Effect of Wood on the Curing Behavior of Commercial Phenolic Resin Systems

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ABSTRACT: Differential scanning calorimetry (DSC) was used to study the effect of wood on the curing behavior of two types of commercial oriented-strand-board phenolic resins. DSC analysis showed that the curing behavior of the core resin differed significantly from that of the face resin in terms of the peak shape, peak temperature, and activation energy. The addition of wood to the resins moved the two separated peaks in the DSC curves of the core resin adjacent to each other. It also accelerated the addition reactions in the curing processes of both the core and face resins. The two peaks in the DSC curves were the result of the high pH values of the resins. These two peaks became either jointed together or overlapped when the pH value of the resin was reduced. Wood also reduced the activation energies for both the core and face resins by decreasing the pH values of the curing systems. Moreover, the effects of wood on the curing behavior of the resins among the five species studied were similar. The lowest activation energy for a phenolic resin probably appeared at pH 10–11 under alkaline conditions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 185–192, 2005

Key words: curing of polymers; differential scanning calorimetry (DSC); resins

INTRODUCTION

Phenol–formaldehyde (PF) resol resin, used as an exterior wood binder, has been widely used in the manufacturing of wood panels, such as plywood, oriented strand board (OSB), particleboard, medium-density fiber board, and engineered lumber products. The curing behavior of the resin and resin/wood mixture has a direct influence on both the production process and the final properties of the products.

It has been established[1] that the polymerization of phenolic resins contains two main types of reactions: addition reactions and condensation reactions. These reactions involved in the synthesis and curing processes of PF resins are very complicated and uncertain because of the different reactivities of various functional groups, the functionalities of phenol and formaldehyde, and their dependence on the process variables. In the formulation of resol PF resins, variables such as the formaldehyde/phenol ratio,[2,3] the type and content of the catalyst,[4–6] and the pH value[7,8] determine the structure and composition of the resin and hence influence the curing behavior of the resin as well. Additives for accelerating the curing rate of PF resins may also change the curing kinetics and even the reaction mechanism.[9,10] Recently, the addition of urea to PF resins to accelerate the curing rate and lower the cost has made the curing process even more complicated in comparison with that of pure PF resins.[11–13] As a result, a full kinetic analysis of the curing processes of PF resins is complex, and data reported in the literature can differ considerably.[1]

The curing behavior of PF resins is affected by the wood substrates in the PF-resin/wood mixtures.[14–19] In the presence of wood, the activation energies for the curing reactions are lower than those of the PF resin alone. This result has been attributed to the catalytic activation of condensation reactions induced by carbohydrates in the wood substrates.[14,17] In other studies, the curing reactions of PF resins have been retarded by wood and have resulted in higher activation energies.[16,19] Results from gel time tests have indicated that the gel time has no direct correlation with the pH values and buffering capacity of wood species.[18] A recent study[19] has shown that wood can accelerate addition reactions and retard condensation reactions. The same study has shown that wood also reduces the reaction enthalpy of the PF resin through diffusion and changes in the phase of the curing systems, and this suggests that the curing reaction reaches lower final degrees of conversion in mixtures of the PF resin with wood than in the PF resin alone. These results show that the basic factors in the curing system, such as the pH value, structure, and compo-

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TABLE I
Composition and Physical Properties of PF Resins

Resin	Solid content (%)	pH	Viscosity (mPa s)	C (%)	N (%)
Core PF	51.5	12.98	164	44.99	10.67
Face PF	57.0	11.05	172	50.82	11.03

sition of both the resin and wood and the phase of the curing system, are significant in the curing process. However, the effects of these factors still unclear because of the complex interactions in wood/resin mixtures.

There are two typical resin systems that are being used in OSB manufacturing: core and face resins. The core resin, which is used in the middle layer of the panel, generally has a higher molecular weight and a faster curing rate than the face resin,[20] which is used in the surface layers. In this study, commercial OSB core and face PF resins were measured in terms of their curing behavior by differential scanning calorimetry (DSC). To analyze the effect of wood on the curing behavior, we also characterized freeze-dried PF resins and mixtures of PF resins with various wood species.

EXPERIMENTAL

Materials

One commercial liquid core PF resin and one commercial liquid face PF resin were used in this study. The compositions and basic physical properties of the resins are listed in Table I. The elemental content was measured with a 2400 series II CHNS/O analyzer (PerkinElmer Inc., Wellesley, MA). Other parameters were supplied by the producer. Freeze-dried resins were obtained via the freeze drying of the corresponding liquid resins in our laboratory. Five wood species, including aspen, birch, red maple, red pine, and southern yellow pine (SYP), were used in the experiments. The moisture content of the wood for all the species was about 6%.

Preparation of the resin/wood mixtures

To make the PF-resin/wood mixtures, wood was first ground into flour. The wood flour was then screened, and wood flours of 35–60 mesh for all species were retained for the experiments. Aspen and maple flours of sizes passing 120 mesh were also used to make mixtures with the face resin. The mixtures of the hybrid wood species were made through the mixing of two species in a 50/50 (w/w) ratio. The resin/wood mixtures were prepared through the mixing of the liquid PF resins with the wood flour in a 50/50 (w/w) ratio.

Determination of the wood pH value and buffering capacity

Wood flour (oven-dried; 25 g) was refluxed in 250 g of distilled water for 20 min, and the cooked mixture was cooled and filtered with Whatman #1 filter paper (Whatman International Ltd., Kent, UK) under an aspirator vacuum to obtain an aqueous wood extractive solution. The pH values of the wood extractive solution were determined at room temperature with a pH meter calibrated with buffering solutions at pH values of 4 and 7.

The acid buffering capacity was measured through the titration of a 50-mL wood extractive solution with a 0.025*N* NaOH aqueous solution to reach the titration terminal at pH 7. The acid buffering capacity was calculated with the following equation:

$$\begin{aligned}&\text{Acid buffering capacity (mequiv/100 g of wood)}\\&\quad= \text{Volume of NaOH titrant used for 100 g of wood}\\&\qquad\qquad\times \text{Normality of NaOH}\end{aligned}$$

The base buffering capacity was measured through the titration of a 50-mL wood extractive solution with a 0.025*N* H_2SO_4 aqueous solution to reach the titration terminal at pH 3. The base buffering capacity was calculated as follows:

$$\begin{aligned}&\text{Acid buffering capacity (mequiv/100 g of wood)}\\&\quad= \text{Volume of } H_2SO_4 \text{ titrant used for 100 g of wood}\\&\qquad\qquad\times \text{Normality of } H_2SO_4\end{aligned}$$

DSC measurements

All DSC measurements and analysis were made with a Q1000 DSC instrument and Universal analysis software from TA Instruments (New Castle, DE). High-volume pans (TA Instruments) that could withstand vapor pressures up to 3.8 MPa were used to prevent the components of the test samples from evaporating at higher temperatures up to 250°C. Dynamic scans were conducted at heating rates of 2, 5, and 10°C/min, and the scanning temperature ranged from 25 to 250°C.

The activation energy of the curing process was evaluated by isoconversional methods with the peak temperatures of the DSC scans at three different heating rates. These methods used the relationship between the heating rate and temperature at the peak of the DSC curve or at a given degree of conversion. Based on the work of Ozawa[21] and Flynn and Wall,[22] an equation connecting the temperature (T) and heating rate (Φ) was obtained under the assumption that the pre-exponential factor (A), the activation energy

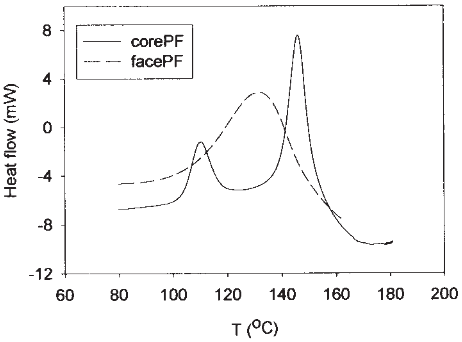

Figure 1 DSC scanning curves for the liquid PF resin (heating rate = 5°C/min).

(E), and the function of α [$f(\alpha)$] were independent of T and Φ:

$$\log \Phi = -2.315 - 0.4567E/(RT) + \log(AE/R) - \log F(\alpha) \quad (1)$$

where $F(\alpha)$ is equal to $F\alpha = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$, α is the degree of conversion, and R is the gas constant. E was calculated from the plot of log Φ versus $1/T$. Another expression relating Φ and T was developed from the work of Kissinger[23] for the nth-order reaction as follows:

$$\ln(\Phi/T^2) = -E/(RT) + \ln(RA/E) \quad (2)$$

A plot of $\ln(\Phi/T^2)$ versus $1/T$ is a straight line, from which E and A can be obtained.

RESULTS AND DISCUSSION

Curing processes of the phenolic resins

Core and face phenolic resins, which are used in the middle and surface layers of OSB panels, have different compositions and physical properties (Table I). The core PF resin, the molecular weight of which is generally higher than that of the face resin, tends to have a higher viscosity. However, the viscosity of the core resin used in this study was slightly lower than that of the face resin because of the lower solid content in the core resin. The pH value of the core resin was higher than that of the face resin. Elemental analysis showed that there was about 11% nitrogen in both PF resins, indicating that the urea component was present in these two PF resins.

Dynamic DSC scanning curves for both the core and face resins are shown in Figure 1. These two curves have different shapes. The curve for the face resin has one peak, whereas the curve for the core resin has two peaks. As stated earlier, the reaction processes of phenolic resins are multiple, including several steps and many individual reactions.[1] It has been shown in previous research that the DSC curves for phenolic resins can have two or multiple peaks under certain conditions, including high formaldehyde residues in the curing systems[3] and high NaOH/phenol molar ratios.[5] The urea component in phenolic resins can result in more reactions with different activation energies,[12,13] which can possibly lead to separated peaks under particular conditions. The two peaks in the core resin used in this study may be the result of the factors mentioned previously; the high pH value of 12.98 is probably the main factor responsible for the formation of the two peaks.

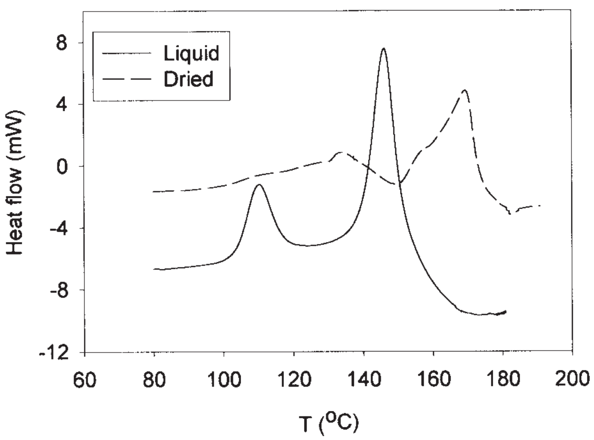

Figure 2 DSC scanning curves for the core PF resin (heating rate = 5°C/min).

To better understand this observation, freeze-dried resins were also subjected to DSC scans (Figs. 2 and 3). In comparison with the liquid resins, the two peaks shifted to higher temperatures for the freeze-dried core resin, whereas the single peak was split into two peaks for the face resin. This indicated that the high pH value was the main reason for the separated peak

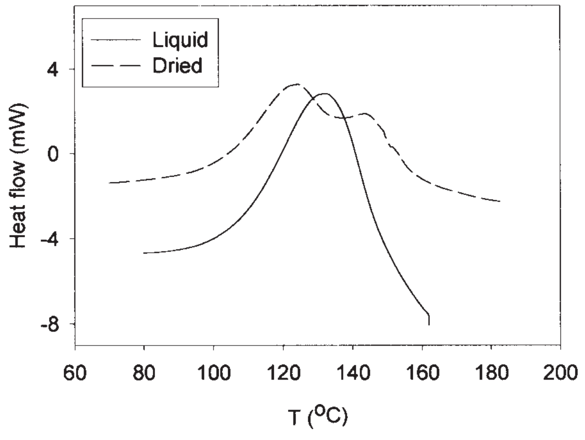

Figure 3 DSC scanning curves for the face PF resin (heating rate = 5°C/min).

TABLE II
Peak Temperature (T_p) and Activation Energy (E_k and E_w) for the Pure PF Resins

	T_p (°C)						
Sample	2°C/min	5°C/min	10°C/min	E_k (kJ/mol)	R^2	E_w (kJ/mol)	R^2
Face-lq	119.58	132.26	142.40	89	1	91	1
Face-sd-p1	112.77	124.32	133.51	95	1	96	1
Face-sd-p2	132.81	143.50	152.25	112	0.9998	113	0.9999
Core-lq-p1	102.03	110.57	118.63	112	0.9971	113	0.9974
Core-lq-p2	134.31	146.20	156.23	100	0.9997	102	0.9997
Core-sd-p1	122.71	134.30	142.85	102	0.9995	104	0.9995
Core-sd-p2	157.52	169.49	177.28	123	0.9968	124	0.9971

lq = liquid resin; sd = solid resin; p1 = first (lower temperature) peak; p2 = second (higher temperature) peak.

because the pH values of the freeze-dried resins became higher with the removal of water from the resins. The increased pH value could also retard the curing reactions, leading to much higher peak temperatures in the core resin. Condensation reactions could also be retarded because of the effect of diffusion-controlled kinetics, but addition reactions could be accelerated because of the increased concentration of the reactants in the freeze-dried resin.[20] That was the reason that the first peak (the peak at the low temperature) for the freeze-dried core resin became wider and a wide shoulder appeared in the lower temperature range of this peak.

Table II shows the activation energies and regression coefficients (R^2) for the liquid and freeze-dried resins calculated with both the Kissinger method (E_k) and Ozawa method (E_w). The two methods were consistent with each other. The activation energies for the two peaks of the liquid core resin were higher than those of the face resin, and this could mainly be attributed to the difference in the pH values (11.05 vs 12.98) of these two resins. The same trend was observed for the activation energies of the freeze-dried resins, except for the value for the first peak of the core resin. The effect of pH on the activation energy is discussed in more detail in the following section.

Effects of the wood flour on the curing processes

For PF resol resins used as wood adhesives, the curing reactions occur under alkaline conditions. Meanwhile, most wood species are acidic. As a result, an important factor that influences the curing behavior of the resin is the pH value and buffering capacity of wood. Table III shows the pH values and buffering capacities of the wood flours used in our experiments. The pH values and the acid buffering capacities are plotted in Figure 4. The pH values of the wood flours ranged from 4.13 (red pine) to 5.15 (aspen), and the acid buffering capacities varied from 0.88 (aspen) to 3.52 (red pine). Figure 4 shows that the order of the acid buffering capacity is the reverse of that of the pH values, except for the values of maple and aspen/SYP. As shown in Figure 4, the differences in the pH values are not significant, and the acid buffering capacities are relatively low. Therefore, the effect of these wood species on the pH values of the resins was expected to be small, especially on the relatively high pH values of the resins.

TABLE III
pH and Buffering Capacity of Wood Flours

		Buffering capacity[b]		
Species	pH[a]	Acid	Base	Total
Aspen	5.15 (0.03)	0.88	5.58	6.46
Red pine	4.13 (0.07)	3.52	3.30	6.82
Red maple	4.76 (0.10)	2.4	2.48	4.88
SYP	4.30 (0.04)	2.08	3.35	5.43
White birch	4.64 (0.07)	1.12	2.65	3.77
Aspen/maple	4.95 (0.03)	0.95	3.87	4.82
Aspen/SYP	4.68 (0.04)	1.37	3.90	5.27

[a] pH values were obtained by the averaging of four measurements from two extractives. The values in parentheses are standard deviations.

[b] Buffering capacity is the average of two measurements from two extractives.

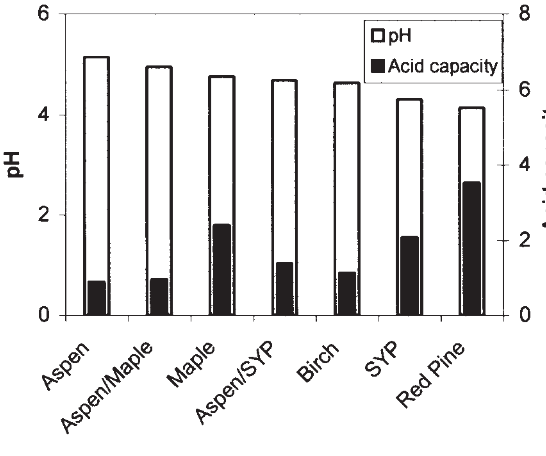

Figure 4 pH and acid capacity of the wood flours.

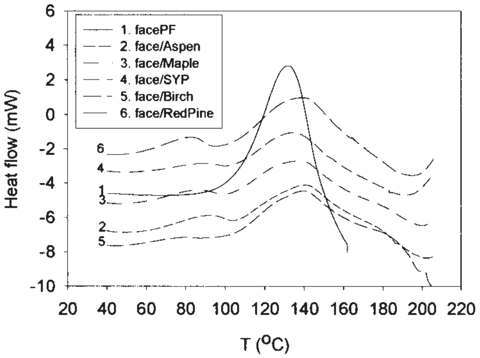

Figure 5 DSC scanning curves for the face resin and its mixtures with wood (heating rate = 5°C/min).

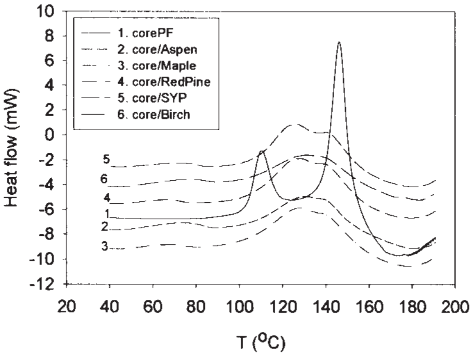

Figure 6 DSC scanning curves for the core resin and its mixtures with wood (heating rate = 5°C/min).

Figure 5 shows the DSC curves for the pure face resin and the corresponding resin/wood mixtures. A small but wide peak appeared in the lower temperature range between 60 and 100°C in the DSC curves after the addition of wood flours to the resin. A similar peak has been reported in the literature;[19] it was described as addition reactions accelerated by wood through the increased concentrations of reactants because wood absorbed most of water in the PF resin. It is also probable that the catalysis of wood to the addition reactions contributed to this peak similarly to the reported catalysis of wood to self-condensations.[9,19]

The activation energies of the curing processes for the face-PF-resin/wood mixtures were evaluated with both the Kissinger and Ozawa methods, as shown in Table IV. The activation energies varied from 79 to 89 kJ/mol, generally being lower than those of the face resin alone. This was mainly because the addition of wood resulted in lower pH values. However, the effect of wood on the activation energy seemed not to be directly related to either the pH values or the acid buffering capacities of the wood among the different wood species. The effect of the wood particle size on the activation energy depended on the species, as shown by the values for aspen/resin and maple/resin mixtures in Table IV. The activation energy for the extracted birch was higher than that for the corresponding unextracted birch, and this showed the impact of acid extractives on the activation energy.

The effect of wood on the curing process was stronger for the core resin, as illustrated in Figure 6. For the core/wood mixtures, the two peaks in the DSC curves of the pure core resin merged into one peak. It was clear that the first peak (low temperature) in the DSC curve of the pure resin shifted to the higher temperature, whereas the second one (high temperature) slightly shifted to the lower temperature. This is consistent with a review[24] that found that the rate of formaldehyde addition to the phenolic ring increases, whereas the rate of formation of methylene linkages between the methylol groups decreases, under strong alkali conditions. This may also be the reason that there was only one peak in the DSC curve of the pure face resin with the lower pH value of 11.05, whereas two peaks appeared in the core resin with the higher

TABLE IV
Peak Temperature (T_p) and Activation Energy (E_k and E_w) of the Face-PF–Resin/Wood Mixtures

	T_p (°C)						
Sample	2°C/min	5°C/min	10°C/min	E_k (kJ/mol)	R^2	E_w (kJ/mol)	R^2
Aspen	126.88	140.57	152.37	83	0.9995	85	0.9996
Aspen-120m[a]	126.80	140.19	151.12	86	1	89	1
Maple	125.28	137.75	149.36	87	0.9979	89	0.9982
Maple-120m[a]	125.40	139.59	151.18	81	1	83	1
Birch	125.33	139.75	151.85	79	0.9998	81	0.9998
Ext-birch[b]	125.99	139.75	150.80	84	1	87	1
Red pine	124.88	139.47	149.53	84	0.9980	86	0.9982
SYP	120.53	134.12	146.10	80	0.9992	82	0.9993
Aspen/maple	126.45	140.12	150.02	89	0.9991	91	0.9992
Aspen/SYP	124.51	138.51	148.40	87	0.9986	89	0.9988

[a] Aspen-120m and maple-120m mean the wood flours in the resin/wood mixtures were of sizes passing 120 mesh.
[b] Ext-birch means extracted birch sample.

TABLE V
Peak Temperature (T_p) and Activation Energy (E_k and E_w) of the Core-PF–Resin/Wood Mixtures

	T_p (°C)						
Sample	2°C/min	5°C/min	10°C/min	E_k (kJ/mol)	R^2	E_w (kJ/mol)	R^2
Aspen	119.36	130.74	140.77	95	0.9991	97	0.9992
Maple	116.81	128.64	138.73	91	0.9996	93	0.9996
Birch	122.31	129.67	139.11	122	0.9785	122	0.9807
Red pine	116.14	128.04	137.91	92	0.9998	94	0.9998
SYP	115.07	126.40	136.36	93	0.9991	95	0.9992
Aspen/maple	118.12	130.43	140.73	89	0.9998	91	0.9998
Aspen/SYP	117.24	128.74	138.13	96	0.9999	98	0.9999

pH value of 12.98. However, further work is needed to identify the exact types of reactions associated with these two peaks. Moreover, a small and wide peak appeared in the low temperature range in the DSC curves of the core-resin/wood mixtures, just as for the face-resin/wood mixtures.

Similarly, the activation energies for the core resin were also influenced by wood, as shown in Table V. The activation energies varied from 89 to 96 kJ/mol, being lower than the values for both peaks of the pure core resin, except for the value of the birch/resin mixture. The value for the birch/resin mixture was higher than that of the pure core resin. The value for the core-resin/birch mixture might be inaccurate because of the error introduced in the determination method associated with the identification of the peak temperatures at different heating rates. Figure 7 shows the DSC curves for the core-resin/birch mixture. The two distinctive peaks observed in the pure core resin did not completely overlap each other in the DSC curves for the resin/birch mixture, and the combined peak was asymmetric. The peak temperature used to calculate the activation energy was actually for the second peak at the heating rate of 2°C/min, whereas the first peak temperatures were used for heating rates of 5 and 10°C/min. As a result, the peak temperature determined at the heating rate of 2°C/min was overestimated, and this resulted in an overestimated activation energy calculated from these peak temperatures. In fact, the activation energies for the other core-resin/wood mixtures were calculated with the first peak temperatures, although these two peaks almost overlapped each other.

Modulated differential scanning calorimetry (MDSC) is a newer method that superposes a sinusoidal signal onto the linear temperature program of the standard DSC scan during the measurement. This technique may separate reversible (e.g., glass transition) and irreversible (e.g., chemical reactions and evaporation) transitions and improve the precision of measurements. To verify the activation energy for the core-resin/birch mixture calculated from DSC data, we subjected the core-resin/birch sample to MDSC measurements with a sinusoidal signal amplitude of 0.5°C and a periodic time of 100 s. The activation energy calculated from MDSC data by the Kissinger method was 127 kJ/mol (R^2 = 0.9794), which was close to the value calculated from the standard DSC data. It is evident from Figure 8 that the MDSC curves

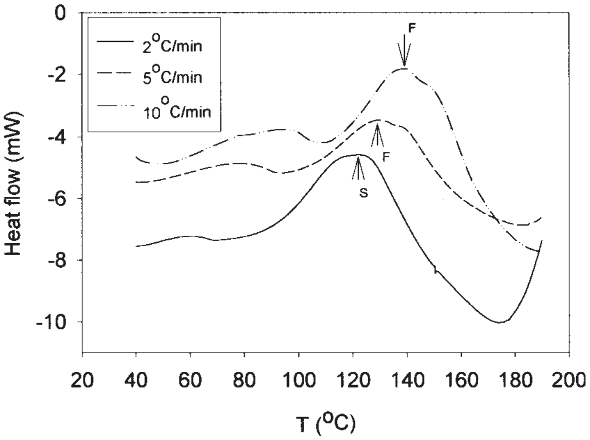

Figure 7 DSC scanning curves for the core-resin/birch mixture (F = first peak; S = second peak).

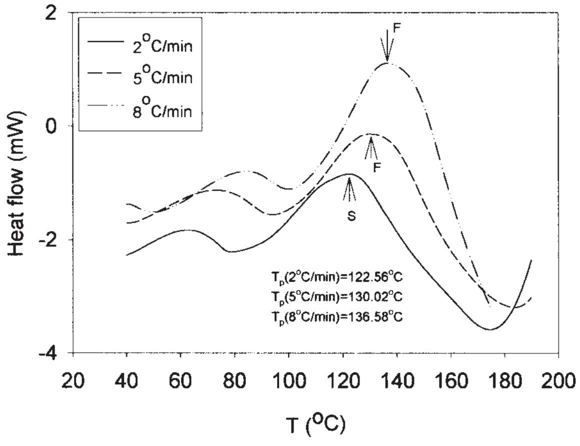

Figure 8 MDSC scanning curves for the core-resin/birch mixture (F = first peak; S = second peak; T_p = peak temperature).

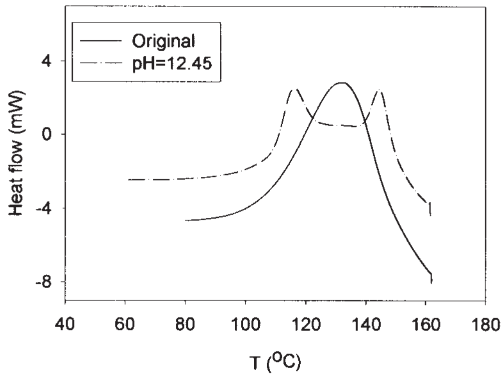

Figure 9 DSC scanning curves for the face resin before and after pH adjustment (heating rate = 5°C/min).

for the core-resin/birch mixture were similar to the DSC ones, although the two peaks seemed to be slightly more overlapped in the MDSC curves.

The activation energies for the core and face resins were influenced by the wood flours because the wood acidity made the pH value of the curing system lower. However, among the different wood species, the extent of this effect was not directly correlated to either the pH value or the acid capacity of the wood species. One probable reason is that the differences in the pH values and the acid capacities among the wood species used in this study were small. It is also possible that the pH value of the resin was influenced not only by the pH value and acid capacity of the wood but also by the reduction of the catalysts in the resin. The catalysts and water, as small molecules, more easily penetrated the wood than the resin molecules, and this resulted in a decrease in the catalyst concentration in the resin system.

As mentioned previously, the activation energies for both the core and face resins decreased under the influence of wood. This result seems to contradict a previous report,[19] in which wood increased the activation energies. However, the pH value of the pure resin used in that research was around 10.5, lower than the pH values of the resins used in this study. That is, the activation energy for the PF resin decreased with an increase in the pH value in the lower pH range but increased with an increase in the pH value in the higher pH range under alkaline conditions. This suggestion was consistent with another report,[8] which showed that a resol PF resin presented the highest reactivity in the pH range of 9–11. It seems that the lowest activation energy for a PF resin appears at pH 10–11 according to results from both previous studies and this study.

To confirm the effect of the pH value on the curing behavior of the resin, we modified the face resin only by adjusting the pH value from 11.05 to 12.45 with sodium hydroxide. Figure 9 shows the DSC curves for the face resin before and after the pH value was adjusted. The single peak for the face resin split into two peaks, similarly to the core resin, after the pH value reached 12.45. The activation energies (E_w) obtained from these two peaks were 110 and 108 kJ/mol, respectively, much higher than those of the unadjusted face resin.

Several repeats were made to determine the reproducibility of the tests. The standard deviation of the measurements, as given in Table VI, showed that the tests were fairly reproducible.

CONCLUSIONS

The commercial core and face phenolic resins had distinctively different curing processes in terms of their DSC curing curves and activation energies. The existence of one or two peaks in the DSC curves for the

TABLE VI
Standard Deviation (SD) of E_k for the DSC Measurements

Sample	Peak temperature (°C)			E_k (kJ/mol)	$\bar{E}_k$ (kJ/mol)	SD
	2°C/min	5°C/min	10°C/min			
Core PF (first peak)	102.03	110.57	118.63	112.2		
	102.17	111.16	118.68	112.8	112.3	0.46
	101.99	111.28	118.60	111.9		
Core PF (second peak)	134.31	146.20	156.23	99.9		
	134.00	145.56	155.32	102.6	101.7	1.59
	134.21	145.50	155.54	102.7		
Face/aspen	126.20	140.34	152.02	81.1		
	127.05	140.42	151.21	87.1	83.6	3.14
	126.88	140.57	152.37	82.5		
Face/maple	125.28	137.76	149.36	86.8		
	124.84	138.07	148.29	88.7	87.1	1.43
	124.71	138.22	148.93	85.9		
Core/SYP	114.92	126.18	137.20	89.0		
	115.07	126.40	136.36	93.4	92.1	2.66
	115.60	126.45	136.85	93.8		

curing reactions of the phenolic resins was mainly affected by the pH value of the curing system. A higher pH value yielded separate peaks and a higher activation energy. Wood had an influence on the curing behavior of both the core and face resins in terms of the shape of the DSC curves and the activation energies. This influence was mainly found through changes in the pH values of the resin systems. The two peaks for the core resin shifted adjacent to each other after the wood flours were added because of the pH reduction by wood. There existed a small peak in the lower temperature range of 50–100°C for both the core and face resins after the addition of the wood flours. This small peak was thought to be associated with the addition reactions accelerated by wood. Wood also decreased the activation energies for both the core and face resins by reducing the pH values. This suggests that the lowest activation energy for PF resins probably appears at pH 10–11 under alkaline conditions. The different wood species had similar effects on the curing behavior of both resins.

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