Thermal Cure Behavior of Unsaturated Polyester/ Phenol Blends

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Received 19 July 1999; accepted 30 May 2003

ABSTRACT: Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to detect and simulate the cure behavior of unsaturated polyester (UP), phenol, and UP/phenol blends and to calculate and predict the cure rate, cure temperature, conversion, and changes in the glass-transition temperature along with various cure orders in order to obtain the optimum parameters for processing. With dynamic scanning and isothermal DSC procedures and Borchardt–Daniels dynamic software, cure data for the UP resin were obtained, 90% of the conversion rate at 100°C being achieved after 15 min. However, for the phenol and UP/phenol blends, gradually increasing the temperature was found to be best for curing according to the DSC and DMA test results. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1041–1058, 2004

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

INTRODUCTION

Because the unsaturated polyester (UP) resin is characterized by ease of processing and excellent features after formation at a low price, it has been applied extensively in industry as a thermally cured resin; nevertheless, its inflammability and great volume of smoke are shortcomings.

We attempted to blend phenol and UP in different proportions in this study because we intended to use the heat resistance of phenol to change the properties of UP. The effect of flame retardancy had already been verified in a previous study.[1] To further explore the thermal cure behavior of these two polymers and to determine the optimum conditions for processing, we used differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) to estimate the cure rate, cure temperature, and cure conversion.

For DSC testing, we considered the heat of reaction to be directly proportional to the reaction order; that is, we measured the heat of reaction of a sample during temperature scanning over the entire course. This provided extremely useful data for a kinetic analysis of the reaction.[2,3] In other words, we considered the separated curve height (dH/dt) as a function of temperature at a fixed rate of increasing temperature (dT/dt is constant), and the volume of heat released was directly proportional to the specific heat of the resin.[4] For the curing reaction, three DSC tests were applied to the dynamic reaction formula for simulation, and these three tests were as follows:

1. Isothermal test.
2. Dynamic scanning.
3. Dynamic scanning with different rates of increasing temperature.

Moreover, we obtained the heats of reaction of partly cured remains by measuring partly cured resins to understand the curing level of the partly cured resins.[4]

As for the cure reaction of the thermally cured resin, many researchers, using various kinetic models, have performed studies[4–10] with the aim of verifying if the theory is consistent with experimentation. Thermal, chemical, and physical changes inside the material under certain temperatures and pressures were obtained, and this led to relationships between the reaction heat, cure conversion time, cure conversion temperature, and reaction conversion rate. Therefore, the optimum operational parameters during resin processing can be predicted. According to research articles published previously, the cure reaction kinetic equations of a thermally cured resin can be categorized as follows:

1. *N*th-order model:[5,6]

$$\frac{d\alpha}{dt} = k_1(1 - \alpha)^n$$

or

$$\frac{dx}{dt} = k_1x^n = R_A$$

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Journal of Applied Polymer Science, Vol. 91, 1041–1058 (2004)
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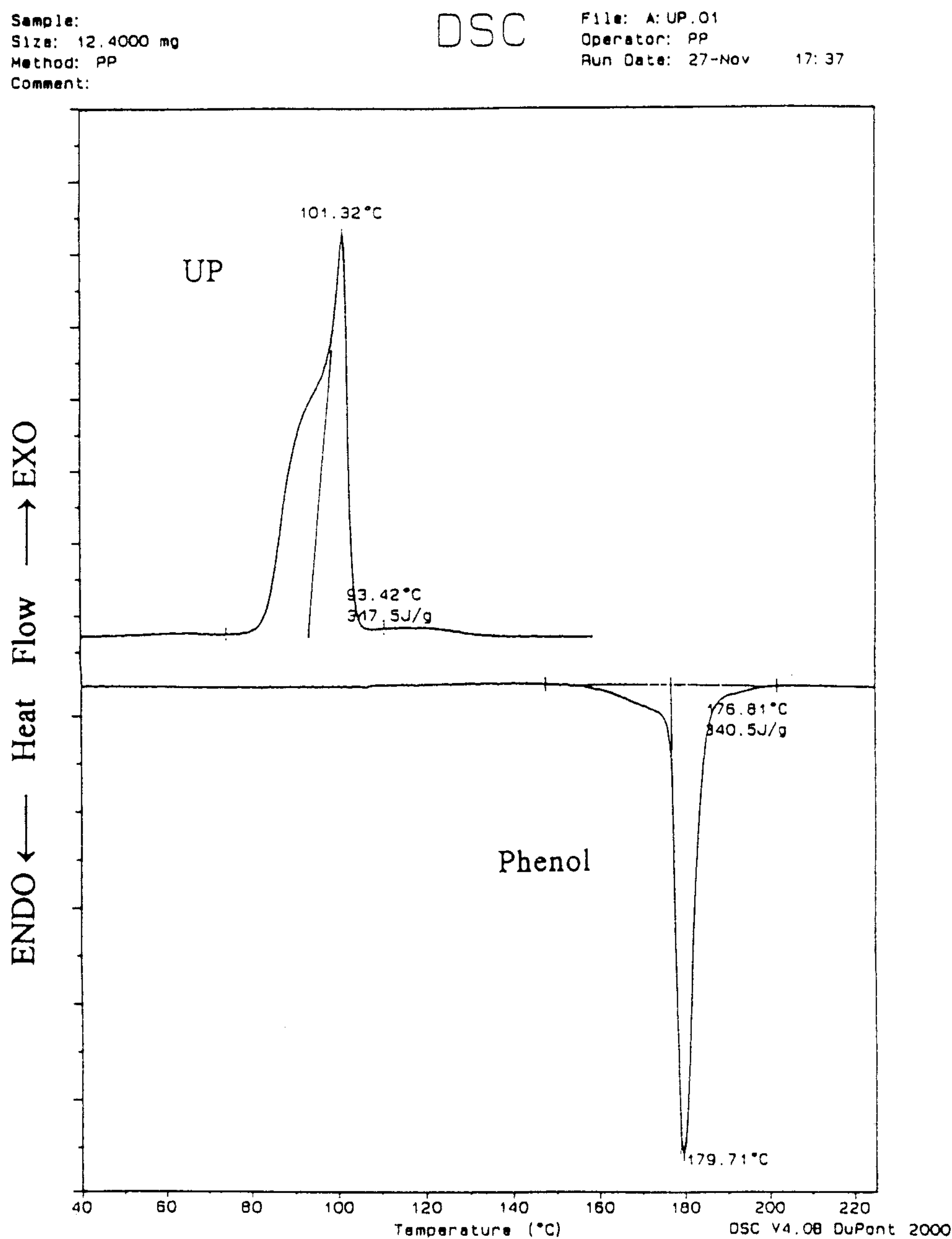

Figure 1 DSC dynamic scanning thermograms of UP and phenol resins at a heating rate of 2°C/min.

TABLE I
Isothermal Scanning of the UP Resin

Isothermal temperature (°C)	Time of the maximum peak of BPO (min)	Time of the maximum peak of TBPB (min)
75	17.8	36.94
80	10	24.16
85	6.75	18.04
90	3.81	11.73
95	3.16	7.7
100	2.54	5.9

2. Autocatalytic model:[7,8]

$$\frac{d\alpha}{dt} = k_1\alpha^m(1 - \alpha)^n$$

where m and n are constant, regardless of the temperature.

3. Combinative model:[7]

$$\frac{d\alpha}{dt} = k_1\alpha^m(1 - \alpha)^n$$

TABLE II
Isothermal Scanning of the Resol-Type Phenol Resin

Isothermal temperature (°C)	Time of the maximum peak (min)	Time of onset of cure (min)	Heat of reaction (J/g)
160	213.2	211.7	353.6
162	181.8	169.8	349.7
165	58.8	57.9	347.2
167.5	35.7	33.94	338.7
170	18.9	18.66	330.8
175	9.24	8.9	319.3

Because it is second-order, $m + n$ is equal to 2.

4. Parallel model:[9]

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)(B - \alpha) \quad \alpha \leq 0.3$$

$$\frac{d\alpha}{dt} = k_3(1 - \alpha) \quad \alpha > 0.3$$

X is the consistency of the reactant, R_A is the reaction speed (L/s), $d\alpha/dt$ is the reaction rate (L/s), α is the conversion rate, k is the ratio function of the temperature function (L/s), and n is the reaction order.

All of the equations presume reaction rate constant k as the function of temperature and the following Arrhenius equation:

$$K = A \exp\left[\frac{-E}{RT}\right]$$

where A is the Arrhenius frequency factor (L/s), E is the activation energy of reaction (J/mol), R is the gas constant (8.314 J/mol/k), and T is the absolute temperature (K).

However, the saved and dissipated energy of an elastic material at a certain temperature and a fixed amplitude of vibration can be measured with DMA. The saved energy varies with the type of polymer, temperature, and imposed vibration frequency, which can be represented as the elastic modulus (bending) or rigidity (shear). Moreover, the dissipated energy due to the friction of molecular movement inside an elastic material can be represented by the loss modulus (E'').[10]

Many reports on measurements of the gelation, vitrification time, cure temperature and time, glass-tran-

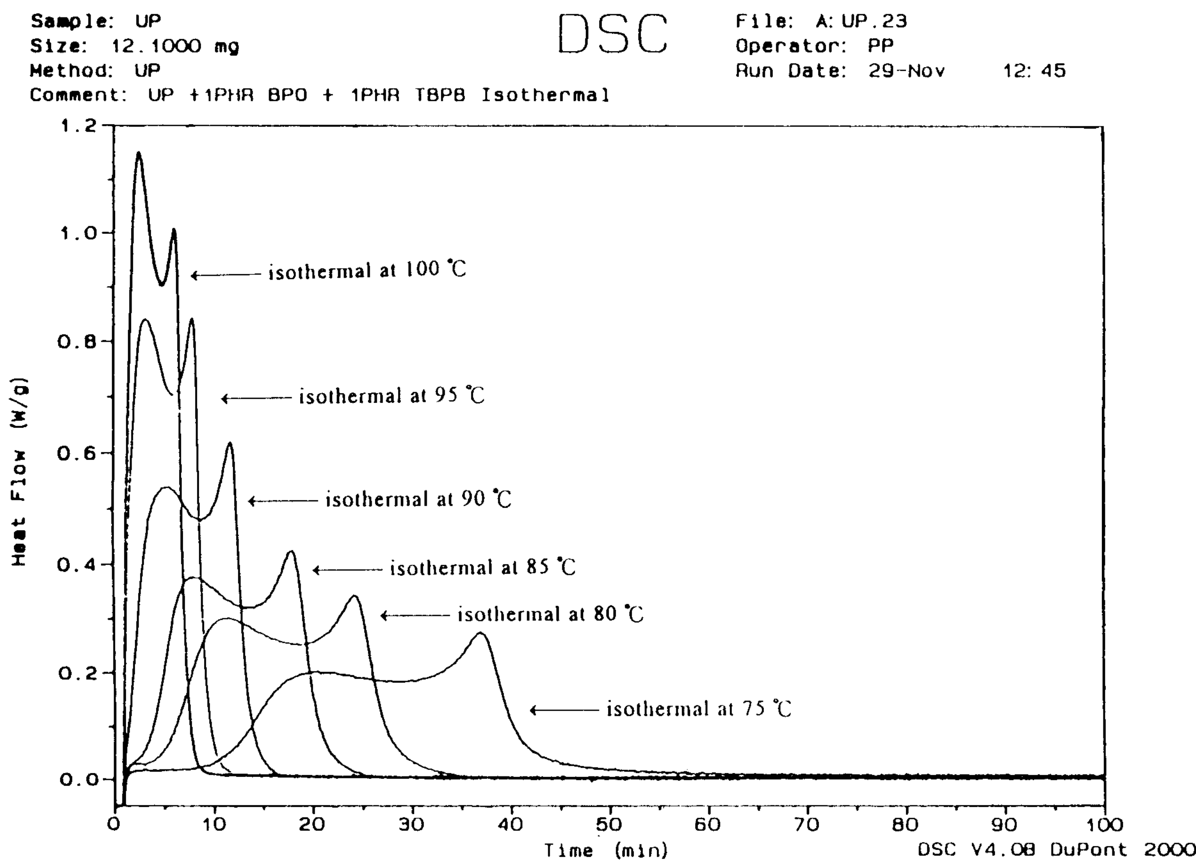

Figure 2 Set of isothermal cure curves of the UP resin.

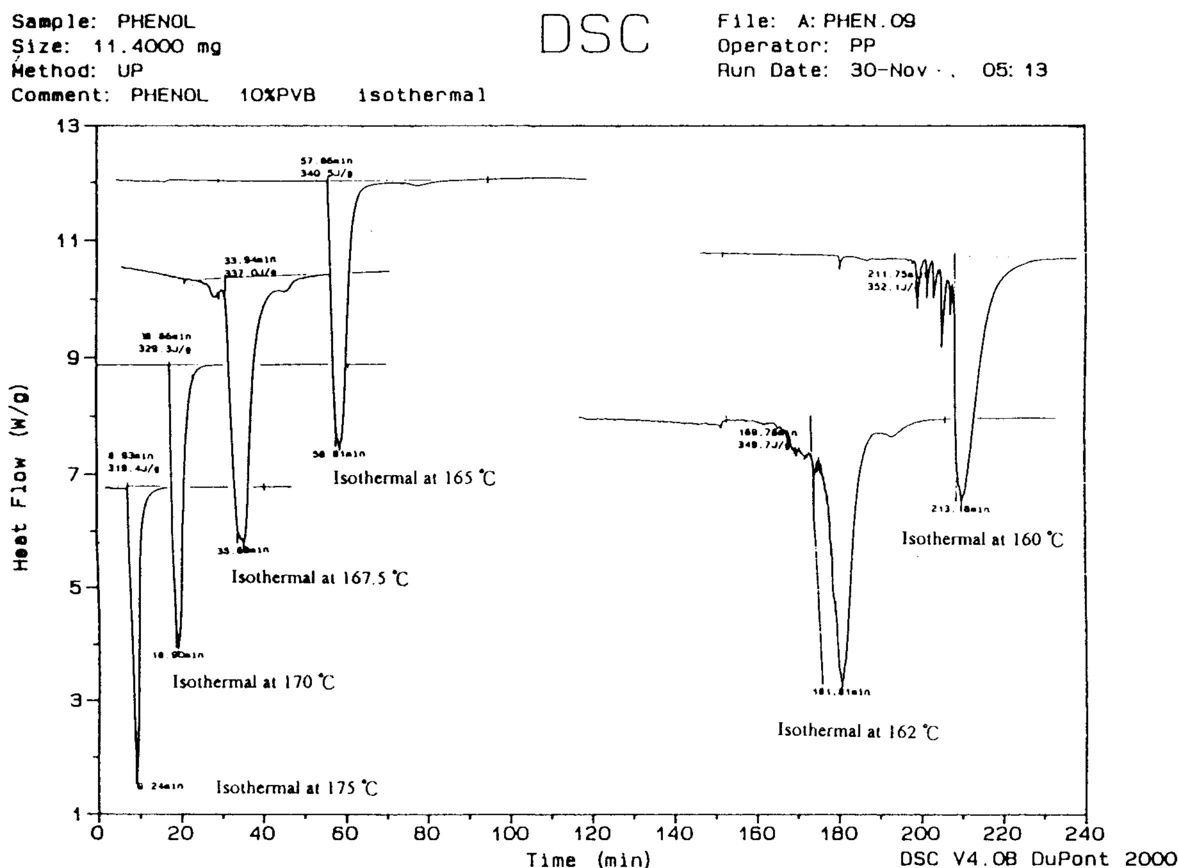

Figure 3 Set of isothermal cure curves of the phenol resin.

sition temperature (T_g), and reaction processes of various thermally cured resins (e.g., epoxy, up, phenol), as well as the kinetic relationships of other thermally cured resins through DMA, have been presented by many researchers.[2,10–17] Normally, a piece of cloth (e.g., fiber-glass cloth) has been used to soak the resin, and a torsion braid analysis by DMA has been conducted. Finally, resin cure parameters can be obtained via an isothermal increasing or isothermal heating process.

In 1953, Flory[11] indicated that the gelation and vitrification of a thermally cured resin occurred at the maximum dissipation factor (tan δ). The network structure of an infinite molecule was formed after gelation.

Gillham and a coworker[12,13] claimed that the mechanical response of a resin showed a higher value in two ways: (1) gelation, resulting from chemical crosslinking, and (2) vitrification, resulting from the partly stable physical properties of a molecular chain.

Strauss[15] applied uncured and ultimate cured values to explain the fully cured value from 0 to 100%. He also measured the maximum possible hardness at a fixed temperature.

Steiner and Warren[15] concluded that E'' changed as the temperature increased because of thermal softening and lost moisture.

So and Rudin[16] and Acitelli, Prime, and Sacher[17] indicated that an increased cure order at a fixed heating rate could be revealed by the shear storage modulus [$G'(t,T)$] and temperature. When the temperature was increased, the test piece started to soften, and this resulted in a decrease in G', which stopped at order G_O'. During the follow-up curing, G' continued to increase to another higher value. The curing rate at any point in the scanning curve could be calculated with G_O' and G' (t,T).

According to the results of the study conducted by Kim and Nieh,[10] tan δ at the peak and the curing time tended to be lower at a higher isothermal curing temperature.

DSC was applied in this study to estimate the relationship of the processing temperature, time, and conversion order for UP, phenol, and UP/phenol blends. The storage modulus (E'), E'', and tan δ (E''/E') from DMA were used to observe the postcure and changes in T_g.

EXPERIMENTAL

Materials

A UP resin (157BQD, Yung-Chun Chemical Industrial Co., Ltd., Taiwan) was used. The curing agents were

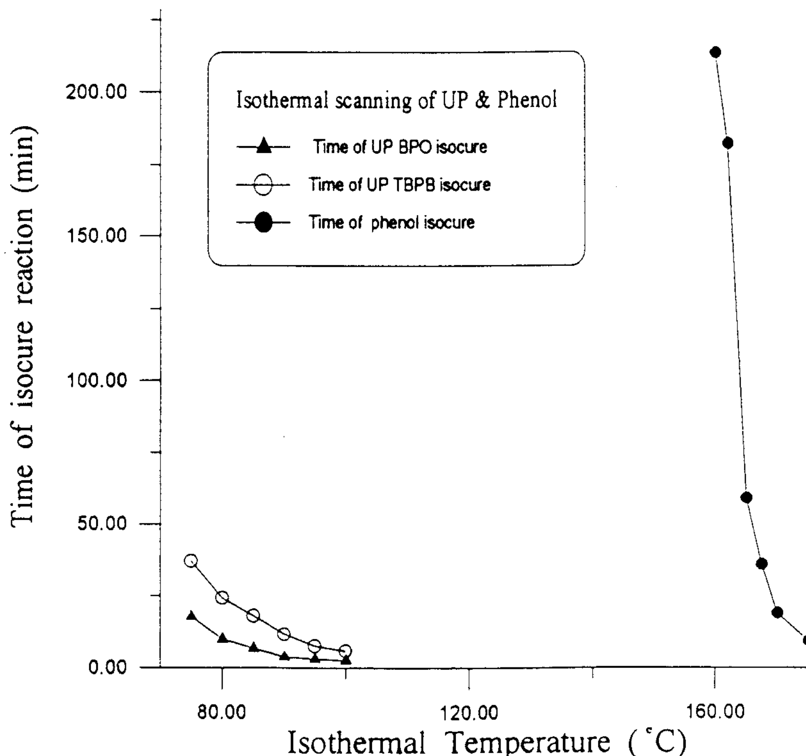

Figure 4 Isocure peak time versus the isothermal temperature of UP/phenol resin blends.

tetrabutyl perbenzonate (TBPB) and benzyl peroxide (BPO). Moreover, a resole-type phenol resin (Shonol BLS-794Z, Showa Hipolymer Co., Ltd., Tokyo, Japan) was also used; it was 10% polyvinyl butyryl (PVB) fiber adhesive modifier and 46.0 ± 2% solid.

DSC testing

Formulation of the sample

The UP resin (100 phr), 1 phr TPBP, and 1 phr BPO were mixed and stirred evenly. The mixture was mixed with phenol in different proportions. About 5–15 mg was placed in an aluminum cell and sealed for DSC testing.

DSC testing

A TA-9900 DSC instrument (DuPont, New Castle, DE) was used to test the samples (5–15 mg) at a rate of 2°C/min within the range of 30–250°C. The heat of reaction and the curing reaction curve of the UP/phenol blends were measured and drafted.

DMA

A Gabo Gualimeter 3031 Ahlder/Aller Eplexor 150N instrument (Germany) was used. The tension mode was adopted, and the temperature increased at 2°C/min at 10 Hz. The test piece was 70 ± 20 mm × 10 ± 0.1 mm × 2 ± 0.15 mm.

Production of the test piece

Production of the UP test piece. BPO (1 phr) and 1 phr TBPB were added to 100 phr UP resin, and the mixture was vacuum-stirred for 30 min at 100 rpm. This was placed in a mold cavity and then placed in a vacuum oven for 2 h at 100°C for the curing reaction. After it

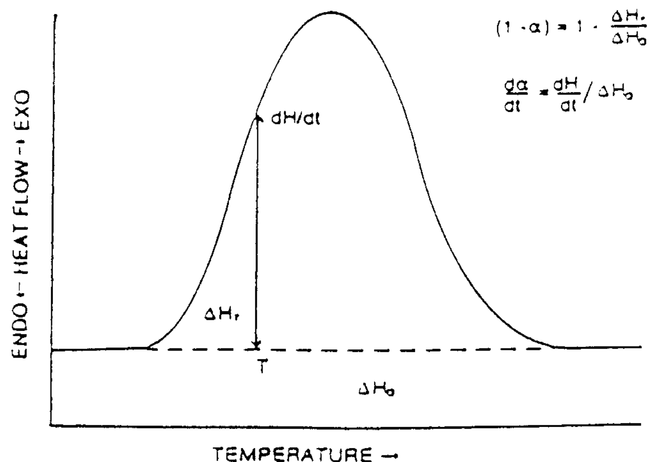

Figure 5 BD kinetic exothermic reaction.

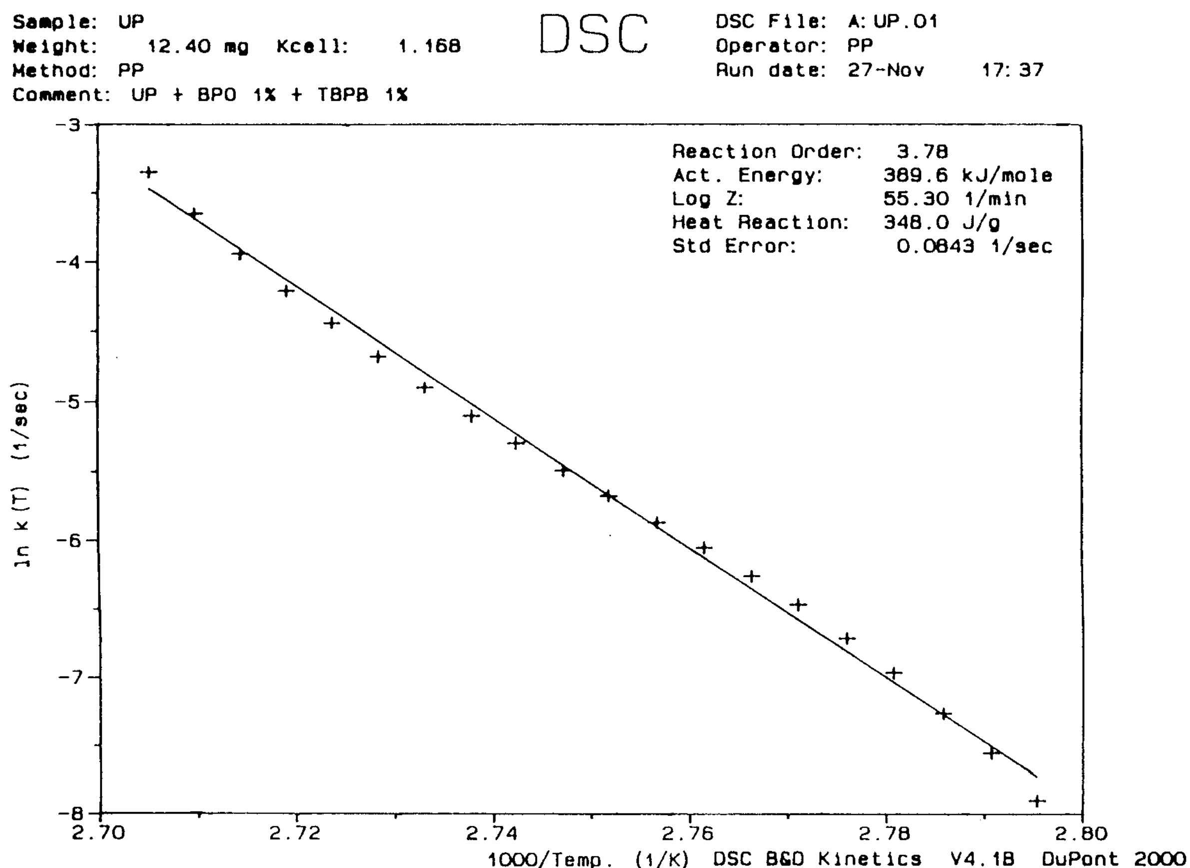

Figure 6 Arrhenius plot of the UP cure kinetics.

cooled naturally, it was removed from the mold and cut to a proper size for testing.

Production of phenol and UP/phenol blend test pieces. After 1 phr BPO and 1 phr TBPB were stirred evenly, UP and phenol were mixed in various proportions before 30 phr acetone was added for vacuum stirring and vaporizing for 30 min at 100 rpm (200 rpm for the first 5 min). The casting was placed on a flat plate mold and put it into an oven at 40°C for 15 h, at 50°C for 12 h, at 60°C for 24 h, at 80°C for 6 h, at 100°C for 2 h, at 120°C for 2 h, and at 140°C for 3 h for curing. It was removed from the mold after hardening and cut to a proper size for testing.

RESULTS AND DISCUSSION

Thermal cure reaction of the UP and phenol resins

Generally, as the molecular chain of a thermally cured resin changes from high entropy to a networklike structure with low entropy during thermal curing, an exothermic reaction occurs, which can be represented by UP and epoxy. However, when a networklike structure is formed because of the vaporization of a low-molecular-weight (e.g., water) byproduct during curing, an endothermic reaction occurs (e.g., phenol resin).[18,19] Therefore, DSC of exothermic and endothermic reactions can be measured and can serve as a beneficial index for evaluating the thermal cure behavior of UP and phenol resins.

Dynamic scanning curves (DSC) of UP and phenol resins is shown in Figure 1. DSC of the UP resin indicates that an exothermic reaction starts at about 76°C and deviates from the baseline gradually. The exothermic reaction is completed at 108°C, and the exothermic peak is at 101.32°C with a heat release volume of 347.5 J/g. For phenol, an endothermic curve comes into existence. A slight reaction begins at 150°C, and the endothermic peak is at 179.71°C with a heat absorption volume of 340.5 J/g.

For a further understanding of the curing reactions, a series of isothermal curing reactions for UP and phenol were conducted (Tables I and II). The isothermal curing reaction curves for UP and phenol are shown in Figures 2 and 3, respectively. When the isothermal curing temperature is lower, a longer curing time is required. For example, it takes nearly 60 min to complete isothermal curing at 75°C for a UP resin, but it only takes 13 min to achieve balance at 100°C. For the isothermal curing of phenol, there is still no reaction at 150 and 155°C after 6 h; how-

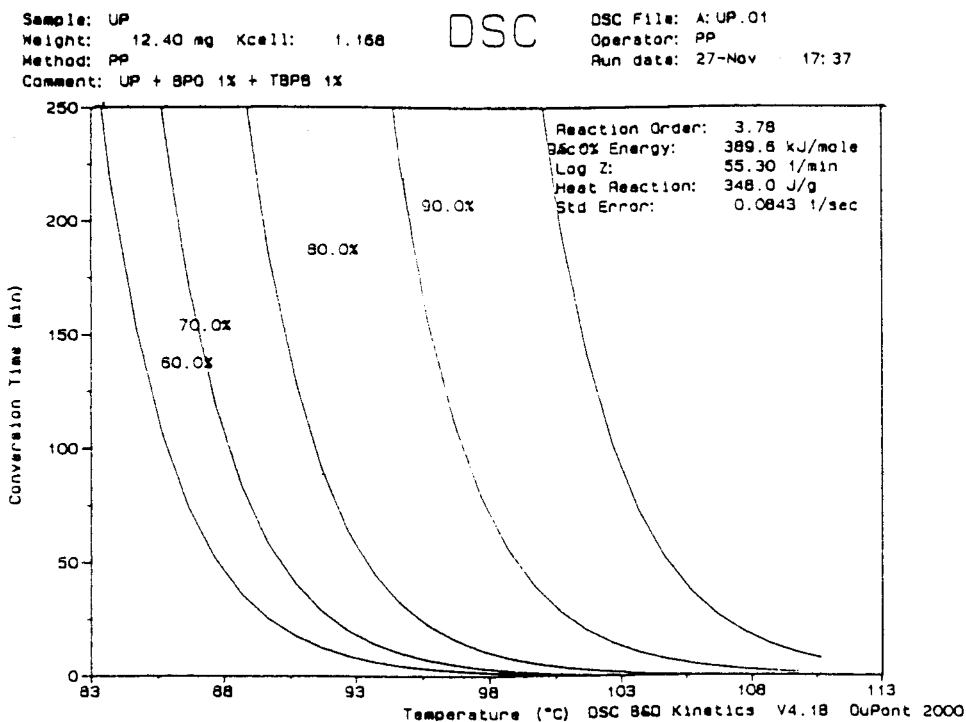

Figure 7 Isoconversion multiplot of the conversion time versus the temperature for the UP cure kinetics.

ever, gas is released dramatically when the temperature is increased beyond 177°C. Extreme pressure not only explodes phenol but also breaks the sealed DSC aluminum plate used to contain the sample. In Figure 3, the phenol resin is shown to become tremendously sensitive to temperature around the critical curing point. For instance, the reaction peak takes 181.8 min at 162°C and only 58.8 min at 165°C.

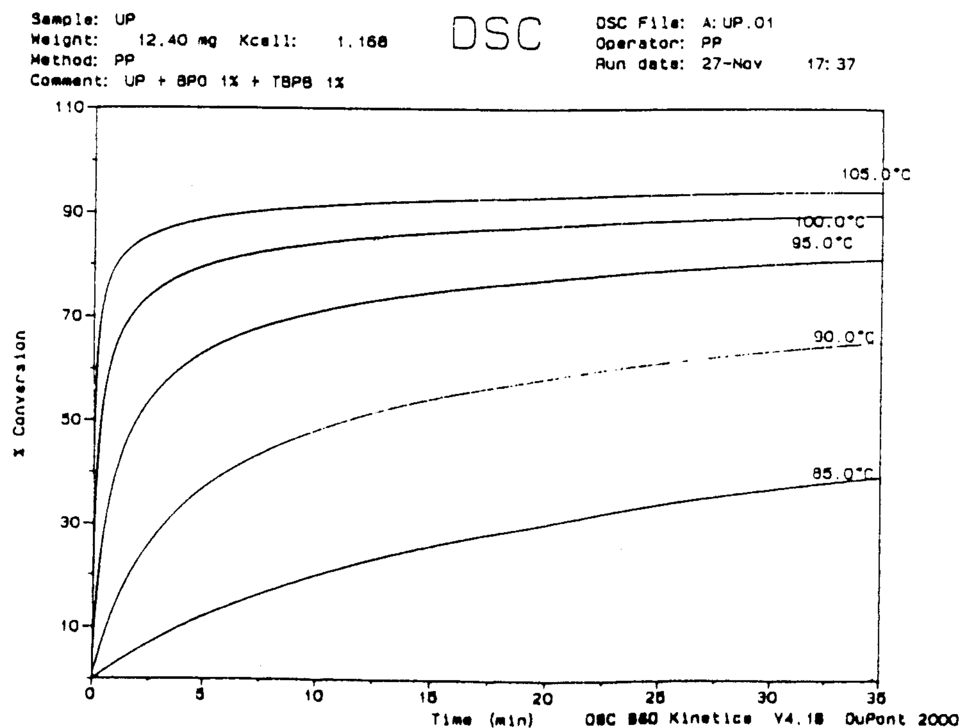

Figure 8 Isothermal multiplot of the conversion versus the time for the UP cure kinetics.

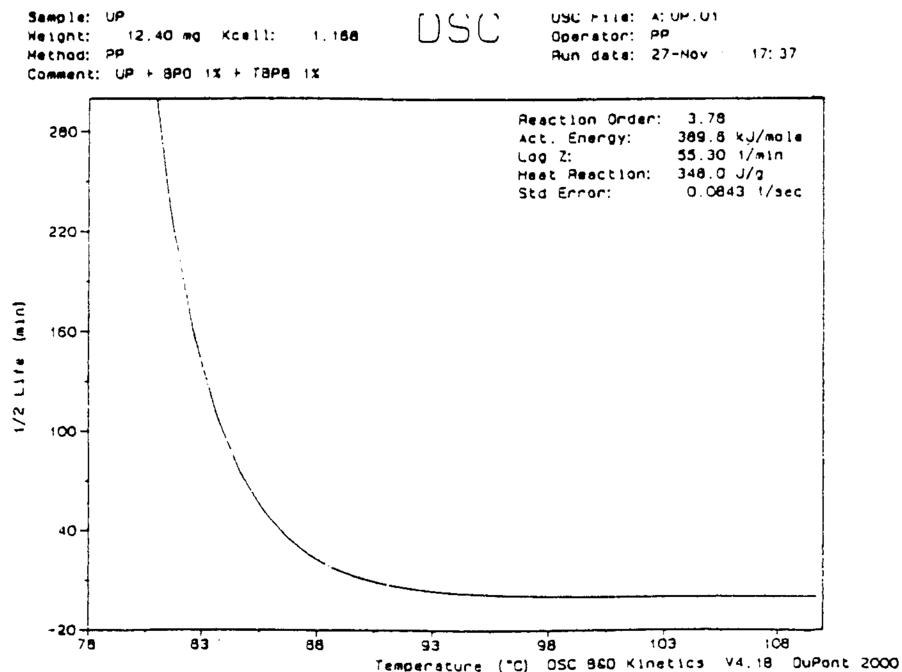

Figure 9 Half-life versus the temperature for the UP cure kinetics.

This difference of 3°C results in an extreme reaction time difference of 123 min. A difference of 5°C shortens the reaction time from 58.8 min to 18.9 min. The reaction rate becomes even greater closer to 177°C. Measurements cannot be made beyond 177°C.

The isothermal curing reactions of UP and phenol resins are integrated in Figure 4. The curing reaction temperatures of UP and phenol are very different. The temperature of a dramatic UP reaction only initiates a slight reaction or none at all for phenol. However, if the temperature is increased to 179.71°C, as shown by DSC for phenol curing, the UP resin will generate a fast curing reaction and release a tremendous amount of heat; this not only results in a cracking reaction but also reduces the bridging density and physical properties. Because

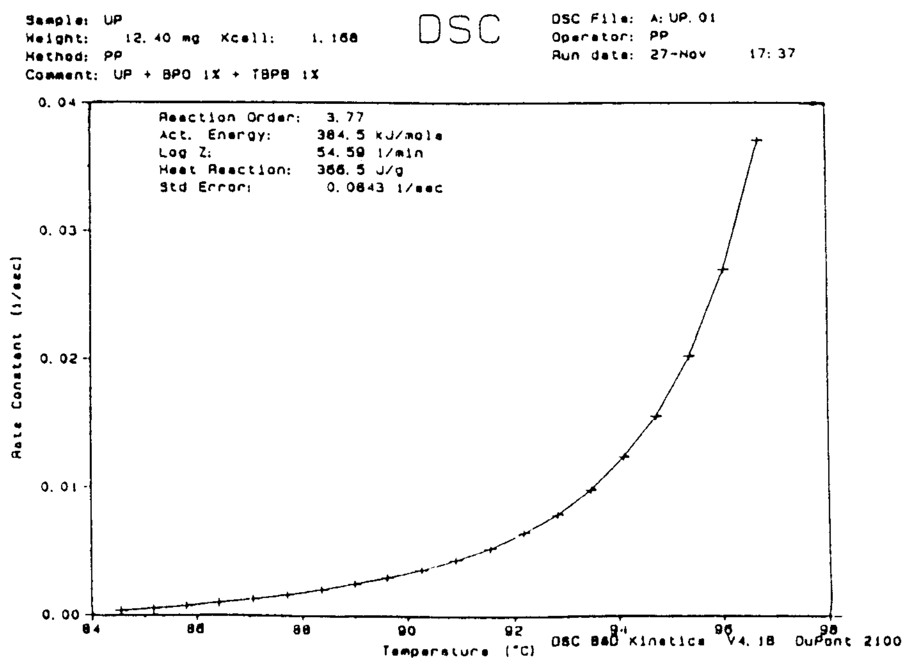

Figure 10 *k* versus the temperature for the UP cure kinetics.

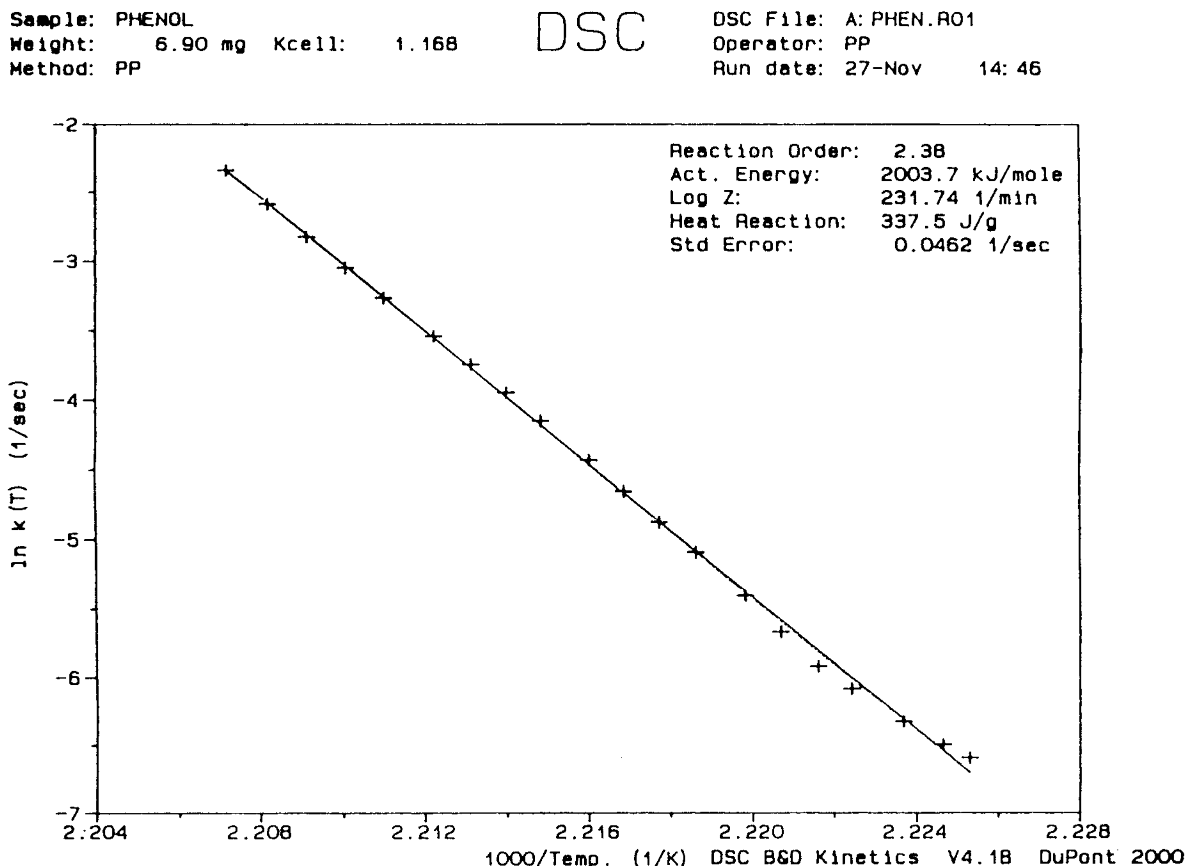

Figure 11 Arrhenius plot of the phenol cure kinetics.

phenol curing is a condensation reaction, byproducts such as the solvent, moisture, or small molecules will be generated. If the reaction rate is too high, the gas release rate will be much greater than the gas diffusion rate. When the released gas proliferates and explodes, irregular holes and cracks will form on the resin. Along with an increase in the heating rate, the diffusion of the released gas becomes more and more difficult. When such a situation becomes serious, various mechanical properties will be reduced tremendously because of the formation of rough holes. This formation might not be possible sometimes.

The curing reaction conversion rates of UP and phenol resins can be estimated through kinetic analysis. As the curing reaction of the phenol resin is quite complicated,[20,21] the Borchardt–Daniels method (BD) of an *N*th-order model was applied in this study to explore and simulate the reaction process and conditions.[22,23] The BD method requires only a single heating scanning test (as Fig. 1). In theory, dynamic DSC includes all normal and specific dynamic messages in a series of isothermal experiments.[24] An *N*th-order reaction is presumed in this reaction kinetic equation:

$$d\alpha/dt = k(T)(1 - \alpha)^n \tag{1}$$

where $d\alpha/dt$ is the reaction rate (L/s), α is the fractional conversion, and $k(T)$ is the specific rate constant at temperature T (L/s).

$k(T)$ is subject to an Arrhenius equation as follows:

$$k(T) = Z \exp(-E/RT) \tag{2}$$

where Z is the pre-exponential factor or Arrhenius frequency factor (L/s).

By taking the logarithm of eq. (2), we obtain

$$\ln k(T) = \ln Z - E/RT \tag{3}$$

We drafted a chart of $\ln k(T)$ versus $1/T$ and obtained a line, as shown later in Figure 6. E was obtained from the slope ($-E/R$) of the linear line in Figure 11 (shown later) with an intercept of $\ln Z$.

We combine eq. (2) and eq. (1) to obtain the following:

$$d\alpha/dt = Z \exp(-E/RT)(1 - \alpha)^n \tag{4}$$

Taking the logarithm of eq. (4), we obtained

$$\ln(d\alpha/dt) = \ln Z - E/RT + n \ln(1 - \alpha) \tag{5}$$

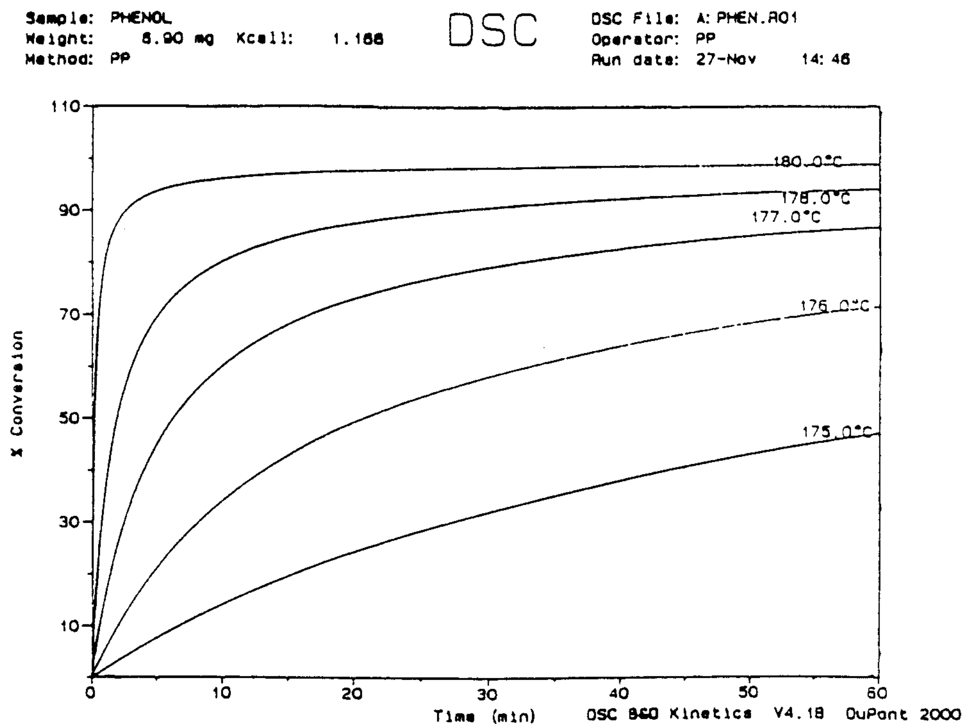

Figure 12 Isothermal multiplot of the conversion versus the time for the phenol cure kinetics.

The general equation, $Z = a + bx + cy$, of multiple linear regression was used for eq. (5) to calculate n.

In Figure 5, two basic parameters ($d\alpha/dt$ and α) can be measured by the exothermal curve of DSC to solve eq. (5). It is presumed that the heat release volume is directly proportional to the number of reacted mole-

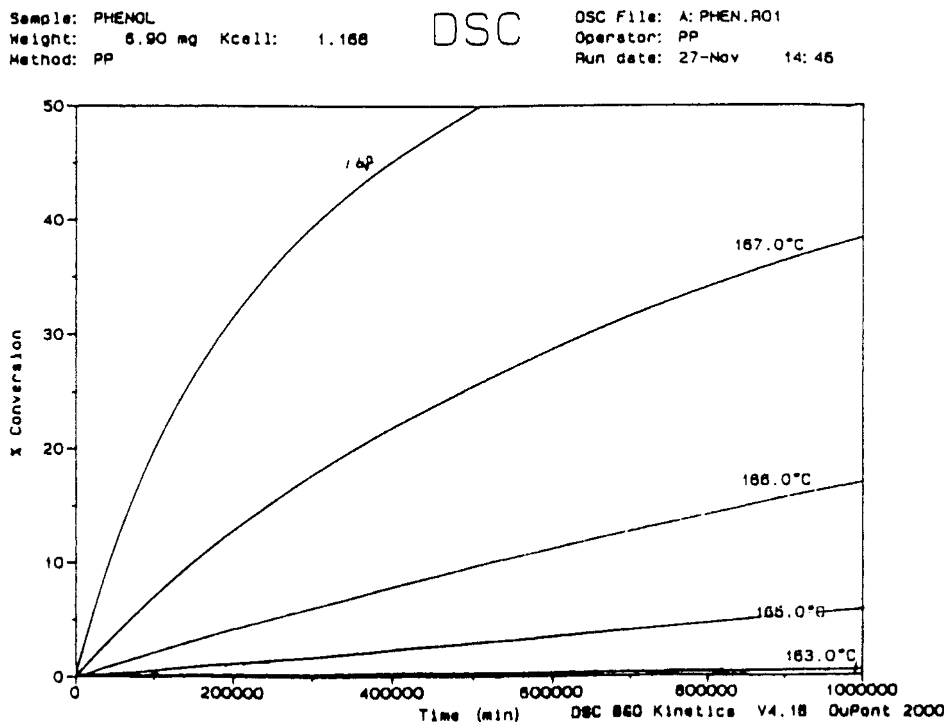

Figure 13 Isothermal multiplot of the conversion versus the time for the phenol cure kinetics.

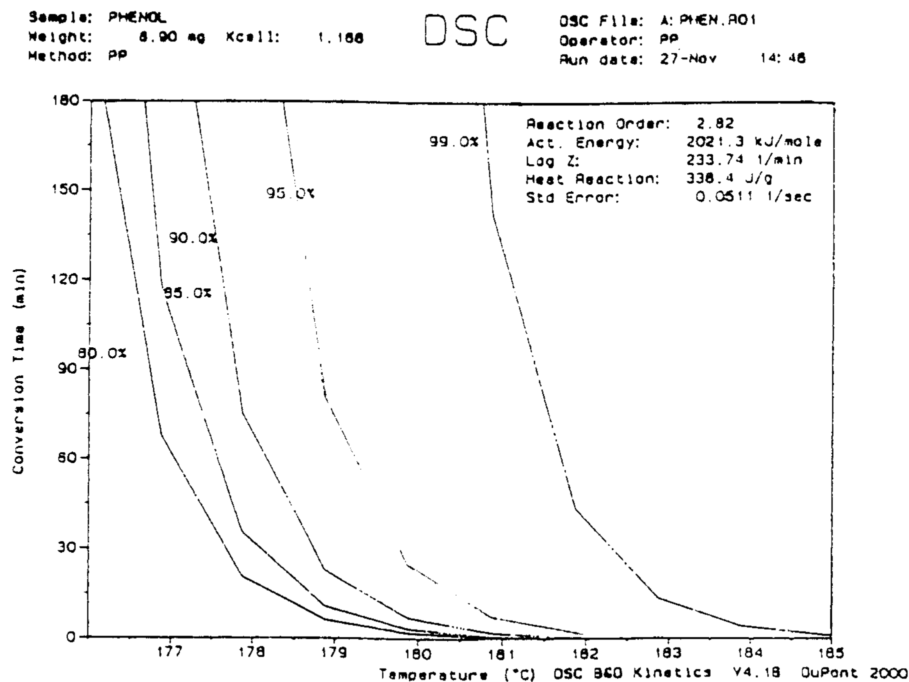

Figure 14 Isoconversion multiplot of the conversion time versus the temperature for the phenol cure kinetics.

cules within a short period of time.[24] The reaction rate at temperature T was obtained by dH/dt being divided by the total reaction heat:

$$d\alpha/dt = (dH/dt)/\Delta H_0$$

where ΔH_0 is the total peak area or theoretical enthalpy.

We calculated the conversion rate by measuring part of the area at temperature T against ΔH_T (entropy at temperature T after time t; refer to Fig. 5):

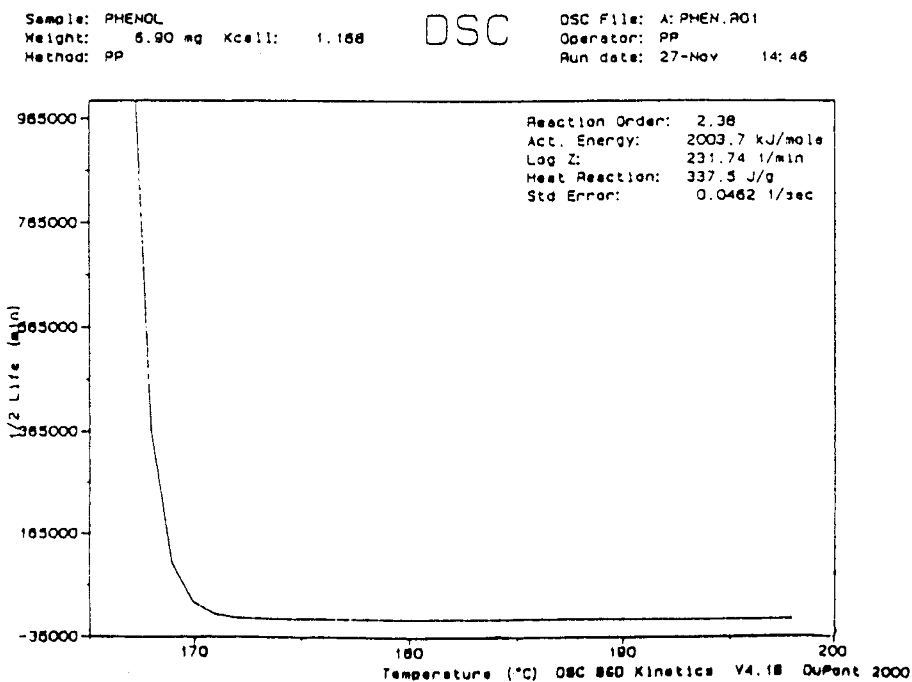

Figure 15 Half-life versus the temperature for the phenol cure kinetics.

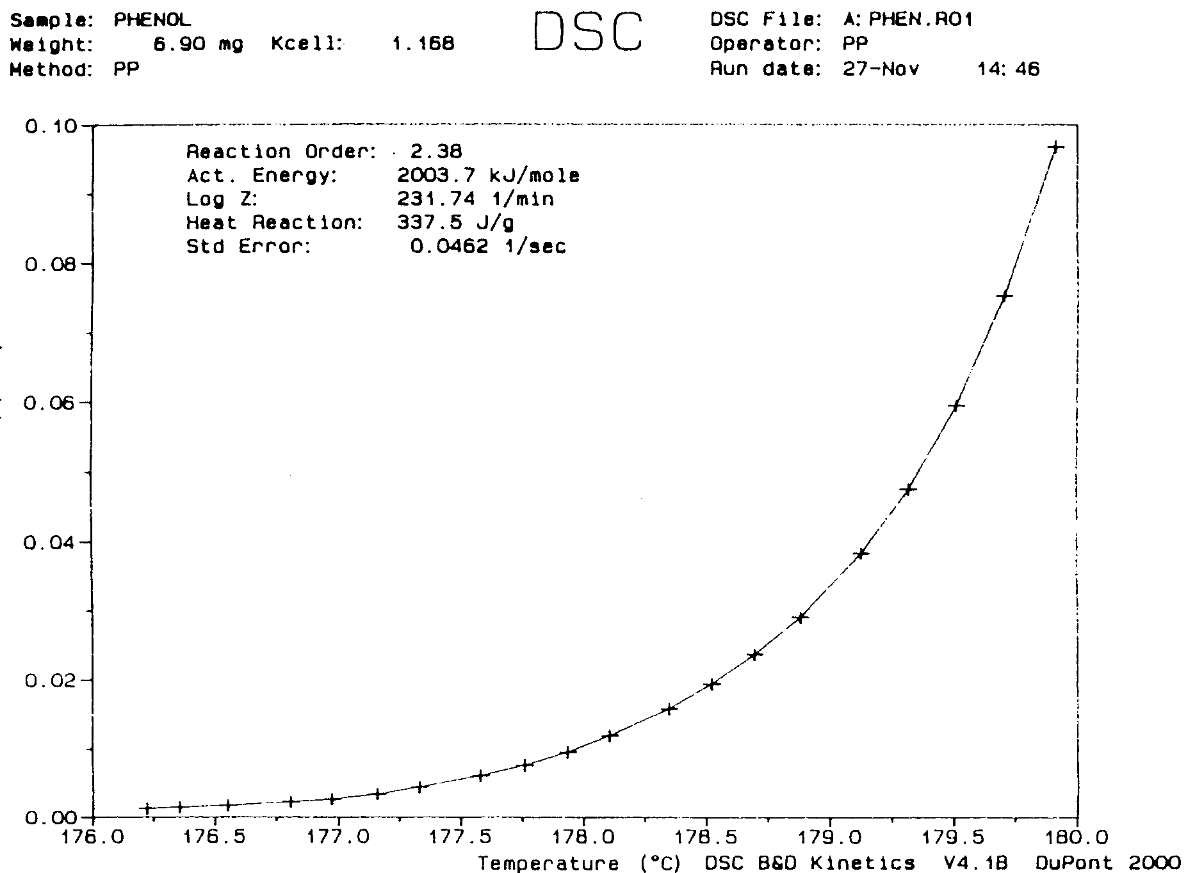

Figure 16 k versus the temperature for the phenol cure kinetics.

$$\alpha = \Delta H_T / \Delta H_0$$

Information on the thermal cure reaction rates for UP and phenol resins was obtained through an analysis with BD dynamic software with an Nth-order model. For the UP resin, $\ln k$ versus $1/T$ is shown in Figure 6. E was obtained from the slope, and intercept $\ln Z$ was obtained from frequency constant Z. Using all these data in the equation, we obtained n. The relationship between the conversion time and the temperature at a fixed conversion rate for the UP resin is shown in Figure 7. The relationship between the conversion rate and time in the isothermal curve of the UP resin is shown in Figure 8. Figure 9 shows the relationship between the half-life and temperature, and Figure 10 indicates the correlation between the rate constant and temperature. As for the phenol resin, $\ln k$ versus $1/T$ is shown in Figure 11. The relationships between the conversion rate and time for the phenol resin are shown in Figures 12 and 13. The relationship between the conversion time and temperature for phenol is shown as Figure 14. A chart showing the correlation between the half-life and temperature is given in Figure 15, and Figure 16 shows the relationship between the rate constant and temperature for the phenol resin. There is no 100% conversion rate in these figures because long molecular chains of the thermally cured resin twine and form globe-shaped microgels; this makes many reactive chains embedded and unable to react.[25]

According to a comparison of the curing kinetics of the UP and phenol resins, the reaction rate of UP is much greater than that of phenol because the latter only produces a slight reaction, whereas the former already starts. However, phenol has a fast reaction rate above 175°C but an extremely slow reaction rate below 165°C.

Furthermore, various reaction kinetic parameters, from an analysis of the Nth reaction kinetics for the UP and phenol resins, are listed in Table III.

TABLE III
Kinetic Parameters of UP and Phenol

Kinetic reaction parameter	UP	Phenol
n	3.78	2.38
E (kJ/mol)	389.6	2003.7
log Z (1/min)	55.3	231.74
Heat of reaction (J/g)	348.0	337.5

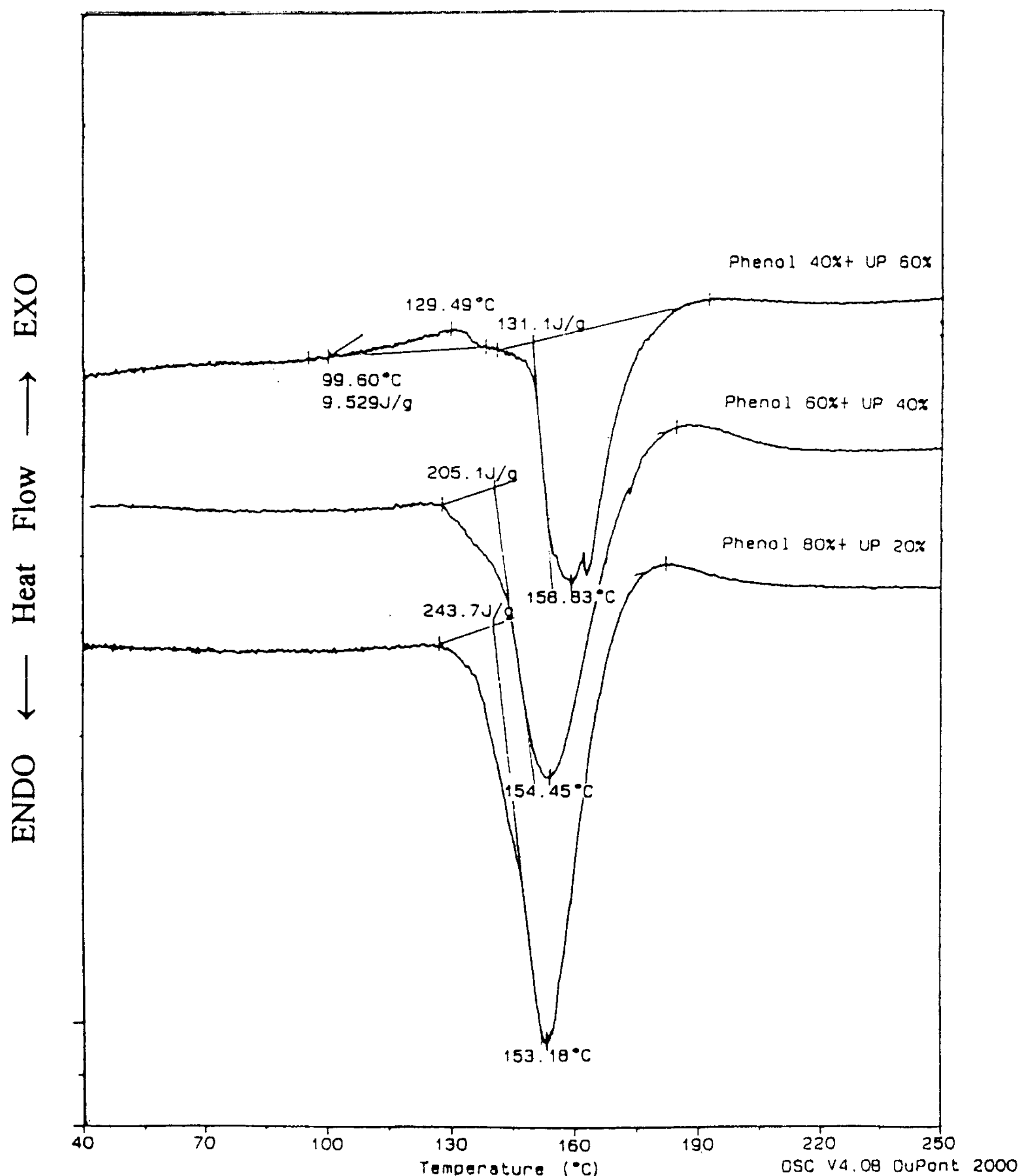

Figure 17 Set of dynamic scanning curves for UP/phenol resin blends.

Thermal cure behavior of the UP/phenol blends

With respect to the thermal cure behavior of UP and phenol, the former belongs to exothermic reactions, and the latter belongs to endothermic reactions. Meanwhile, the reaction rate of UP is much greater than that of phenol. Consequently, this will be an interesting subject of research for exploring the cure behavior and structure of cured objects of UP/phenol blends.

Dynamic scanning curves of UP/phenol blends (UP20/Ph80, UP40/Ph60, and UP60/Ph40) are shown in Figure 17. The exothermic peak of UP disappears at 101.32°C; however, the endothermic peak of phenol at 179.71°C moves toward low temperature as UP is added. The main peaks in the dynamic scanning curves of the UP/phenol blends are as follows: UP20/Ph80, 153.18°C; UP40/Ph60, 154.45°C; and UP60/Ph40, 158.83°C. As the proportion of phenol increases, the endothermic peaks move toward low temperatures with an increasing endothermic volume (UP20/Ph80, 243.7 J/g; UP40/Ph60, 205.1 J/g; UP60/Ph40, 131.1 J/g). In the curve of UP60/Ph40, a small peak appears indistinctly at 129.49°C. Phase separation is considered because when the proportion of UP is less than that of phenol, UP is scattered and the exothermic volume due to curing first is lower; however, such reaction heat

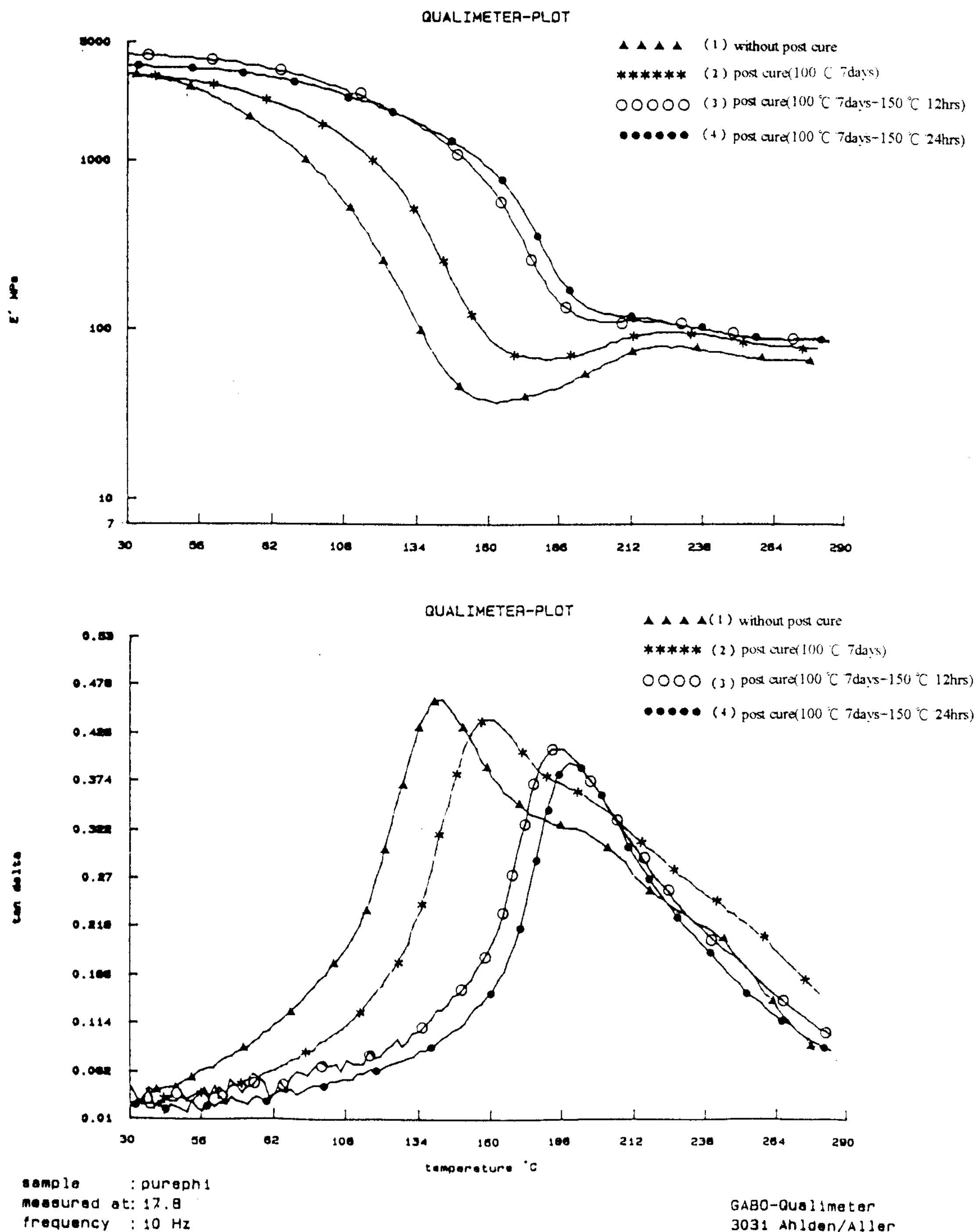

Figure 18 Dynamic mechanical properties of the phenol resin with various postcures.

can motivate the slow cure mechanism of phenol. Thus, it moves toward the low-temperature area between the UP and phenol reaction peaks. In addition, when the proportion of UP is greater than that of phenol, UP starts to cure first, and phenol has a much slower reaction mechanism; this causes the two macromolecules to cure independently. Therefore, in the curve of UP60/Ph40, a small peak appears at 129.49°C that is close to the UP curve at 101.32°C, and the main endothermic peak is closer to the reaction peak of phenol than in any other proportion. However, when phenol is scattered in UP, UP starts to cure first, and this wraps phenol inside the system and forms a microgel. Byproducts generated by phenol, such as water, cannot be released. As the positive reaction process cannot continue, curing is not complete. Although the proportion of UP is greater with a large exothermic vol-

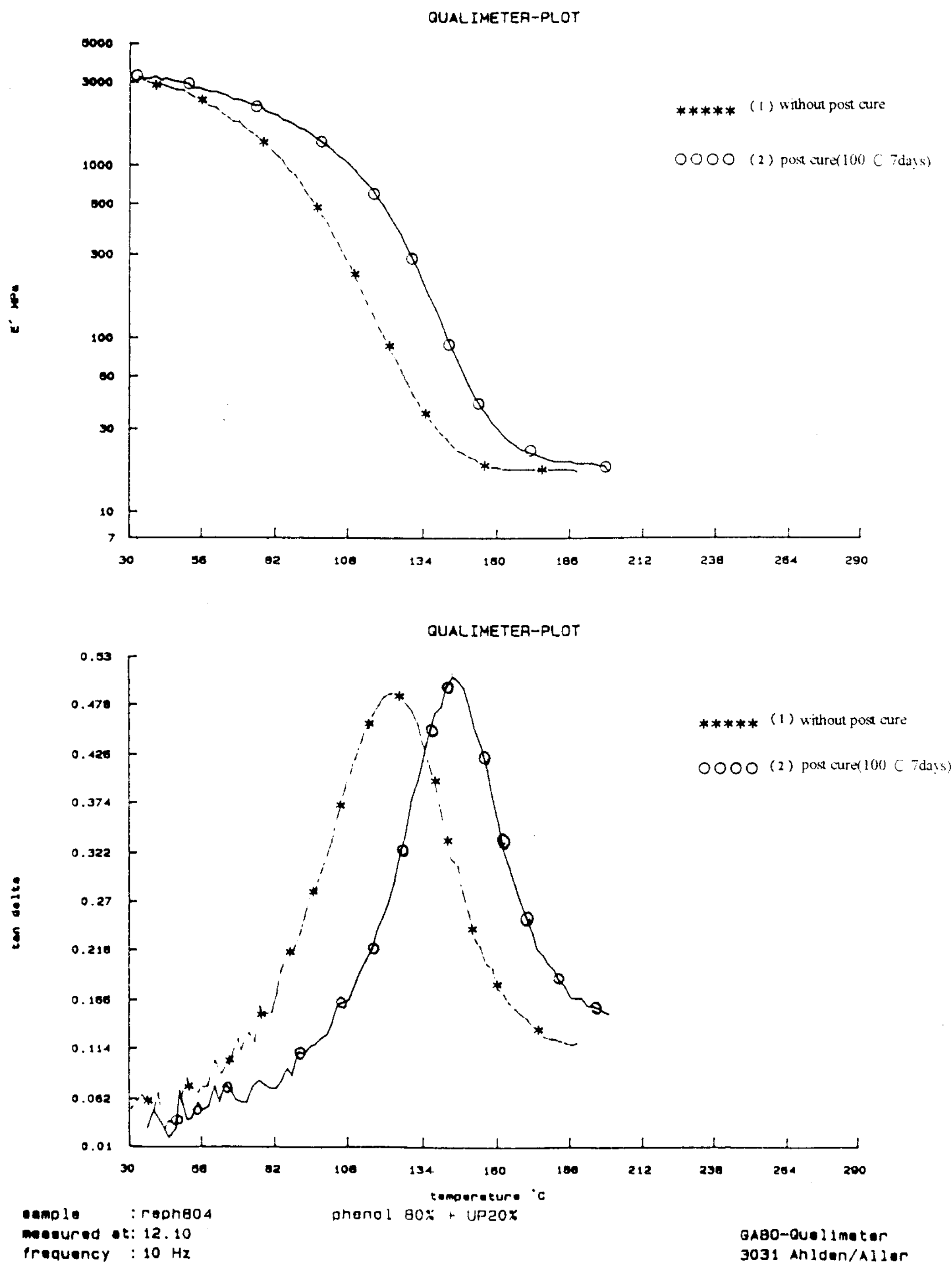

Figure 19 Dynamic mechanical properties of the UP20/Ph80 resin without postcure and with postcure (100°C for 7 days).

ume, which initiates phenol to react, the oligomer of phenol that does not react completely cracks because the reaction of phenol is slow, the positive reaction cannot continue, and UP releases a great amount of heat. Thus, the UP80/Ph20 blend cannot be cured and formed.

Effect of postcuring

From the discussion of the thermal cure behavior, it is known that UP/phenol blends achieve a better curing effect at a low temperature after a long period of time. In addition, curing at a low temperature with a long period of time also makes the crosslinking structure of UP/phenol blends complete; however, the chemical crosslinking activity decreases tremendously upon gelation and vitrification. To continue crosslinking for a certain curing effect, postcuring procedures[12,13] need to be implemented, and this means increasing the temperature above T_g for devitrification in order to enhance the bridging density. Therefore, upon the

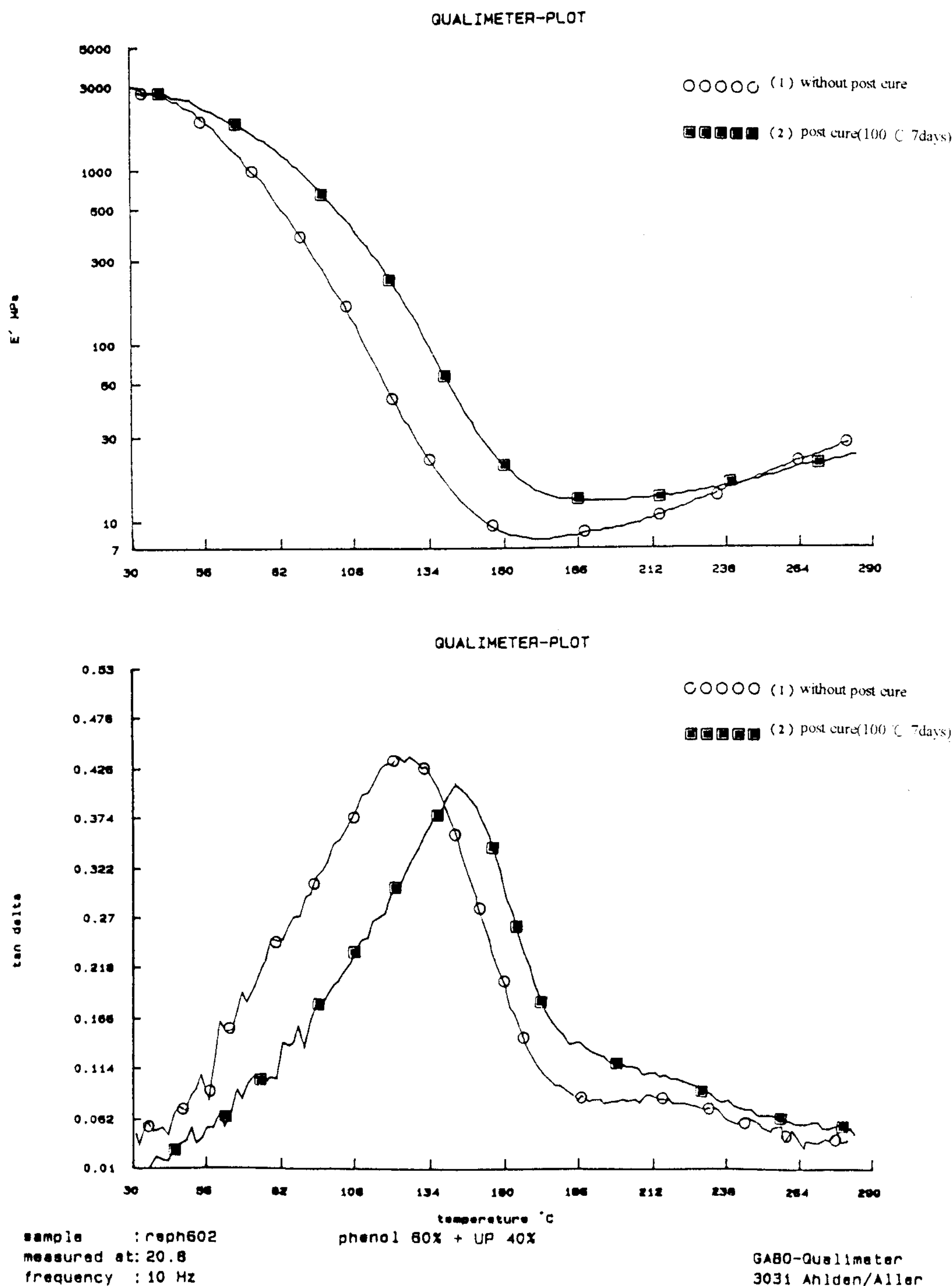

Figure 20 Dynamic mechanical properties of the UP40/Ph60 resin without postcure and with postcure (100°C for 7 days).

curing of phenol, the postcure process is as follows: (1) 100°C for 7 days, (2) 100°C for 7 days and 150°C for 12 h, and (3) 100°C for 7 days and 150°C for 24 h. In short, postcuring procedures have to be performed on the test piece at 100°C for 7 days after UP/phenol blends are cured, and then DMA is conducted to evaluate E' and the changes in tan δ for the observation of the effects of postcuring. A DMA spectrum of phenol after different postcuring procedures is shown in Figure 18. E' increases as crosslinking increases and falls at a higher temperature. The E' curve without a postcure process begins to fall gradually at 40°C; however, the same curve with the postcure procedure of 100°C for 7 days and 150°C for 24 h starts to descend slowly at 65°C. T_g moves toward a high temperature after the postcure process is implemented.

For the phenol resin without the postcure process, increasing the temperature motivates more remaining

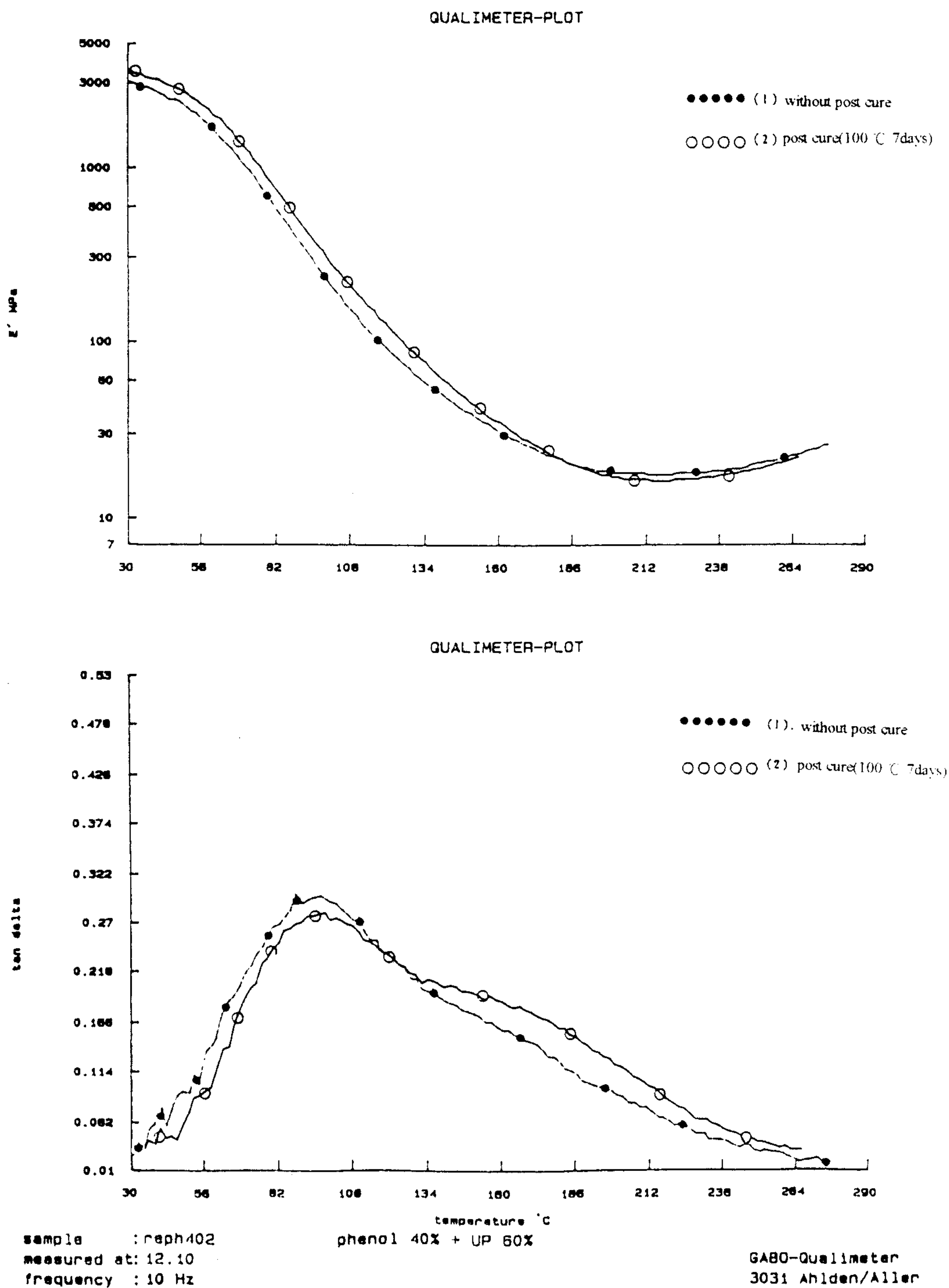

Figure 21 Dynamic mechanical properties of the UP60/Ph40 resin without postcure and with postcure (100°C for 7 days).

reactions to continue. Whitehouse et al.[26] indicated that —CH_2—O—CH_2—, formed earlier by incomplete crosslinking of the phenol resin, was easily broken at 150°C and higher, lost CH_2O, and transformed into more thermally stable —CH_2—. Therefore, in Figure 18, E' (curve 1) with less crosslinking increases crosslinking at about 160°C and higher, and this makes E' ascend gradually after descending. E' tends to achieve balance at 220°C as the reaction is mostly completed. As crosslinking increases E', byproducts of small molecules are generated and are dissipated continuously, and this increases energy dissipation. Consequently, tan δ forms a small peak between 160 and 200°C and then starts to decrease gradually. Nevertheless, samples with the postcure process do not have such problems.

UP20/Ph80, UP40/Ph60, and UP60/Ph40 blends without postcure procedures at 100°C for 7 days are shown from Figures 19–21. The DMA curves present single peaks, and this means that compatibility possibly exists between these two macromolecules. Crosslinking increases after the postcure process, and E' and T_g increase as well. However, as there is UP, an extremely high temperature and an excessively long period of time are not allowed to prevent cracking.

CONCLUSIONS

An exploration of the thermal cure behavior and postcure effect between incompatible UP and phenol blends was conducted with DSC, thermal kinetic analysis, and DMA. The following results were obtained:

1. For the DSC kinetic analysis, the exothermic peak of UP and the endothermic peak of phenol were used for analysis.
2. According to isothermal testing and *N*th kinetic model analysis, the curing temperature of UP was lower than that of phenol, and the curing rate of the former was much greater than that of the latter.
3. DMA analysis proved that the postcure process was closely related to a complete network structure of the UP/phenol blends.

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