Cure Kinetics of Aqueous Phenol–Formaldehyde Resins Used for Oriented Strandboard Manufacturing: Analytical Technique

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ABSTRACT: The cure kinetics of commercial phenol–formaldehyde (PF), used as oriented strandboard face and core resins, were studied using isothermal and dynamic differential scanning calorimetry (DSC). The cure of the face resin completely followed an nth-order reaction mechanism. The reaction order was nearly 1 with activation energy of 79.29 kJ mol^{-1}. The core resin showed a more complicated cure mechanism, including both nth-order and autocatalytic reactions. The nth-order part, with reaction order of 2.38, began at lower temperatures, but the reaction rate of the autocatalytic part increased much faster with increase in curing temperature. The total reaction order for the autocatalytic part was about 5. Cure kinetic models, for both face and core resins, were developed. It is shown that the models fitted experimental data well, and that the isothermal DSC was much more reliable than the dynamic DSC in studying the cure kinetics. Furthermore, the relationships among cure reaction conversion (curing degree), cure temperature, and cure time were predicted for both resin systems. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1642–1650, 2006

Key words: resins; curing of polymers; oriented strandboard; modeling; differential scanning calorimetry

INTRODUCTION

Phenol–formaldehyde (PF) resins are thermosetting polymers, which are widely used in many fields. One such application is as wood adhesives for the manufacture of wood-based composites, including plywood, oriented strandboard (OSB), and fiberboard. The consolidation of these composites is achieved by a hot-pressing process. This process involves simultaneous heat and mass transfer, curing of adhesives, and forming panel strength. A better understanding and optimization of this operation can be achieved through simulation using large mathematical models, in which adhesive curing models are critically important.[1]

It is known that the curing behavior of wood adhesives directly affects both hot-pressing procedures and physical properties of wood products, during their manufacture.[2] Differential scanning calorimetry (DSC) is a well-established technique to study the polymer curing process and to detect involved heat flow, from which analytical models are formulated to obtain kinetic information. This technique has been widely used to analyze the cure process of the thermosetting polymers, including epoxy resins,[3–10] isocyanate resins,[11,12] and PF.[2,13–20]

Although there are quite a few reports about the cure kinetics of PF resins, studied by DSC, most of the research treated the cure reaction of PF resins simply as an nth-order reaction and studied the effect of other ingredients on the cure processes by dynamic DSC. Among the studies reported, a kinetic study of the polymerization of PF resin in the presence of cellulosic materials was carried out by Chow,[13] using DSC. Mizumachi and Morita[15] obtained the activation energy of the curing reaction of phenolic resin in the presence of wood. To evaluate the effect of lignin addition on the curing of phenolic resin, Barry et al.[16] obtained the activation energy, the heat of the reaction, and the order of the reaction, using the Borchardt–Daniels' nth-order reaction model. Pizzi et al.[17] found that the reaction of polycondensation of PF resins in the presence of wood had a lower energy of activation than that of the PF resin alone. He et al.[18] studied the role of water in the curing system of powered PF resol resins by investigating the relationship between the conversion and the activation energy. He and Riedl[2] studied the influence of wood–resin interaction on the curing

kinetics of PF with DSC and FTIR, using the Kissinger model. Alonso et al.[19] compared the difference of cure kinetics between lignin–PF and PF resol resins to evaluate the effect of methylolated ammonium lignin sulfonate, and fitted the data by means of the Borchardt–Daniels, Ozawa, and Kissinger methods for nth-order reactions.

Many PF resins, especially those containing complexing agents used to accelerate their cure reactions at low temperatures, do not show an nth-order reaction, which can be distinguished clearly by isothermal DSC, rather than by dynamic DSC. Park et al.[20] characterized the thermal behavior of carbonate-modified PF resol resins with both dynamic and isothermal methods. The isothermal method revealed that the curing of propylene carbonate-modified resins followed pure autocatalytic reaction kinetics, whereas the resins modified by the other two additives, sodium carbonate and potassium carbonate, showed nth-order reactions. Liu and Gao[21] also found that the isothermal cure reaction of a boron-containing PF resin followed an autocatalytic reaction mechanism, and the kinetic parameters were derived. In general, the cure of PF resin can be influenced by the interactions between resin and wood,[2,13,15,17,22,23] as well as those between resin and inorganic or organic additives. Understanding these interactions is fundamental to improve the productivity and physical properties of wood-based panels.

This work is part of a large project dealing with the influence of wood, chemical additives, and processing technology on curing kinetics of structural wood composite adhesives. The specific objectives of this study were to investigate and model curing kinetics of neat PF resins for OSB manufacturing, using DSC techniques.

METHODS

Materials

Two aqueous PF resins, for OSB face (called face resin) and OSB core (called core resin), were obtained from Borden Chemical (Springfield, OR). The face resin has total alkalinity of 2.69 wt % and pH of about 10. The solid content, viscosity, and specific gravity are 45.0 wt %, 143 mPa s, and 1.17, respectively. The core resin, containing a complexing agent, has total alkalinity of 6.85 wt % with pH between 11 and 12. The solid content, viscosity, and specific gravity for the core resin are 45.2 wt %, 95 mPa s, and 1.22, respectively. Both resins were stored in a freezer prior to measurements.

Differential scanning calorimetry

The cure reaction rates of the core and face reins were measured using a differential scanning calorimeter (DSC-TA Q100). Adhesive samples were removed from the freezer and were allowed to warm to room temperature. Small samples (30–40 mg) were taken and placed in hermetically sealed steel capsules (TA high-volume pans) that can withstand vapor pressures up to 10 MPa.

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 100–170°C. Before the test, the temperature of the base heating block was maintained at 40°C. The thermal equilibrium of the sample and the reference holders was achieved quickly, and nitrogen gas was introduced into the DSC cell. A continuous curve was obtained, showing the rate of heat generation for a given weight of the sample as a function of time. 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 heating rates of 2.5, 5, 7.5, 10, 15, and 20°C min, respectively. The scanning temperature ranged from 40 to 220°C, and the base heating block was cooled to 10°C and was maintained at this temperature level before scanning.

Cure kinetic models

The basic equation that relates the conversion rate at a constant temperature to some function of the reactant concentration has the following form:

$$\frac{d\alpha}{dt} = k f(\alpha) \tag{1}$$

where, α is chemical conversion of reaction, t is reaction time (s), k is rate constant (s^{-1}), and $f(\alpha)$ is a function describing the reactant concentration and is assumed to be independent of temperature. The temperature dependence of the conversion rate is assumed to reside in the constant (k) through the Arrhenius equation:

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

where, A is preexponential factor (s^{-1}), E is activation energy (J mol^{-1}), R is gas constant (J mol^{-1} K^{-1}), and T is reaction temperature (K).

The basic assumption for the application of DSC to the curing of thermosets is that the reaction rate is proportional to the measured heat flow rate[24]:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{RXN}} \frac{dH}{dt} \tag{3}$$

where, H is heat flow (J g^{-1}), and ΔH_{RXN} is the total exothermic heat of the cure reaction.

Mechanistically, thermoset curing reactions can be divided into two general categories: nth-order and autocatalytic. The function $f(\alpha)$ has the following form:

$$f(\alpha) = (1 - \alpha)^n \tag{4}$$

for an nth-order reaction, and

$$f(\alpha) = \alpha^m (1 - \alpha)^n \tag{5}$$

for a pure autocatalytic reaction. In eqs. (4) and (5) n and m are reaction orders. Thus, systems obeying nth-order reaction kinetics will obviously have the maximum reaction rate at $t = 0$, while the reaction rate of the systems obeying autocatalytic reaction kinetics passes through the maximum and then decreases with time.

For an nth-order cure reaction, the conversion rate is given by

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n = A \exp\left(-\frac{E}{RT}\right)(1 - \alpha)^n \tag{6}$$

To model the cure process, the values of n, A, and E need to be determined. At an isothermal condition, these three parameters can be obtained through a two-step linear regression analysis, using transformed eqs. (2) and (6):

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k + n \ln(1 - \alpha) \tag{7}$$

$$\ln k = \ln A - \frac{E}{RT} \tag{8}$$

where ln represents natural logarithm. For dynamic DSC procedure, temperature varies, but the heating rate can be fixed. By differentiating eq. (6) one has

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = \frac{d\alpha}{dt}\left[\frac{E\varphi}{RT^2} - An(1 - \alpha)^{n-1} \exp\left(-\frac{E}{RT}\right)\right] \tag{9}$$

where $\varphi = dT/dt$ is heating rate (K s^{-1}). In a dynamic DSC spectrum, the heat flow rate rises to the maximum value at the temperature T_p, then returns to zero

as the reactant is exhausted with the temperature increasing. Thus, when T reaches T_p, $d(dH/dt)dT = 0$ (i.e., $d(d\alpha/dt)dt = 0$ at $T = T_p$ when φ is fixed). After expanding eq. (9) and neglecting small quantities,[25] one has the Kissinger equation

$$\frac{d \, [\ln(\varphi/T_p^2)]}{d(1/T_p)} = -\frac{E}{R} \tag{10}$$

from which the activation energy, E, can be determined. After rearranging and taking natural logarithm, eq. (6) becomes

$$\ln\left[\frac{d\alpha/dt}{\exp(-E/RT)}\right] = \ln\left[\varphi \frac{d\alpha/dT}{\exp(-E/RT)}\right]$$
$$= \ln A + n \ln(1 - \alpha) \tag{11}$$

with E known, a linear regression can lead to the values of A and n.

For an autocatalytic cure reaction, the cure kinetics are described as

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{RXN}} \frac{dH}{dt} = k\alpha^m (1 - \alpha)^n \tag{12}$$

eq. (12) describes a typical autocatalytic reaction, where the rate is zero when $t = 0$, and the maximum value appears at some intermediate conversion, usually 30–40%. Since there is a possibility that reactants can be converted into products via alternative paths and only one of the paths is autocatalytic, the initial rate is not necessarily zero.[26] The more accurate description should be

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{RXN}} \frac{dH}{dt} = (k' + k\alpha^m)(1 - \alpha)^n \tag{13}$$

where $k' = (d\alpha/dt)$ at $t = 0$.

The OSB core adhesive normally contains a complexing agent to speed up its cure at low temperatures. The complexing agent complicates curing reactions, and thus, new models are needed to take into account this reaction. The whole cure reaction comprises nth-order and autocatalytic reactions simultaneously. In this case, the following expression is proposed based on eqs. (6) and (13):

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_{nth} + \left(\frac{d\alpha}{dt}\right)_{auto}$$
$$= k_1(1 - \alpha)^{n_1} + (k_2 + k_3\alpha^{n_2})(1 - \alpha)^{n_3} \tag{14}$$

where $(d\alpha/dt)_{nth}$ represents the conversion rate of the nth-order portion, and $(d\alpha/dt)_{auto}$ is for the autocatalytic portion; k_1 and n_1 are the reaction rate constant

and reaction order of the nth-order part, respectively; n_2 and n_3 are the reaction orders of the autocatalytic part, and k_2 and k_3 are the corresponding reaction rate constants. If the kinetic parameters of the nth-order cure reaction part can first be derived from eqs. (7) and (8), the kinetic indexes for the autocatalytic portion can be calculated. A first estimate of the reaction order n_3 can be determined from the slope of the $\ln (d\alpha/dt)_{\text{auto}}$ versus $\ln (1 - \alpha)$ plot, as described in eq. (15):

$$\ln\left[\left(\frac{d\alpha}{dt}\right) - \left(\frac{d\alpha}{dt}\right)_{\text{nth}}\right] = \ln\left(\frac{d\alpha}{dt}\right)_{\text{auto}} = \ln(k_2 + k_3\alpha^{n_2})$$
$$+ n_3 \ln(1 - \alpha) \quad (15)$$

and the constant k_2 is given by the intercept at $\alpha = 0$. Equation (15) can be rearranged to give

$$\ln\left[\frac{(d\alpha/dt)_{\text{auto}}}{(1 - \alpha)^{n_3}} - k_2\right] = \ln k_3 + n_2 \ln\alpha \quad (16)$$

from which the reaction order n_2 and constant k_3 can be obtained with a linear regression analysis. Moreover, eq. (15) can be rearranged again to give

$$\ln\left[\frac{(d\alpha/dt)_{\text{auto}}}{k_2 + k_3\alpha^{n_2}}\right] = n_3 \ln(1 - \alpha) \quad (17)$$

from which the new value of the reaction order n_3 can be obtained, with the values of n_2 and k_3 known. This new n_3 is applied again in eq. (16) for the new values of n_2 and k_3. This interactive procedure is repeated until the obtained values for n_3, n_2, and k_3 show less than 1% difference between subsequent calculations.

Cure prediction

A prediction of the relationship among cure reaction conversion (curing degree), cure temperature, and cure time can be performed by integrating the kinetic equation. For a cure reaction that follows the cure mechanism described by eq. (1), the following equation on reaction time can be derived:

$$t = \int_0^t dt = \int_0^\alpha \frac{1}{\kappa f(\alpha)} d\alpha = \int_0^\alpha \frac{1}{Af(\alpha)} \exp\left(\frac{E}{RT}\right) d\alpha \quad (18)$$

The prediction for the cure process of a thermosetting adhesive can be successfully made by solving eq. (18) In this work, eqs. (1)–(18) were used to model the cure process of both OSB face and core adhesives.
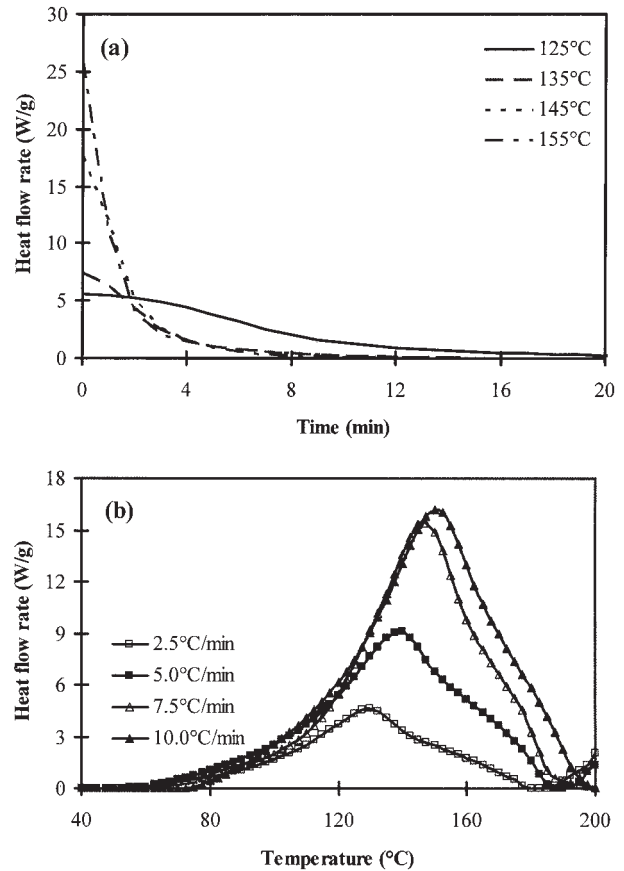

Figure 1 Isothermal (a) and dynamic (b) DSC curves from curing of the face resin.

RESULTS AND DISCUSSION

Cure kinetics of the face resin

Isothermal and dynamic DSC curves for the face resin are shown in Figures 1(a) and 1(b), respectively. Under the isothermal condition (Fig. 1(a)), the heat flow rate was the highest when $t = 0$, and then decreased with increasing cure time. Apparently, the cure of the face resin followed an nth-order reaction mechanism. The value of the peak at $t = 0$ for the cure reaction was increased, and the time needed for the cure reaction to reach the endpoint was shorter with increasing temperature. At 125°C, the whole time for the cure reaction was about 30 min, while only several minutes were needed at 145°C.

The isothermal DSC data were used to calculate the kinetic parameters k and n according to eq. (7) (Table I). As shown, the mean cure reaction order was about 1. Further analysis with eq. (8) showed that the activation energy E was 62.30 kJ mol^{-1}, and the preexponential factor A was 4.48×10^5 s^{-1}. Thus, the kinetic equation derived from isothermal DSC analysis can be described as

$$\frac{d\alpha}{dt} = 4.48 \times 10^5 \exp\left(-\frac{7497}{T}\right)(1 - \alpha)^{1.02} \quad (19)$$

TABLE I
Cure Kinetic Parameters of the Face Resin under Isothermal Temperatures

	Model parameter		
Temperature (°C)	Reaction order, n	Reaction rate constant, k (10^{-3}) (s^{-1})	r^a
125	0.884	2.64	0.99
135	0.985	5.79	0.99
145	1.083	8.05	0.99
155	1.113	10.16	0.99

[a] Correlation coefficient.

Figure 2 Theoretical (lines) and experimental (symbols) conversion rates versus conversion of the face resin.
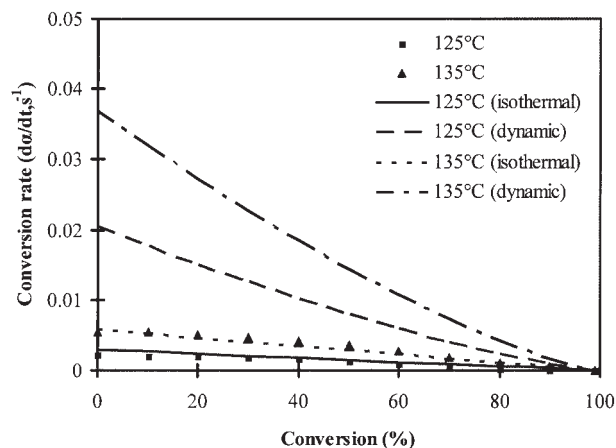
Under dynamic conditions (Fig. 1(b)), onset cure temperatures and peak temperatures of the cure reaction at different heating rates were obtained, and the data are shown in Table II. The higher the heating rate was, the higher the onset cure temperature and the peak temperature were. Actual cure temperatures, which are independent of heating rates, are those when the heating rate is zero. These values were calculated according to the intercepts of the plots of onset temperature and peak temperature versus heating rate. Thus, the cure reaction happened only when the temperature was higher than 94.8°C, and at about 128°C, the cure rate was the highest.

The activation energy calculated by the Kissinger equation (eq. (10)) was 79.29 kJ mol^{-1}. According to eq. (11) the remaining kinetic parameters were obtained (Table II). The mean cure reaction order was 1.35, and the mean preexponential factor was 5.21 × 10^8 s^{-1}. The kinetic equation obtained by dynamic DSC method is thus

$$\frac{d\alpha}{dt} = 5.95 \times 10^8 \exp\left(-\frac{9541}{T}\right)(1-\alpha)^{1.35} \quad (20)$$

Comparing eq. (19) with (20), it can be seen that there is an obvious difference between the cure kinetic

parameters obtained from isothermal and dynamic DSC analysis, respectively. To test the reliability of these two methods, a direct comparison was made, and the results are shown in Figure 2. It can also be seen that the cure reaction model constructed using isothermal DSC method fits the experimental data much better than that from the dynamic DSC, just as Park et al.[20] reported, although dynamic DSC is simpler and easier to use.

Cure kinetics of the core resin

The quantitative change of enthalpy (heat flow rate) as a function of temperature of the core resin is shown in Figure 3. It is a plausible assumption that there are two dominant reactions involved, and that the curve is composed of two individual ones with overlapping initial and final parts. Compared with the DSC pattern of the mixture of monomers of phenol and formaldehyde, reported by He et al.,[18] the two peaks for the core resin include one for a typical addition reaction

TABLE II
Cure Temperatures and Kinetics of the Face Resin under Various Heating Rates

			Model parameter		
Heating rate, φ (°C/min)	Onset temperature (°C)	Peak temperature(°C)	Reaction order, n	Pre-exponential constant, A (10^8) (s^{-1})	r^a
0	94.8[b]	128.4[b]	—	—	—
2.5	95.81	129.06	1.523	10.98	0.99
5.0	103.60	138.57	1.507	6.22	0.99
7.5	115.04	146.91	1.179	3.55	0.99
10.0	116.76	150.34	1.198	3.05	0.99
15.0	126.12	158.70	—	—	—
20.0	132.22	165.55	—	—	—

[a] Correlation coefficient.
[b] Extrapolated values from the intercepts of the onset temperature–heating rate and peak temperature–heating rate plots, respectively.
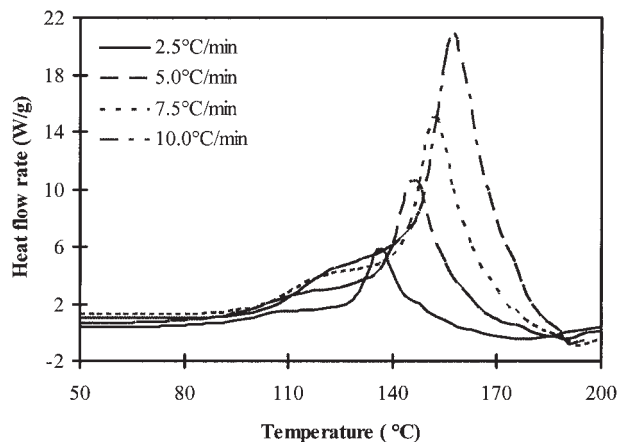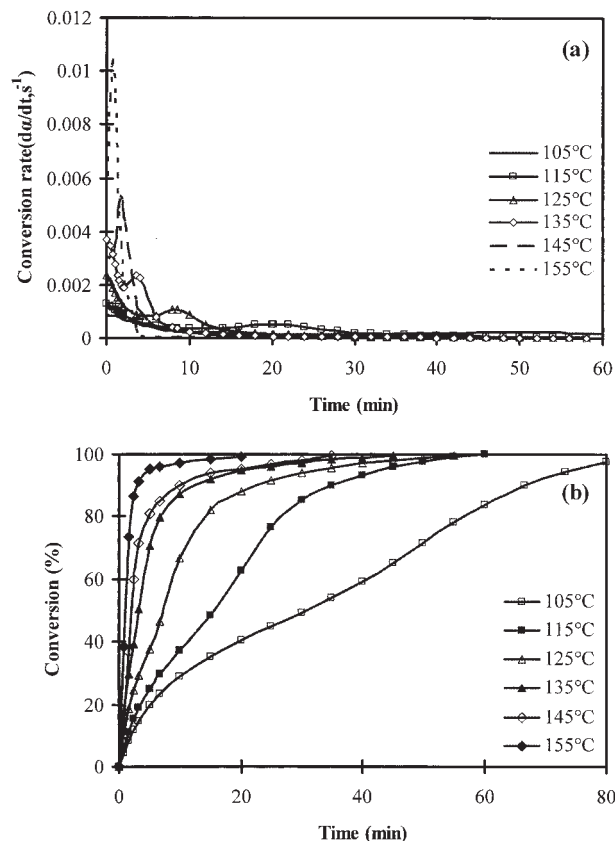
Figure 3 Typical dynamic DSC curves from curing of the core resin.

and the other for a condensation reaction. This also means that the addition reaction occurred first during the cure of the core resin, and that its onset cure temperature was about 89°C, when the heating rate was 5°C min^{-1}.

The onset temperatures and the peak temperatures for the cure reaction at different heating rates are listed in Table III. The extrapolated onset and peak temperatures, for the heating rate equal to zero, were 82.5 and 36.4°C, respectively. Compared with the data from the face resin, the onset temperature of the cure reaction of the core resin was lower by about 10°C, but the peak temperature was higher by about 10°C. Thus, the face resin was more stable at lower temperature, but more active at temperatures higher than 120°C.

A series of isothermal reaction rate curves, as a function of cure time for the core resin, are shown in Figure 4(a). Obviously there existed two kinds of reaction, one followed an nth-order cure kinetic mechanism, and the other followed an autocatalytic mechanism. At temperatures lower than 140°C, the nth-order

TABLE III
Cure Temperatures of the Core Resin under Various Heating Rates

Heating rate, φ (°C/min)	Onset temperature (°C)	Peak temperature (°C)
0	82.50[a]	136.40[a]
2.5	84.96	136.43
5.0	89.02	145.94
7.5	96.39	152.11
10.0	103.54	157.37
15.0	103.92	163.30
20.0	111.29	169.27

[a] Extrapolated values from the intercepts of the onset temperature–heating rate and peak temperature–heating rate plots, respectively.

Figure 4 Conversion rate (a) and conversion (b) as a function of curing time at various isothermal temperatures for the core resin.
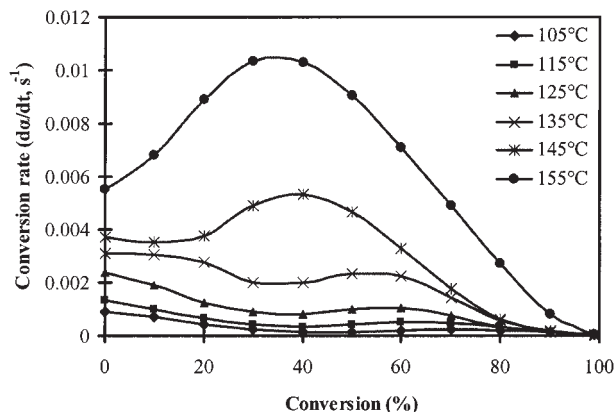
cure reaction occurred first, and then, the autocatalytic reaction ensued. At the same time, the peak corresponding to the autocatalytic reaction was increased significantly and clearly shifted to a shorter time with the temperature increase. Thus, the overlapped section between the nth-order and autocatalytic reactions increased. At 155°C, these two reactions overlapped completely. Figure 4(b) shows a series of conversion curves as a function of time. Before the conversion increased to 70%, the curves at 125, 115, and 105°C had apparent points of inflection, while at 155°C, there was no inflection point at all.

To visualize the phenomenon clearly, the conversion rate is plotted as a function of conversion in Figure 5. It is shown that the curing reaction proceeded through an nth-order kinetic mechanism first, which was followed by an autocatalytic one, with the maximum conversion rate in a conversion range of 30–70%. The lower the isothermal temperature was, the higher the conversion for the maximum reaction rate of the autocatalytic section became. At 105°C, or even lower temperatures, it can be assumed that the nth-order cure reaction absolutely contributed to the increase of conversion, when the conversion was lower than 20%. With the isothermal data at 110, 105,

Figure 5 Conversion rate of the core resin versus conversion at various isothermal temperatures.

and 100°C, the kinetic parameters for the nth-order part were calculated according to eq. (7), when the conversion was low, and the data are summarized in Table IV. The addition kinetics of the base-catalyzed phenol–formaldehyde addition reactions were usually observed as a second-order reaction.[27] For the core resin, the mean reaction order for the nth-order cure section was 2.38. According to eq. (8) the activation energy was 43.53 kJ mol^{-1}, and the preexponential factor was 1502 s^{-1}. Thus, the kinetic equation for the nth-order part can be described as

$$\left(\frac{d\alpha}{dt}\right)_{n\text{th}} = 1502 \exp\left(-\frac{5238}{T}\right)(1-\alpha)^{2.38} \quad (21)$$

The kinetic parameters for the autocatalytic part of the cure reaction were evaluated using eqs. (15)–(17) The obtained data are summarized in Table IV. With

the data of corresponding A and E from eq. (8) the kinetic equation for the autocatalytic part is

$$\left(\frac{d\alpha}{dt}\right)_{\text{auto}} = \left[2.74 \times 10^{14} \exp\left(-\frac{16{,}866}{T}\right) + 2.46\right.$$
$$\left. \times 10^{16} \exp\left(-\frac{16{,}558}{T}\right)\alpha^{3.04}\right](1-\alpha)^{2.26} \quad (22)$$

When the temperature was not higher than 145°C, the total reaction order of the autocatalytic cure part was about 5 (Table IV), and the rate constants increased with the temperature, following the Arrhenius equation. However, beyond 155°C, the total reaction order obviously decreased, and the rate constant k_3 decreased with increasing temperature. This deviation was mainly ascribed to fast vitrification, where the mobility of the reacting groups was hindered, and the cure reactions became diffusion-controlled reactions.

Figure 6 shows a comparison of experimental and predicted cure conversion rates. As shown, the predicted values matched the experimental data well. It should be pointed out that commercial OSB core adhesives from various manufacturers may contain different complexing agents, which certainly change the model parameters. However, the analytical technique is applicable to different adhesives.

Prediction for the cure of the face or core resin

The prediction of the relationship among reaction conversion (curing degree), cure temperature, and cure time was made by using eq. (18). For the face resin, the following equation was derived from eq. (19):

$$t = 1.3646 \times 10^{-4} \exp\left(\frac{7497}{T}\right)[(1-\alpha)^{-0.02} - 1] \quad (23)$$

TABLE IV
Isothermal Cure Kinetic Parameters of the Core Resin

Temperature (°C)	Model parameters[a]						
	nth-order part			Autocatalytic part			
	n_1	k_1 (10^{-4}) (s^{-1})	n_2	k_2 (10^{-4}) (s^{-1})	n_3	k_3 (10^{-2}) (s^{-1})	r[b]
100	2.447	7.86	—	—	—	—	0.98
105	2.404	9.06	—	—	—	—	0.97
110	2.293	11.47	—	—	—	—	0.99
115	—	—	3.547	0	1.476	0.71	0.96
125	—	—	3.239	0.06	1.950	1.78	0.99
135	—	—	2.990	0.44	2.678	8.72	0.99
145	—	—	2.390	3.62	2.909	12.42	0.99
155	—	—	1.404	5.50	1.940	8.02	0.99
160	—	—	1.134	34.93	1.527	6.89	0.99
165	—	—	0.821	48.82	1.112	4.53	0.99
170	—	—	0.652	84.11	0.983	2.48	0.99

[a] n_1, n_2, n_3 = reaction order; k_1, k_2, k_3 = reaction rate constant.
[b] Correlation coefficient.
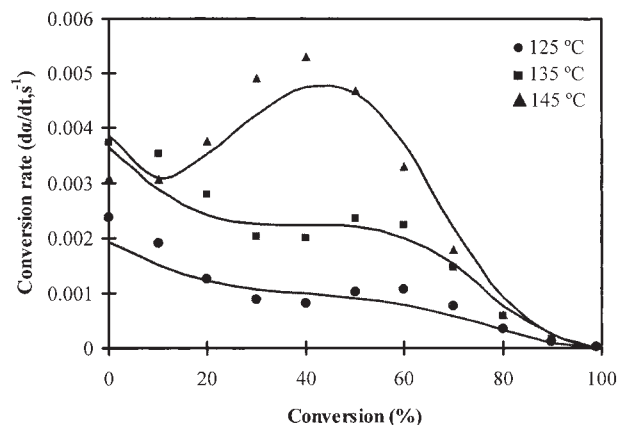
Figure 6 Theoretical (lines) and experimental (symbols) conversion rates as a function of conversion of the core resin.

The prediction of the cure reaction of the face adhesive is shown in Figure 7(a). The curves provide necessary information for deciding the actual curing technology.

For the core resin, there are two kinds of cure reaction involved, and their corresponding portions in the whole cure reaction are listed in Table V. It is assumed that the conversion is directly proportional to the sum of heat generation. Thus, the ideal temperature to cure

Figure 7 Curing time of the face resin (a) and the core resin (b) as a function of conversion at isothermal temperatures.

TABLE V
Component Percentages for the Cure Reaction of the Core Resin

Temperature (°C)	Enthalpy (kJ/g)	nth-order part (%)	Autocatalytic part (%)
105	1.76	86	14
115	2.20	66	34
125	2.85	46	54
135	3.34	32	68
145	3.35	32	68
155	2.40	20	80
165	1.59	13	87

the core resin was about 140°C, according to the values of enthalpy in this Table. The portion of the nth-order cure reaction was assumed to be about 32%, although this portion was as high as 86% at 105°C when most of the autocatalytic cure reaction did not happen. On the other hand, it is believed that the cure time for the whole cure reaction was up to the autocatalytic cure reaction. Thus, on the basis of eq. (22) the following equation was obtained after neglecting small quantities:

$$t = 2.90 \times 10^{-15} \exp\left(\frac{16{,}866}{T}\right)[(1 - 0.68\alpha)^{-1.26} - 1]$$

$$(24)$$

The predicted results are shown in Figure 7(b), which provides information for the actual curing technology of the core adhesive.

CONCLUSIONS

The cure kinetics of commercial PF used as OSB core and face resins were studied by dynamic DSC at different heating rates and isothermal DSC at different temperatures. Isothermal DSC method was shown to be much more reliable than dynamic DSC method in determining the cure kinetic parameters.

The results indicate that the curing mechanisms of these two adhesives differed significantly. The cure of the face resin was a nearly 1st-order reaction with the high activation energy of 79.29 kJ mol^{-1} and the onset cure temperature of about 95°C, while an nth-order reaction and an autocatalytic one amalgamated the cure of the core resin. The nth-order part with the reaction order of 2.38 began at 89°C, and the autocatalytic one with the total reaction order of about 5 occurred at the highest rate when the temperature reached 136°C. The proposed model for the core resin fitted experimental data well when the temperature was lower than 155°C. The ideal cure temperature was about 140°C, and the portion of the nth-order cure reaction was about 32%.
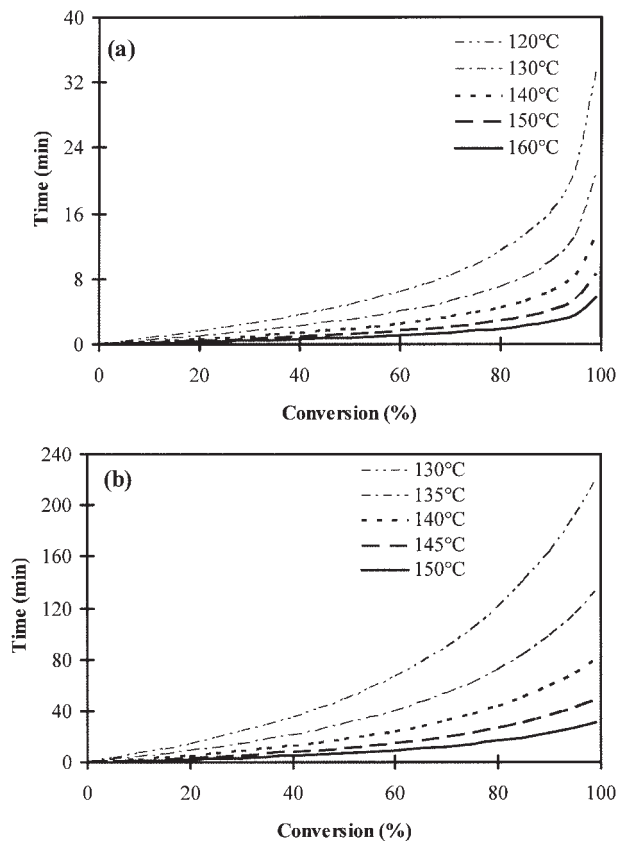
With the developed models and the obtained kinetic parameters, the relationships among reaction conversion (curing degree), cure temperature, and cure time were predicted. The predictions provide necessary information for deciding the actual cure technology for both adhesives. Future work will deal with cure kinetics of the adhesives under the influence of wood and chemical additives.

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