Curing Process of Powdered Phenol–Formaldehyde Resol Resins and the Role of Water in the Curing Systems

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ABSTRACT: The curing behavior of two kinds of commercial powdered resol phenolic resins was studied by differential scanning calorimetry. Liquid-state ^{13}C-NMR spectroscopy was used to aid in understanding the curing behavior by detecting the structure of powdered resins. The reaction mechanism was interpreted with the dependency of activation energy on the degree of conversion. The results indicate that there are differences in the curing mechanism between core and face phenolic resins. The curing process of core resin was faster than that of face resin at the same reaction temperature. The water added in the curing system played an important role of plasticizer or diluent according to different curing stages and water content. In the initial curing stage, water mainly diluted the system and retarded the curing reactions. However, at the higher degrees of conversion, water played the role of plasticizer to decrease the effect of diffusion on the curing reactions to make the curing reactions more complete. The excess water added in the curing system played the role of diluent at almost all stages during the curing process. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1371–1378, 2003

Key words: differential scanning calorimetry (DSC); kinetics; curing of polymers; powdered PF resins; role of water

INTRODUCTION

Powdered phenol–formaldehyde (PF) resins have been used in the North American waferboard and oriented strand board (OSB) industries since 1975.[1] Advantages of powdered PF resins over their corresponding liquid counterparts include lower resin quantity requirements in panel manufacture, better resin distribution on wood flakes, shorter panel pressing time, and no complicated spraying system. In addition, powdered PF resins exhibit better stability and lower transportation costs. For the manufacture of OSB panels, there is a temperature gradient from the core to the surface of panels during the hot-pressing process. Hence two different resin systems have been developed for OSB: core resin and surface resin. The core resin is used for the middle layers of the panel, where a slow increase in temperature occurs and the final temperature is lower than that in the surface layers of the panel.

Some chemical and physical characteristics of powdered phenol–formaldehyde resins differ from those of liquid resins because of the influence of spray-drying (or freeze-drying) parameters and the role of water in phenolic systems. Ellis and Steiner[1–5] have carried out effective work in understanding the cure and flow parameters for powdered phenolic resins as they are used as face resins, core resins, and resins for use throughout the panel. However, that research was not concerned with the curing reactions of powdered PF resins. In fact, the kinetic parameters of the curing reactions for a powdered phenolic resin are different from those of a liquid resin, and this is attributed to the scarcity of water in the reaction system. Water, as plasticizer or diluent, may accelerate or retard the curing reactions. UV spectroscopy measurements on aqueous extracts from cured PF resins[6,7] showed that the presence of water in the resin during cure plays an important role. At 100°C, the curing rate of aqueous resins decreases with increasing water dilution. The extra water acts as an energy barrier to resin crosslinking. However, the influence of moisture diminishes with increasing temperature. Studies on the cure of solid two-step phenolic molding compounds[8,9] showed that moisture can enhance the curing rate and the degree of cure. Increased reactivity is primarily attributed to moisture accelerating the decomposition of hexamethylenetetramine and also might be partially attributed to moisture improving the flowability

of the compounds by plasticization. Wang et al.[10] studied the effect of temperature and humidity on phenol–formaldehyde resin cure by DSC and obtained similar results.

This study analyzes the curing behavior of core and face commercial resol phenol–formaldehyde resins, mainly by DSC. A model-free kinetics technique[11,12] was used to interpret the curing mechanism. The molecular structure of resins was characterized by nuclear magnetic resonance (NMR) spectroscopy. To study the effect of water in the curing systems of phenolic resins on the curing process, the curing reactions of powdered phenolic resins mixed with water were measured.

EXPERIMENTAL

Materials

Core and surface powdered phenolic resins were commercial ones (Tembec Products, Temiscaming, Canada). To measure the effect of water on the cure of powdered phenolic resins, powdered phenolic resin/water mixtures were produced by adding distilled water into the powdered resins. The solid content of the mixture was obtained from the weight of resin divided by the sum of the weight of resin and water added.

DSC measurements

A Mettler (Columbus, OH) DSC 20 with a Mettler TA400 thermal analysis system with STAR^e software was used in the experiments. Because the adhesives are water-based, high-pressure steel crucibles that can withstand vapor pressure up to 10 MPa were used. Dynamic scans were made at heating rates of 5, 10, and 20°C/min, respectively, and a scanning temperature range from 30 to 250°C.

NMR measurements

High-resolution ^{13}C-NMR spectra in liquid were recorded with a Bruker AM 300 spectrometer (Bruker Instruments, Billerica, MA). Spectra were measured using a 5-μs pulse width 45° and 1-s pulse delay. The Waltz 16 decoupling method was used to suppress the nuclear Overhauser effect. In all, 2560 scans were accumulated to obtain reliable spectra. No relaxation reagent was used in NMR measurement. Samples were dissolved in deuterated dimethysulfoxide (DMSO-d_6). ^{13}C chemical shifts were measured with respect to tetramethylsilane as internal standard (δ value of DMSO-d_6: 39.5 ppm).

RESULTS AND DISCUSSION

Kinetic computational method for DSC measurement

Isoconversional method can be utilized to evaluate the activation energy of curing reactions at each degree of conversion from multiple DSC data, including at least three DSC scans at different heating rates.[13–17] Based on the work of Ozawa[14] and Flynn and Wall,[15] a plot of ln Φ (the logarithm of heating rate) versus $1/T$ is a straight line at a given conversion. The activation energy can be obtained from the slope of the line. Kissinger[13] developed another equation for curing reaction, expressed as follows:

$$\ln \Phi/T_i^2 = -E_\alpha/RT_i + \ln RA/E_\alpha \qquad (1)$$

where E_α is the activation energy at conversion α, and A is the preexponential factor. In the same way, a plot of ln Φ/T_i^2 versus $1/T_i$ is also a straight line at a given conversion. The activation energy can be obtained from the slope. The Kissinger equation was utilized to evaluate the activation energy in this study. By the model-free kinetic technique,[11,12] the dependency of activation energy on the degree of conversion is obtained by evaluating activation energy at each degree of conversion during the overall curing process of PF resins.

A prediction of isothermal kinetic parameters can be done through nonisothermal DSC data and the activation energy obtained above. The reaction time to reach a given conversion at an arbitrary temperature can be calculated by introducing an integrated equation,[11,12] as follows:

$$t_\alpha = \left[\Phi\exp\left(-\frac{E_\alpha}{RT_{iso}}\right)\right]^{-1} \int_{T_0}^{T_\alpha}\exp\left(-\frac{E_\alpha}{RT}\right)dT \qquad (2)$$

where t_α is the reaction time to reach conversion α, at isothermal temperature T_{iso}. T_0 and T_α are the scanning temperature at conversion 0 and α, respectively.

NMR analysis for the structure of phenolic resins

The ^{13}C-NMR spectra of several model compounds, such as phenol, 2-methylolphenol, 4-methylolphenol, 2,6-dimethylolphenol, 2,4-dimethylolphenol, 2,4,6-trimethylolphenol, 2,4′-dihydroxyldiphenylmethane, and 4,4′-dihydroxyldiphenolmethane, were obtained and interpreted.[18–20] The information obtained from the spectra of model compounds was used to assign and interpret the spectra of powdered PF resins. The chemical shifts of liquid ^{13}C-NMR of powdered PF resins are shown in Table I.

For the face powdered phenolic resin, the chemical shift of methylene bridges occurs at 30–45 ppm. The

TABLE I
Chemical Shifts of ^{13}C-NMR of Powdered Phenolic Resins

Chemical shift (ppm)	Assignment of carbons
34.8[a] (34.7)[b]	*ortho–para* methylene bridges
59.1–61.7 (58.8–61.6)	*ortho* methylol
63.0–63.7 (62.9–63.2)	*para* methylol
114.7–115.7 (114.5–115.6)	Free *ortho*
117.3–118.0 (118.3)	Free *para*
125.0–131.9 (125.6–131.6)	*meta,* substituted *ortho,* substituted *para*
153.5–155.8 (151.1–155.8)	Phenoxy, alkylated in *ortho* position
157.4–157.5 (156.9)	Phenoxy, alkylated in *para* position
158.7 (158.2)	Phenoxy

[a] Values of face resin.
[b] Values of core resin.

ortho– para bridges can be seen at 34.8 ppm. However, *ortho–ortho* methylene bridges, which appear at about 30 ppm,[18] were not detected. This indicates that *ortho–ortho* bridges are scarce in the powdered resins studied. Unfortunately, the signal of *para– para* bridges at about 40 ppm overlaps with that of dimethylsufoxide solvent. The chemical shifts at 59.1– 61.7 and 63.0– 63.7 ppm belong to *ortho* and *para* methylol, respectively. Free *ortho* and *para* carbons produce signals at 114.7– 115.7 and 117.3– 118.0 ppm, respectively. It appears that the signals of *ortho* positions are wider than those of *para* positions because there are two kinds of *ortho* carbons that may emit different signals attributed to other substituents on the benzene rings.

The core phenolic resin displays chemical shifts similar to those of the face resin. However, further examination of the spectra reveals some differences. The ratio of the signal intensity of methylol to *ortho– para* bridges is 4.23 : 1 for face resin and 3.73 : 1 for core resin, respectively, which indicates that more condensation reactions possibly occur to form methylene bridges in the core resin than in the face resin. Furthermore, the ratio for free *ortho* and *para* positions to methylol is 0.18 : 1 for face resin and 0.44 : 1 for core resin, respectively. The ratio for free *ortho* and *para* positions to *ortho– para* bridges is 1.05 : 1 for face resin and 1.66 : 1 for core resin, respectively. Because substitution on phenolic rings is favored at high ratios of formaldehyde to phenol (F/P) during PF resin synthesis, it is probable that the F/P ratio in the formula of face resin is higher than that in the formula of core resin. The above conclusions could not be confirmed, based partly on the amount of *ortho– para* methylene bridges, because of the lack of information on *para– para* bridges. Further evidence can be taken in the following DSC analysis. In addition, a few methylene ether bridges and hemiformals were detected in the face resin, corresponding to the chemical shifts of 73.8, 85.6, and 87.9 ppm.[19,21]

Reaction kinetics and mechanism of powdered phenolic resins

There is a variation of activation energy with the degree of conversion in a complicated reaction system, which is made up of various kinds of individual reactions. This variation generally results from the change in individual reactions, even the change in a reaction mechanism with degree of conversion. Therefore, the curing mechanism of powdered PF resins may be interpreted according to the dependency of activation energy on the degree of conversion during the overall curing process.

Figure 1 shows the dependency of activation energy on the degree of conversion for core and face powdered phenolic resins. Although the two curves seem quite different from each other, does that mean quite different mechanisms existing from core resin to face resin during the curing process? Gardziella et al.[22] established that there are two main kinds of reactions occurring in the reaction system of phenolic resins, which are addition and condensation reactions. For the core resin, first the curve increases, indicating that there are parallel reactions occurring in the reaction system.[23] It is clear that the parallel reactions are addition and condensation reactions. However, the activation energy rapidly increases to a maximum value at a low degree of conversion, indicating that the addition reactions are scarce and almost completed.[12] After the maximum value is attained, the activation energy decreases with convex shape with the degree of conversion, indicating that a change in reaction mechanism occurs from a kinetic to a diffusion regime. It is seen that this change occurs early during the curing process of core resin because the core resin has reached a relatively higher degree of conversion during the manufacture of the resin, which was shown by the above NMR analysis. The resin with a higher degree of conversion undergoes early gelation, vitrifi-
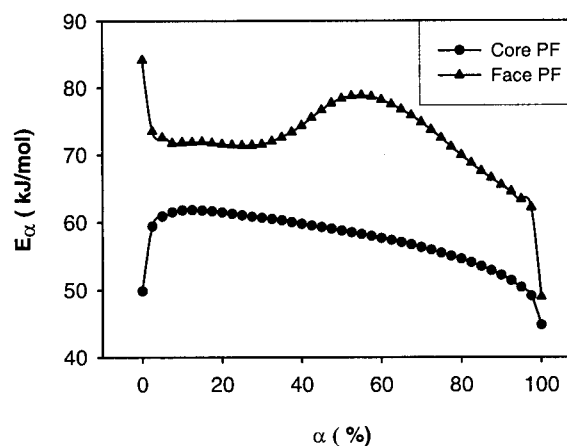

Figure 1 Activation energy dependency on the degree of conversion for powdered PF resins.
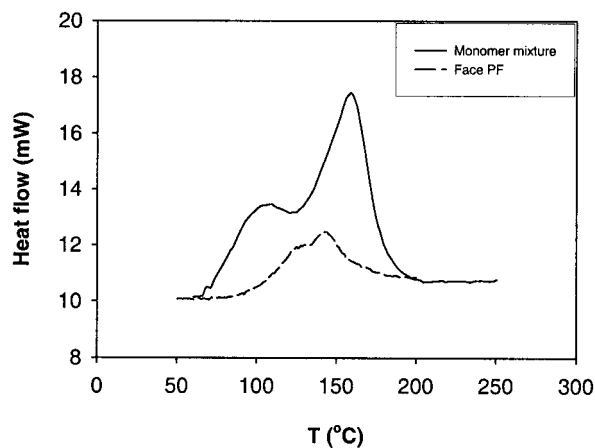
Figure 2 DSC curves of face resin and the mixture of monomers (heating rate: 5°C/min).

cation, and crosslinking at a low degree of conversion during the subsequent curing process.

For the face resin, the change in activation energy with conversion is more complicated than that of core resin. The curve decreases with concave shape at the beginning of cure, indicating the addition reactions occur first during the initial stage of the curing process.[12] However, the curve stops decreasing at a low degree of conversion and levels off, after which it increases to a maximum. This change indicates that the condensation reactions start to occur after a short term, during which the addition reactions occur first.

Figure 2 shows the DSC curves for the face PF resin and a mixture of monomers of phenol and formaldehyde. The latter curve comes from previous experiments.[12] Compared with the typical addition and condensation reactions in the mixture, the two peaks for face PF resin overlap more and the first peak is much smaller. This also indicates that addition reactions occur first during the cure of the face PF resin, even though the fraction of addition reactions is small. According to NMR spectra analysis, the face PF resin contains some hemiformals and methylene ether bridges, which may exist in PF resins with high F/P ratios. Because the content of formaldehyde is low in PF resin, it is possible that the hemiformals in face powdered PF resin are also the source of addition reactions.

The curve of the face resin, like that of the core resin, decreases at a higher degree of conversion, indicating the change in mechanism from a kinetic to a diffusion regime. However, the curve does not decrease with an exact convex shape at the final section of the curve and displays a leveling-off trend, which can also be seen in other curves of face resin mixtures, discussed below. It is probable that this trend is attributable to new individual reactions, which are the decomposition reactions of methylene ether bridges to form methylene bridges and formaldehyde (**Scheme 1**). In general, the

formation of ether bridges can be envisioned only in neutral or acidic conditions in phenolic systems, although it also can be detected in resol phenolic resins with high F/P ratios. A high F/P ratio enhances the concentration of methylol groups, increasing the condensation reactions between two methylol groups to form methylene ether bridges. Methylene ether bridges may also exist in the commercial powdered resol phenolic resins.[2] At higher temperatures, these methylene ether bridges decompose to form more stable methylene bridges.[19,24,25] These reactions may be the origin of the changed trend in activation energy with conversion for face resin in the latter stage of the curing process.

By use of the kinetic computational method described above, a prediction was made of the conversion advancement with reaction time in the isothermal curing process. Figure 3 shows conversion advancement with reaction time at an isothermal temperature of 120°C. It is clear that the curing reaction time is shorter for the core resin than for the face resin at the same curing temperature, given that the core resin reached a higher degree of conversion during the manufacture of resin. Therefore, the core resin can reach the same degree of conversion at lower curing temperature as the face resin does at higher curing temperature. It is noted that the reaction rate of face resin is more rapid than that of core resin in the initial stage. This is reasonable because there are smaller molecules and more reactive groups in the face resin.

Effect of water on the cure of powdered phenolic resins

The basic role of water in the curing systems of phenolic resins is plasticizer or diluent, depending on the molecular structure of the resin and the concentration of water. The effect of water on the activation energy of the curing system for core powdered phenolic resin and its mixture with water is shown in Figure 4. The tendency of the variation of activation energy with conversion is the same for the powdered resin and its mixture. It is seen that the values of activation energy are slightly lower for the mixture than for the powdered resin. Furthermore, the change in reaction mechanism from a kinetic to a diffusion regime occurs at a slightly higher degree of conversion for the mixture because the water in the curing system plasticizes
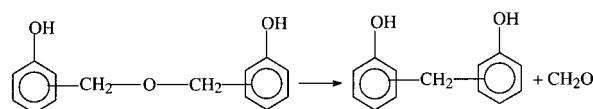
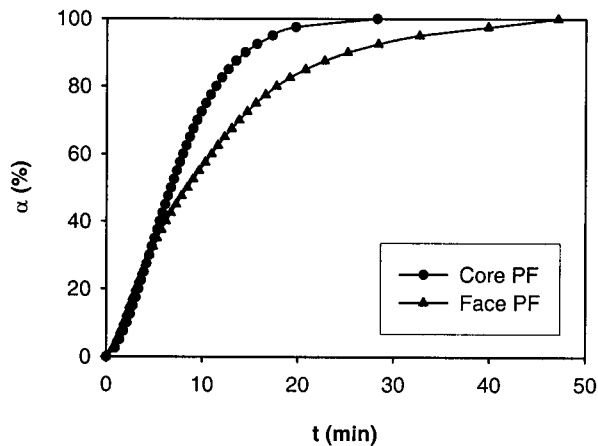**Scheme 1** Decomposition reaction of a methylene ether bridge to form a methylene bridge.

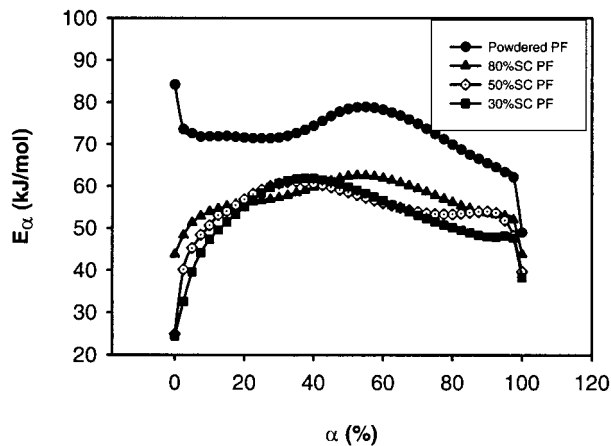**Figure 3** Conversion advancement of powdered resins with reaction time at 120°C.

Figure 5 Activation energy dependency on the degree of conversion for face resin.

the reaction system and increases the mobility of reactive molecules.

The effect of water on the activation energy of the curing system for the face powdered phenolic resin and its mixtures is shown in Figure 5. The curves of powdered face resin and its mixtures with several solid contents are different in some sections of the curves. Compared with the curves of the other mixtures, the curve of the mixture with a solid content of 80% is more similar to that of the powdered face resin except in the initial section. For the mixtures with solid contents of 50 and 30%, the curves display significant differences from that of powdered face resin, which are more similar to that of liquid phenolic resin.[12] It can be seen that the change in reaction mechanism from a kinetic to a diffusion regime occurs at lower degrees of conversion for these two mixtures. This seems to contradict the theory of diffusion because the role of water would decrease the viscosity of reaction systems and postpone the diffusion, discussed below.

The prediction of conversion advancement with reaction time at an isothermal condition was made for powdered resins and their mixtures. Figure 6 shows the conversion advancement of the core resin and its mixture at 120°C. The curves indicate that the water added in the core resin seems to retard the curing reactions except in the final section. Figure 7 shows the conversion advancement of face resin and its mixtures at 120°C. It is seen that the curing reactions were accelerated by the water for the mixtures with solid contents of 80 and 50%. The reaction rate increases with increasing content of added water. However, the reaction rate of the mixture with a solid content of 30% tends to decrease compared with that of the mixture with a solid content of 50%. On the other hand, the reaction rate in the initial step always decreases with the increase of the water content added in the face curing systems. Generally, the conversion advancement of the core and face resins seems not to be influenced significantly by the water added in the
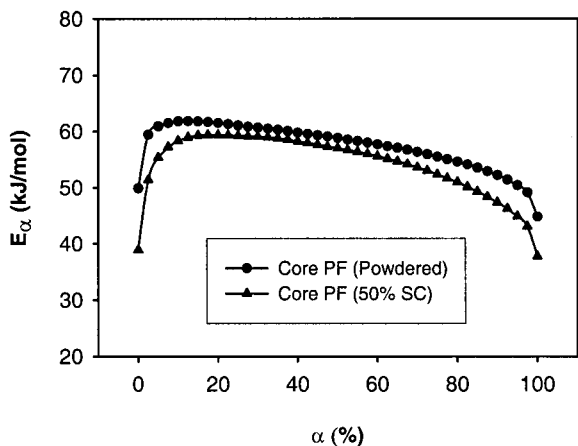

Figure 4 Activation energy dependency on the degree of conversion for core resin.
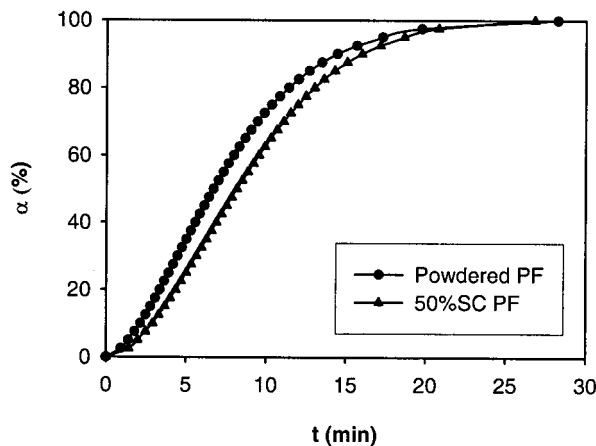

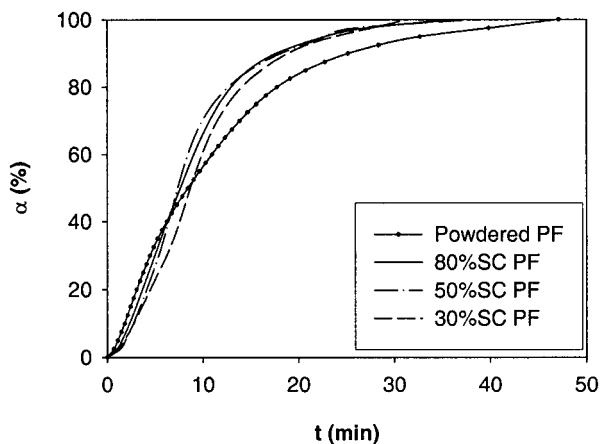**Figure 6** Conversion advancement of core resin and its mixture with reaction time at 120°C.

Figure 7 Conversion advancement of face resin and its mixtures with reaction time at 120°C.
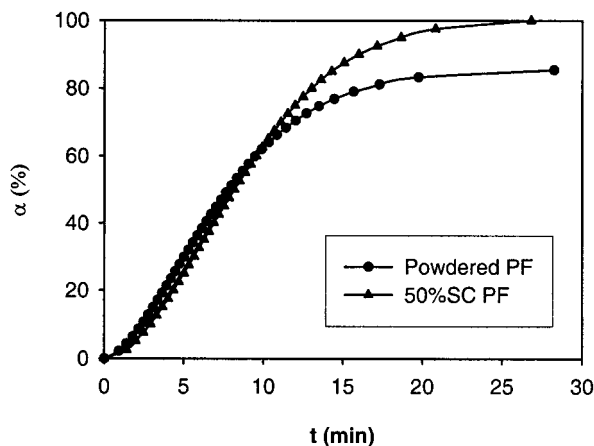

Figure 8 Modified conversion advancement of core resin and its mixture with reaction time at 120°C.

curing systems. Further research in this field is necessary, as explained later in this study.

Table II lists some DSC scanning parameters of phenolic resins. What is worth noting is the variation of total reaction enthalpy in the curing systems. The reaction enthalpy increases with added water and with the increase of the water content in the curing systems. The increased enthalpy means that the curing reactions tend to be carried out more completely because of the plasticization of the added water. In the curing systems of powdered resins, the mobility of reactive molecules and functional groups decreases with increasing molecular weight, especially with gelation, vitrification, and crosslinking phenomena. At a certain degree of conversion, unreacted molecules and functional groups are restricted in their movement and collide with each other because of substantially greater viscosity and network formed in the curing systems. This probably results in an early termination of curing reactions before reactive functional groups are used up. In the mixtures of powdered resin and water, the added water is able to dissolve the lower molecular weight fraction and swell the network to increase the mobility of unreacted molecules and functional groups at the final step of the curing process. Therefore, the curing reactions in the mixture system

are probably carried out to a higher degree of conversion than in the powdered system. In the range of measurement performed, it was found that the higher the water content, the higher the reaction enthalpy.

It is necessary to recalculate conversion advancement with reaction time at isothermal temperature by considering the different enthalpies of cure. To do that, we simply introduce a coefficient, $f = \Delta H / \Delta H_{max}$, for each resin and its mixtures, where ΔH_{max} is the highest enthalpy in the corresponding resin. The modified degree of conversion is obtained from the multiple of original degree of conversion with the above coefficient. Therefore, the predictions of the conversion advancement with reaction time shown in Figures 6 and 7 are modified as shown in Figures 8 and 9, respectively.

From Figures 8 and 9, it can be seen that the prediction curves are separated into two sections, in which the conversion advancements with reaction time are different from each other. The degree of con-
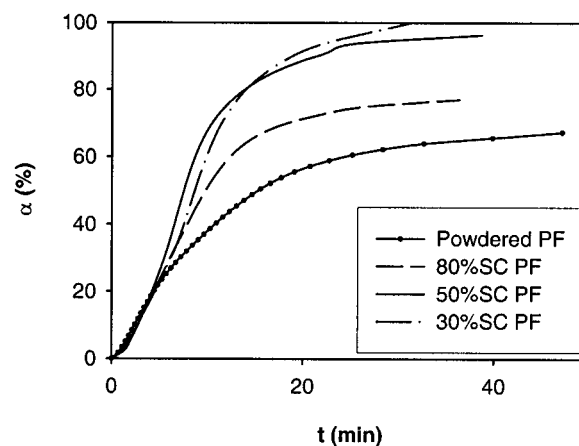
TABLE II
DSC Parameters of Powdered Phenolic Resins

PF resin	ΔH (J/g)	T (°C) ($\Phi = 10°C/min$)		
		α (20%)	α (50%)	α (80%)
Powdered core	129	133.0	145.7	157.9
50%SC core	151	135.8	148.9	161.3
Powdered face	181	130.8	146.9	162.4
80%SC face	199	132.6	147.0	159.7
50%SC face	259	134.2	146.3	159.7
30%SC face	269	136.1	149.7	163.4

Figure 9 Modified conversion advancement of face resin and its mixtures with reaction time at 120°C.

version of the powdered resins is higher than that of the mixtures at the same reaction time at lower conversion, whereas the situation is opposite at higher conversion. Furthermore, the final degree of conversion increases when the water content added in the powdered resins increases.

Why do these samples indicate this difference? It might be interpreted with taking into account the plasticization and dilution of water on the curing system. At the initial stage of curing reactions, the molecules of powdered phenolic resins are relatively small and the mobility of reactants is sufficient to cause them to collide and react with each other. Therefore, the effect of diffusion in the curing system on the reactions can be ignored. When water is added into the powdered resin, the curing system does not need the plasticization of water at the initial stage, but the water added makes the concentration of reactants decrease, so the water added in the curing system entails dilution on the curing reactions but not plasticization. However, the reaction rate becomes slower at a higher degree of conversion because of the effect of diffusion on the overall reactions. This effect of diffusion can even terminate the reactions in advance, resulting in some unreacted groups remaining in the curing system. Therefore, the water added in the powdered resin decreases the effect of diffusion and encourages further reactions, as mentioned above. This is the reason that the water added in the curing system plays the more important role of plasticizer, but not diluent, at higher degrees of conversion. However, it could be noted that excess water in the curing system still dilutes the system and retards the reactions at higher degrees of conversion.

A further study indicates that water in the curing system seems able to accelerate condensation reactions or retard addition reactions. As shown above about the curing steps of face phenolic resin, the cure begins with addition reactions for the powdered resin, but the cure begins with both addition and condensation reactions for its mixtures with water. This change can also be interpreted with the DSC curves shown in Figure 10. For the powdered face resin, the curve has two overlapping peaks, indicating the addition and condensation reactions, respectively. However, the two peaks continue to overlap until they eventually become one peak with the increase of water added in the curing systems. One probable interpretation is that addition reactions occur between smaller molecules, whereas condensation reactions occur between larger molecules. Therefore, addition reactions are affected more significantly by dilution of water, whereas condensation reactions are affected more significantly by plasticization of water.
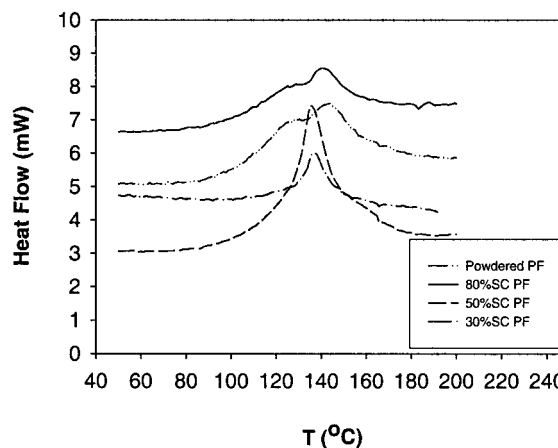

Figure 10 DSC curves of face resin and its mixtures with water (heating rate: 5°C/min).

CONCLUSIONS

There are some differences in the curing behavior of two kinds of commercial powdered phenolic resins. For the core resin, the curing reactions are influenced by diffusion earlier because it has reached a higher degree of conversion during the manufacture of the resin. Moreover, it takes a shorter time to complete the overall curing process than for the face resin. On the other hand, the curing process of the face resin starts with addition reactions, followed by both addition and condensation reactions, even though the addition fraction is small. At the final stage of the curing process, the reactions from methylene ether bridges to methylene bridges may lead to a deviation of the decreasing tendency of activation energy in the face resin. The water added in the curing system plays an important role of plasticizer or diluent according to different curing stages and solid content. In the initial curing stage, water mainly dilutes the system and retards the curing reactions because the small molecules are mobile enough to collide and react with each other. In the later curing stage, water plays the role of plasticizer such that it decreases the effect of diffusion on the curing reactions and allows more complete curing reactions. The excess water added in the curing system plays the role of diluent at almost all stages during the curing process.

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