Cure Processing Modeling and Cure Cycle Simulation of Epoxy-Terminated Poly(phenylene ether ketone). II. Chemorheological Modeling

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ABSTRACT: Chemorheology and corresponding models for an epoxy-terminated poly-(phenylene ether ketone) (E-PEK) and 4,4′-diaminodiphenyl sulfone (DDS) system were investigated using a differential scanning calorimeter (DSC) and a cone-and-plate rheometer. For this system, the reported four-parameter chemorheological model and modified WLF chemorheological model can only be used in an isothermal or nonisothermal process, respectively. In order to predict the resin viscosity variation during a stepwise temperature cure cycle actually used, a new model based on the combination of the four-parameter model and the modified WLF model was developed. The combined model can predict the resin viscosity variation during a stepwise temperature cure cycle more accurately than the above two models. In order to simplify the establishment of this model, a new five-parameter chemorheological model was then developed. The parameters in this five-parameter model can be determined through very few rheology and DSC experiments. This model is practicable to describe the resin viscosity variation for isothermal, nonisothermal, or stepwise temperature cure cycles accurately. The five-parameter chemorheological model has also successfully been used in the E-PEK systems with two other curing agents, i.e., the diamine curing agent with the addition of a boron trifluride monoethylamine (BF$_3$-MEA) accelerator and an anhydride curing agent (hexahydrophthalic acid anhydride). © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 799–808, 1997

Key words: epoxy resin; poly(phenylene ether ketone); chemorheology; model and simulation; composite

INTRODUCTION

Perhaps the most important property of a polymer with regard to the polymer processing conditions is its rheological behavior. For a given thermoplastic material, viscosity, temperature, and shear rate relationships are basically stable criteria for pro-

cessing because there is no considerable change in the chemical structure of material. In the case of a thermosetting resin, however, the processing is not only a physical process, but also a chemical process. The increase in viscosity as the resin is transformed into crosslinked networks is a main characteristic, hence the viscosity variation becomes more complex. Once the gelation of a resin has occurred, the resin loses its fluidity and cannot be shape-altered thereafter. Therefore, the prediction of viscosity variation during a given cure cycle is an essential requirement for the manufacture of thermosetting

composites. The most direct way to gain understanding of a rheological process for a thermosetting resin is to build a process model, which is called a chemorheological model. Over the past 20 years, scientists have developed more than 10 mathematical models to describe the viscosity variation during the curing process.[1-7] All these models generally can be classified as two types, i.e., the poly-parameter model and the modified WLF model.

Viscosity–temperature functions have been derived either from the application of free volume theory or from the assumption that flow is an activation process. The poly-parameter chemorheological models are examples of relationships that have been derived from the activation process theory. The four-parameter model is one representative[3]:

$$\ln \eta(t)_T = \ln \eta_\infty + \Delta E\eta/RT$$
$$+ tk_\infty \cdot \exp(-\Delta E_k/RT) \quad (1)$$

where $\eta(t)_T$ is viscosity as a function of time at temperature T, η_∞ is calculated viscosity at $T = \infty$, ΔE_η is Arrhenius activation energy for viscosity, R is universal gas constant, T is absolute temperature, t is time, K_∞ is kinetic analog of ln η_∞, and ΔE_k is kinetic analog of ΔE_η.

It is reported that eq. (1) can be used to describe the viscosity variation for an isothermal (constant temperature) process, and the integrated form of eq. (1) can be used to describe a dynamic (nonisothermal with constant heating rate) process.[1] However, as previously discussed,[8] the mechanism of the epoxy curing reaction is highly complex: more than one kind of curing reaction takes place at the same time and the ratio among them changes with temperature. For this reason, disagreement between models and experiments occurs sometimes for the nonisothermal curing process of epoxy systems. Thus, two modified forms of the four-parameter model were developed.[2,3]

The other type of chemorheological model[4-6] is based on the WLF equation: a typical example is derived from the free volume theory. By allowing the model parameters to adjust with the changing structure of curing resin, Chiou and Letton developed a modified WLF equation to predict the viscosity change during a nonisothermal curing process[9]:

$$\ln \frac{\eta(T)}{\eta(T_g)} = \frac{-C_1(\alpha)[T - T_g(\alpha)]}{C_2(\alpha) + [T - T_g(\alpha)]} \quad (2)$$

where α is the extent of reaction, T_g is the glass transition temperature, $\eta(T)$ is resin viscosity at temperature T, $\eta(T_g)$ is resin viscosity at temperature T_g, and C_1 and C_2 are materials-dependent parameters. T_g, C_1, and C_2 are correlated to the extent of reaction.

The authors have studied the curing process of a novel epoxy, epoxy-terminated poly(phenylene ether ketone) (E-PEK). A curing kinetics submodel has been reported in the first article of this series.[8] In this article, the second in the series, the chemorheological behavior of the E-PEK with various curing agent systems was characterized by differential scanning calorimeter (DSC) and cone-and-plate rheometer. Two reported chemorheological models, i.e., a four-parameter model and a modified WLF model, were applied to describe the rheological behavior of our reaction system. Modification to the reported chemorheological models and a new chemorheological model are also proposed in this article.

EXPERIMENTAL

The resin material used is a novel E-PEK which has been described previously.[8] 4,4′-Diaminodiphenyl sulfone (DDS) (Shanghai Shijisanchang, China) with or without the use of a boron trifluoide monoethylamine (BF$_3$·MEA) as accelerator and hexahydrophthalic acid anhydride (Nadic) were chosen as curing agents, respectively. The mixing process and storing condition of the resin and curing agent mixtures are the same as previously described.[8]

A cone-and-plate rheometer (model Rheomat 120, Contraves Co., Switzerland) was used to measure the viscosity variation with shear rate 1 s^{-1}. The cone with 20 mm diameter and 0.5 radian angle was used. The weight of samples used in these tests was ~ 0.25 g. Both the isothermal and nonisothermal tests were performed on E-PEK/DDS samples. The isothermal tests were performed on fresh samples, and both the fresh and partially cured samples were used for nonisothermal tests. In order to obtain samples with various extents of reaction, E-PEK/DDS mixture samples were put in a special lab-made oven with a certain flowing rate of nitrogen into the oven. The samples were kept in the oven at several different temperatures for different lengths of time to obtain partially cured samples. Then the samples were quickly removed from the oven and put into a liquid nitrogen bath to stop further curing reaction. The extent of reaction for partially cured samples was determined by compar-
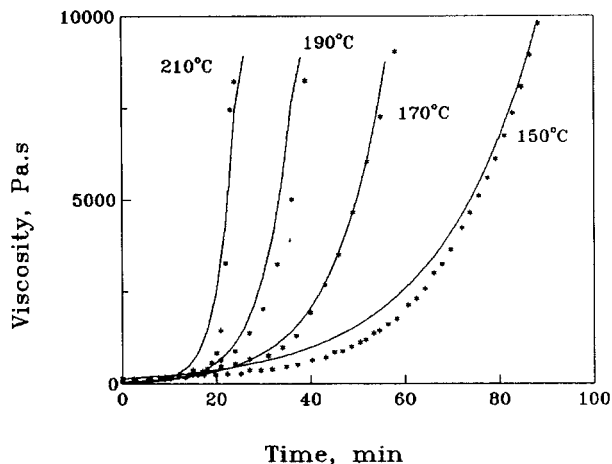
Figure 1 Viscosity versus cure time for the E-PEK/DDS system at different temperatures. (*) experimental results by the rheometer; (—) theoretical predictions by the four-parameter model [eq. (1)]. The value near the curve indicates the isothermal hold temperature.

ing the residual reaction heat to the whole reaction heat of a fresh sample derived from nonisothermal DSC. The glass transition temperature for partially cured samples was also determined simultaneously.

RESULTS AND DISCUSSION

Chemorheological Description by the Reported Models

First of all, we tried to use the reported chemorheological model, i.e., the four-parameter model, and the modified WLF model to describe the rheological behavior of the E-PEK/DDS system.

Nine isothermal viscosity tests were run at various constant temperatures from 130°C to 230°C. Some of the typical viscosity profiles are shown by asterisks in Figure 1. The parameters in eq. (1) were calculated using the best-fit method on the isothermal viscosity data obtained in the above tests. The corresponding parameters in eq. (1) are listed below.

$$\eta_\infty = 8.1 \times 10^{-8} \text{ Pa}^{-1} \text{ s}^{-1}$$

$$\Delta E_\eta = 749433.21 \text{ J/mol}$$

$$K_\infty = 1005.27 \text{ s}^{-1}$$

$$\Delta E_k = 49398.4 \text{ J/mol}$$

Viscosity changes predicted by eq. (1) with the parameters shown above are shown by solid lines

in Figure 1. Figure 1 shows that, at isothermal conditions, the theoretical predictions by the four-parameter model agree well with the experimental results for our system.

It has been reported that the modified WLF model [eq. (2)] can be used to predict the viscosity changes for a nonisothermal process.[9] The DiBenetto's equation [eq. (3)] can be used to represent the relationship between T_g and α in eq. (2):

$$\frac{T_g - T_{g_o}}{T_{g_o}} = \frac{(\varepsilon_x/\varepsilon_m - F_x/F_m)\alpha}{1 - (1 - F_x/F_m)\alpha} \quad (3)$$

where T_{g_o} is the glass transition temperature of the uncured resin, $\varepsilon_x/\varepsilon_m$ is the ratio of lattice energies for the cured and uncured polymers, and F_x/F_m is the corresponding ratio of the segmental mobilities. To calculate the constants $\varepsilon_x/\varepsilon_m$ and F_x/F_m, eq. (3) can be rewritten as

$$\frac{T_g - T_{g_o}}{\alpha} = (\varepsilon_x/\varepsilon_m - 1)T_{g_o} + (1 - F_x/F_m)T_g \quad (4)$$

where $(\varepsilon_x/\varepsilon_m - 1)T_{g_o}$ and $(1 - F_x/F_m)$ become the intercept and slope of the plot of $(T_g - T_{g_o})/\alpha$ versus T_g.

Partially cured samples were scanned at 10°C/min by DSC to determine T_g and residual heat of reaction, which enabled the extent of reaction to
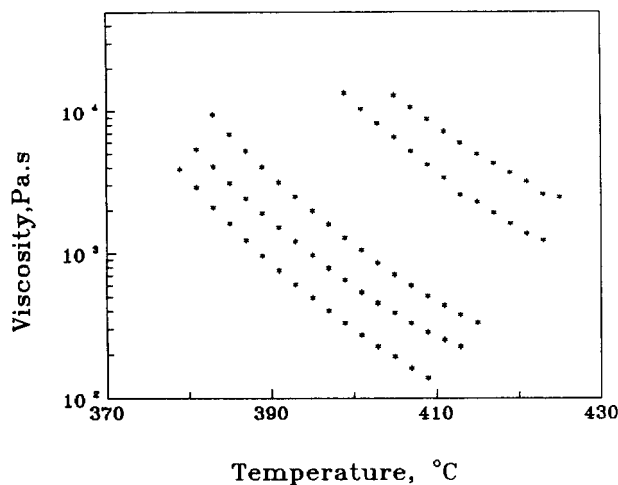

Figure 2 Nonisothermal viscosity curves for resin samples of the E-PEK/DDS with various extents of reaction: extents of reaction for each curve are A: 0, B: 0.041, C: 0.110, D: 0.345, E: 0.455, respectively. Heating rate is 2.5°C/min. For clarity, not all the viscosity curves are shown. (From bottom to top are A, B, C, D, and E, respectively)
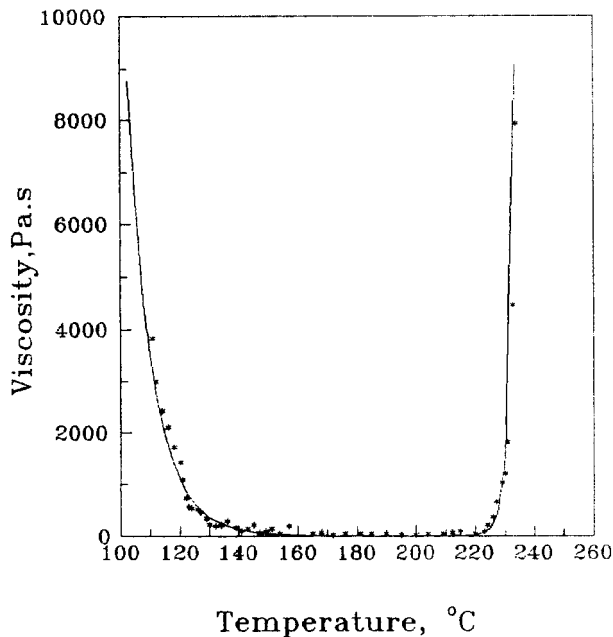
Figure 3 Comparison between the theoretical predicted viscosity variation and the experimental results for the E-PEK/DDS system during a dynamic process. (*) experimental results; (—) theoretical predictions by the modified WLF model [eq. (2)].

be determined. The relationship between T_g and α for various partially cured samples determined from DSC was used to determine the ratios of $\varepsilon_x/\varepsilon_m$ and F_x/F_m in eq. (3) by the curve fitting method. The two values obtained for the E-PEK/DDS system are $\varepsilon_x/\varepsilon_m = 0.589$ and $F_x/F_m = 0.426$, respectively.

The extent of reaction dependent parameters C_1 and C_2 in eq. (2) were determined following the method in ref. 9. Five nonisothermal viscosity curves for partially cured samples were measured. The experimental data are shown in Figure 2. To determine the relationships of C_1, C_2, and α, two assumptions were made. First, the reference viscosity at $\eta(T_g)$ can be chosen as a constant of $10^9 \, \text{Pa}^{-1} \, \text{s}^{-1}$. Second, in the temperature ranges shown in Figure 2, the dominant effect on decrease in viscosity is temperature, and the extent of reaction of the resin for each curve in this temperature range can be considered constant. That means the decrease in viscosity is considered solely to be due to the changes in temperature, and the changes in C_1 and C_2 associated with each viscosity curve can be obtained from the slopes and intercepts of the plots of $(T - T_g)/\ln[\eta(T)/\eta(T_g)]$ versus $(T - T_g)$. In the case of the E-PEK/

DDS system the relationships between C_1 and C_2 and the extent of reaction α are

$$C_1 = 22.12 + 20.93\alpha \qquad (4)$$

$$C_2 = \exp(3.49 + 2.78\alpha) \qquad (5)$$

The parameters of the modified WLF model [eq. (2)] for the E-PEK/DDS system are listed below.

$$\varepsilon_x/\varepsilon_m = 0.589$$

$$F_x/F_m = 0.454$$

$$C_1 = 22.12 + 20.93\alpha$$

$$C_2 = \exp(3.49 + 2.78\alpha)$$

The comparison between the theoretical predictions [from eqs. (2)–(5)] and the experimental viscosity profiles in a nonisothermal process for the E-PEK/DDS system are displayed in Figure 3. It shows a good agreement between them.

Generally, the practicality of the established chemorheological model depends on whether the model can describe the actual stepwise cure cycle, such as is shown in Figure 4. The viscosity profiles for the stepwise cure cycle as predicted by the four-parameter model and the modified WLF model are compared with the experimental results in Figures 5 and 6, respectively. It is very interesting to note that the four-parameter model, in which the model parameters were derived from the isothermal process, can well predict the viscosity variation during the isothermal step of a stepwise cure cycle accurately, but gives a relatively high error in the nonisothermal step of the
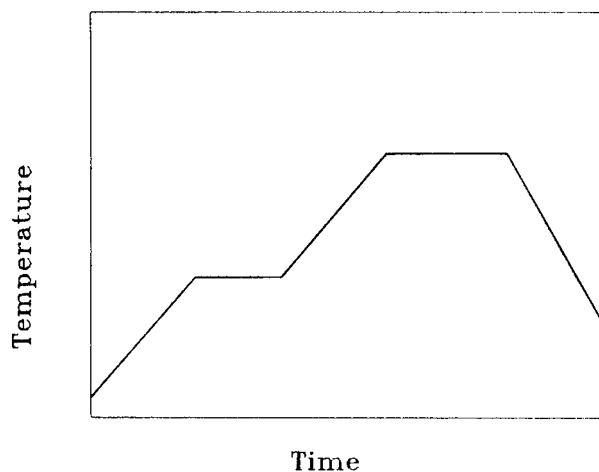

Figure 4 A cure cycle (stepwise temperature cure cycle) actually used in manufacture of composite.
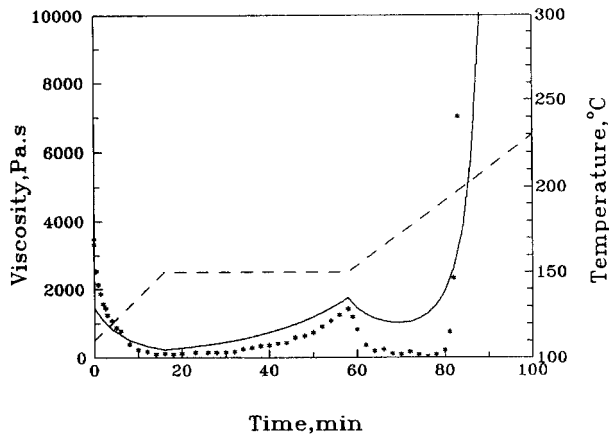
Figure 5 Comparison between the theoretical predicted viscosity variation and the experimental results for the E-PEK/DDS system during a stepwise cure cycle. (*) experimental results; (− −) temperature; (—) theoretical predictions by the four-parameter model [eq. (1)].

stepwise cure cycle, as shown in Figure 5. The same conclusion was also reported in ref. 10. In contrast, the modified WLF model, in which the model parameters were derived from the nonisothermal process, can well predict the viscosity variation during the nonisothermal process of a stepwise cure cycle accurately, but also gives a high error in the isothermal process of the stepwise cure cycle, as shown in Figure 6. This means the two models can only be suitable for the isothermal or nonisothermal step of the stepwise cure cycle for our reaction system, respectively,
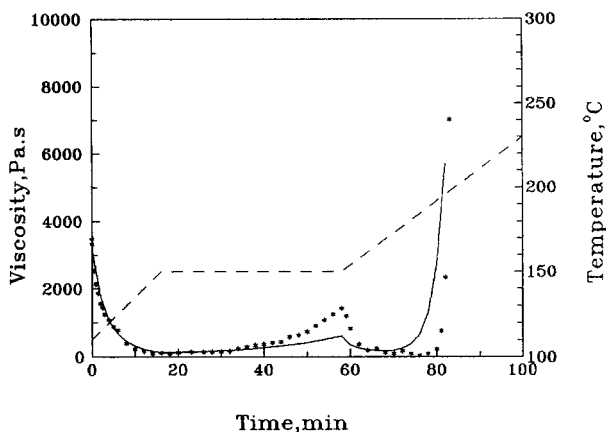

Figure 6 Comparison between the theoretical predicted viscosity variation and the experimental results for the E-PEK/DDS system during a stepwise cure cycle. (*) experimental results; (− −) temperature; (—) theoretical predictions by the modified WLF model [eq. (2)].
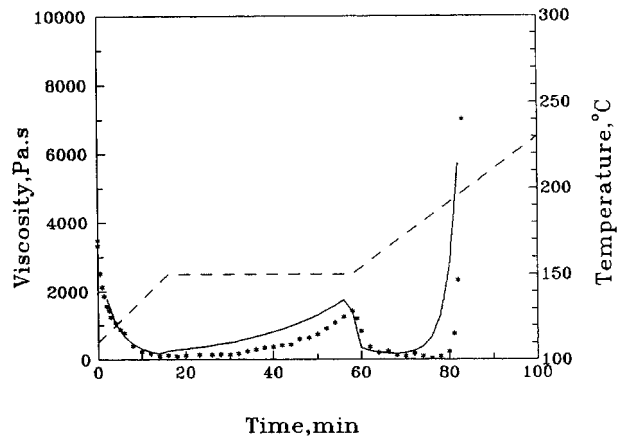

Figure 7 Comparison between the theoretical predicted viscosity variation and the experimental results for the E-PEK/DDS system during a stepwise cure cycle. (*) experimental results; (− −) temperature; (—) theoretical predictions by the combined model, in which the four-parameter model [eq. (1)] is used in an isothermal step, and the modified WLF model [eq. (2)] is used in a nonisothermal step.

but not for the whole stepwise cure cycle. The above conclusions were also reached in the literature.[10] Chiou and Letton's modified WLF model[9] was successfully applied in calculating the viscosity variation under nonisothermal cure conditions, but no data or calculation under isothermal conditions were presented.

Since neither of the above two models can be used for a stepwise cure cycle, it is necessary to search for a new way to reach our goal. A simple alternative approach is to combine the two models into one. This is not only convenient but also reasonable because, as previously proved, the two models can be used in the isothermal or nonisothermal process, respectively, so a new chemorheological model was developed by the combination of the above two models. The new model was a combined one in which the four-parameter model was used in the isothermal step while the modified WLF model was used in the nonisothermal step. Since the viscosity variation during the stepwise temperature cure cycle predicted by the combined model agrees well with the experimental data (Fig. 7), the combination of the four-parameter model [eq. (1)] and the modified WLF model [eq. (2)] can well describe the chemorheological behavior for the E-PEK/DDS system.

A New Chemorheological Model

Although the above-combined model with eqs. (1)−(6) can predict the viscosity variation during
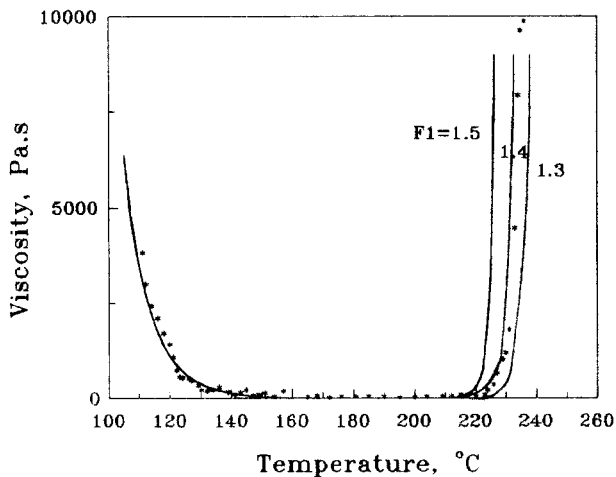
Figure 8 Influence of the proportionality factor, ϕ, on the predicted viscosity by the five-parameter chemorheological model developed for the E-PEK/DDS system.

a stepwise temperature cure cycle accurately, its establishment is very complex. A new chemorheological model established from as few experiments as possible is desirable.

Parameters of the four-parameter chemorheological model can be divided into two parts. The parameters η_∞ and ΔE_η relate to the resin viscosity, and k_∞ and ΔE_k to the level of advancement. Thus they may be determined from different approaches. For instance, the value of η_∞ and ΔE_η can be determined by rheometer, while the parameters k_∞ and ΔE_k can be determined by DSC.

In all poly-parameter chemorheological models, the flow viscosity activation energy is treated as being process independent.[1–3] To simplify the establishment of the new chemorheological model, it was also assumed that the parameter ΔE_η is independent of the extent of reaction for the E-PEK/DDS system. Under this assumption the parameters η_∞ and ΔE_η can be determined by the same method as used for thermoplastic materials.

For the E-PEK/DDS system, it has been proved that the curing reaction kinetics k_∞ and ΔE_k are reaction process-dependent.[8] Therefore, to describe a stepwise temperature cure cycle, both isothermal and nonisothermal reaction kinetics parameters have to be considered. The isothermal reaction kinetics parameters can be used in the isothermal process, and the nonisothermal reaction kinetics parameters can be used in the nonisothermal process. However, a potential problem can be raised if the assumption that the total reaction order is constant is not considered. Isothermal and nonisothermal kinetics parameters are

all determined under the assumption that the reaction order is unchangeable, but actually the reaction order and even the reaction activation energy for epoxy systems are not constant but rely on both the temperature and extent of reaction.[4,11] Therefore, the four-parameter model must be modified when the isothermal and nonisothermal reaction kinetics parameters are used in combination. Hence a proportionality factor ϕ was introduced into the integration part of the four-parameter model:

$$\ln \eta(T, t) = \ln \eta_\infty + \Delta E_\eta/RT$$
$$+ \phi \int k_\infty \cdot \exp(-\Delta E_k/RT) \quad (6)$$

Equation (7) is named as the five-parameter chemorheological model.

For a thermoplastic material, the flow viscosity activation energy is generally measured from a nonisothermal process. Therefore, it is important to find a process in which the resin viscosity change mainly relies on the temperature, while the effect of the curing reaction on the viscosity increase can be eliminated. Considering the nonisothermal viscosity curve for the E-PEK/DDS system at a heating rate of 2.5°C/min (Fig. 3), in the temperature range of 110°C–140°C the initial lowering of viscosity shown on the viscosity curve is due to the melting of the resin. During this stage the effect of changing temperature on the viscosity is much more dominant than the effect of changing resin structure. The state of the resin sample in this temperature range can be considered constant, which has been proved by the nonisothermal DSC results previously reported in this series of articles (Fig. 4 in ref. 8), in which the extent of reaction reached before 140°C during the same nonisothermal process is < 0.5%. Then it is easy to calculate the η_∞ and ΔE_η from such a viscosity curve because the integrated part in eq. (7) is approximately equal to zero, and then eq. (7) can be rewritten as

$$\ln \eta(T, t) \cong \ln \eta_\infty + \Delta E_\eta/RT \quad (7)$$

$\ln \eta_\infty$ and ΔE_η are the intercept and slope of the plot of $\ln \eta(T, t)$ versus $1/RT$. Thus, obtained values of η_∞ and ΔE_η for the E-PEK/DDS system are $4.53E - 17 \text{ s}^{-1}$ and 146 kJ/mol, respectively.

The curing reaction kinetics parameters determined by DSC at isothermal and nonisothermal processes for the E-PEK/DDS system have been reported earlier (Tables I and II in ref. 8).

The modifying factor ϕ in eq. (7) can be determined through the correlation of the predicted viscosity variation from eq. (7) with different values of ϕ and experimental viscosity profile at isothermal, nonisothermal, or stepwise temperature processes. The selection of the process is arbitrary, but the nonisothermal process is the simplest one. Following such a procedure, the optimal value of ϕ obtained is between 1.3 and 1.4, as shown in Figure 8. Now, a new five-parameter chemorheological model for the E-PEK/DDS system has been established, and the parameters determined are listed below.

$$\eta_\infty = 4.53E - 17 \text{ Pa}^{-1} \text{ s}^{-1}$$

$$\Delta E_\eta = 145845 \text{ J/mol}$$

$$\phi = 1.4$$

$$\text{isothermal step} \begin{cases} k_\infty = 21.98 \text{ s}^{-1} \\ \Delta E_k = 36117 \text{ J/mol} \end{cases}$$

$$\text{nonisothermal step} \begin{cases} k_\infty = 6.092E10 \text{ s}^{-1} \\ \Delta E_k = 118780 \text{ J/mol} \end{cases}$$
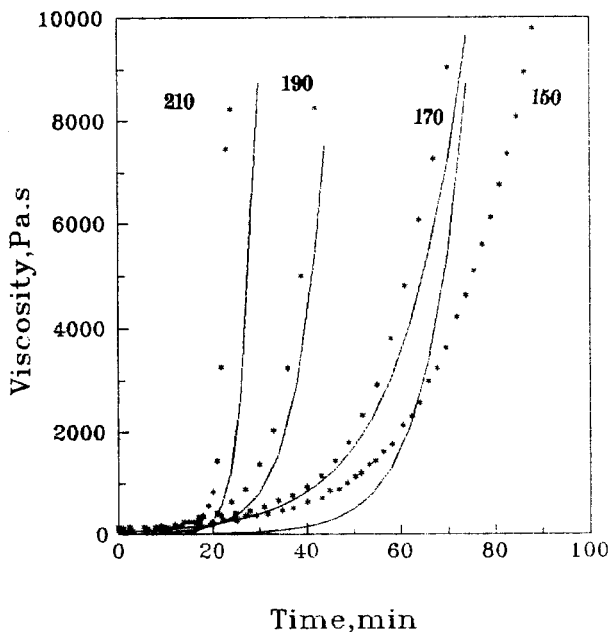
The correlation between the predicted and ex-

Figure 9 Comparison between the theoretically predicted and the experimental viscosity profiles at different constant temperatures for the E-PEK/DDS system. (*) experimental results; (—) theoretical predictions by the developed five-parameter chemorheological model [eq. (6)].
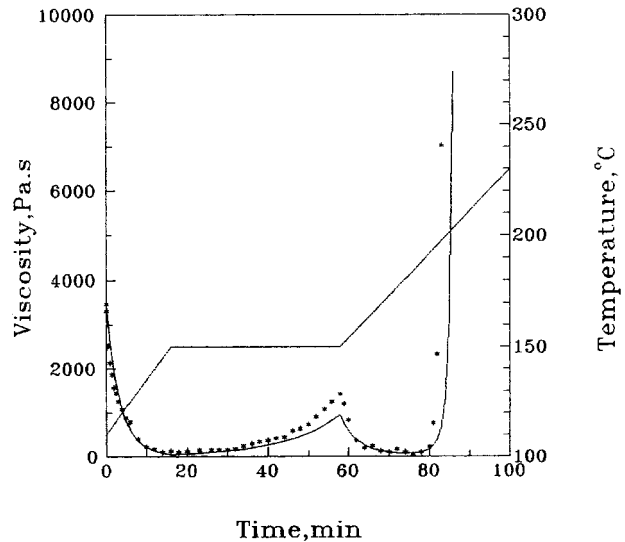

Figure 10 Comparison between the theoretically predicted and the experimental viscosity profiles during a stepwise cure cycle for the E-PEK/DDS system. (*) experimental results; (– –) temperature; (—) theoretical predictions by the developed five-parameter model [eq. (6)].

perimental viscosity profiles under different isothermal conditions for the E-PEK/DDS system is shown in Figure 9. Figures 8 and 9 show that the predicted and experimental results in both isothermal and nonisothermal processes are in good agreement. Then it can be predicted that the five-parameter model can be used in the actual stepwise cure cycle. This prediction is true and was proved by Figure 10, in which the predicted results agree well with the experimental results in both isothermal and nonisothermal steps of a stepwise cure cycle.

The new chemorheological model has been established, but it is necessary to know if the model can be used in other thermosetting systems. Therefore, the same procedures were performed on both the E-PEK/(DDS + BF$_3 \cdot$MEA) and the E-PEK/Nadic systems. Corresponding model parameters for these two systems have also been determined. The comparisons between the predicted and experimental viscosity profiles for E-PEK/(DDS + BF$_3 \cdot$MEA) and E-PEK/Nadic systems are shown in Figure 11. It is found from Figure 11 that the predicted data are in good agreement with the experimental results for the stepwise cure cycles. But it is interesting to note that the experimental viscosity curve in Figure 11(a) looks like a zigzag shape at the second valley. The reason is still not apparent.
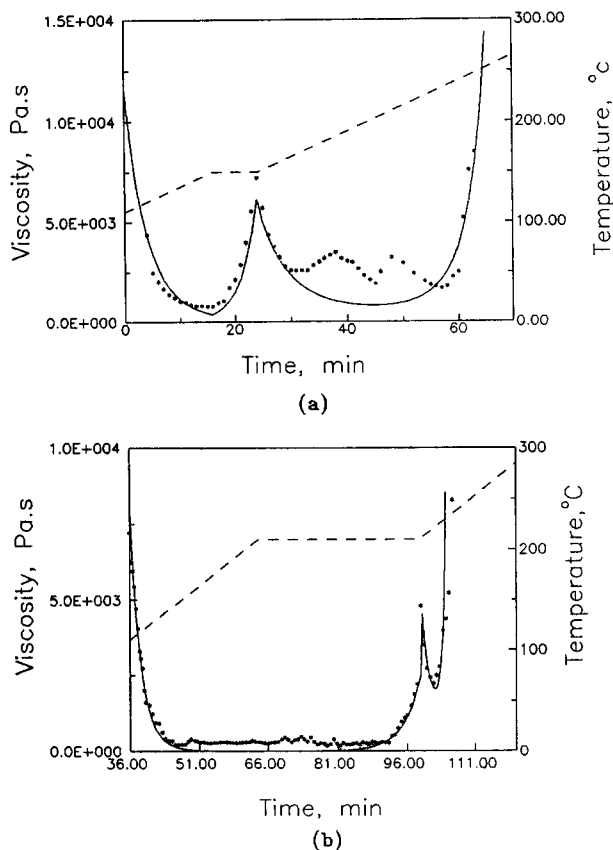
Figure 11 Comparison between the theoretically predicted and the experimental viscosity profiles during a stepwise cure cycle for an E-PEK/(DDS + BF$_3 \cdot$MEA) system (a) and an E-PEK/Nadic system (b). (*) experimental results; (— —) temperature; (——) theoretical calculations by the developed five-parameter model [eq. (6)].

One may argue that the flow viscosity activation energy is dependent on the extent of reaction. For our system, the opposite assumption is right. To realize it, the viscosity curves for the nonisothermal process for partially cured E-PEK/DDS samples (Fig. 2) can be redrawn as in Fig. 12. For partially cured samples with various extents of reaction, only a small variation of the slopes of the viscosity curves in Figure 12 was observed. That means the calculated flow viscosity activation energy for partially cured samples can be considered as constant (the calculated ΔE_η from Figure 12 varies between 135 and 150 kJ/mol, near the value for an uncured sample 146 kJ/mol). The same phenomena can also be observed from ref. 6 for another reaction system. However, the calculated η_∞ for the E-PEK/DDS system increases significantly with the extent of reaction. Such results are not surprising because, for a partially cured sample, the reaction time t is not equal to zero at

the beginning of the reaction. Since we usually treat the beginning of the reaction time as zero, that means that a constant associated with the reaction time (or extent of reaction) taken before testing should be introduced into the model, and it is reflected by the increase of η_∞.

Keenan also found limitations in the four-parameter model and suggested another modified model [eq. (8)][3]:

$$\ln \eta(T, t) = \ln \eta_\infty + \Delta E_\eta / RT$$
$$+ \phi \int k_\infty \cdot \exp(-\Delta E_k / RT) \quad (8)$$

Keenan's model looks like our five-parameter model since there are also five parameters in his model. However, the determination of the parameters in his model was different from that of our model. The parameters in his model, as well as the four-parameter model, were mathematically fitted results from a series of isothermal viscosity curves. Keenan's model has also been used here to describe the E-PEK/DDS system (Fig. 13). The correlation of predicted and experimental viscosity profiles during a stepwise temperature cure cycle shows that there are significant errors between the predicted data and the experimental results.

One of the possible sources of error, when Keenan's model was used in the stepwise temperature cure cycle for our system, is that the flow viscosity activation energy in his model was determined in a different way from our five-parameter model. There are three traditional methods used to calculate ΔE_η. The first can be named the extrapola-
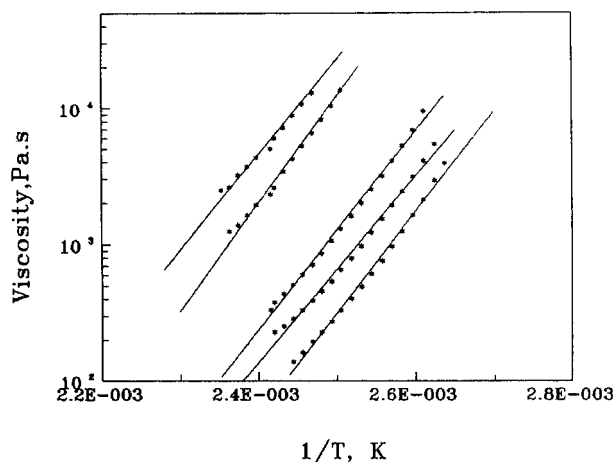

Figure 12 Influence of the extent of reaction on the viscosity curves for a nonisothermal process.
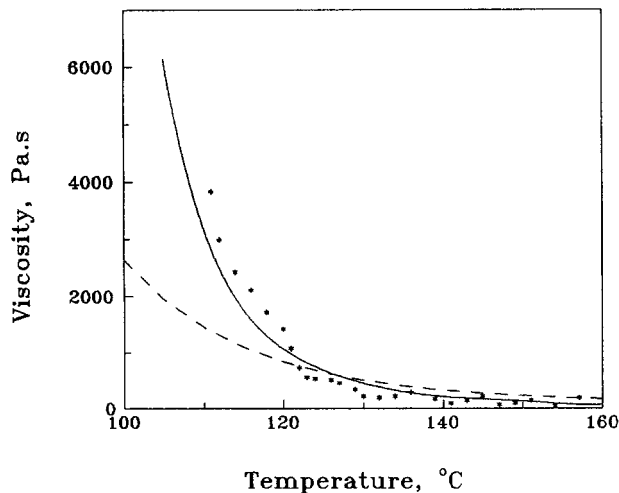
Figure 13 Influence of the determination method of the flow viscosity activation energy on the predicted low initial viscosity. (*) experimental results; (– –) theoretical predictions by the four-parameter model [eq. (1)] and Keenan's model [eq. (9)]; (—) theoretical predictions by the developed five-parameter model [eq. (6)].

tion method. From the starting linear region of the isothermal viscosity curves, ΔE_η can be obtained through extrapolation to the reaction time of 0 min, but the starting region of the isothermal viscosity curve doesn't always change regularly and there may be some curing reaction taking place before the isothermal hold temperature is achieved, if the isothermal hold temperature is high. It is evident that the extrapolated results from these curves is unreliable. The second method is the Arrhenius method. Equation (1) can be rewritten as

$$\eta(T, t) = \eta_o \cdot \exp(kt) \tag{9}$$

where

$$\eta_o = \eta_\infty \cdot \exp(\Delta E_\eta / RT)$$

$$k = k_\infty \cdot \exp(-\Delta E_k / RT)$$

For each isothermal viscosity profile, a pair of η_o and k can be determined. Then, the constant η_∞ and ΔE_η can be calculated from the Arrhenius plot of $\log \eta_o$ versus $1/T$. The third method to determine the flow viscosity activation energy ΔE_η for a thermosetting system, named the non-linear curve fitting method, was developed by Eley [12]. The latter two methods give pure mathematical fitting results, and the occurrence of error when the pure fitted results are used in the five-parameter model is not surprising. The parame-

ters of the four-parameter model and in Keenan's model for the E-PEK/DDS system were all determined by the Arrhenius method. The comparison (Fig. 13) of the predicted viscosity profiles at the initial stepwise lowering, calculated from Keenan's (the same as the four-parameter model) model and our suggested five-parameter model, respectively, and the experimental results (Fig. 12), show that the flow viscosity activation energy obtained from our method is more accurate.

CONCLUSIONS

The two reported chemorheological models, i.e., the four-parameter model and the modified WLF model, have been used for an E-PEK/DDS system. It is found that, for this reaction system, the first model is only suitable for an isothermal process, and the second one only for a nonisothermal process. Neither of them can be used for stepwise temperature cure cycles, which are actually the cure cycles used in composite manufacture.

A new combined chemorheological model has been developed. It is combined with the four-parameter model and modified WLF model. The combined model can be used to predict the resin viscosity variation during a stepwise temperature cure cycle.

A new five-parameter chemorheological model for the E-PEK system has been developed. The parameters in the model can be determined through very few rheology and DSC experiments. The parameters η_∞ and ΔE_η were determined from the starting region of a nonisothermal viscosity curve. The isothermal and nonisothermal curing reaction kinetics parameters, determined by isothermal DSC and nonisothermal DSC, were directly introduced into the model. A proportionality factor ϕ was introduced into the integration part of the equation, which was determined by the comparison of viscosity variation predicted with different values of ϕ with the experimental results for a nonisothermal process. The five-parameter chemorheological model thus obtained can predict the resin viscosity variation in isothermal, nonisothermal, and especially stepwise temperature cure cycles accurately. The new five-parameter model has also successfully been used in the E-PEK systems with two other curing agents, i.e., diamine curing agent with addition of boron trifluoride ethylamine ($BF_3 \cdot MEA$) accelerator and an anhydride curing agent, hexahydrophthalic anhydride.

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