

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

IV. Cure Cycle Simulation

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ABSTRACT: Epoxy-terminated poly(phenylene ether ketone) (E-PEK) developed in this Institute is a candidate matrix resin for polymer composites as structural materials. Cure cycles for this reaction system were simulated according to the previously established processing model. It is found that for the E-PEK system, the curing process is best completed by a stepwise cure cycle comprising two isothermal processes at different temperatures, T_1 and T_2 . The cure cycles over a wide range of processing parameters simulated, based on the established processing model, indicate that the processing window is width-adjustable. Analysis of the mechanical properties of the composite sheets showed that the simulated cure cycles are acceptable and reliable. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1751–1757, 1997

Key words: model and simulation; cure cycle; epoxy; poly(phenylene ether ketone); composite

INTRODUCTION

Recently, computer-aided modeling and processing simulation techniques have demonstrated appreciable potential in fabrication of thermosetting composites, especially in the cure cycle design.^{1–6} As a result, the amount of experimentation necessary for a cure cycle design can be minimized. Eventually, this leads to reduce manufacturing costs, shorter lead time, and improved control and prediction of the properties of the finished product.

The authors have studied the curing process of

the epoxy-terminated poly(phenylene ether ketone) (E-PEK) system and established four cure processing submodels, i.e., curing reaction kinetics, reaction limit,⁷ chemorheology,⁸ and applying pressure submodels.⁹ In this article, the fourth in this series, the cure cycles for the manufacture of continuous carbon-fiber-reinforced epoxy-terminated poly(phenylene ether ketone) were simulated based on the previously established four curing processing submodels. Practicality and reliability of the simulated cure cycles were evaluated through characterization of mechanical properties of the composite sheets fabricated according to the simulated cure cycles.

EXPERIMENTAL

Continuous carbon fiber prepreps used in this work were made from T300–(E-PEK–DDS).

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Table I Input and Output Data of the Program for Cure Cycle Simulation of the E-PEK-Based Composite

Input Data	Output Data
(1) Curing temperature cycle (a) heating rate; (b) isothermal temperatures and holding time. ^a	(1) Curing reaction rate and reaction content at any time of the cure cycle.
(2) Reaction kinetics parameters ^b (a) reaction order; (b) reaction activation energy; (c) preexponential factor.	(2) Viscosity variation with temperature and time during any cure cycle.
(3) Five-parameter chemorheological model ^c ($\eta_{\infty} = 4.53\text{E}-17 \text{ Pa}\cdot\text{s}$; $\Delta E_{\eta} = 146 \text{ kJ/mol}$; $\phi = 1.4$) ^d (a) isothermal process ($K_{\infty} = 21.98 \text{ s}^{-1}$; $\Delta E_k = 36 \text{ kJ/mol}$); (b) nonisothermal process ($K_{\infty} = 6.09\text{E}10 \text{ s}^{-1}$; $\Delta E_k = 119 \text{ kJ/mol}$).	(3) The optimal cure cycle, including heating rate, first and second isothermal temperatures, and corresponding holding time; time of pressure application; and postcure conditions.

^a The selection of (a) and (b) is arbitrary.^b Tables I and II in Wang et al.⁷^c Equation (7) in Wang et al.⁸

This E-PEK resin and curing agent, 4,4'-diaminodiphenyl sulfone (DDS), have been previously described in the first article of this series.⁷ T300 carbon fiber was used as reinforcement.

Impregnation of the carbon fiber was performed on a small-scale winding machine. Carbon fiber was continuously passed through the impregnation solution made from E-PEK dissolved in acetone, then through two metering bars to remove excess resin. After the prepregs were taken from the roller, they were put in an oven to evaporate most of the solvent at about 413 K. The prepregs were then stored under 248 K to prevent premature curing reaction. Before use, the prepregs were vacuum-dried for four hours (313 K).

Cure cycles were simulated using our program based on the previously established processing submodels. The input and output data of the program for cure cycles simulation are listed in Table I.

All laminate specimens, 50 by 60 mm, were prepared by stacking 10 layers of prepregs together. Laminates were molded under compression. Practicality and reliability of the simulated cure cycles are evaluated through mechanical properties characterization of composite sheets fabricated by the simulated cure cycles. The mechanical properties of composites, interlaminar shear strength, flexural strength, and modulus measurement were carried out according to ASTM D-2344, ASTM D2733-70, and ASTM D790-81. The interlaminar fracture toughness

measurement was carried out according to the procedure reported in He and Zhou.¹⁰

RESULTS AND DISCUSSION

There are three basic processing parameters for the cure processing of thermosetting composites, i.e., temperature, pressure and reaction time. The effect of them should all be considered when simulation is carried out to determine cure cycles.¹ To simulate a practical cure cycle, it is better at first to get a glimpse at the essential requirements for a cure cycle and the information that each submodel could give. The cure processing of a thermosetting composite is a complex physiochemical process in which curing reaction and resin flow take place at the same time. Generally, the curing process is accomplished by exposing the materials to a certain temperature and pressure for a predetermined length of time. A proper cure cycle has to meet some major requirements, as follows, in manufacturing and quality control of the finished composite products: (1) to make the resin uniformly and completely cured; (2) to yield cured composites with as low a void content as possible and an optimal fiber volume fraction; and (3) to have the curing process complete in as short a time as possible.

To fulfill the above requirements, the main target of processing simulation of the E-PEK-DDS system is to determine the time of pressure appli-

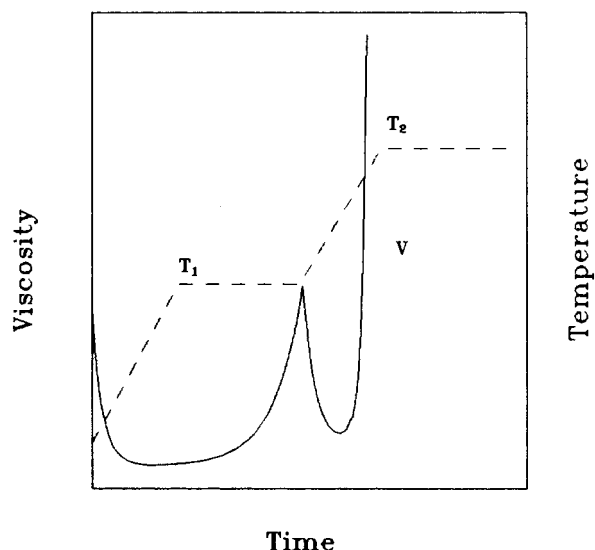


Figure 1 Schematic of stepwise cure cycle and viscosity variation during such a cure process.

cation and the total curing time based on the analysis of the effect of changing temperature and time on the viscosity variation, reaction rate, and extent of reaction. Considering the requirements in industry, the pressure applied, 0.6 MPa, was chosen as a constant.

It is found that the stepwise cure cycle, as shown in Figure 1, which is widely used in the manufacture of thermosetting composites and includes both isothermal and nonisothermal processes, is suitable for the manufacture of E-PEK-based composite.⁹ As shown in Figure 1, there are two viscosity valleys associated with temperature during such a stepwise cure cycle. The first one is the result of competition between viscosity reduction, due to resin melting, and viscosity increase, due to resin reaction. Although this first viscosity valley could be considered as an opportunity to apply pressure, a relatively rapid increase in viscosity around this valley area narrows processing window. The second viscosity valley arises from the second nonisothermal process, the width of which can be manipulated through controlling the preceding isothermal process. The width-adjustable second viscosity valley provides a suitable pressure window. Analysis of the effect of reinforcement fraction and defect content on the quality of the composite sheets indicates that a viscosity ranging from 400 to 1200 Pa·s at the second viscosity valley is an acceptable region to apply pressure.⁹ Therefore, the purpose of the first isothermal process (T_1) is to provide a wider processing window for pressure application; that of

the second isothermal process (T_2) is to make the resin completely cured in a shorter time. The total curing time is dependent on these two isothermal processes. The softening point of E-PEK is about 378 K, and gelation would occur at about 498 K in a nonisothermal (2.5 K/min^{-1}) process. It seems that the temperature range from 383 K to 498 K can be chosen as the processing region; but the resin viscosity changes with temperature too quickly at high temperatures, which would make control of applying pressure difficult. Conversely, the curing rate is very low at low temperatures. Thus, the first isothermal temperature (T_1) can be selected from the range of 403 K to 453 K. Under the assumption that the cure is complete when the extent of reaction is 0.9 at all points of the composite,¹ the second isothermal temperature can be selected from 473 K to 513 K because the reaction limit submodel⁷ reveals that such an extent of reaction can be achieved if the isothermal temperature is higher than 473 K.

The change in viscosity associated with varying the first isothermal temperature and varying the holding time at those isothermal temperatures, is simulated (the heating rate at nonisothermal process is chosen as 2.5 K/min^{-1} to meet the requirement in industry) based on the previously established five-parameter chemorheological model [eq. (1)]⁸ and the applied pressure submodel⁹ to determine the time of pressure application.

$$\ln \eta(T, t) = \ln \eta_{\infty} + \frac{\Delta E \eta}{RT} + \varphi \int K_{\infty} \cdot \exp(-\Delta E/RT) dt \quad (1)$$

The change in viscosity associated with varying the first isothermal temperature for same holding time of 50 min is shown in Figure 2. As seen from the viscosity curves in Figure 2, the viscosity at the second viscosity valley increases rapidly with the first isothermal temperature. The change in viscosity, associated with various holding time at the first isothermal temperature of 453 K, is simulated in Figure 3. As seen from Figure 3, the viscosity at the second viscosity valley increases with holding time; and the viscosity range of 400 to 1200 Pa·s is located in the area of the second viscosity valley, corresponding to a holding time of from 37 to 43 min. The processing window for pressure application at different first isothermal temperatures (T_1) is displayed in Figure 4. Pressure must be applied in this critical time-temperature band to achieve a void-free laminate with

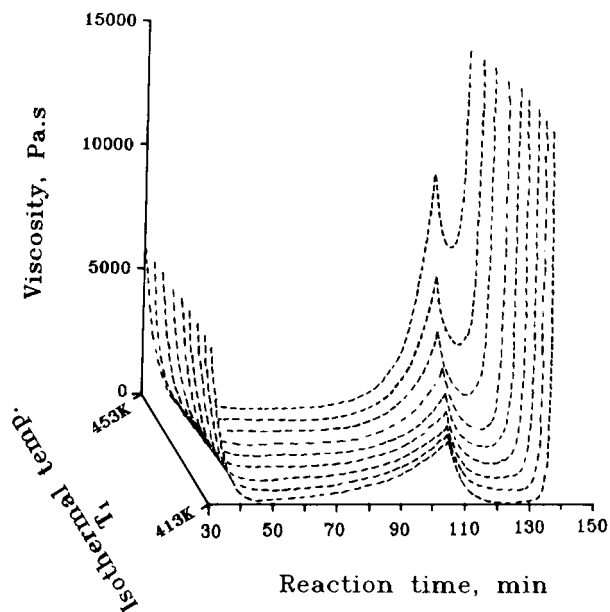


Figure 2 The change in viscosity associated with various first isothermal temperatures (T_1) at the same holding time of 50 min, calculated by eq. (1).

an optimal resin-fiber ratio. Correlation of the total curing time (t_{tol}) versus different first and second isothermal temperatures (T_1 and T_2) are

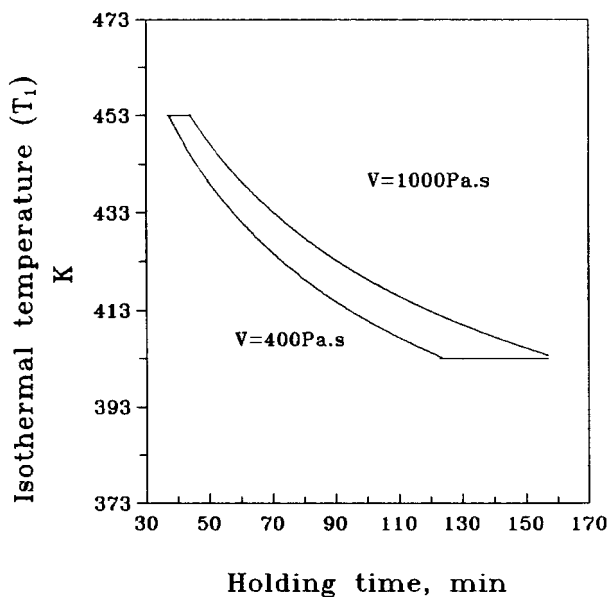


Figure 4 Processing window for pressure application at different first isothermal temperatures (T_1).

simulated (Fig. 5), based on the previously established reaction kinetics submodel.⁷ The total curing time decreases with an increase in the first and second isothermal temperatures.

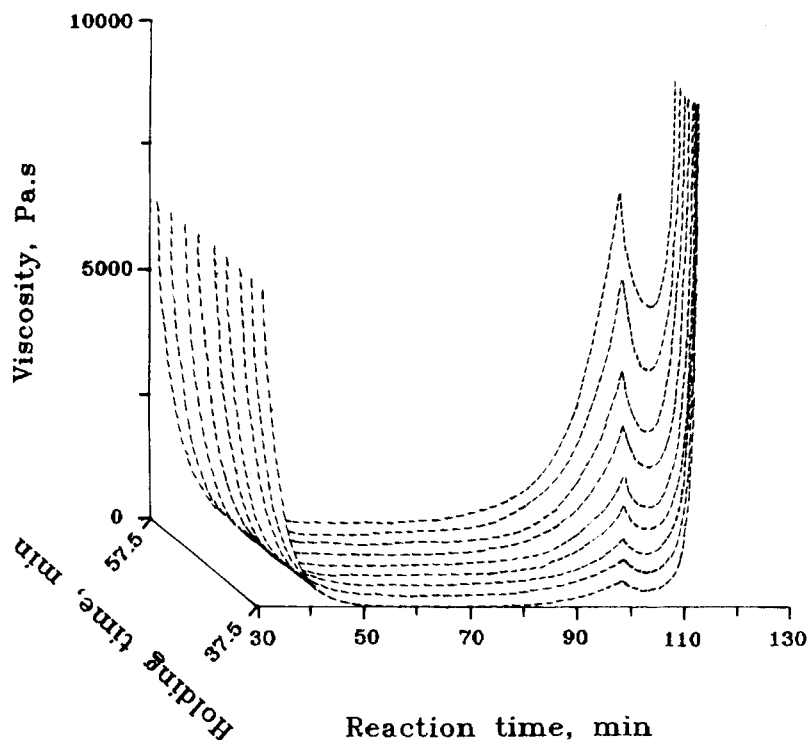


Figure 3 The change in viscosity associated with various holding times at the same first isothermal temperature (T_1) of 453 K, calculated by eq. (1).

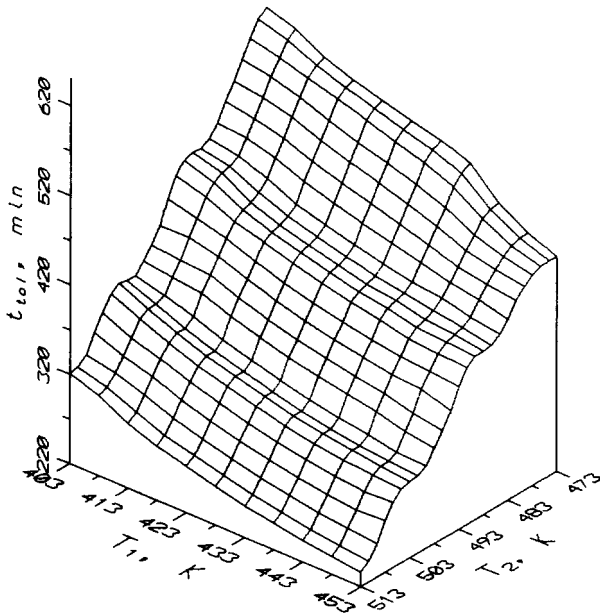


Figure 5 Predicted correlation of the total curing time (t_{tot}) versus different first and second isothermal temperatures (T_1 and T_2).

Twelve composite sheets were prepared according to the simulated cure cycles in Figures 4 and 5. As seen from the data listed in Table II, the interlaminar shear strength of the composite sheets does not change significantly with the isothermal temperatures. The standard deviation of interlaminar shear strength of composite sheets, however, increases with the second isothermal temperatures. This means that the first isother-

mal temperature mainly affects the resin flow, providing little effect on the interlaminar shear strength of the composite when there is enough resin flow. The second isothermal temperature mainly affects the uniformity of the composite and would result in composites with nonuniform quality, even at as high a temperature as 513 K. There is a temperature region, outlined in Table II, which is the acceptable processing window. Although temperatures on the left side of the region would also give higher interlaminar shear strength of the composite, the total curing time is too long (longer than 500 min) and lowers the productivity. And although, within the right side of this region, the curing process can be completed in a very short time (shorter than 300 min), the standard deviation of interlaminar shear strength would be very large, inferring nonuniformity in quality of the composite. Therefore, the cure cycles in the outlined area are all acceptable processing conditions; and for both productivity (total curing time) and high quality (uniformity of the finished products), the shaded area in the outline, i.e., at $T_1 = 423$ to 438 K, $T_2 = 488$ to 503 K, a total curing time of 326–465 min, and the viscosity range suitable for applying pressure from 400 to 1200 Pa · s, is the most promising processing window. The mechanical properties of the composite sheets fabricated by the processing conditions of the left upper corner in the shaded area in Table II are listed in Table III. As seen from the data listed in Table III, the interlaminar fracture toughness (G_{IC}) of E-PEK-based composite is 428

Table II Interlaminar Shear Strength (MPa) and the Standard Deviation (%) of the Composite Sheets Fabricated According to the Simulated Cure Cycles with Different T_1 and T_2

T_1 (K)	T_2 (K)			
	473	488	503	513
408	89 (±5%)	89 (±6%)		
423	82 (±5%)	88 (±6%)	86 (±7%)	81 (±19%)
438	87 (±5%)	89 (±8%)	87 (±7%)	79 (±19%)
453			82 (±9%)	81 (±19%)

* The outlined area is discussed in the text.

Table III Mechanical Properties of the Composite Fabricated According to the Simulated Cure Cycle ($T_1 = 423$ K, $T_2 = 473$ K)

Interlaminar shear strength (MPa)	
RT^*	88
393 K	46
Flexural strength (MPa)	
RT	1526
393 K	1052
Flexural modulus (GPa)	
RT	103
393 K	109
Interlaminar fracture toughness G_{IC} (J/m^{-2})	423

* Room temperature.

J/m^{-2} , which indicates good toughness compared with conventional epoxy-based composites, such as T300/5208 with $G_{IC} = 93 J/m^2$,¹¹ AS4/Epon828 with $G_{IC} = 390 J/m^2$,¹² and IM6/F584 with $G_{IC} = 372 J/m^2$.¹³ The general mechanical properties of the E-PEK-based composite are similar to those of widely used composites obtained from matrix epoxy resin; but its interlaminar fracture toughness is significantly high due to the fact that the E-PEK has a special chain structure different from the other epoxy resins.

In order to evaluate whether the post-cure process is necessary or not, composite samples obtained from the previously prepared twelve composite sheets were put in an oven to provide the same post cure process, i.e., heated from room temperature to 473 K and 493 K with 1 h hold, respectively; and then to 513 K, holding for 2 h; and then cooled down. The interlaminar shear strength of the post-cured composite samples were also measured. According to the simulation, the extent of the curing reaction of the resin in-

creases less than 2%; but, as seen from the data listed in Table IV, the interlaminar shear strength of the composite sheets increases after post curing; at the same time, the standard deviation for the interlaminar shear strength decreases. This means that the post-cure process is able to increase the interlaminar shear strength and lower the residual thermal stress and shows that the post-cure process has to be considered during the cure cycle simulation.

CONCLUSIONS

Based on the previously established curing processing model, cure cycles of continuous carbon-fiber-reinforced E-PEK were simulated. It was found that a stepwise temperature cure cycle, which includes two isothermal processes, was suitable for an E-PEK system. The holding time at the first isothermal temperature (T_1) determines the resin fluidity at the pressure application, and the second isothermal temperature (T_2) determines the cure uniformity. The simulated cure cycles, with processing parameters over a wide range, indicates that the processing window is width-adjustable, which is of great significance in actual application. The analysis of the interlaminar shear strength of the fabricated composite sheets indicates that the simulated stepwise cure cycles, in which the first and second isothermal temperatures range from 423 K to 438 K and 488 K to 503 K, respectively, with total curing time ranging from 326 to 465 min, and with the most suitable viscosity in the region of 400 to 1200 Pa·s to apply pressure are the most promising processing window. The simulation method is not only able to yield practicable and reliable cure

Table IV Effect of the Postcure Process on the Interlaminar Shear Strength (MPa) and the Standard Deviation (%) of the Composite Sheets

T_1 (K)	T_2 (K)			
	473	488	503	513
408	95 ($\pm 9\%$)	93 ($\pm 1\%$)		
423	91 ($\pm 6\%$)	94 ($\pm 4\%$)	91 ($\pm 4\%$)	85 ($\pm 15\%$)
438	90 ($\pm 6\%$)	92 ($\pm 2\%$)	93 ($\pm 5\%$)	94 ($\pm 2\%$)
453			85 ($\pm 4\%$)	83 ($\pm 6\%$)

cycle but also leads to reduced manufacturing costs and minimizes the amount of experimentation necessary for cure cycle development.

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