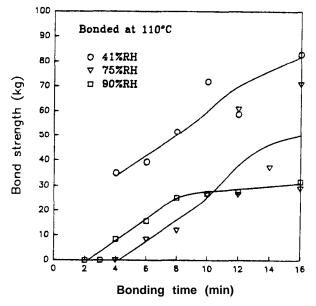
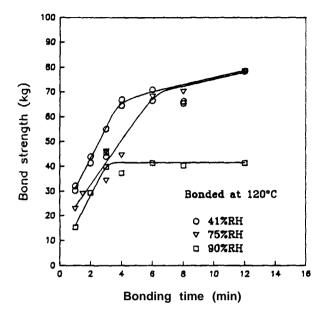


Fig. 1. Bond strength development of phenol-formaldehyde resin on aspen flakes at  $110^{\circ}$ C and 41%, 75% or 90% RH. All lap-shear specimens were conditioned at 50% RH (22°C) for at least 24 hr prior to test

et al. 1994). We found that the resin cured faster at 90% RH than it did at 75% or 41% RH. An interesting point is the effect of relative humidity on the resin cure showing a different trend as to its effect on the resin bonding. This indicates that optimum conditions for resin cure are not necessarily the same as those which promote the best resin-wood bonding.

## Bond strength development at 120°C

The bond strength development at 120°C is shown in Fig. 2. An increase in bonding temperature of only 10°C caused significant changes in the bond strength development overall as compared with the results shown in Fig. 1. The minimum times to achieve bonds at 120°C were 1 min at 41%, 75% or 90% RH; these were much less than the times required at 110°C: 4 min at 41% and 90% RH, and 6 min at 75% RH. The bond strength at 120°C increased linearly with increasing press time up to approximately 4 min at each relative humidity. Increasing exposure time beyond 4 min did not improve bonds made at 90% RH. However increasing time did improve bond strengths at the lower relative humidities, but at a reduced rate. The absolute differences in bond strength buildup caused by bonding relative humidity at 120°C were much less significant than at 110°C. In Fig. 2, it is also observed that the bonding strength curves at 41% and 75% RH came closer to each other with an increase in press time, especially after 6 min. The maximum bond strength obtained at 90% RH at 120°C was also higher than it was at 110°C. This effect is probably caused by less resin cure at 110°C. The level of cure attained by phenolic resins is limited not only by time but by the temperature during cure, as shown by Nachtrab (1970) for phenolic novolacs and Schindlbauer and others (1976) for phenolic resoles. The results indicate that 41% was still the favored relative humidity for resin bonding at 120°C but less determinant than it was at 110°C (Fig. 1).



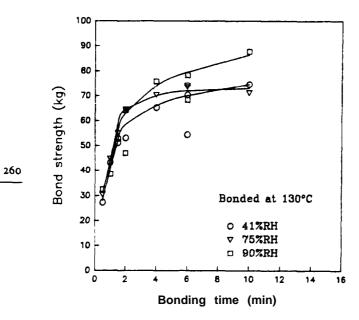
**Fig. 2.** Bond strength development of phenol-formaldehyderesin on aspen flakes at 120°C and 41%, 75% or 90% RH. All lap-shear specimens were conditioned at 50% RH (22°C) for at least 24 hr prior to test

The importance of relative humidity thus decreased with increasing temperature. This relationship appears to be dependent on the rate of resin cure, as will be shown in the following discussion.

## Bond strength development at 130°C and 140°C

Increasing bonding temperatures from 110°C to 140°C caused the bond strength to develop at a much higher rate, while the absolute inhibiting effect of relative humidity on bonding greatly decreased, as seen in Figs. 3 and 4. Formation of bonds took only 0.5 min at 130°C and 0.25 min at 140°C. Bonding curves showed linearly rising strengths versus bonding time at each bonding condition, and the strengths reached their plateaus at about 2 min at 130°C and 1 min at 140°C. Evaluations of bond strength beyond the early linear regions at each bonding temperature were limited due to wood substrate failure or partial wood failure (at the interface and in the phases of the wood and resin) when the specimens were tested. In other words, there was often cohesive failure in the wood, which suggests the bonds were at least as strong as the bulk wood phase. So the actual bond strengths are possibly higher than the values shown in the latter regions.

Bonding conditions vs. failure patterns for all measurements are summarized in Table 2. Maximum strength of the tensile lap-shear specimens was between 60 and 85 kg for all specimens when partial or full wood failure occurred. Before reaching the bond strength plateaus or conditions where flake (wood) failure occurred, the bond strength development as a function of bonding time is characterized by actual failure in the bond. The inherent tensile strength of a single aspen flake with a length of 76 mm and the same cross-sectional area as other flakes used in this study was approximately 120 kg. The most likely cause for the lower failure loads on the bonded joints, compared to



**Fig. 3.** Bond strength development of phenol-formaldehyde resin on aspen flakes at  $130^{\circ}$ C and 41%, 75% or 90% RH. All lap-shear specimens were conditioned at 50% RH ( $22^{\circ}$ C) for at least 24 hr prior to test

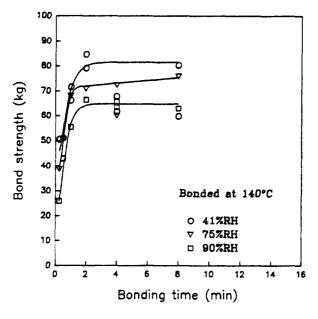


Fig. 4. Bond strength development of phenol-formaldehyde resin on aspen flakes at 140  $^{\circ}$ C and 41%, 75% or 90% RH. All lap-shear specimens were conditioned at 50% RH (22  $^{\circ}$ C) for at least 24 hr prior to test

strengths of simple flakes, is that the structure of the joint leads to peeling forces and stress concentrations at the ends of lap-shear joints. The effect of stress concentrations is evident in the pattern of failures among tested flakes. Wood failure in almost every case occurred at the ends of the overlap. Other factors can also affect bond strength. Variations in the temperature and relative humidity used during the bond pressing period can cause dimensional changes in the flake adherend and/or bondline, affecting the stress concentration as Krueger (1981) noted. Dimensional changes in the flakes can either strengthen the wood by increasing specific gravity or decrease the strength of the wood by inducing damage (Price 1976; Geimer 1985). In our study it was observed that the thickness of lap bonded flakes decreased with increasing bonding temperature, relative humidity, and time. As techniques become more refined, this side effect of pressing environment variables on the adherend may be shown to be an important part of the total bonding picture.

By comparing the results in Figs. 1 to 4, it is observed that scattering of data occurs under almost every bonding condition. The variability of the data appeared more extensive in Fig. 4 for 41% RH than for 75% or 90% RH. We do not know the reason for this, but there are many factors which could cause the variability of the data beside the aforementioned stress concentrations. These factors include individual flake strength and surface texture, combined effects of temperature and humidity on resin penetration and steam hydrolysis of wood, variability in bonding chamber operation, indentation during bonding of one flake by the other where the laps end, poor alignment of flakes in the specimen, and possible problems during testing such as poor specimen alignment or nonlinear force fields from bending of the flexible adherends. More data would be necessary to clarify this issue.

## **Bonding kinetics**

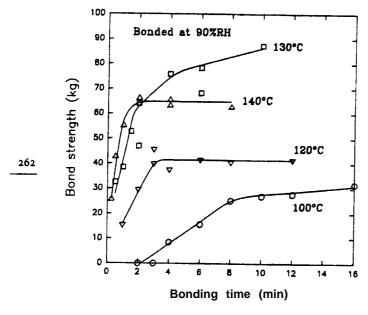
Wood contains active hydroxyl groups which enable a PF resin to bond to it in a high temperature environment. Thus, the activation energy required to form a resin-wood bond is influenced by both resin and wood factors. A larger value of activation energy in wood-resin formation, as compared with curing of the resin alone, may indicate that bond formation is actually retarded, rather than enhanced, by the presence of wood.

Bond strength development at bonding temperatures of  $110^{\circ}$ C,  $120^{\circ}$ C,  $130^{\circ}$ C and  $140^{\circ}$ C is summarized for the 90% RH data in Fig. 5. Each bonding curve shows a linear slope prior to reaching its plateau. Since the bonding rate, expressed as the slope of the initial line, increased with increasing bonding temperature, it is possible to correlate the bonding rate to bonding temperature. A plot of the logarithm of the bonding rate (kg min<sup>-1</sup>) versus the reciprocal of absolute temperature is illustrated in Fig. 6. Since the plot shows an excellent linear correlation ( $r^2 = 0.99$ ) at this humidity bonding condition, we believe that the bond strength development follows classical kinetics, and the activation energy can be calculated by using the Arrhenius equation:

$$\Phi = A \cdot \exp(-E_a/RT)$$

where  $\phi$  is the rate of bond strength development (kg min<sup>-1</sup>), A is the pre-exponential factor, E<sub>a</sub> is the activation energy (kJ mol<sup>-1</sup>), R is the universal gas constant (8.314 J K<sup>-1</sup>mol<sup>-1</sup>) and T is the absolute temperature (K).

The same approach was also used to calculate activation energy for bond formation at 41% and 75% RH. All kinetics results are shown in Table 3. The activation energies calculated at 41%, 75% and 90% RH were 93, 99 and 98 kJ mol<sup>-1</sup>, respectively. Note that little resin cure information at exposure times less 4 min was obtained for exposures at



**Fig. 5.** Bond strength development as a function of bonding temperature  $(110^{\circ}C, 120^{\circ}C, 130^{\circ}C \text{ and } 140^{\circ}C)$  at 90% RH. All lap-shear specimens were conditioned at 50% RH  $(22^{\circ}C)$  for at least 24 hr prior to test

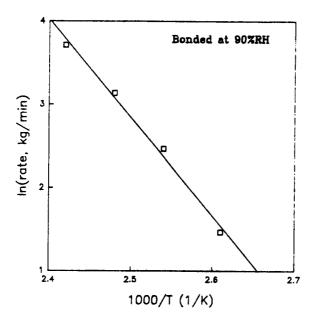


Fig. 6. Rate of bond strength development at 90% RH versus the reciprocal of absolute bonding temperature

Table 3. Curing and bonding kinetics for PF resin

Method	Relative humidity (%)	Activation energy, E <sub>a</sub> (kJ mol <sup>-1</sup> )	Pre-exponential factor, In A <sup>a</sup>			
DSC cure	-	80	17.52			
Flake bond	41	93	30.68			
Flake bond	75	99	32.51			
Flake bond	90	98	32.38			

A is expressed in kg min-1 for flake bonding

110°C. The activation energies observed in this study were very close to the value of 96 kJ mol<sup>-1</sup> measured by Humphrey and Ren (1989) for the activation energy of bond strength development of a powdered PF resin. Since the activation energies measured here for the three relative humidities are close to each other, it indicates that the bonding relative humidity had little effect on the rate of resin bond strength development, especially between 75% and 90% RH. Considering Figs. 1-4 again, we note that the early linear parts of the bonding curves, which are used to calculate the rate of bond strength development (as shown in Fig. 6), are generally parallel to each other and have the same slope, or rate, at each temperature and for all the three levels of relative humidity. But the bond strengths at different RH values were more widely separated at lower temperature; however this influence of humidity diminished with increasing temperature. This indicates that relative humidity did influence the extent, but not the rate of bond strength development in the early stages (before 4 min) at lower temperatures (110°C – 120°C), and humidity did limit the maximum strength development. These effects are relatively important in curing composite board resins where heat transfer depends on the development of successive steam fronts progressively moving into the center of the panel from the heated faces.

Although the effect of environmental relative humidity on bond strength development could not be detected by the simple evaluation of activation energy, it still reveals some important information about resin curing in the presence of wood and about formation of a strong resin-wood bond. The activation energy of the liquid PF resin determined by DSC was 80 kJ mol<sup>-1</sup>, as shown in Table 3. Since this E<sub>a</sub> value is smaller than that from the flake bonding, it indicates that the formation of a resin-wood bond may require a larger energy than resin cure alone. This result agrees with Chow (1969)'s finding in his kinetic study by ultraviolet spectroscopy of the polymerization of PF resin mixed with wood powders. Chow (1969) pointed out that the polymerization of PF resin involved two steps: (a) the substitution reaction between wood carbohydrate and resin, (b) the condensation reaction of resin with resin. The former required about one half the activation energy (28 kJ mol<sup>-1</sup>) required for resin alone (47 kJ mol<sup>-1</sup>). Since the wood-resin reaction reduces the probability of reaction between resin molecules, Chow (1969) proposed that to complete the resin cure or form a strong bond, a higher energy level is required than for a resin-resin bond.

The chemical interaction between resin and wood also varies with wood species. Mizumachi and Morita (1975) compared the activation energy of the curing reaction of a dry PF resin alone (75 kJ mol<sup>-1</sup>) with that of the PF resin filled with various wood powders, using differential thermal analysis. They found that some wood species enhanced the resin curing reaction (activation energy ranged from 59-71 kJ mol<sup>-1</sup>), and some inhibited resin cure (96–109 kJ mol<sup>-1</sup>), and some seemed to have little effect

on resin cure (75-88 kJ mol<sup>-1</sup>). The effects of woods on the curing reaction of PF resin might be attributed to the wood extractives (Mizumachi and Morita 1975). Extractives may become a serious problem to resin bonding when concentrated on the wood surface even at low contents. Excessive amounts of water-soluble extractives may dilute the resin system (Wellons 1981). Some resinous or oily extractives may partially block resin bonding or diffusion (FPL 1987). Extractives also influence the chemical activity of a wood surface. Since basic conditions are required to complete cure of PF resins (resoles), extractives making the wood surface very acidic possibly inhibit the resin cure, and the reverse case would favour the resin cure (Wellons 1981; FPL 1987).

PF resin curing and bonding in the presence of wood is a complex process. Any changes in wood aspect (such as wood surface chemistry and texture) or resin aspect (such as viscosity and composition) may influence the rate of resin cure and bonding quality. Kinetic study of PF resin will provide a useful and more direct way in understanding the basic interaction between wood and resin. This information will also help the manufacturers of wood composites to develop or formulate a suitable adhesive for a particular wood species.

#### Conclusions

The bonding of PF resin under various environmental temperature and relative humidity has been studied. The important points obtained from this work can be summarized as below.

- 1. At 110°C, 41% environmental relative humidity provides better bonding conditions than relative humidities of 75% or 90%. With increasing temperature, the bond strength developed faster and the effect of relative humidity became less significant.
- 2. Condition for optimum resin cure determined by a DSC measurement may not be suitable for the resin-wood bonding due to the interaction between the resin and wood.
- 3. The activation energy required to form a resin-wood bond is larger than that required for the resin cure alone.
- 4. The technique to follow the bond strength development between two flakes in a lap-shear configuration provides a direct way (a) to monitor and characterize resin bonding processes and (b) to understand the basic interaction between wood and resin under various environmental conditions. Information similar to that acquired in this study is helpful to resin manufacturers to optimize resin for specific wood composite manufacturers, and on the other hand, wood composite manufacturers who are seeking to improve their products by optimizing manufacturing conditions.

## References

Burns, R. E.; Orrell, W. 1967: A thermal analytical study of phenol formaldehyde resins. J. Mater. Sci. 2: 72-77

Chow, S.-Z. 1969: A kinetic study of the polymerization of phenol-formaldehyde resin in the presence of cellulosic materials. Wood Sci 1: 215-221

Chow, S.-Z. 1972: Thermal analysis of liquid phenol-formaldehyderesin curing. Holzforschung 26: 229–232

Chow, S.-Z.; Hancock, W. V. 1969: Method for determining degree of cure of phenolic resin. Forest Prod. J. 19: 21-29

Chow, S.-Z.; Mukai, H. N. 1972: Polymerization of phenolic resin at high vapor pressure. Wood Sci. 5: 65-72

Chow, S.; Steiner, P. R.; Troughton, G. E. 1975: Thermal reactions of phenol-formaldehyde resins in relation to molar ratio and bond quality. Wood Sci. 8: 343-349

- Christiansen, A. W.; Follensbee, R. A.; Geimer, R. L.; Koutsky, J. A.; Myers, G. E. 1993: Phenol-formaldehyde resin curing and bonding in steam injection pressing. II. Differences between rates of chemical and mechanical responses to resin cure. Holzforschung 47: 76–82 Christiansen, A. W.; Gollob, L. 1985: Differential scanning calorimetry of phenol-formaldehyde resoles. J. Appl. Polym. Sci. 30: 2279–2289
- Follensbee, R. A. 1990: Using dynamic mechanical analysis to characterize the cure of phenolic resins. Ph.D. thesis, University of Wisconsin-Madison, USA
- Follensbee, R. A.; Koutsky, J. A.; Christiansen, A. W.; Myers, G. E.; Geimer, R. L. 1993: Development of dynamic mechanical methods to characterize the cure state of phenolic resole resins. J. Appl. Polym. Sci. 47: 1481-1496
- Forest Products Laboratory (FPL). 1987: Wood Handbook: wood as an engineering material. Chapter 9: 1-21. Forest Products Laboratory, Agric. Handb. 72. Washington, DC: U.S. Department of Agriculture
- Geimer, R. L.; Christiansen, A. W. 1994: Adhesive curing and bonding: response to real time conditions. To be published in: Proceedings of Adhesive and bonding Wood Products Symposium, 19-21 November 1991, Seattle, WA
- Geimer, R. L.; Follensbee, R. A.; Christiansen, A. W.; Koutsky, J. A.; Myers, G. E. 1990: Resin characterization. In: Maloney, T. M. (Ed.): Proceedings 24th International Washington State University, Particleboard/Composite Materials Symposium, 3-5 April 1990, Pullman, WA. Pullman, WA: Washington State Univ. pp. 65-83
- Geimer, R. L.; Mahoney, R. J.; Loehnertz, S. P.; Meyer, R. W. 1985: Influence of processing induced damage on strength of flakes and flakeboards. FPL Res. Pap. No. 463. U.S. Forest Products Laboratory, Madison, WI
- Humphrey, P. E.; Ren, S. 1989: Bonding kinetics of thermosetting adhesive systems used in wood-based composites: the combined effect of temperature and moisture content. J. Adhesion Sci. Technol. 3: 397-413
- Kay, R.; Westwood, A. R. 1975: DSC investigations on condensation polymer I: Analysis of the curing process. Eur. Polym. J. 11: 25-30
- Kelley, S. S.; Gollob, L.; Wellons, J. D. 1986: The effects of resin formulation variables on the dynamic mechanical properties of alkaline curing phenolic resins. Holzforschung 40: 303-308 Kim, M. G.; Nieh, W. L.-S.; Meacham, R. M. 1991: Study on the curing of phenol-formaldehyde resol resins by dynamic mechanical analysis. Ind. Eng. Chem. Res. 30: 798-803
- Krueger, G. P. 1981: Design methodology for adhesives based on safety and durability. In: Blomquist, R. F.; Christiansen, A. W.; Gillespie, R. H.; Myers, G. E. (Eds.): Adhesive bonding of wood and other structural materials, pp. 319–364. The Pennsylvania State University, University Park, Pa.
- Kurachenkov, V. I.; Igonin, L. A. 1971: Curing mechanism for phenol-formaldehyde resin. J. Polym. Sci. Part A-I. 9: 2283-2289
- Maciel, G. E.; Chuang, I.-S.; Gollob, L. 1984: Solid-state <sup>13</sup>C NMR study of resol-type phenol-formaldehyde resins. Macromolecules 17: 1081-1087
- Marian, J. E.; Stumbo, D. A.; Maxey, C. W. 1958: Surface texture of wood as related to glue-joint strength. Forest Prod. J. 8: 345-351
- Mizumachi, H.; Morita, H. 1975: Activation energy of the curing reaction of phenolic resin in the presence of woods. Wood Sci. 7: 256-260
- Myers, G. E.; Christiansen, A. W.; Geimer, R. L.; Follensbee, R. A.; Koutsky, J. A. 1991: Phenol-formaldehyde resin curing and bonding in steam-injection pressing. I. Resin synthesis, characterization, and cure behavior. J. Appl. Polym. Sci. 43: 237-250
- Nachtrab, G. 1970: Untersuchung des Aushärtungsgrades von Duromeren mit Hilfe der Differential-Thermoanalyse. Kunststoffe 60: 261-265
- Price, E. W. 1976: Determining tensile properties of sweetgum veneer flakes. Forest Prod. J. 26: 50-53 Provder, T. 1989: Cure characterization in product research and development. J. Coat. Technol. 61: 33-50
- Schindlbauer, H.; Henkel, G.; Weiss, J.; Eichberger, W. 1976. Quantitative study of the curing behavior of phenoplasts during differential thermal analysis measurements (DSC). Angew. Makromol. Chem. 49: 115-128
- Steiner, P. R.; Warren, S. R. 1981: Rheology of wood-adhesive cure by torsional braid analysis. Holzforschung 35: 273-278

Wang, X.-M.; Riedl, B.; Christiansen, A. W.; Geimer, R. L. 1994: Differential scanning calorimetry of the effects of temperature and humidity on phenol-formaldehyde resin cure. Polymer 26: 2485-2492

Wellons, J. D. 1981: The adherends and their preparation for bonding. In: Blomquist, R. F.; Christiansen, A. W.; Gillespie, R. H.; Myers, G. E. (Eds): Adhesive bonding of wood and other structural materials, pp. 85-134. The Pennsylvania State University, University Park, Pa. White, R. H.; Rust, T. F. 1965: Cure rates of phenolic resins by differential thermal analysis. J. Appl. Polym. Sci. 9: 777-784

Woodbrey, J. C.; Higginbottom, H. P.; Culbertson, H. M. 1965: Proton magnetic resonance study on the structures of phenol-formaldehyde resins. J. Polym. Sci. Part A. 3: 1079-1106 Young, R. H.; Kopf, P. W.; Salgado, O. 1981: Curing mechanism of phenolic resins. Tappi 64: 127-130

Young, R. H. 1986a: Adhesive cure as determined by dynamic mechanical analysis and its effect on wood composite performance. In: Christiansen, A. W.; Gillespie, R. H.; Myers, G. E.; River, B. H. (Eds.): Wood adhesives in 1985: status and needs: Proceedings of a conference; 1985 May 14-16; Madison, Wl. Madison, Wl. Forest Products Research Society, pp. 267-276
Young, R. H. 1986b: Cure and durability of adhesives for wood-based composites. In: Salmén, A.; Ruvo, A.; Seferis, J. C.; Stark, E. B. (Eds.): Composite Systems from Natural and Synthetic Polymers, pp. 225-231. Elsevier Science Publishers B.V., Amsterdam

on recycled paper