Cure Kinetics of Aqueous Phenol-Formaldehyde Resins Used for Oriented Strandboard Manufacturing: Effect of Wood Flour

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ABSTRACT: The effect of wood flour on the cure kinetics of commercial phenol-formaldehyde resins used as oriented strandboard face and core adhesives was studied using differential scanning calorimetry. The wood flour did not change the cure mechanism of the face resin, but lowered its cure temperature and activation energy and increased its cure reaction order. For the core resin (CR), the wood flour lowered the onset cure temperature, and caused separation of the addition and condensation reactions involved in curing of CR. Compared with neat CR, the addition reaction of CR/wood mixture also followed an nth-order reaction mechanism but with a lower reaction order, while the condensation was changed from an autocatalytic reaction to an nth-order one. The addition reaction happened at temperatures lower than 90°C, and the condensation reaction was dominant at temperatures higher than 110°C. The proposed models fitted the experimental data well. Relationships among cure reaction conversion (cure degree), cure temperature, and cure time were predicted. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3774–3781, 2006

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

INTRODUCTION

The curing behavior of phenol-formaldehyde (PF) resins used for bonding structural wood composites directly affects both hot pressing processes during the manufacture and properties of the resultant composites. Studying the influence of wood on the cure of PF resins and obtaining the corresponding cure kinetic parameters is thus fundamental to the understanding and optimization of the hot pressing process of structural wood composites.[1]

It has been reported that the cure of PF resins can be influenced by the interactions between the resins and wood.[2–9] As early as 1969, the kinetics of the polymerization of PF resin in the presence of Douglas-fir heartwood and cotton cellulose were studied by Chow[2] with ultraviolet spectrometry. The activation energy of the polymerization of PF in the presence of cellulosic materials depended on the number of accessible hydroxyl groups in the carbohydrates. The greater the number of accessible hydroxyl groups, the less energy required. Pizzi's group have made much work on the curing of PF, and they found that wood substrates have a marked modifying influence on a well-defined region of the continuous heating-transformation diagrams during hardening of PF resin using thermomechanical analysis.[3,4]

Most of the reported research on the influence of wood on the curing behavior of PF resins treated the cure reaction simply as an nth-order reaction and evaluated the activation energy using the data from dynamic differential scanning calorimetry (DSC). Pizzi et al.[5] found that the lowering of activation energy by wood appeared to result from the catalytic activation induced particularly by carbohydrates such as crystalline and amorphous cellulose and hemicelluloses and from the formation of resin/substrate covalent bonding, particularly in the case of lignin. He and Yan[6] attributed the reduced activation energy to the decreased pH value of the resin (i.e., 12.98 for core PF and 11.05 for face PF) by wood, and the lowest activation energy for a phenolic resin probably appeared at pH 10–11. But the measured gel time of phenolic resin/wood mixtures indicated that the gel time had no direct correlation to the flake pH and buffering capacity of various wood species.[7]

On the other hand, Mizumachi and Morita[8] reported that the curing reaction of phenolic resin could be retarded by some species of wood. After treating the complex cure reaction of PF resin/wood mixtures as a 1st-order reaction, He and Riedl[9] found that the activation energy of the mixtures was

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higher than that of the pure PF resin, and that wood accelerated the addition reaction but retarded the condensation. Different results are probably ascribed to the complicated components of wood and complex formulations of PF resins used.[10–18]

It is well known that addition reactions between formaldehyde and phenol are the 2nd order reactions and that the PF condensation typically follows a 1st-order reaction. Actually, the cure of PF resins which contain complexing agents and additives usually do not follow a single nth-order reaction mechanism.[19–21] To identify a reaction which follows an autocatalytic reaction mechanism, isothermal DSC is much more useful than dynamic DSC.[19,20] However, little effort has been made to study the influence of wood on the cure kinetics of PF resins using isothermal DSC techniques.

In a previous study,[20] the cure kinetic models of aqueous PF resins for OSB face and core adhesives were developed, and the corresponding kinetic parameters were obtained. As 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 objective of this study was to investigate the influence of wood substrates on the curing behavior of PF resins with DSC techniques.

MATERIALS AND METHODS

Materials

Two aqueous PF resins, one for OSB face (called face resin, FR) and one for OSB core (called core resin, CR), were obtained from Hexion Specialty Chemicals (Springfield, Oregon). FR has total alkalinity of 2.69 wt % and a pH of about 10. The solid content, viscosity, and specific gravity are 45.0 wt %, 143 mPa s, and 1.17, respectively. CR-containing additives has total alkalinity of 6.85 wt % with pH between 11 and 12. The solid content, viscosity, and specific gravity for CR are 45.2 wt %, 95 mPa s, and 1.22, respectively. Both resins were stored in a freezer prior to measurements.

Maple (*Acer* sp.) and pine (*Pinus* sp.) flours with a 120-mesh particle size from American Wood Fibers Company (Columbia, MD) were used in the experiment. The moisture content of the wood was controlled at about 2% at time of testing. The typical acidity (pH) of the maple and pine flours is 5.0 and 4.7, respectively.

Preparation of the resin and wood flour mixture

All resin and wood mixtures, including FR/maple (FRM), FR/pine (FRP), CR/maple (CRM), and CR/pine (CRP), were prepared by mechanically mixing the aqueous FR or CR with the wood flour at a 50/50 (wt/wt) loading ratio for 10 min at room tempera-

ture. The obtained mixtures were stored in a freezer prior to DSC measurements.

Differential scanning calorimetry

The cure reaction rates of samples were measured using a differential scanning calorimeter (TA DSC Q100). Prior to analysis, the samples were removed from the freezer and then 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 paper.[20] 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 70–140°C. Before the test, the temperature of the base heating block was maintained at 40°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 reaction heat 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 the heating rate of 5°C/min, and 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 wood flour on curing behavior of the face resin

Dynamic DSC curves for FR, maple flour, pine flour, and their corresponding mixtures are shown in Figure 1(a). At the 5°C/min heating rate, the cure temperature range for FR was from 90 to 180°C, with one peak at about 140°C. The maple flour itself did show a wide exothermal peak between 75 and 165°C, and the pine flour showed a peak between 150 and 200°C. However, these peaks were so weak that they could be ignored. The FR/wood mixture showed one cure peak similar to neat FR. However, its cure temperature range became wider, and the onset cure temperature was significantly lowered. The cure temperature range was from 64 to 210°C for FRM and from 70 to 215°C for FRP. The maximum heat flow rate was shifted to lower temperatures, especially for FRP. He and Riedl[9] reported two wide cure peaks after the addition of wood flour to the resin. One peak was between 60 and 100°C, and
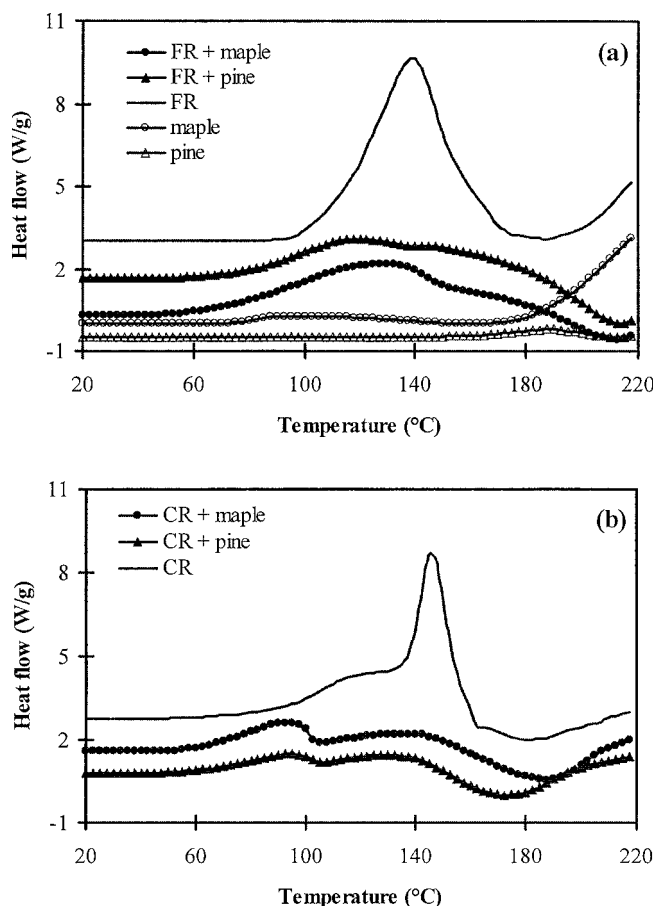
Figure 1 Dynamic DSC curves at a heating rate of 5°C/min. (a) FR, wood flour, and their mixtures. (b) CR and its mixtures with the wood.

another peak was between 100 and 200°C. The former was smaller and weaker than the latter. The difference probably resulted from the different formulations of PF resins.

Under the isothermal condition [Fig. 2(a)], the conversion rates for FR, FRM, and FRP were the highest in the beginning, and then decreased with an increase of the cure time. This was typical for an nth-order cure reaction. However, the shape of curves differed significantly from each other, which implied a difference between their reaction orders.

The conversion rate of an nth-order cure reaction is given by:[20]

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

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

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 obtained cure kinetic parameters for FR/wood mixtures are shown in Table I. The mean cure reaction order of neat FR was about 1,[20] while it increased to 2.05 for FRM and to 1.81 for FRP. The activation energy of neat FR was 62.30 kJ/mol, and it was decreased to 29.11 kJ/mol for FRM and to 39.51 kJ/mol for FRP. The corresponding kinetic equations are summarized as:
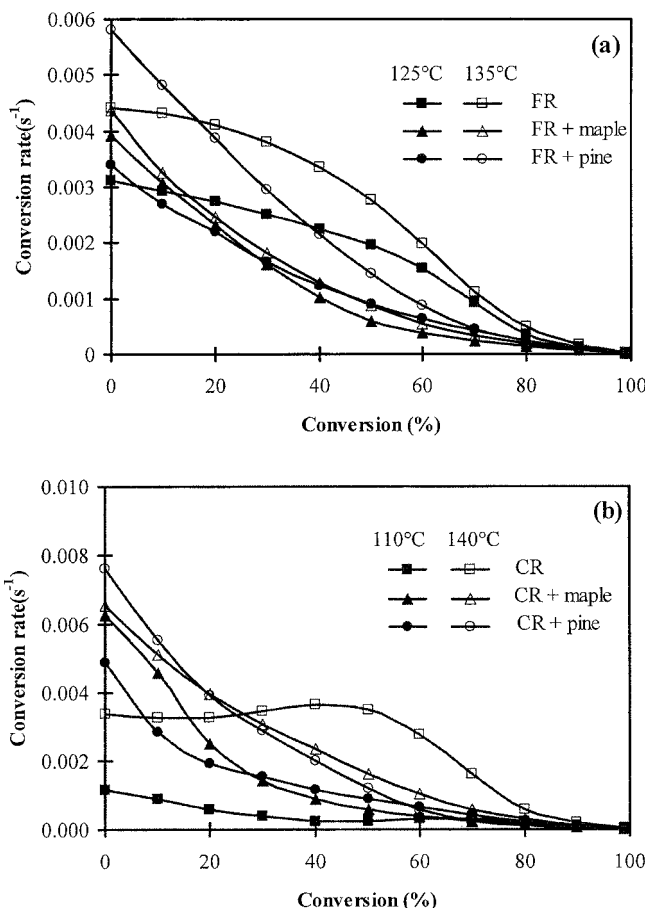

Figure 2 Conversion rate as a function of percent conversion at different temperatures. (a) FR and its mixtures with the wood. (b) CR and its mixtures with the wood.

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

| Temperature (°C) | Model parameters[a] | | | | |
| | Face resin/maple | | Face resin/pine | | |
	n	k (s^{-1} × 10^{-3})	n	k (s^{-1} × 10^{-3})	r^b
105	–	–	1.95	2.02	0.99
115	–	–	1.80	2.59	0.99
125	2.10	3.06	1.65	3.09	0.99
135	1.97	3.79	1.85	5.39	0.99
145	2.10	4.25	–	–	0.99
155	2.03	5.93	–	–	0.99

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

$$\left(\frac{d\alpha}{dt}\right)_{FR} = 4.48 \times 10^5 \exp\left(-\frac{7497}{T}\right)(1-\alpha)^{1.01} \quad (5)$$

$$\left(\frac{d\alpha}{dt}\right)_{FRM} = 2.32 \times 10^1 \exp\left(-\frac{3504}{T}\right)(1-\alpha)^{2.05} \quad (6)$$

$$\left(\frac{d\alpha}{dt}\right)_{FRP} = 6.09 \times 10^2 \exp\left(-\frac{4754}{T}\right)(1-\alpha)^{1.81} \quad (7)$$

for FR, FRM, and FRP, respectively. Figure 3(a) shows the comparison of the cure reaction rate between experimental data and predicted values from eqs. (6) and (7), which shows close agreement between the two.

The cure reaction of the PF resin is typically exothermic. Thus, it is assumed that the cure degree (i.e., the degree of conversion) is proportional to the exothermic heat (i.e., the reaction enthalpy) for the same system. According to the enthalpy at different temperatures (Table II), the ideal cure temperature, at which the enthalpy and cure degree were the biggest, was 135°C for FR. For FRM, the ideal cure temperature was 125°C, and it was as low as 115°C for FRP. The data in Table II indicate that the reaction enthalpy of the resin decreased by the addition of wood, especially on adding the pine flour. At the higher temperatures, the reaction enthalpy decreased because of the fast vitrification. The mobility of the reacting groups was then hindered and the cure reaction was controlled by diffusion.[22,23]

Results from dynamic and isothermal DSC showed that the onset cure temperature and activation energy of FR were greatly lowered by the addition of maple or pine flour. Therefore, the existence of catalytic activation of self-condensation of PF resin induced by the substrates must be considered.[2,4] The strong secondary interactions (i.e., dipolar forces and hydrogen bonds formed between PF oligomers and wood substrate) may weaken the O—H bond of phenol, leading to a stronger negative charge on the ortho and para positions of the phenolic ring. Thus, the PF self-con-

densation reactions were accelerated. The different effect of wood types on the curing behavior of PF resins may depend on the number of accessible hydroxyl groups in the carbohydrates of wood.

Effect of the wood flour on curing behavior of the core resin

The quantitative change of enthalpy (i.e., heat flow rate) as a function of temperature of CR and its mix-
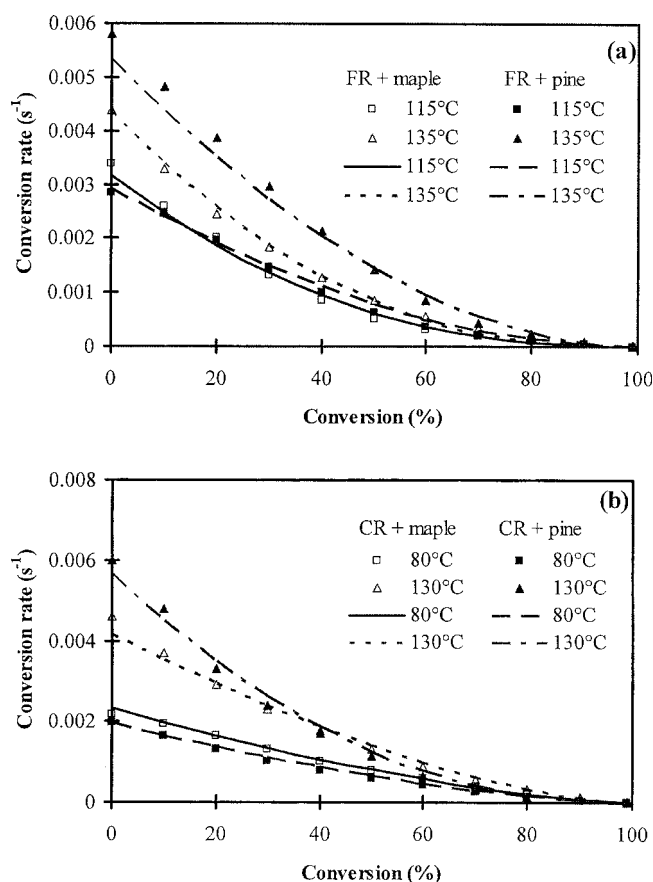

Figure 3 Comparison of measured (symbols) and predicted (lines) conversion rates as a function of percent conversion. (a) FR/wood mixtures. (b) CR/wood mixtures.

TABLE II
Enthalpy of the Face Resin and Its Mixtures with Wood

Temperature (°C)	Enthalpy (kJ/g)		
	Face resin	Face resin/maple	Face resin/pine
105	–	–	0.82
115	–	0.78	0.84
125	1.79	1.06	0.69
135	2.22	1.02	0.66
145	2.04	0.85	–
155	2.03	0.82	–

tures with wood flour is shown in Figure 1(b). It was reported that the cure processes of phenolic resins were multiple, including several steps and many individual reactions.[24] It is a plausible assumption that there were two dominant reactions involved (i.e., the addition and condensation). The two peaks for CR included one at about 125°C for the addition and another at about 146°C for the condensation.[20] For CRM, the first peak moved to a lower temperature of 92.5°C, and the other changed to 137.5°C. The onset cure temperature was as low as about 40°C when the heating rate was 5°C/min. The same results were for CRP. He and Yan[6] reported two peaks in the DSC curves of CR merged into one peak between 90 and 180°C for the PF CR/wood mixtures, and another very small and wide peak appeared between 50 and 90°C. Different additives in various CRs may have contributed to the difference.

The interaction between wood flour and CR not only decreased the cure temperature, but also influenced the addition and condensation reaction rates in a different way. When the resin was mixed with the maple or pine flour, the reaction rate of addition reaction increased. According to the report from He and Riedl,[9] wood absorbed most of the water in the mixtures, resulting in a diffusion-limited mechanism

for PF cure. The addition reaction was not influenced significantly by diffusion-control, since the addition reactants were small molecules, but the condensation was retarded by diffusion because it occurred among bigger molecules. The relative concentrations of addition reactants increased when water was absorbed by wood, which possibly accelerated the addition reaction.

A series of isothermal reaction rate curves as a function of conversion for CR and its mixtures with wood flours is shown in Figure 2(b). The cure rate of CR was significantly accelerated by the wood flour, especially at low temperatures. Another interesting finding was the change of the cure mechanism. For CR, there obviously existed two kinds of cure mechanisms. The addition reaction followed an nth-order reaction mechanism, while the condensation followed an autocatalytic one. However, there was only one cure kinetic mechanism for the mixtures of CR and wood flour, i.e., an nth-order reaction mechanism. The interaction, the strong secondary interactions between the resin and wood molecules, might change the cure mechanism of the condensation reaction. The different shapes among the curves for CR/wood mixtures at 80 (data not shown), 110, and 140°C indicated that the reaction orders varied with temperatures, since the shape of curve had a close relation with the reaction order.

The nth-order cure kinetic parameters obtained by linear regression (eq. (3)) are shown in Table III. There seemed to be three stages for the whole cure process of CR/wood mixtures. The first was at the temperatures lower than 90°C; the second was from 90 to 110°C; and the last was at temperatures higher than 110°C. Combining the results from Figure 2(b), the addition reaction was mainly attributed to the first cure stage, the third stage mostly resulted from the condensation, and both addition and condensation acted in the second cure stage.

TABLE III
Isothermal Cure Kinetic Parameters of the Core Resin/Wood Mixtures

Temperature (°C)	Model parameters[a]					
	Core resin/maple			Core resin/pine		
	n	k (s^{-1} × 10^{-3})	r[b]	n	k (s^{-1} × 10^{-3})	r[b]
70	1.39	1.65	0.99	1.46	1.11	0.99
75	1.48	1.69	0.99	1.60	1.57	0.99
80	1.70	2.45	0.99	1.65	1.90	0.99
90	2.59	4.96	0.99	2.14	2.97	0.98
100	2.22	1.31	0.98	2.09	1.25	0.86
110	2.77	3.40	0.96	2.10	4.41	0.98
120	1.37	3.88	0.99	1.78	4.69	0.99
130	1.59	4.27	0.99	2.14	5.31	0.99
140	1.76	5.75	0.99	2.63	7.21	0.99

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

TABLE IV
Enthalpy of the Core Resin and Its Mixtures with Wood

Temperature (°C)	Enthalpy (kJ/g)		
	Core resin	Core resin/maple	Core resin/pine
70	–	0.48	0.46
80	–	0.54	0.55
90	–	0.61	0.66
100	1.04	0.34	0.24
120	2.53	0.37	0.36
130	3.10	0.57	0.56
140	3.35	0.56	0.46
150	2.88	–	–
160	1.64	–	–

Additional information was obtained from the enthalpy at different temperatures (Table IV). The result indicates that the reaction enthalpy decreased when the wood was added. The ideal cure temperature for CR was 140°C, at which the enthalpy was the highest. For both mixtures, there were two peaks, one at 90°C and the other at 130°C. From 100 to 120°C, reaction enthalpy of the mixtures became lower. The result implied little overlapping between the addition and condensation reactions when the wood flour was added [Fig. 1(b)]. It seemed that the addition reaction generally happened at lower temperatures, while the condensation replaced the addition at higher temperatures. This was evidenced by the relationship between cure reaction rate constant and temperature (Fig. 4). According to the Arrhenius equation, the reaction rate constant increases with the increase of a temperature for an exothermal reaction. However, the cure reaction rate constants decreased with the increase of temperature from 90 to 100°C (Fig. 4). This was possibly due to the fact that the addition under fast vitrifying was gradually replaced by the condensation with a low reaction rate.

Based on the discussion earlier, the nth-order cure kinetic parameters of the addition reaction for CRM can be obtained with the isothermal data below 90°C, and those of the condensation reaction can be derived from the data over 110°C. In Table III, the kinetic parameters at temperatures lower than 90°C were for the addition reaction, and those at temperatures higher than 110°C were for the condensation. For CR, the reaction order for the addition reaction was 2.38, and the total reaction order of the autocatalytic condensation reaction was about 5.[20] For CRM, the addition reaction had the lower reaction order of 1.52, and the condensation had the similar reaction order of 1.57. For CRP, the reaction order of the addition reaction was 1.57, and that of the condensation was 2.18. With the values of A and E from linear regressions of eq. (4), the corresponding kinetic equations for CRM are:

$$\left(\frac{d\alpha}{dt}\right)_{\text{addition}} = 1.736 \times 10^3 \exp\left(-\frac{4779}{T}\right)(1-\alpha)^{1.52}$$
$$(T < 90°C) \quad (8)$$

$$\left(\frac{d\alpha}{dt}\right)_{\text{condensation}} = 1.213 \times 10^1 \exp\left(-\frac{3217}{T}\right)(1-\alpha)^{1.57}$$
$$(T > 110°C) \quad (9)$$

and

$$\left(\frac{d\alpha}{dt}\right)_{\text{addition}} = 2.005 \times 10^5 \exp\left(-\frac{6516}{T}\right)(1-\alpha)^{1.57}$$
$$(T < 90°C) \quad (10)$$

$$\left(\frac{d\alpha}{dt}\right)_{\text{condensation}} = 3.169 \times 10^1 \exp\left(-\frac{3479}{T}\right)(1-\alpha)^{2.18}$$
$$(T > 110°C) \quad (11)$$

for CRP. Figure 3(b) shows the comparison of the experimental and predicted cure conversion rates at temperatures of 80 and 130°C. The result shows a good agreement between measured and predicted data. At temperatures between 90 and 110°C, the corresponding kinetic equations could not be obtained because it is difficult to know the exact portion of the addition or condensation reaction.

According to dynamic DSC and isothermal DSC results, the cure temperature of CR was significantly decreased by the wood flour. This may result from the strong secondary interactions formed between PF oligomers and wood substrate.[5] The reason why the cure mechanism of the condensation part was changed from the autocatalytic reaction to the nth-order reaction probably was that the interaction between PF oligomers and wood matrix was much stronger than that between PF oligomers and complexing agent, which caused the autocatalytic cure reactions to happen.
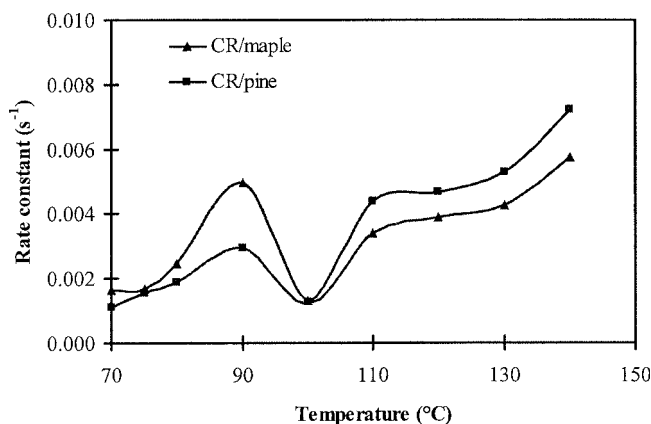

Figure 4 Cure reaction rate as a function of temperature for the CR/wood mixtures.

Prediction of the cure of the resin and wood mixtures

For the mixtures of FR with wood flour, the prediction of the relationship among the reaction conversion (curing degree), cure temperature, and cure time was performed by integrating the kinetic equations (eqs. (6) and (7)). The obtained equations are:

$$t_{FRM} = 4.066 \times 10^{-2} \exp\left(\frac{3504}{T}\right)\left[(1-\alpha)^{-1.05} - 1\right] \quad (12)$$

$$t_{FRP} = 2.027 \times 10^{-3} \exp\left(\frac{4754}{T}\right)\left[(1-\alpha)^{-0.81} - 1\right] \quad (13)$$

The predicted curing curves for FRM are shown in Figure 5(a). The predicted curing curves for FRP can also be done in the same way.

For CR/wood mixtures, the prediction was done by integrating the corresponding kinetic equations (eqs. (8)–(11)). The obtained equations for CRM are:

$$t = 1.108 \times 10^{-3} \exp\left(\frac{4779}{T}\right)\left[(1-\alpha)^{0.52} - 1\right]$$
$$(T < 90°C) \quad (14)$$

$$t = 0.145 \exp\left(\frac{3217}{T}\right)\left[(1-\alpha)^{0.57} - 1\right] \quad (T > 110°C)$$
$$(15)$$

and

$$t = 8.750 \times 10^{-6} \exp\left(\frac{6516}{T}\right)\left[(1-\alpha)^{-0.57} - 1\right]$$
$$(T < 90°C) \quad (16)$$

$$t = 2.674 \times 10^{-2} \exp\left(\frac{3479}{T}\right)\left[(1-\alpha)^{-1.18} - 1\right]$$
$$(T > 110°C) \quad (17)$$

for CRP. The predicted curing curves for CRM at temperatures less than 90°C and at higher than 110°C are shown in Figure 5(b). The predicted curing curves for CRP can also be done in the same way. The predicted curing curves as shown in Figure 5 provide guiding information for deciding actual curing technology of various resin/wood systems.

SUMMARY AND CONCLUSIONS

The wood effect on the cure behavior of commercial PF Resin used for OSB face and core was studied using DSC. The wood flour not only decreased the cure temperatures and activation energy of FR, but also increased its cure reaction order. The initial cure temperature of FR/wood mixtures was lower than 70°C. The reaction order and activation energy were 2.36 and 29.11 kJ/mol for FRM, and 1.88 and 39.51 kJ/mol for FRP.

The onset cure temperature of CR was lowered significantly by the wood flour. Compared with neat CR, the addition reaction of the mixtures also followed an *n*th-order reaction mechanism with a lowered reaction order. However, the condensation changed from an autocatalytic reaction to an *n*th-order reaction, with the reaction order of 1.57 for CRM and 2.18 for CRP. The addition reaction of the mixtures usually occurred at temperatures less than 90°C, and at temperatures higher than 110°C, the condensation reaction replaced the addition.

The kinetic models fitted the experimental data well. With the obtained kinetics parameters, the relationships among reaction conversion (cure degree), cure temperature, and cure time for various resin/wood systems were developed. The future work will deal with cure kinetics of the resins under the influence of chemical additives, such as biocides.
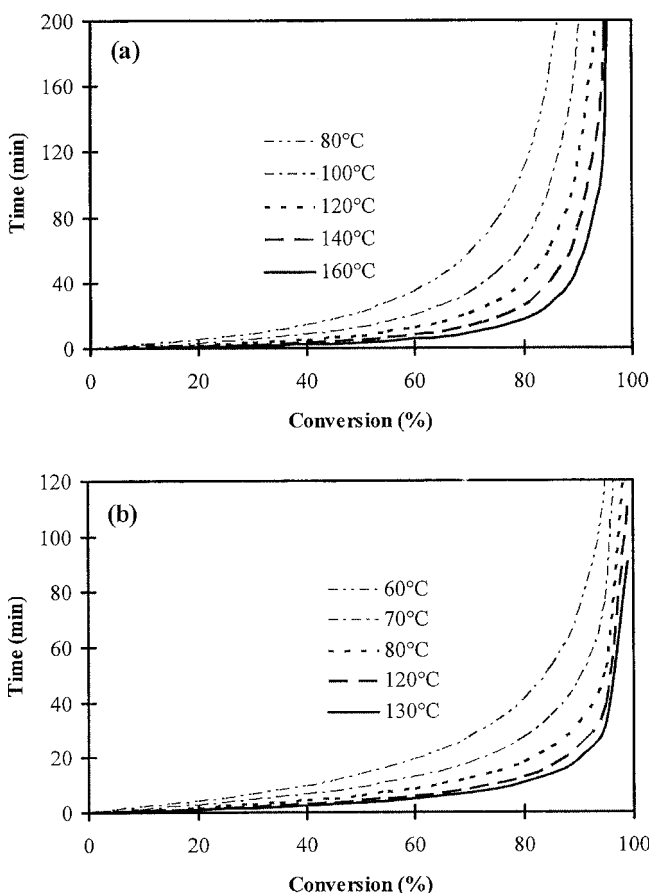
Figure 5 Predicted cure time as a function of percent conversion at various isothermal temperatures. (a) FRM mixture. (b) CRM mixture.

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