

## Curing of Phenol-Formaldehyde Resin Mixed with Wood Preservatives

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**ABSTRACT:** The effects of preservatives used for glue-line treatment on the curing of phenol-formaldehyde resin (PF) were studied by dynamic mechanical analysis and differential scanning calorimetry. Storage modulus,  $G'$ , loss modulus,  $G''$ , and loss tangent,  $\tan \delta$ , of PF with and without preservatives were recorded as a function of time under isothermal heating. The time required for  $G'$ ,  $G''$ , and  $\tan \delta$  to reach steady values increased with addition of preservative. The  $G'$ ,  $G''$ , and  $\tan \delta$  curves of PF containing benzyl alcohol (used in the preservative as a diluent) were almost identical to those of PF containing preservative. However, the addition of antitermite and anti-fungal compounds alone had no effect on the curing process. There were no differences in total reaction enthalpy or dependence of activation energy on degree of conversion between pure PF and mixtures. Our results indicate that benzyl alcohol in preservatives plasticizes the curing system for PF. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

One method for preserving wood composites such as plywood and laminated veneer lumber (LVL) is to incorporate preservatives in the glue-line by mixing them with the adhesive. Glue-line treatment has the advantage that the only change is in the formulation of the glue and, therefore, requires no additional process or special equipment, unlike pressure treatment, for example. However, it should be noted that the preservatives must not interfere with the curing of the adhesive.

In some cases, a longer hot-pressing time has been required for the glue-line treatment of plywood/LVL.<sup>1,2</sup> Understanding the curing process of mixtures of phenol-formaldehyde resin (PF) and preservatives is important for optimizing the manufacturing process for glue-line-treated plywood/LVL. Identifying the constituents that cause retardation during PF curing is also important for selecting chemicals that have no negative impact on the manufacturing process or the adhesive properties of the final products.

Dynamic mechanical analysis (DMA) has been used to study the curing process in PF.<sup>3–7</sup> Materials change from a viscous to a rubbery or glassy state during curing. The study of these marked changes in rheological properties during curing is important when considering the adhesive condition and improving

the final properties. However, there is no straightforward relationship between these rheological changes and the individual reactions that occur during the curing process.

Differential scanning calorimetry (DSC) is the most common method for monitoring the curing of thermoset resins.<sup>8–18</sup> The kinetic analysis of DSC thermograms gives dynamic information during curing because it provides the quantitative heat flow associated with the polymerization process. Two peaks are evident in the DSC thermograms for curing of PF. These peaks have been interpreted using the structural information provided by nuclear magnetic resonance and gel permeation chromatography.<sup>8,9</sup> The first peak was attributed to hydroxymethylphenol formation and condensation, while the second peak was attributed to further reactions, for example, the condensation of dibenzyl ether bridges to methylene bridges.<sup>9</sup> The kinetics of complex processes such as the curing reaction for PF can be described by model-free kinetics.<sup>10,13,14</sup> Model-free kinetics does not require a specific model because the model-fitting step is eliminated through use of multiple heating rate experiments and is based on the isoconversional principle (i.e., that the reaction rate at a constant conversion is a function only of temperature).<sup>11</sup> The Friedman method<sup>12</sup> is appropriate for gaining insight into the curing mechanisms of commercial PF.<sup>10</sup>

The aim of this work was to show the effects of the addition of wood preservatives on the PF curing process. The variation in the mechanical properties of PF and mixtures of PF and preservative during curing was examined by DMA. A model-free kinetic analysis of DSC data was used to examine the chemical transformations taking place during curing of the PF and the mixtures.

## EXPERIMENTAL

### Materials

PF was obtained from DIC Kitanihon Polymer Corporation, Miyagi, Japan. Sodium hydrogen carbonate from Kanto Chemical Co., Inc., Tokyo, Japan was used as a catalyst. Commercial wood preservative used for the glue-line treatment was obtained from Lanxess K.K., Tokyo, Japan. This preservative consists of imidacloprid, tebuconazole, and triadimefon dissolved in benzyl alcohol. Benzyl alcohol and imidacloprid were obtained from Kanto Chemical Co., Inc. and tebuconazole and triadimefon were obtained from Dr Ehrenstorfer GmbH, Augsburg, Germany.

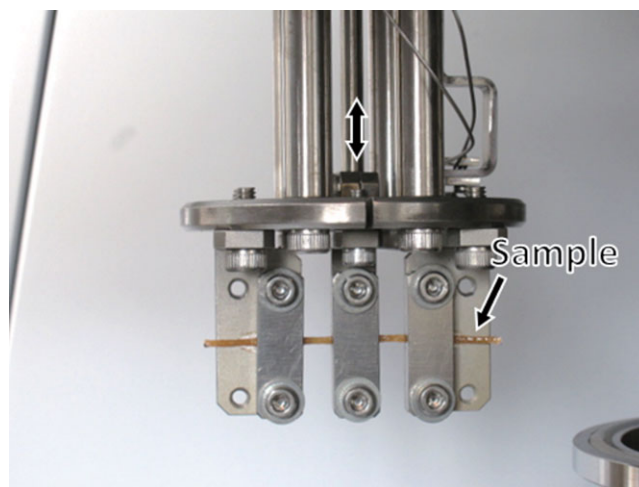
### Dynamic Mechanical Analysis

To prepare the PF glue and preservative mixture, 100 parts by weight of PF and three parts of sodium hydrogen carbonate were first mixed to prepare the PF glue and then 7.3 parts of preservative was added to the PF glue, based on the dose recommended by the manufacturer. Samples were also prepared by adding each of the main components of the preservative individually to glue samples, as follows. With the exception of benzyl alcohol, the individual preservative components were diluted with methyl alcohol before addition to the PF glue; imidacloprid was prepared as a 110 mg/mL solution, while tebuconazole and triadimefon were prepared as 220 mg/mL solutions. Samples were then prepared by mixing 1 mL of each solution with 34 g of glue. Finally, samples containing 10.3 g of glue and 0.3 g or 0.6 g of benzyl alcohol were prepared. A glass fiber bundle was impregnated with each prepared mixture and placed under vacuum for 15 min and then held at atmospheric pressure for 1 h. The impregnated fiber was clamped by two arms to straighten it, dried at room temperature for 3 h and then dried under vacuum at room temperature over phosphorous pentoxide for 20 h. The dimensions of the samples were approximately 1 mm  $\varnothing$   $\times$  55 mm length.

DMA measurements were made on an EXSTAR DMS6100 instrument with the film shear measurement head (Figure 1; SII NanoTechnology Inc., Chiba, Japan). The measurements were conducted in shear mode using a frequency of 1 Hz. DMA measurements started at room temperature and the temperature was then increased at about 20°C min<sup>-1</sup> until reaching various isothermal conditions at 90, 100, 110, and 120°C. The measurements were continued for 60–120 min after reaching the target isothermal conditions until the loss tangent,  $\tan \delta$ , reached a constant value. Each sample was run in triplicate.

### Differential Scanning Calorimetry

Samples were prepared by adding preservative to PF (without sodium hydrogen carbonate). Samples were also prepared by mixing PF with each of the main components of the preservative in a similar manner to that described above for DMA experiments. Approximately 8 mg of each sample was sealed in



**Figure 1.** Film shear measurement head. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

stainless steel, high-pressure crucibles. DSC measurements were made using a DSC 8230 instrument (Rigaku, Tokyo, Japan). Samples were heated from 15 to 220°C at rates of 2, 3, 5, and 7°C min<sup>-1</sup> under a nitrogen atmosphere (flow rate 50 mLmin<sup>-1</sup>). An empty stainless steel crucible was used as a reference. After each sample had returned to room temperature, a second scan was performed under similar conditions to obtain the baseline response. The change in enthalpy,  $\Delta H$ , was calculated from the area under the peak in the DSC curve. The degree of conversion ( $\alpha$ ) and the rate of conversion with respect to time ( $d\alpha/dt$ ) were obtained by following formulae:

$$\alpha = \frac{\Delta H(t)}{\Delta H} \quad (1)$$

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H} \quad (2)$$

where  $t$  is the time,  $\Delta H(t)$  is the heat released up to  $t$ ,  $\Delta H$  is the total heat of reaction, and  $dH/dt$  is heat flow (mW).

### Kinetic Analysis by the Friedman Method

The kinetic analysis of the resin curing reaction can be described by the following equation:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (3)$$

where  $A$  (s<sup>-1</sup>) and  $E$  (kJ mol<sup>-1</sup>) are the Arrhenius pre-exponential factor and activation energy, respectively,  $R$  is the gas constant,  $T$  (K) is the absolute temperature, and  $f(\alpha)$  is the reaction model associated with a certain reaction mechanism.

The Friedman method<sup>12</sup> allows the model-fitting step to be eliminated by using DSC data from multiple heating rates. The method is based on eq. (4):

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha_i} = \ln(A_2 f(\alpha)) - \frac{E_{\alpha}}{RT_{\alpha_i}} \quad (4)$$

For a specific  $\alpha_i$ , a plot of  $\ln(d\alpha/dt)_{\alpha_i}$  versus  $T_{\alpha_i}^{-1}$  was obtained from DSC thermograms at various heating rates. The slope

allows the determination of the apparent activation energy. This procedure was repeated for various values of  $\alpha$  and the kinetic parameters were extracted by MATLAB<sup>®</sup> programs using the smoothing spline algorithm.

## RESULTS AND DISCUSSION

### Mechanical Cure Development of PF by DMA

Figure 2 shows the mechanical cure development of PF glue without preservative when heated at various constant temperatures. The lowest graph shows the change of temperature in the sample chamber. The storage modulus,  $G'$ , decreased and then increased markedly until reaching a maximum steady state value. The loss modulus,  $G''$ , began to decrease after the onset of the decrease in  $G'$ , then increased, passing through a maximum peak, and then decreased until reaching a minimum steady state value. The  $\tan \delta$  curve displayed three peaks, which coincided with the changes in the  $G'$  and  $G''$  curves. In previous work,<sup>3–6</sup> the number of peaks shown in the  $\tan \delta$  curves was between one and three. Differences in the number of  $\tan \delta$  peaks would result from differences in the chemical structure of the PF oligomer, heating temperature, and heating rate.

Four distinct stages were evident in the  $\tan \delta$  curve: (1) a region where  $\tan \delta$  increased before reaching a maximum, (2) from the maximum to the first shoulder peak, (3) from the first shoulder peak to the second shoulder peak, (4) from the second shoulder peak to the minimum plateau.

In the first region, the increase in  $\tan \delta$  was accompanied by decreases in  $G'$  and  $G''$ . The time required to reach the maximum for  $\tan \delta$  corresponds to the gel point, where the molecules lose the ability to flow.<sup>4,7</sup>

In the second region, the decrease in  $\tan \delta$  was accompanied by an increase in  $G'$ . The value of  $G'$  increased first gradually, then rapidly. At the inflection point for  $G'$ , a shoulder peak appeared in the  $\tan \delta$  curve. A broad, concave peak appeared in the  $G''$  curve in this region. The moderate increase in  $G'$  indicates that both curing and softening of the resin occurred, while the subsequent increase in steepness of the incline indicates that resin curing outpaced softening.

The values of  $G'$  and  $G''$  increased where the second shoulder peak appeared in the  $\tan \delta$  curve (the third region). The value of  $G'$  indicates the stiffness and that of  $G''$  indicates that energy is converted to heat. Therefore, the increase in these two curves indicates that a network structure was generated but still retained flexibility because of a lower crosslinking density. Following this,  $G''$  decreased gradually, indicating that molecular motion was restricted by crosslinking. After  $G'$  reached its maximum steady state value,  $G''$  continued to decrease, indicating that additional crosslinking occurred (the fourth region).

The time at which the maximum plateau for  $G'$  was reached increased with decreasing curing temperature and the peaks for  $G''$  and the shoulder peaks in  $\tan \delta$  were shifted toward a longer time, while the gel time was not affected by the difference in heating temperature. The curing after the gel point was retarded by a decrease in the curing temperature.

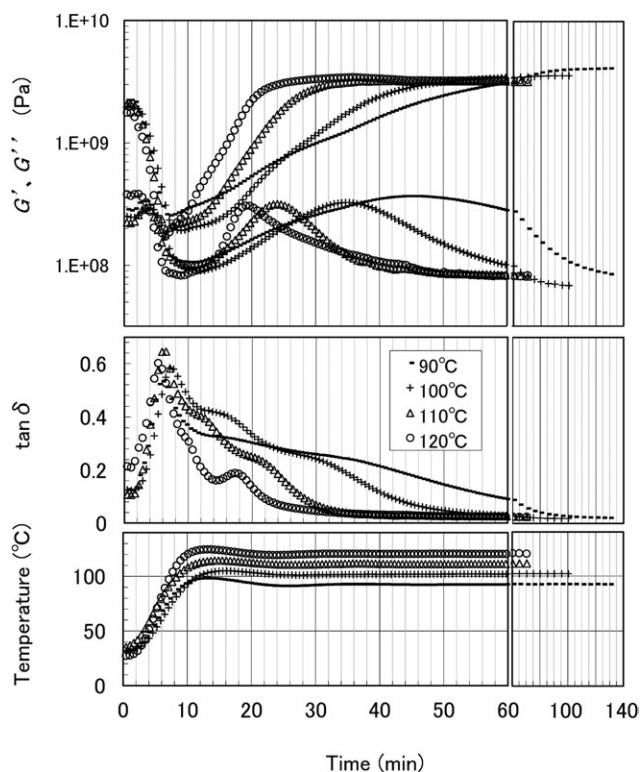


Figure 2. Typical DMA profiles for curing of PF glue at various temperatures.

### Effect of Preservative Addition on the Mechanical Curing of the PF

Figure 3 shows typical DMA cure profiles of PF glue containing preservative as a function of time during isothermal curing at various temperatures. The curing after the gel point was

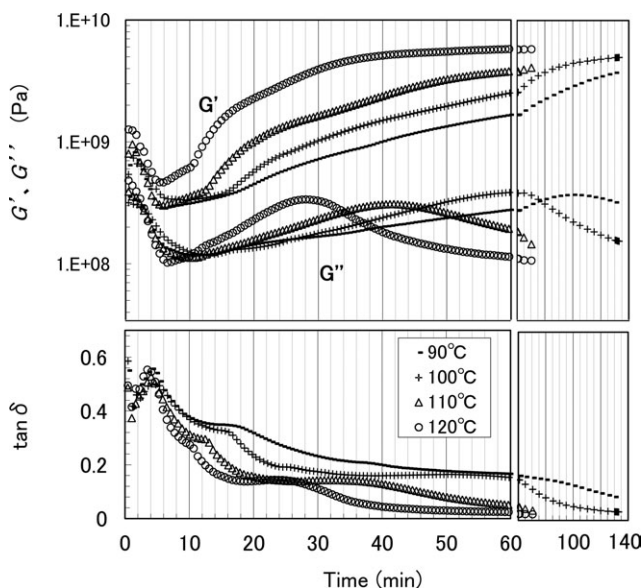
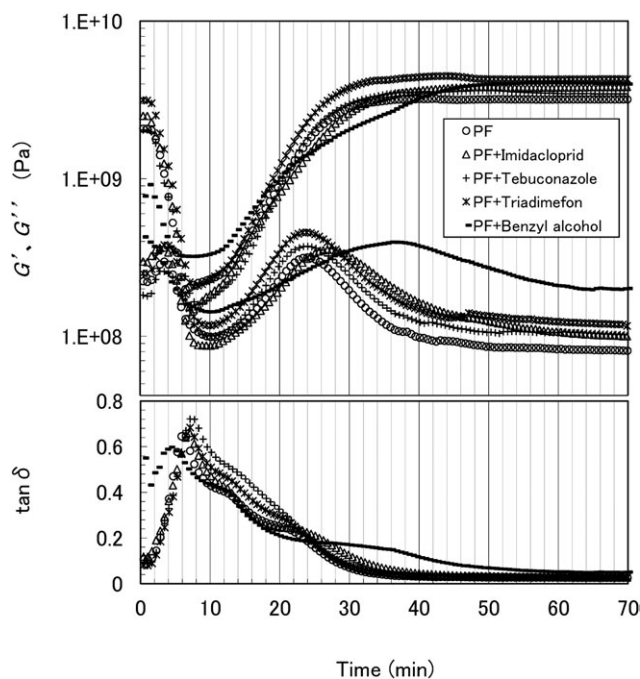
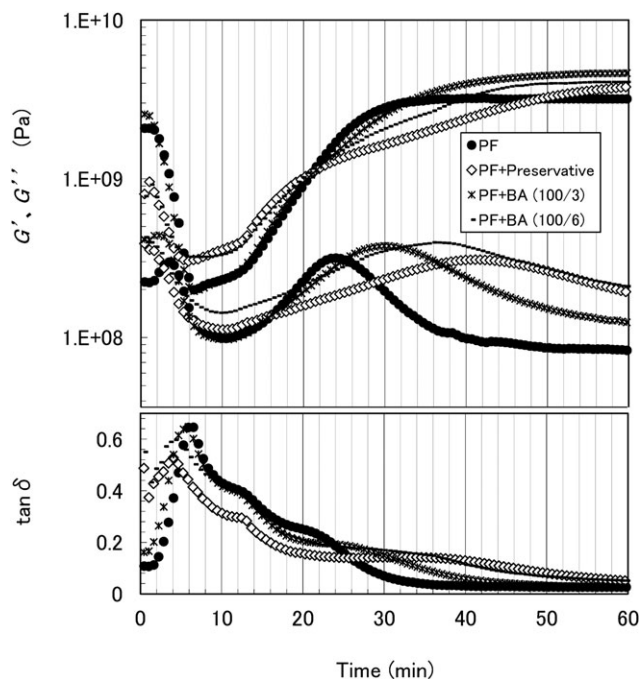


Figure 3. Typical DMA profiles for curing of PF glue containing preservative at various temperatures.



**Figure 4.** Typical DMA profiles for curing PF glue containing the individual preservative components at 110°C.

retarded by a decrease in the curing temperature. The upward slope of  $G'$  was lower and the time required to reach the maximum steady state value was longer than for glue with no preservative (Figure 2). The peaks in the  $G''$  and  $\tan \delta$  curves were shifted towards a longer time. This indicates that the addition of preservative retarded the mechanical curing of PF.



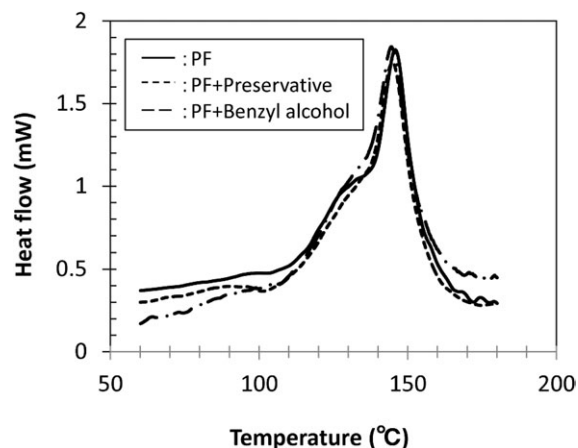
**Figure 5.** Comparison of the DMA profiles for curing PF glue, mixtures of PF glue and preservative, and mixtures of PF glue and benzyl alcohol (BA) at 110°C.

Figure 4 shows the DMA profiles of glue samples containing the individual main preservative constituents for curing at 110°C. The curves for PF glue containing benzyl alcohol (as noted in the Materials, used as a diluent in the preservative) were similar to those for PF glue containing preservative, while the curves for PF glue containing individual antitermite (imidacloprid) and antifungal (tebuconazole and triadimefon) compounds were similar to PF glue without the preservative.

Figure 5 compares the changes in  $G'$ ,  $G''$ , and  $\tan \delta$  with time for PF glue, PF glue containing preservative and PF glue containing benzyl alcohol. The benzyl alcohol content in the mixture of the PF glue and the preservative was equal to the ratio PF/benzyl alcohol = 100/6. The first shoulder peak in the  $\tan \delta$  curve appeared almost simultaneously in all four samples, while the second shoulder peak was shifted towards a longer time for PF glue samples containing preservative or benzyl alcohol. For PF glue containing preservative or benzyl alcohol at a ratio of 100/6, the second shoulder peaks appeared simultaneously and the  $\tan \delta$  curves reached a steady value at almost the same time. When the benzyl alcohol content was diminished to three parts per 100 parts of PF by weight, the second shoulder peak appeared between that of glue without preservative and glue with benzyl alcohol at a ratio of 100/6. The changes in the  $G'$  and  $G''$  curves corresponded to those in  $\tan \delta$ . The addition of benzyl alcohol appears to retard the complete curing of PF glue and the larger the amount of benzyl alcohol added, the slower the complete curing of the PF glue.

#### Kinetic Analysis of the Curing Process of PF Containing Preservative

Figure 6 shows the DSC thermograms for PF, a mixture of PF and preservative, and a mixture of PF and benzyl alcohol. Two overlapping exothermic peaks appeared, with the first peak being much smaller. There was practically no difference between these DSC curves. The peak temperatures of the second peak ( $T_p$ ) for PF containing preservative and PF containing any of the individual components of the preservative were almost the same as for PF without preservative (Table I). The total reaction enthalpy, which is the total heat released due to the curing



**Figure 6.** DSC thermograms for PF, mixtures of PF and preservative, and mixtures of PF and benzyl alcohol (heating rate: 3°C min<sup>-1</sup>).



**Table I.** Peak Temperature ( $T_p$ ) and Reaction Enthalpy ( $\Delta H$ ) of PF and the Mixtures

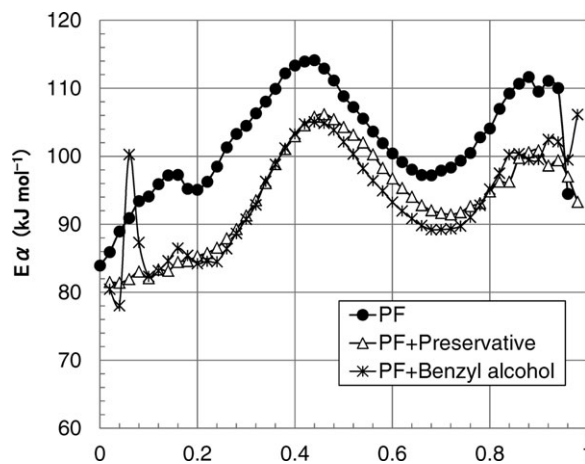
|                     | $T_p$ ( $^{\circ}\text{C}$ ) | $\Delta H$ ( $\text{J g}^{-1}$ ) |                 |
|---------------------|------------------------------|----------------------------------|-----------------|
|                     |                              | Average                          | SD <sup>a</sup> |
| PF                  | 145.3                        | 77.0                             | 1.4             |
| PF + Preservative   | 145.4                        | 78.8                             | 1.1             |
| PF + Benzyl alcohol | 144.5                        | 75.9                             | 4.4             |
| PF + Imidacloprid   | 145.4                        | 75.9                             | 2.6             |
| PF + Tebuconazole   | 145.7                        | 74.4                             | 4.0             |
| PF + Triadimefon    | 145.7                        | 78.8                             | 6.1             |

<sup>a</sup>Standard deviation.

reaction, did not change significantly with addition of preservative or individual components.

Figure 7 shows the dependence of  $E_x$  on  $\alpha$  for PF, PF containing preservative, and PF containing benzyl alcohol (100/6). Activation energies ranged between 80 and 120  $\text{kJ mol}^{-1}$ , which is consistent with the  $E_x$  for commercial PF computed using the Friedman and other algorithms.<sup>10</sup> The  $E_x$  curves for PF and the mixtures displayed three maximum peaks and two minimum peaks. An analysis of the form of the dependence of activation energy on the degree of conversion can identify the type of reactions in complex processes such as PF curing.<sup>18</sup> For PF, an increase in  $E_x$  up to an  $\alpha$  of 0.15 reveals that the curing process involved parallel reactions. A concave decrease in  $E_x$  reveals a change in the reaction process to a reversible intermediate stage. Above an  $\alpha$  of 0.2, the  $E_x$  curve again increased, up to an  $\alpha$  of 0.45, indicating that parallel reactions once again occurred, followed by the curve decreasing until 0.65, indicating that the reaction process changed to one involving a reversible intermediate. The first  $E_x$  peak may be attributed to the addition and condensation reaction for the higher molecular weight fraction of PF oligomer, while the second  $E_x$  peak may be attributed to the addition and condensation reaction for the lower molecular weight fraction of PF oligomer.<sup>10,13,14</sup> In addition, the  $E_x$  curve increased until the third peak, shown at  $\alpha = 0.88$ , followed by a convex decrease, indicating that the curing process changed from a kinetic-controlled to a diffusion-controlled regime.<sup>10,13,14,18</sup> The shapes of these three curves are closely similar (Figure 7). The addition of preservative and benzyl alcohol to the PF barely affected the reaction process during curing.

The results of DMA measurements indicate that the mechanical cure was retarded by the addition of the preservatives and benzyl alcohol, while the results of DSC measurements indicate that there was no effect on the reaction process through their addition. Considering the results of both DSC and DMA, benzyl alcohol added to PF could act as a plasticizer. The DMA specimen was dried in a vacuum at room temperature immediately prior to measurement. Water was removed from the specimen during drying but benzyl alcohol was still present in the specimen because of its relatively high boiling point of 205 $^{\circ}\text{C}$ . The residual benzyl alcohol acts as a plasticizer in the PF curing system, so the mechanical curing of PF was retarded. According to diffusion theory, a plasticizer decreases the viscosity of a reac-



**Figure 7.** Dependence of activation energies on the degree of conversion for PF, PF containing preservative and PF containing benzyl alcohol (at the ratio 100/6).

tion system, so that the transition to the diffusion-controlled regime should be retarded.<sup>13</sup> There was no retardation observed, however, during the curing of PF containing preservative or benzyl alcohol (Figure 7). He et al.<sup>13</sup> reported that during the curing of powdered PF containing a small amount of water, the  $E_x$  curve is similar to that of powdered PF without water. The amount of benzyl alcohol contained in the preservative used in this study had no effect on the curing reaction, as measured by kinetic analysis with DSC.

## CONCLUSIONS

Addition of preservative slowed the increase in  $G'$  and the maximum peak in the  $G''$  curve, while the second shoulder peak in the  $\tan \delta$  curves were shifted to longer times. Longer time was required to reach steady state  $G'$ ,  $G''$ , and  $\tan \delta$  values. The mechanical curing process of PF glue containing benzyl alcohol, as represented by the  $G'$ ,  $G''$ , and  $\tan \delta$  curves, appeared to be similar to that of glue containing preservative. The individual addition of imidacloprid, tebuconazole, or triadimefon, the antitermite and antifungal compounds contained in the preservative used in this study, has no significant effect on the mechanical curing process.

There was no difference in the total reaction enthalpy between PF, PF mixed with preservative, and PF mixed with the individual preservative components. The dependence of the activation energies on the degree of conversion was similar for PF and the mixtures, indicating that the addition of the preservative has no effect on the PF curing reaction. The combined results of DMA and DSC measurements indicate that the addition of benzyl alcohol plasticizes the PF curing system.

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