Cure Processing Modeling and Cure Cycle Simulation of Epoxy-Terminated Poly(phenylene ether ketone). I. DSC Characterization of Curing Reaction

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ABSTRACT: The curing reaction process of epoxy-terminated poly(phenylene ether ketone)(E−PEK) with 4,4′-diaminodiphenyl sulfone (DDS) and hexahydrophthalic acid anhydride (Nadic) as curing agents was investigated using isothermal differential scanning calorimetry (IDSC) and nonisothermal differential scanning calorimetry (DDSC) techniques. It was found that the curing reactions of E−PEK/DDS and E−PEK/Nadic are n th-order reactions but not autoaccelerating. The experimental results revealed that the curing reaction kinetics parameters measured from IDSC and DDSC are not equivalent. This means that, in the curing reaction kinetics model for our E−PEK system, both isothermal and nonisothermal reaction kinetics parameters are needed to describe isothermal and nonisothermal curing processes. The isothermal and nonisothermal curing processes were successfully simulated using this model. A new extrapolation method was suggested. On the basis of this method the maximum extent of the curing reaction (A_{ult}) that is able to reach a certain temperature can be predicted. The A_{ult} for the E−PEK system estimated by the new method agrees well with the results obtained from another procedure reported in the literature. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 789−797, 1997

Key words: epoxy resin; poly(phenylene ether ketone); curing reaction kinetics; model and simulation; differential scanning calorimetry

INTRODUCTION

Cure Processing Modeling and Cure Cycle Simulation

The use of thermosetting polymers for composite matrices is widespread as a result of their many desirable properties that include high modulus and mechanical strength, excellent heat and chemical resistance, and good dimensional stability.[1]

During the manufacture of a thermosetting composite part, temperature, pressure, and reaction time must be maintained at certain preferred values to ensure that the process meets well-defined objectives with minimum materials wastage and good productivity. This set of processing conditions is referred to as the cure cycle or cure schedule.

It is difficult to describe the whole curing process of a thermosetting composite, since the processing of a thermosetting composite is a complicated physiochemical process in which curing reaction and resin flow take place at the same time. Traditionally, thermosetting composite cure cy-

cles were determined by trial and error, which is an empirical approach rather than a scientifically sound procedure. Generally, it would take over 30 to 50 thousand U.S. dollars and at least 6 months of time for a cure cycle design.[2] Therefore, how to determine a cure cycle efficiently and economically is a key point to which scientists have paid attention for a long time.

A new approach was introduced about 12 years ago[3] through the development of some mathematical models to describe the composite manufacturing process. This is a better way to determine a cure cycle because it is helpful to get a better understanding of the laws of curing processes for thermosetting polymers and their composites, and, as a result, the amount of experimentation necessary for a cure cycle determination can be minimized. Eventually this advantage results in reduced manufacturing costs, shorter lead time, and improved control and prediction of the properties of the finished products. It is also of benefit to realize *in situ* control of composite quality.

The curing process for a composite generally involves exposing the material to certain temperatures and pressures for a predetermined time. Therefore, the processing model for the manufacture of a thermosetting composite should take account of the effects of temperature, time, pressure, and thermal transfer because the performance of the finished product is significantly affected by them. On the basis of these considerations, the cure processing model for a thermosetting composite should be classified as several submodels relating to reaction kinetics, chemorheology, the effect of applied pressure, and thermal transfer. According to these submodels, a proper cure cycle for a special system can be selected based on the prediction analysis of the curing process.

We have studied the curing process of a novel epoxy resin, epoxy-terminated poly(phenylene ether ketone) (E–PEK). The main goal of our work is to simplify the cure cycle design for a thermosetting composite through simulation based on cure processing modeling. In this series of articles, cure cycles of a carbon-fiber-reinforced E–PEK composite were simulated based on the process modeling. The differential scanning calorimetry (DSC) characterization of the curing processes is described in this article, and the discussion of the chemorheology based on a reported model in the literature and our suggested model is presented in Part II. Part III will discuss the determination of the time of pressure application, and Part IV will address the simulation of cure cycle and eval-uate the simulated cure cycle through characterization of the mechanical properties of composite sheets. The last article will discuss the thermal transfer affecting the simulation.

Curing Kinetics Model

It is known that the curing kinetics and the maximum extent of reaction to be attained in an isothermal curing process have to be considered because they are the basic requirements for the determination of a cure cycle. The reaction rate and extent of reaction as a function of temperature and time can be calculated from a kinetics equation. There are many techniques that can be used to study curing reaction kinetics such as Fourier transform infrared spectrometry (FTIR),[4,5] high-performance liquid chromatography (HPLC),[5,6] torsional braid analysis (TBA),[4-7] and DSC.[6,8,9] One of the simple and fast methods to characterize the curing reaction kinetics is DSC, which is classified as an isothermal method (IDSC, constant temperature process) or a nonisothermal method (DDSC, scan with constant heating rate).

In this article the curing reaction kinetics of the E–PEK system is characterized by isothermal differential scanning calorimetry (IDSC) and nonisothermal differential scanning calorimetry (DDSC), and a new method to estimate the maximum extent of reaction completed at a certain isothermal curing process is introduced.

EXPERIMENTAL

Materials

A novel epoxy-terminated poly(phenylene ether ketone) (E–PEK) developed in this Institute is used as the resin material. E–PEK is a kind of CET (crosslinkable epoxy thermoplastics) material[1] that has relatively low viscosity in processing compared with thermoplastic poly(phenylene ether ketone). At the same time, because of the crosslinking reaction between the end epoxy groups and a curing agent, E–PEK is able to keep the same high performance as thermoplastic PEK at elevated temperature for a long time. Therefore, E–PEK is a candidate matrix resin of polymer composites as structural materials because it appears to possess a combination of high modulus, high glass transition temperature T_g, good ductility, and processibility.

A polyamine, 4,4′-diaminodiphenyl sulfone

Matrix resin
  Epoxy terminated phenolphthalein
poly(phenyl ether ketone) (E-PEK)
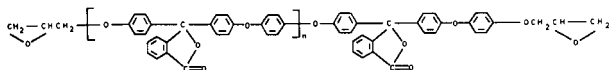
$\overline{Mn}$	1200
EEW	625
Melt viscosity (250℃)	0.1571 Pa.s
Soft point	110℃

Curing agent
  1. 4, 4′ -Diamino diphenyl sulphone (DDS)
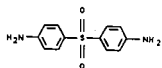
Molecular weig	198.27
Melt point	176～178

  2. Hexahydrophthalic acid anhydride

Molecular weight	154.17
Melt point	32-34

Figure 1 The chemical structure of epoxy-terminated poly(phenyl ether ketone) (E-PEK), 4,4′-diaminodiphenyl sulfone (DDS), and hexahydrophthalic acid anhydride (Nadic).

(DDS) (Shanghai Shijisanchang, China) and an anhydride, hexahydrophthalic acid anhydride (Nadic) (Beijing Huagongchang, China) were chosen as curing agents. The chemical structures of E-PEK, DDS, and Nadic are shown in Figure 1. The stoichiometric ratios of epoxy/amine and epoxy/anhydride are 1 : 1.

Procedure

E-PEK, DDS, and Nadic were vacuum dried, for 12 h (313 K) before mixing. The weighed powders of E-PEK/DDS or E-PEK/Nadic were then mixed. To prevent premature reaction, all the mixtures were stored in a desiccator under 248 K until use. Before measurement, the mixtures were held at room temperature for 2 h.

DSC (Perkin-Elmer Model 7) was used for investigating the curing reaction kinetics parameters. Indium was used for temperature and calorimetric calibration following the procedure described in the operating manual of the instrument. Both IDSC and DDSC tests were performed

on both E-PEK/DDS and E-PEK/Nadic mixtures in a nitrogen atmosphere. The flow rate of nitrogen was 20 ml/min. The weight of the samples used in these experiments ranged from 15 to 20 mg. In an isothermal process, the weighed sample in the aluminum cell was put in a sample holder and then heated to the isothermal temperature with a heating rate of 320 K/min. The duration of these tests was extended until a stable baseline in the thermograms was achieved. The nonisothermal experiments were performed, with five different scan rates (2.5, 5, 10, 15, and 20 K/min) between 323 and 623 K. The same operations using an empty cell as a reference were always made before the IDSC and DDSC measurements.

RESULTS AND DISCUSSION

Isothermal Reaction Kinetics

The curing reaction of E-PEK is an exothermic process. When DSC is used for characterizing the curing reaction kinetics, there is an assumption that the reaction rate is directly proportional to the rate of heat generation as denoted by the following equation:

$$\frac{d\alpha}{dt} = \frac{1}{H_T} \times \frac{dH}{dt} \qquad (1)$$

where α is the extent of reaction, t is the reaction time, and H_T is the total reaction heat. For an nth-order reaction, the kinetics equation can be described as

$$d\alpha/dt = k(1 - \alpha)^n \qquad (2)$$

where k is a temperature-dependent reaction rate constant. According to eqs. (1) and (2), the kinetics parameters can be calculated from DSC curves.

Ten isothermal DSC tests were made at different temperatures from 403 to 503 K for the E-PEK/DDS system and from 403 to 493 K for the E-PEK/Nadic system. One of the typical experimental (IDSC) thermograms is shown in Figure 2, which is a typical nth-order curing reaction exthermal curve according to ref. 10. Its reaction kinetics can be described with eqs. (1) and (2). The average reaction heat of 123 J/g for the E-PEK/DDS system, measured from DDSCs with various heating rates, was used as H_T in eq. (1).
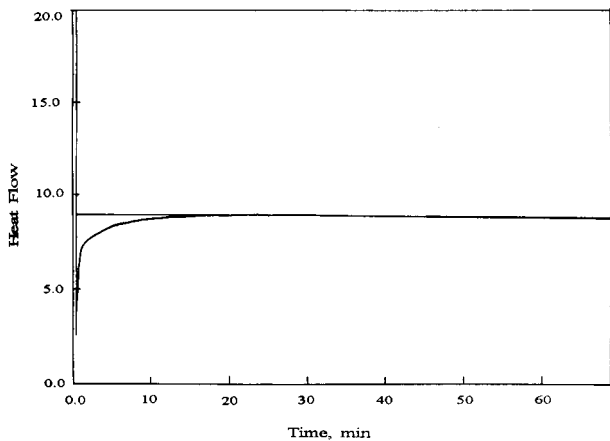
Figure 2 An IDSC thermogram at 210°C for the E–PEK/DDS system. The maximum reaction rate peak is located at the beginning of the scan, which is the typical feature of an nth-order reaction.

Then a pair of curing reaction rate constant k and reaction order n can be calculated from each isothermal DSC thermogram through eq. (2). From the Arrehnius plot of ln k versus $1/T$ (Fig. 3) for the E–PEK/DDS system, the preexponential factor Ao and reaction activation energy Ea were calculated (Table I). The same procedure was also performed on the E–PEK/Nadic system, and the corresponding kinetics parameters were also obtained (Table I). The average values of reaction order n derived from IDSC are also listed in Table I. It is evident from Table I that the reaction activation energy Ea for the E–PEK/DDS system is lower than that for the tetraglycidyl diamino diphenyl methane (TGDDM/DDS) system (62.4 kJ/mol) reported in ref. 11, whereas the reaction order n is higher than that for TGDDM/DDS (n is lower than 3 for the TGDDM/DDS system).[12]

The extents of reaction for the E–PEK/DDS system at different temperatures calculated from eq. (2) and using the parameters in Table I were compared with the experimental results in Figure 4. It was found that there is good agreement between them. The same conclusion was also obtained for the E–PEK/Nadic system.

Nonisothermal Reaction Kinetics

One of the typical nonisothermal DSC thermograms for the E–PEK/DDS system is shown in Figure 5. There are several methods to calculate reaction kinetics parameters from DDSC thermograms.[13–19] It was found that the combination of the Freeman–Carroll equation[16] and Kissinger

equation[19] gives reaction kinetics parameters for our reaction systems accurately. The Freeman-Carroll and Kissinger equations are shown as eqs. (3) and (4), respectively.

$$\frac{\Delta \ln \dfrac{dH}{dt}}{\Delta \ln Hr} = n - \frac{E}{R}\frac{\Delta \dfrac{1}{T}}{\Delta \ln Hr} \qquad (3)$$

$$A = \frac{\Phi Ea \cdot \text{EXP}[E/RTp]}{RTp^2[hn(1 - \alpha p)^{n-1}]}$$

$$= \frac{\Phi Ea \cdot \text{EXP}[E/RTp]}{RTp^2} \qquad (4)$$

where

dH/dt = the heat generation rate
T = the absolute temperature
$Hr = H_T - H$
Ea = the reaction activation energy
n = the reaction order
$h = (dH/dt)/\phi$
ϕ = the scan rate
R = the universal gas constant
Tp = the exothermic peak temperature

The reaction kinetics parameters obtained from eqs. (3) and (4) are listed in Table II, in which reaction order n and activation Ea were calculated from eq. (5), and the preexponential factor Ao was calculated from eq. (6). It has been re-
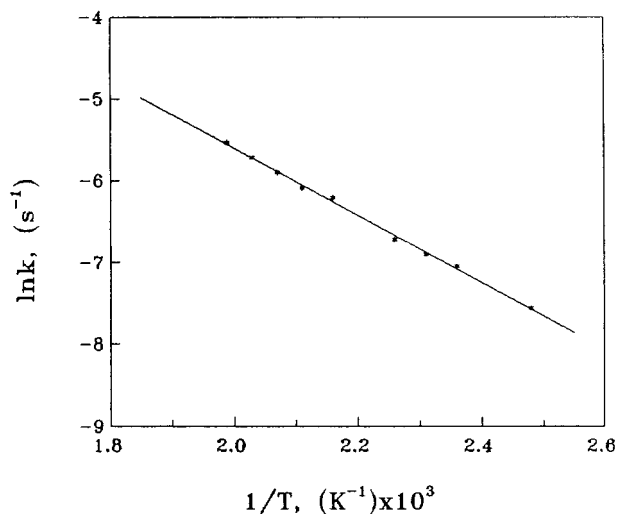
Figure 3 An Arrhenius plot of the isothermal reaction rate constant with isothermal temperature for the E–PEK/DDS system: (*) experimental; (——) the best fit.

Table I Isothermal Reaction Kinetics Parameters

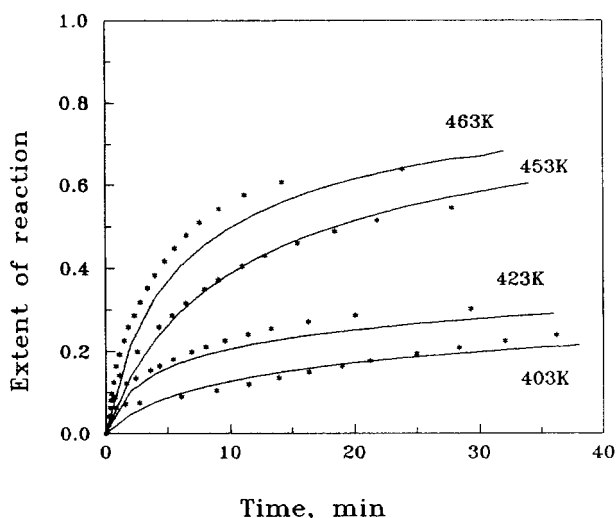| Reaction System/ Kinetics Parameters	Preexponential Factor A_O, s^{-1}	Activation Energy Ea (kJ/mol)	Reaction Order n
E−PEK/DDS System	21.98	1.12	3.167
E−PEK/Nadic System	88.80	40.06	1.646

ported[20] that the Ea for bisphenol *A*-diglycidyl ether (BADGE) and the ethylenediamine (EDA) system determined by DDSC is 102 kJ/mol, which is lower than that for the E−PEK/DDS system (Table II). When the extent of reaction for the E−PEK/DDS system versus temperature during a nonisothermal process predicted using the parameters in Table II is compared with the experimental results (Fig. 6), they are found to be in good agreement.

It is observed that the kinetics parameters determined from IDSC and DDSC are not equivalent. The same reports have been found in refs. 20 and 21. The reaction kinetics parameters in Table II, obtained from nonisothermal processes, cannot be used for describing isothermal processes or vice versa. Moacanin[22] studied the mechanism of the epoxy/DDS system and pointed out that several curing reactions may take place at the same time and that the ratio among them changes with temperature. This viewpoint was supported by research work in refs. 15 and 22. It has been reported[12] that the curing reaction order

for epoxy systems is dependent on both the temperature and the extent of reaction rather than being a constant. It has also been reported[23] that, for an autoaccelerating curing reaction, even if the total reaction order $m + n$ is assumed not to be changeable, the reaction order m is temperature-dependent. In the case of an epoxy/diamine system with an accelerator, the reaction activation energy is also temperature-dependent. In view of the difference in reaction kinetics parameters, isothermal and nonisothermal steps in a cure cycle have to be simulated using the corresponding reaction kinetics parameters.

Prediction of the Maximum Extent of Reaction During an Isothermal Curing Process

Generally, the completion of curing is carried out under a constant temperature. The isothermal curing process of thermosetting resins is usually characterized by gelation and vitrification.[20] Near vitrification, curing reaction kinetics are local viscosity dependent. As long as vitrification is reached, curing reaction ceases. However, this cessation is not necessarily an indication that the curing reaction is completed. Subsequent exposure to a higher temperature could result in further curing reaction. If the maximum extent of reaction (A_{ult}) completed at a certain curing tem-

Figure 4 Changes of the extent of reaction in isothermal processes associated with reaction time for the E−PEK/DDS system: (∗) experimental; (——) calculations from eq. (3) and Table I.
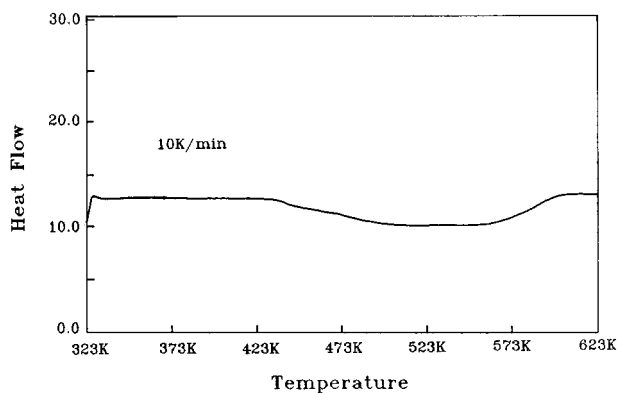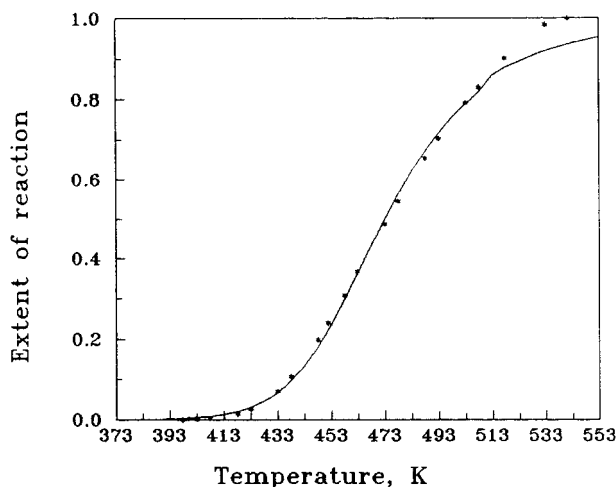
Figure 5 Nonisothermal DSC thermogram for the E−PEK/DDS system at a scan rate of 10 K/min.

Table II   Nonisothermal Reaction Kinetics Parameters

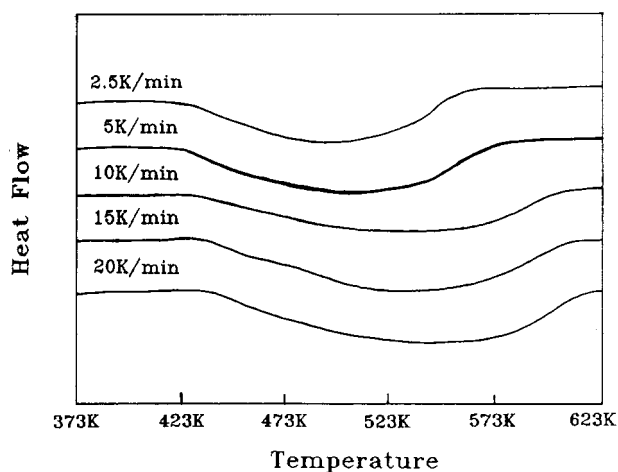| Reaction System/ Kinetics Parameters	Preexponential Factor A_O, s^{-1}	Activation Energy E_a (kJ/mol)	Reaction Order n
E−PEK/DDS System	6.092e10	118.7	2.947
E−PEK/Nadic System	1.611e24	213.0	3.754

perature could be predicted, it would be helpful for the determination of a cure cycle and postcure conditions that lead to continuing curing reaction. The reaction kinetics cannot give information about the maximum extent of reaction, although they can give the reaction rate and the extent of reaction. The traditional method to determine the maximum extent of reaction is IDSC.[21] It is more complicated if we want to know the $A_{ult}(T)$ at each specific temperature by this method because there are usually some difficulties in IDSC measurements. For instance, even though the temperature equilibrium is achieved in a very short time, there is still some reaction heat that may not be recorded before the equilibrium is reached, or the resin may overflow from the DSC cell during the quick heating stage. Another method to determine the maximum extent of reaction is based on the relationship between the T_g and the extent of reaction.[24] But one has to determine the relationship between T_g and α through many experiments.

The DDSC curves for the E−PEK/DDS system

measured with different scan rates are shown in Figure 7. It can be seen from this figure that the extents of reaction at the same specific temperature are not equal to each other when the scan rate is not the same, and the extents of reaction will decrease with the increase of the scan rate. The extents of reaction at the same temperature were correlated to scan rates and a series of curves were obtained (Fig. 8). The curves in Figure 8 look like exponential curves in shape thus they can be redrawn as semilog plots, as shown in Figure 9. Since there are good linear relationships between ln (the extent of reaction) and scan rates, the fitted curves can extend along the horizontal axis. If a fitted curve is extrapolated to the limit case (i.e., extrapolated to the scan rate of zero) an extrapolated value at a special equilibrium state is obtained. This value is the extent of reaction completed, after an unlimited length of time, until the corresponding isothermal temperature has been achieved. It can be used approximately as the maximum extent of reaction completed for an isothermal curing process just under this constant temperature. A series of exponential equations like eq. (5) were fitted from the curves in Figure 9 as follows:
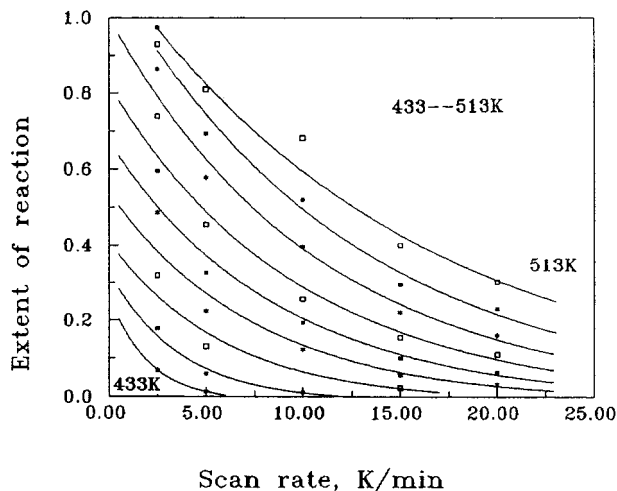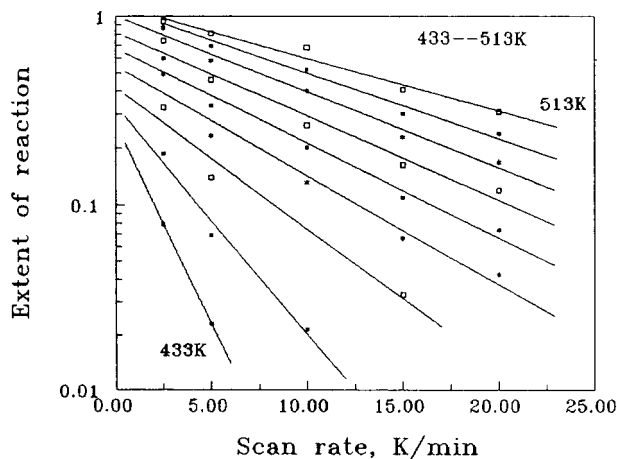
Figure 6   Changes of the extent of reaction during a nonisothermal process associated with reaction time (temperature) for the E−PEK/DDS system at a scan rate of 10 K/min: ($*$) experimental; (——) calculations from eq. 3 and Table II.

Figure 7   Nonisothermal DSC thermograms at different scan rates for the E−PEK/DDS system.

Figure 8 Scan-rate-dependent extent of reaction for the E−PEK/DDS system at various temperatures.

Figure 10 Relationship between the maximum extent of reaction and temperature for (a) E−PEK/DDS system and (b) E−PEK/Nadic system: (∗) extrapolated to a scan rate at zero from Figure 9; (———) the best fit.
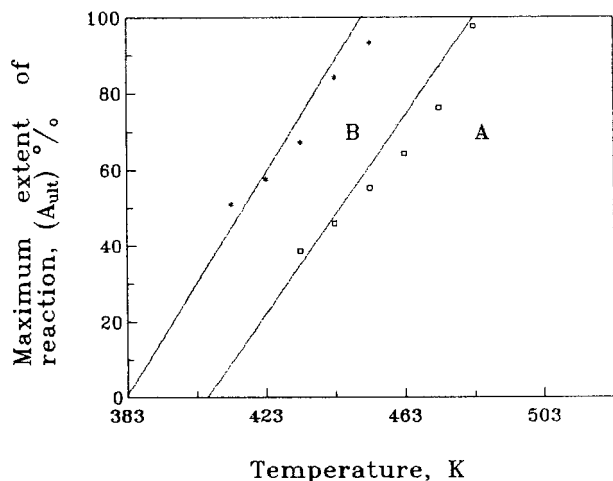
$$A(T) = A \times \exp(-B\phi) \tag{5}$$

where $A(T)$ is the extent of curing reaction, T is the temperature, A and B are temperature-dependent constants, and ϕ is the scan rate. In the case of $\phi = 0$, A is equal to $A(T)$, which refers to the maximum extent of reaction ($A_{ult} = 0$) during an isothermal curing process (reaction temperature T). The fitted linear relationship between the maximum extent of reaction and reaction temperature shown in Figure 9 can be used for predicting the maximum extent of reaction at any constant

temperature. This relationship in Figure 9 is as follows:

E–PEK/DDS system $\quad A_{ult} = -504 + 1.21T \quad (6)$

The same procedure was performed on the E–PEK/Nadic system (Fig. 10), and the corresponding relationship is shown in equation (7):

E–PEK/Nadic system $\quad A_{ult} = -560 + 1.46T \quad (7)$

The maximum extents of reaction A_{ult} experimentally measured from IDSC by the method in ref. 23, are shown in Figure 11 by squares, and the calculated A_{ult} from eqs. (6) and (7) are shown by solid lines. Figure 11 shows that the A_{ult} calculated from eqs. (6) and (7) are in good agreement with the experimental results, which proves the validity of these equations. However, there are two special cases to which attention should be paid. First, when $T \approx 393$ K [in the case of E–PEK/DDS from eq. (6)] and $T \approx 383$ K [in the case of E–PEK/Nadic from eq. (7)], A_{ult} equals zero. This means the curing reaction cannot take place at (or below) such temperatures, which are very close to the actual phase. Second, when $T \approx 493$ K [in the case of E–PEK/DDS from eq. (6)] and $T \approx 455$ K [in the case of E–PEK/Nadic from eq. (7)], A_{ult} calculated from eqs. (6) and (7) is equal to 100, which emphasizes that the complete curing reaction can be achieved at and above such temperatures.

Figure 9 Semilogarithmic plot of the extent of reaction versus scan rate for the E−PEK/DDS system at various temperatures.

Figure 11 Relationship between the maximum extent of reaction and temperature for (a) E−PEK/DDS system and (b) E−PEK/Nadic system: (∗) experimentally measured from the isothermal DSC method reported in ref. 10; (——) calculations from eqs. (6) and (7).

CONCLUSIONS

1. The curing reaction kinetics parameters for the E−PEK/DDS and the E−PEK/Nadic systems were measured using IDSC and DDSC. It was found that the curing reactions of the E−PEK/DDS and the E−PEK/Nadic systems are nth-order reactions but are not autoaccelerating. The experimental results revealed that the curing reaction kinetics parameters measured from IDSC and DDSC are not equivalent. This means that, in the curing reaction kinetics model for our E−PEK system, both isothermal and nonisothermal reaction kinetics parameters are needed to describe isothermal and nonisothermal reaction processes. The isothermal and nonisothermal curing processes were successfully simulated using this model. This result is the same as that reported by several other authors. Similar phenomena were also observed in the chemorheology study for these two systems, and will be published in our next article in this series.[24]

2. A new extrapolation method was suggested. On the basis of this method the maximum extent of curing reaction (A_{ult}) that can be reached at a certain temperature can be predicted. The A_{ult} for the E−PEK system, which can be reached at different isothermal conditions, estimated by the new method agrees well with the results obtained from another procedure reported in the literature. This estimating method is of benefit for determination of cure processing time and postcure conditions.

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