Cure Kinetics of Aqueous Phenol–Formaldehyde Resins Used for Oriented Strandboard Manufacturing: Effect of Zinc Borate

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ABSTRACT: The effect of zinc borate (ZB) on the cure kinetics of commercial phenol–formaldehyde oriented strandboard adhesives was studied using differential scanning calorimetry. ZB caused a separation of the addition and condensation reactions for both face and core resin (CR) systems with lowered cure temperature for the addition reaction. For the face resin, ZB did not change its *n*th-order curing mechanism, but retarded the whole cure reactions, and increased the reaction order and the activation energy. Compared with neat CR, the addition reaction of the CR/ZB mixture, which occurred at temperatures lower than 60°C, also followed an *n*th-order reaction mechanism. The condensation reaction of the mixture was changed from an autocatalytic reaction to an *n*th-order one with the reaction order of about 1. The proposed models fitted the experimental data well. Relationships among cure reaction conversion (i.e., cure degree), cure temperature, and cure time were predicted for various resin/ZB systems. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3886–3894, 2006

Key words: resins; curing of polymers; oriented strandboard; zinc borate; differential scanning calorimetry (DSC)

INTRODUCTION

Chemical treatment of wood-based composites against insects and biodeterioration is gaining importance in the forest product industry.[1,2] Oriented strandboard (OSB), a structural wood composites, is susceptible to biodeterioration by a variety of insects and microorganisms, such as termites and wood-decay fungi, which can severely affect its economic value and usefulness. It is thus important to develop methods for the long-term protection of OSB, which can be applied during the manufacturing process.

Work has been done to incorporate boron-based chemicals such as zinc borate (ZB) into OSB furnish during the blending process.[3–6] Panels with good termite and decay resistant properties have been successfully developed.[6] Borate, however, has an adverse effect on mechanical and physical properties of OSB, especially those bonded with phenol–formaldehyde (PF) resin.[4] As a result, a higher resin-loading rate is usually needed to achieve acceptable board strength and durability at high levels of borate addition. The problem associated with the potential long-term durability of borate-modified OSB has generated controversy in the structural application of the product. This signals the need for studying bonding characteristics and durability of the OSB as influenced by wood properties and levels of borate application.

The adverse effect of borate in OSB has been attributed to the interference of borate with the resin cure process during hot pressing.[3–5] It is believed that boron ions react with the functional methylol groups on resin molecules, which would cause the resin to gel before it is able to develop an effective bond. Sean et al.,[5] in evaluating the effect of borate treatment on the physical and mechanical behavior of OSB, used polyethylene glycol (PEG) as a flow agent to improve resin fluidity during hot-pressing. They reported that the adverse effect of borate on adhesive fluidity could be minimized by the addition of organic flow agents containing hydroxyl (—OH) groups such as PEG. Lee et al.[7] reported that measured resin gel times of PF resins decreased as the amount of ZB increased, and the reduced gel time was partially recovered by using PEG in combination with the borate. Resin gel time is only considered a relative measure of the resin cure rate. It is usually characterized by a sudden, striking increase in the viscosity from liquid to a solid gel, as measured by a suitable gel-time apparatus. The measurement, however, does not lead to curing kinetic information. Jiang and Kamdem[8] investigated the change of the cure temperatures of PF adhesives in the presence of copper-based preservative (i.e., copper

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azole and alkali copper quat-type C) using dynamic differential scanning calorimetry (DSC). A retardant effect on the cure of the OSB PF resins was observed. Very little work has been done so far on the influence of biocides (e.g., ZB) on the curing kinetic behavior of PF resins.

In a previous article,[9] the influence of wood substrates on the cure kinetics of aqueous PF OSB face and core adhesives was investigated using DSC. The specific objectives of this study were to investigate the influence of biocides (i.e. ZB) on curing kinetics of PF OSB resins using DSC techniques and to predict curing reactions for the resin systems containing biocides.

METHODS

Materials

One PF OSB face resin (FR) and one PF OSB core resin (CR) were obtained from Hexon Specialty Chemical (Springfield, OR). The FR has a total alkalinity of 2.69 wt % and pH of about 10. Its solid content, viscosity, and specific gravity are 45.0 wt %, 143 mPa s, and 1.17, respectively. The CR, which contains a complexing agent, has a total alkalinity of 6.85 wt % with pH between 11 and 12. The solid content, viscosity, and specific gravity for the CR are 45.2 wt %, 95 mPa s, and 1.22, respectively. Both resins were stored in a freezer prior to measurements. ZB ($1ZnO–3B_2O_3–3.5H_2O$) was obtained from U.S. Borax Company. The specific density of the borate was 2.79.

Preparation of the resin/ZB mixtures

The FR/ZB mixtures were prepared by mechanically mixing the aqueous FR with the ZB load level of 5, 10, and 20% based on the FR solid weight. The CR/ZB mixture was prepared by mixing the aqueous CR with 5% ZB based on the solid weight of the CR. All these mixtures were stored in a freezer prior to measurements.

Differential scanning calorimetry

The cure reaction rates of neat resins, ZB, and their mixtures were measured using a differential scanning calorimeter (TA DSC Q100). The samples were removed from the freezer and allowed to warm to room temperature. Samples of 10–15 mg were taken and placed in hermetically sealed steel capsules (TA high volume pans) that can withstand vapor pressures up to 10 MPa.

The DSC testing procedures were similar to those reported in the previous article.[9] During DSC runs, a steady isothermal baseline was established at the cure temperature using two empty sample pans. The data acquisition system was then initiated by isothermally carrying the reaction to completion in a temperature range of 50–160°C. Before the test, the temperature of the base heating block was maintained at 10°C. The reaction was considered complete when the rate curve leveled off to the baseline. The total area under the exothermal curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure at a given temperature.

The measurement of the heat flow rate as a function of curing temperature using a dynamic DSC method was also made. Dynamic scans were made with a heating rate of 5°C/min. The scanning temperature ranged from 40 to 230°C. Before scanning, the base heating block was cooled to 10°C and maintained at this temperature level.

RESULTS AND DISCUSSION

Effect of ZB on the cure of the FR

Dynamic DSC curves for the FR, ZB, and their mixtures in different weight ratios are shown in Figure 1(a). At the heating rate of 5°C/min, there was only one exothermal peak at 140°C for the neat FR, and the onset cure temperature was about 100°C. The exothermal peaks of ZB were so weak that it could be ignored. For the FR/ZB mixtures, there were two peaks. One peak was at about 142.5°C, and the other appeared at a lower temperature. The more the added ZB, the lower is this temperature. The onset cure temperature for the mixture containing 20% ZB was only 72.5°C. It was confirmed early that the cure of PF resins was accomplished in a two-step process.[10–12] The first step involved the addition of formaldehyde to phenol to form hydroxymethyl phenol, and the second one involved the condensation of hydroxymethyl phenols to form methylene and methylene-ether-bridged di- or high-molecular compounds. In this work, ZB caused a separation of the addition and condensation reactions of the FR by accelerating the addition reaction.

Under the isothermal conditions [Fig. 2(a)], the conversion rate of the FR/ZB mixture was the highest when $t = 0$, and then decreased with the cure time increased, which is the typical characteristic of a cure reaction obeying an nth-order reaction kinetics. Before the conversion reached 10% at temperatures lower than 135°C, the onset conversion rate was unusually high and decreased very fast with the conversion. This phenomenon should be ascribed to the accelerated addition part of the cure reactions by ZB. At temperatures of 135°C or higher, the main condensation part ran so fast that the influence of the addition was overlapped. The same phenomenon was observed for the FR/ZB mixture containing 10 and 20% ZB.

The conversion rate of an nth-order cure reaction is given by[9]:

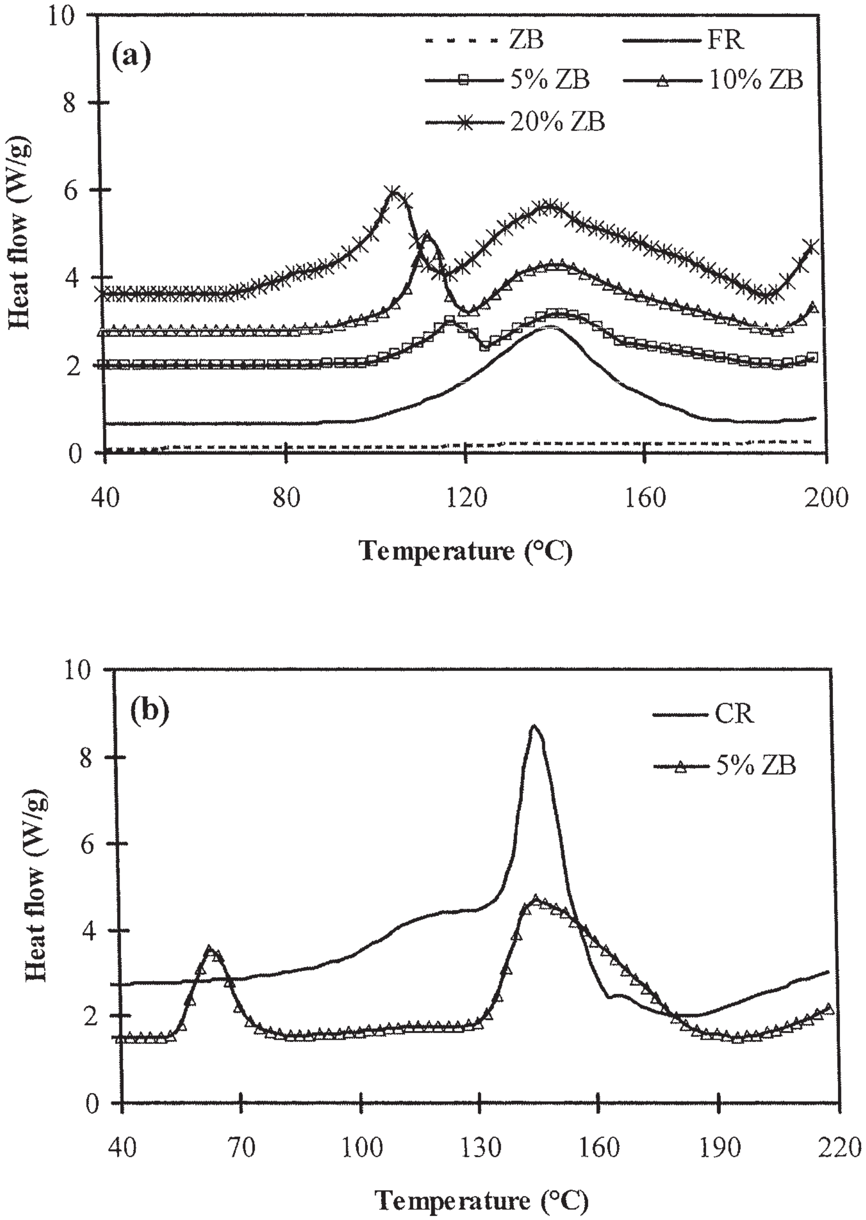

Figure 1 Dynamic DSC curves at the heating rate of 5°C/min: (a) FR, ZB, and their mixtures and (b) CR and its mixture with ZB.

$$\frac{d\alpha}{dt} = \frac{dH}{dt\Delta H_{\mathrm{RXN}}} = k(1-\alpha)^n \tag{1}$$

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where α is the chemical conversion or extent of reaction; t is the reaction time (s); H is the heat flow of reaction (J/g); ΔH_{RXN} is the total exothermic heat of the cure reaction (J); k is rate constant (s^{-1}); n is the reaction order; A is the pre-exponential constant (s^{-1}); E is activation energy (J/mol); R is a gas constant (J/mol K); and T is reaction temperature (K). At an isothermal condition, A, n, and E can be obtained through a two-step linear regression analysis, using the transformed eqs. (1) and (2):

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k + n\ln(1-\alpha) \tag{3}$$

$$\ln k = \ln A - \frac{E}{RT} \tag{4}$$

where ln is natural logarithm. The isothermal DSC data were used to calculate the kinetic parameters based on eq. (3) and the results are shown in Table I.

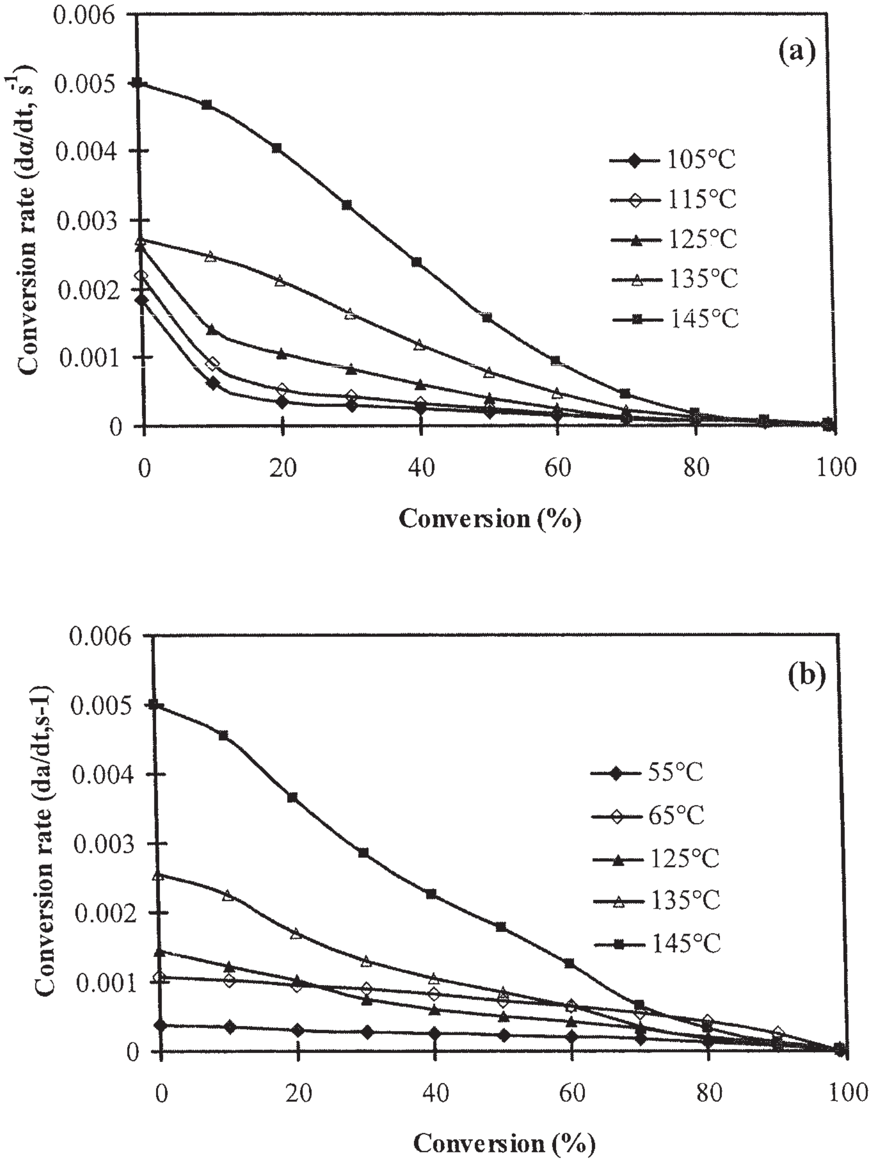

Figure 2 Conversion rate as a function of percent conversion at various isothermal temperatures: (a) FR/ZB (5%) and (b) CR/ZB (5%).

TABLE I
Isothermal Cure Kinetic Parameters of the Face Resin/ZB Mixtures

Temperature (°C)	Model parameters[a]								
	5% ZB			10% ZB			20% ZB		
	n	k (10^{-3} s^{-1})	r^b	n	k (10^{-3} s^{-1})	r^b	n	k (10^{-3} s^{-1})	r^b
100	1.32	0.66	0.94	1.22	0.55	0.96	1.10	0.66	0.92
115	1.50	0.95	0.96	1.35	1.00	0.99	1.22	0.91	0.99
125	1.76	1.60	0.97	1.72	2.09	0.99	1.27	2.22	0.99
135	1.80	2.80	0.99	1.65	2.71	0.99	1.29	3.45	0.99
145	1.97	5.74	0.99	1.72	5.30	0.99	1.57	6.74	0.99

[a] n, reaction order; k, reaction rate constant.
[b] Correlation coefficient.

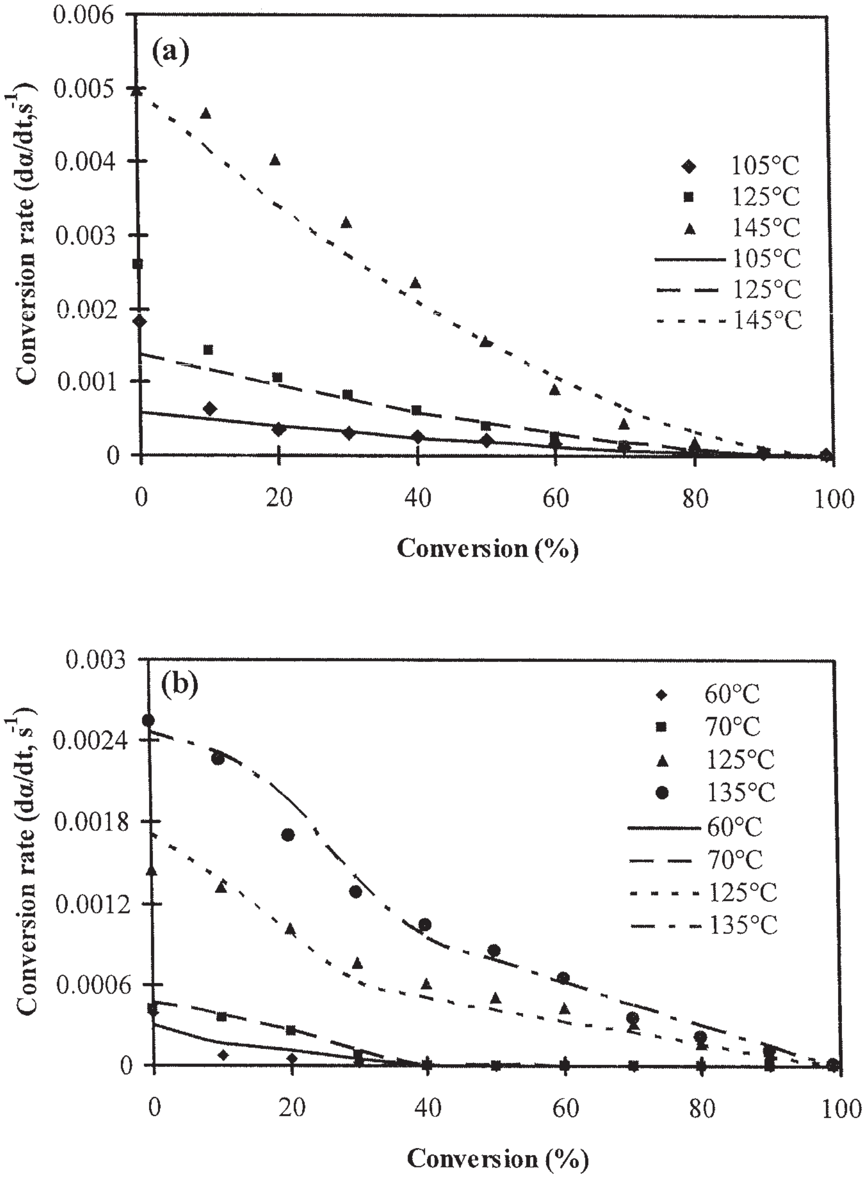

Figure 3 Comparison of predicted (lines) and experimental (symbols) conversion rates versus percent conversion at various isothermal temperatures: (a) FR/ZB (5%) and (b) CR/ZB (5%).

The mean reaction order of the FR is about 1[9]; it increased to 1.67, 1.53, and 1.29 with the ZB loading level of 5, 10, and 20%, respectively. Further linear regressions with eq. (4) showed that the activation energy also increased (i.e. 70.89, 72.90, and 78.59 KJ/mol for the mixture containing 5, 10, and 20% ZB, respectively). The corresponding kinetic equations for the FR/ZB mixtures are summarized as follows:

$$\frac{d\alpha}{dt} = 3.60 \times 10^{6} \exp\left(-\frac{8530}{T}\right)(1-\alpha)^{1.67} \tag{5}$$

$$\frac{d\alpha}{dt} = 6.68 \times 10^{6} \exp\left(-\frac{8772}{T}\right)(1-\alpha)^{1.52} \tag{6}$$

$$\frac{d\alpha}{dt} = 4.24 \times 10^{7} \exp\left(-\frac{9458}{T}\right)(1-\alpha)^{1.29} \tag{7}$$

Equations (5)–(7) are for the FR/ZB mixture containing 5, 10, and 20% ZB, respectively. Figure 3(a) shows the comparison between the experimental and predicted cure reaction rates.

The curing reactions of PF resins are typically exothermic; thus, it is assumed that the cure reaction degree is proportional to the exothermic heat (the reaction enthalpy) for the same system. According to the relationship between enthalpy and temperature (Table II), the ideal cure temperature for both the FR and its mixture with 5% ZB was about 135°C. As shown the maximum reaction enthalpy obviously decreased when ZB was added. The more the added ZB, the more the maximum enthalpy was reduced. However, the enthalpy increased at temperatures lower than 125°C with increasing ZB loading level from 5 to 20%, which may have resulted from the ZB acceleration on the addition reaction.

Results from both dynamic and isothermal DSCs showed that the cure reactions of the FR were retarded by ZB, although introducing ZB accelerated the addition part. There is 37.2 wt % zinc oxide (ZnO) in ZB compound, and ZnO is a Lewis base, which may accelerate the PF cure reaction by forming complexes between borate ions and the functional methylol groups on resin molecules.[5] At the same time, ZB powder absorbed most of the water in the PF resin, and the viscous liquid FR turned into solid even at a loading level of 5%. The addition reaction was not influenced significantly by diffusion, since the addition reactants were small molecules. The relative concentrations of addition reactants increased when water was absorbed, which possibly accelerated the addition. However, the condensation reaction, which occurred among bigger molecules, was obviously retarded by diffusion. Because the condensation reaction was the main reaction during the FR curing,[13] ZB retarded the entire cure reactions for the FR.

Effect of ZB on the cure of the CR

The quantitative change of enthalpy (i.e. heat flow rate) as a function of temperature for the CR and its mixture containing 5% ZB is shown in Figure 1(b). It is a plausible assumption that there were two dominant reactions, the addition and condensation, involved in the cure of the CR/ZB mixture.[10–12] The exothermal peak for the addition reaction appeared at 62.5°C, which was much lower than that of the neat CR (i.e. 125°C).[9] The peak for the condensation was at about 145°C similar to that of the CR. The onset cure temperature for the addition reaction was as low as 50°C when the heating rate was 5 °C/min. Obviously, ZB separated the addition and condensation reactions by accelerating the addition component.

A series of isothermal reaction rate curves as a function of conversion for the CR/ZB mixture are shown in Figure 2(b). The interesting finding was the change of the cure mechanism. For the CR, there obviously existed two kinds of cure mechanisms simultaneously, i.e. the *n*th-order cure kinetics for the addition reaction and the autocatalytic for the condensation reaction.[9] There was only one cure mechanism (i.e. an *n*th-order reaction) for the CR/ZB mixture [Fig. 2(b)]. The interaction, the strong secondary interactions between the resin and ZB, might have changed the cure mechanism.

TABLE II
Enthalpy of the Face Resin/ZB Mixtures

Temperature (°C)	Enthalpy (J/g)			
	Face Resin	5% ZB	10% ZB	20% ZB
105	–	524	617	722
115	–	704	719	777
125	1794	1680	729	792
135	2249	1037	1133	901
145	2041	883	997	589

TABLE III
Enthalpy of the Core Resin/ZB (5%) Mixture

Temperature (°C)	Enthalpy (J/g)	Maximum (J/g)
55	59	245
60	171	
65	245	
70	230	
125	673	733
135	676	
145	733	
155	608	

It is assumed that the conversion degree (i.e. cure degree) is proportional to the exothermic heat (the reaction enthalpy) for the typically exothermic cure reactions of PF resins. Thus, the following equations are defined:

$$Q_t = Q_a + Q_c; \quad \phi = \frac{Q_a}{Q_t}; \quad 1 - \phi = \frac{Q_c}{Q_t};$$

$$\alpha = \phi\alpha_a + (1 - \phi)\alpha_c \quad (8)$$

$$\frac{d\alpha}{dt} = \phi\frac{d\alpha_a}{dt} + (1 - \phi)\frac{d\alpha_c}{dt} \quad (9)$$

where Q_t, Q_a, and Q_c are the total exothermic heat for the whole reactions, the addition reaction, and the condensation reaction, respectively; ϕ is the weighing factor representing the fraction of the addition reaction; $(1 - \phi)$ is the weighting factor for the condensation reaction; α, α_a, and α_c are the conversions (cure degrees) corresponding to the whole cure reactions, the addition reaction, and the condensation reaction, respectively. According to the reaction heat at different temperatures (Table III), the value of $\phi = 0.33$ was estimated by dividing the maximum reaction heat of the addition reaction with the maximum exothermic heat of the whole cure reactions. Based on eq. (1) the whole cure kinetic equation can be described as follows:

$$\frac{d\alpha}{dt} = 0.33A_a \exp\left(-\frac{E_a}{RT}\right)(1 - \alpha_a)^{n_a} + 0.67A_c \exp\left(-\frac{E_c}{RT}\right)(1 - \alpha_c)^{n_c} \quad (10)$$

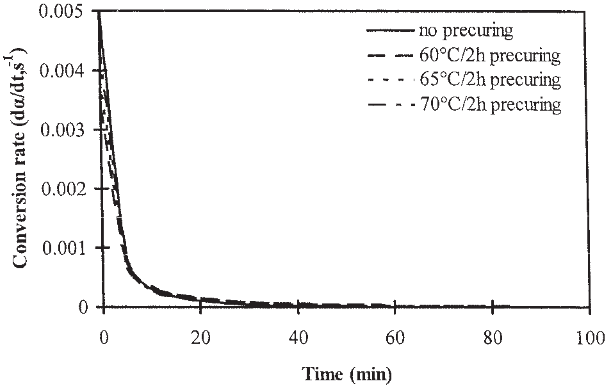

Figure 4 Conversion rate versus conversion for the CR/ZB (5%) mixture at 145°C.

TABLE IV
Comprehensive Cure Kinetic Parameters of the Core Resin/ZB (5%) Mixture

Temperature (°C)	Model parameter Reaction order (n)	Reaction rate constant, k (10^{-3} s^{-1})	r^a
55	0.67	0.35	0.99
60	0.63	0.71	0.99
65	0.63	1.09	0.99
70	0.64	1.31	0.99
125	0.85	0.90	0.99
135	1.03	1.44	0.99
145	1.23	3.05	0.97

[a] Correlation coefficient.

TABLE V
Diffusion-Control Factors of the Face Resin/ZB (5%) Mixture at Different Conversions

Temperature (°C)	Diffusion-control factors (Conversion (%)) 0	10	20
65	1.000	0.996	0.994
70	0.955	0.938	0.941
125	0.064	0.061	0.067
135	0.049	0.051	0.054
145	0.047	0.051	0.050
155	0.044	0.048	0.045

where A_a, E_a, and n_a are the pre-exponential constant, activation energy, and reaction order for the addition reaction; A_c, E_c, and n_c are the corresponding parameters for the condensation reaction. At temperatures lower than 85°C, the value of α_c was 0 since condensation reactions did not happen at all [Fig. 1(b)]. The maximum of the total conversion $\alpha = 0.33\alpha_a$ was 33%. When the cure temperature was above 85°C, the value of α_a was assumed to be 1 soon before the condensation reaction began. As shown in Figure 4, this assumption was proven to be reasonable.

The kinetic parameters, obtained from the corresponding isothermal DSC data according to eqs. (3) and (8), are shown in Table IV. For the CR, the reaction order for the addition reaction was 2.38, and the total reaction order of the autocatalytic condensation reaction was about 5.[9] For the CR/ZB (5%) mixture, the addition reaction had the lower reaction order of 0.64, and the condensation was an nth-order reaction with the reaction order of 1.04. Combining the results from linear regressions with eq. (4), the kinetic equations for the mixture were obtained as

$$\frac{d\alpha}{dt} = 1.62 \times 10^9 \exp\left(-\frac{9891}{T}\right)\left(1 - \frac{\alpha}{0.33}\right)^{0.64} + 6.50 \times 10^7 \exp\left(-\frac{10{,}135}{T}\right) \quad (\alpha \leq 33\%) \quad (11)$$

$$\frac{d\alpha}{dt} = 0.67\frac{d\alpha_c}{dt} = 6.50 \times 10^7 \exp\left(-\frac{10{,}135}{T}\right) \times \left(1 - \frac{\alpha - 0.33}{0.67}\right)^{1.04} \quad (\alpha > 33\%) \quad (12)$$

The diffusion effect on the addition reaction at high temperatures must be considered since the addition reaction can take place at temperatures as low as 50°C [Fig. 1(b)]. Chern and Poehlein proposed a Williams-Landel-Ferry type function that models the change in polymer properties based on the variation in the free volume.[14] It can be combined with eq. (11) to model a change in the reaction rate as

$$\frac{d\alpha}{dt} = \left[1.62 \times 10^9 \exp\left(-\frac{9891}{T}\right)\left(1 - \frac{\alpha}{0.33}\right)^{0.64} + 6.50 \times 10^7 \exp\left(-\frac{10{,}135}{T}\right)\right] f(\alpha) \quad (\alpha \leq 33\%) \quad (13)$$

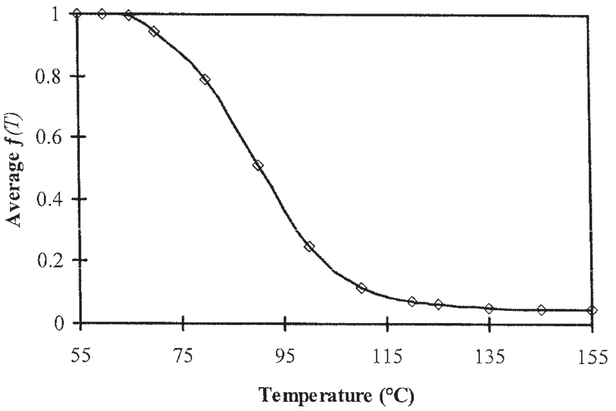

Figure 5 Diffusion-control factor versus temperature for the CR/ZB (5%) mixture.

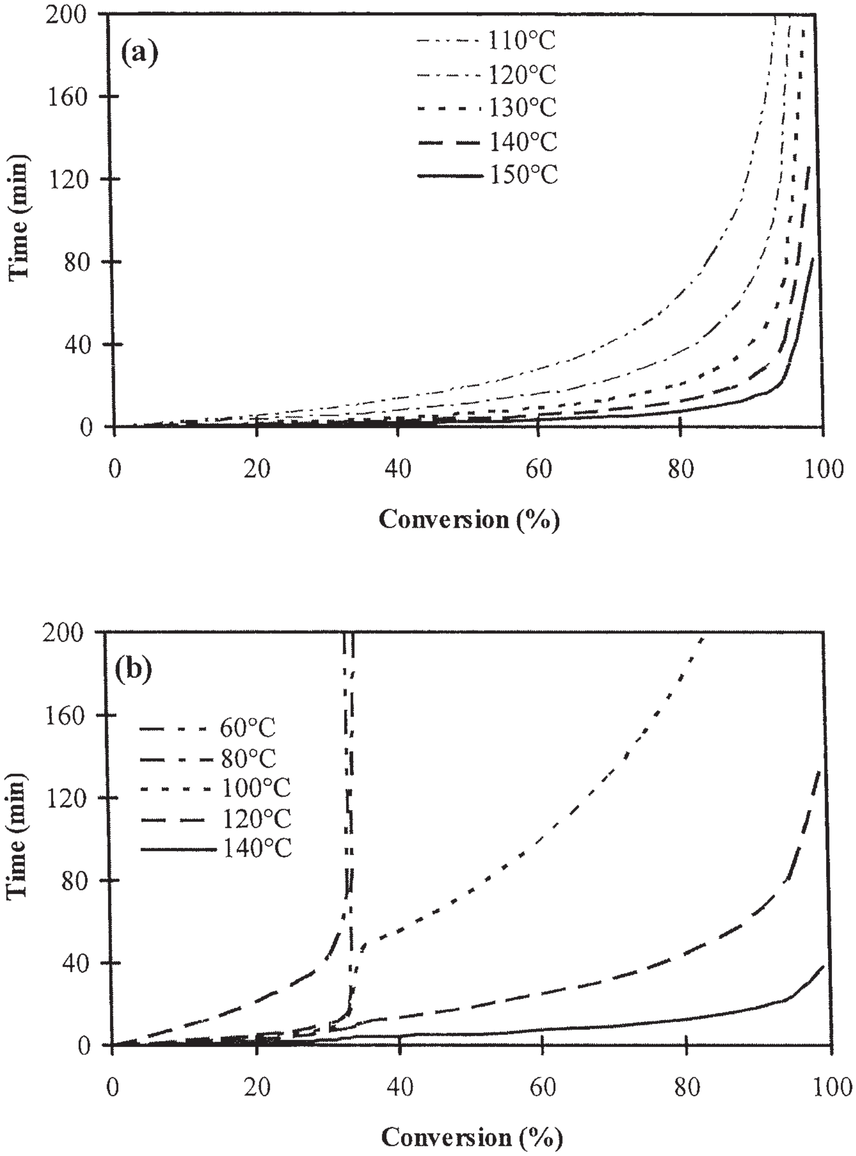

Figure 6 Predicted curing time as a function of percent conversion at various isothermal temperatures: (a) FR/ZB (5%) and (b) CR/ZB (5%).

This involves determination of $f(\alpha)$, which represents the diffusion-control factor and is defined by two empirical parameters as

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha^*)]} \quad (14)$$

where C is the material constant for a given PF resin composition; α^* is the critical conversion that depends on the curing temperature; and $f(\alpha)$ was calculated by dividing the experimental reaction rate ($d\alpha/dt$) by the corresponding calculation from eq. (11) at conversions lower than 33%. The result is listed in Table V. At low conversions, $f(\alpha)$ was almost independent on conversion, and the effect of temperature on $f(\alpha)$ was significant. When the conversion is lower than 33%, the average values of diffusion-control factor $f(T)$ at different temperatures are shown in Figure 5. The comparison of the cure reaction rate between the experimental and the predicted values in Figure 3(b) shows a close agreement.

Prediction for the cure of the face and CR/ZB mixture

The prediction of the relationship among reaction conversion (i.e., curing degree), cure temperature, and cure time was performed by integrating the kinetic equations.[9] For the FR/ZB (5%) mixture, the following equation was obtained from eq. (5):

$$t = 4.15 \times 10^{-7} \exp\left(\frac{8530}{T}\right)[(1 - \alpha)^{-0.67} - 1] \quad (15)$$

For the CR/ZB (5%) mixture, the prediction was done by integrating the corresponding kinetic eqs. (12) and (13) The results are shown as

$$t = \frac{5.67}{f(T)} \times 10^{-10} \exp\left(\frac{9891}{T}\right)\left[1 - \left(1 - \frac{\alpha}{0.33}\right)^{0.36}\right] \quad (\alpha \leq 33\%) \quad (16)$$

$$t = 2.54 \times 10^{-7} \exp\left(\frac{10{,}137}{T}\right)\left[(1-\alpha)^{-0.04} - 1\right] \quad (\alpha > 33\%) \quad (17)$$

The predictions for the cure reactions of the FR/ZB and CR/ZB mixtures are shown in Figure 6, which provide direct information for deciding the actual curing technology of the resin systems.

SUMMARY AND CONCLUSIONS

The effect of ZB on the cure behavior of commercial PF OSB core and FRs was studied by DSC. ZB caused a separation of the addition and condensation reactions involved in the cure of both FR and CR, with the lowered cure temperature of the addition reaction. ZB did not change the cure reaction mechanism of the FR (i.e., *n*th-order), but changed that of the CR.

ZB accelerated the addition part of the FR cure. The more the added ZB, the lower is the onset cure temperature for the addition. The onset cure temperature was only 72.5°C when the loading level of ZB was 20%. ZB retarded the cure reactions of the FR as a whole. The cure reaction order of the FR/ZB mixture was higher than that of the FR, but decreased as the loading level increased. The activation energy of the FR was increased from 62.30 to 70.89, 72.90, and 78.59 KJ/mol after introducing 5, 10, and 20% ZB, respectively.

ZB also lowered the onset cure temperature of the CR, and caused the addition reaction to occur at much lower temperatures. Compared with the neat CR, the addition reaction of the CR/ZB mixture also followed the *n*th-order cure kinetics with the lower reaction order. However, the mechanism of the condensation was changed to follow an *n*th-order cure mechanism with the reaction order of 1.04. The activation energy was also increased.

The models developed to predict the relationships among reaction conversion (i.e. curing degree), cure temperature, and cure time fitted the experimental data well. The predictions provide direct information for deciding the actual cure technology for resin/wood composites containing biocides. Future work will deal with the combined effect of wood and biocides.

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