Cure Processing Modeling and Cure Cycle Simulation of Epoxy-Terminated Poly(phenylene ether ketone). III. Determination of the Time of Pressure Application

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ABSTRACT: The curing temperature, pressure, and curing time have significant influence on finished thermosetting composite products. The time of pressure application is one of the most important processing parameters in the manufacture of a thermosetting composite. The determination of the time of pressure application relies on analysis of the viscosity variation of the polymer, associated with curing temperature and curing time. To determine it, the influence of the time of pressure application on the physical properties of epoxy-terminated poly(phenylene ether ketone) (E-PEK)-based continuous carbon fiber composite was studied. It was found that a stepwise temperature cure cycle is more suitable for manufacture of this composite. There are two viscosity valleys, in the case of the E-PEK system, associated with temperature during a stepwise cure cycle. The analysis on the effects of reinforcement fraction and defect content on the composite sheet quality indicates that the width-adjustable second viscosity valley provides a suitable pressing window. The viscosity, ranging from 400 to 1200 Pa·s at the second viscosity valley, is the optimal viscosity range for applying pressure to ensure appropriate resin flow during curing process, which enables one to get a finished composite with optimal fiber volume fraction and low void content. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1745–1750, 1997

Key words: epoxy; applying pressure; cure cycle; composite; computer modeling

INTRODUCTION

Processing modeling for the manufacture of a fiber-reinforced thermosetting composite is a new way to determine cure cycles and is a more efficient and economical approach than the traditional trial and error method. It is known that processing models can be classified generally as reaction kinetics, applying pressure, chemorheology, and thermal transfer submodels. The authors have studied the curing process of a novel epoxy resin, epoxy-terminated poly(phenylene ether ketone) (E-PEK). The establishment of mathematical models for this epoxy system, including curing reaction kinetics, reaction limit, and chemorheological submodels, have been reported earlier in this series of articles I and II.[1,2]

Manufacture of thermosetting composites is a complex physiochemical process in which curing reaction and resin flow take place at the same time. Two processing parameters have significant influence on the curing reaction and resin flow

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during the processing of a thermosetting composite, i.e., temperature and pressure. The crosslinking reaction is controlled by curing temperature through the curing reaction kinetics. Pressure is applied to compact the individual plies, to squeeze out the excess resin, to adjust the resin content, and to minimize the void content in the composite part.[3,4] For curing process simulation of the E-PEK system, a reaction kinetics model[1] can give information about the changes in both curing reaction rate and the extent of reaction associated with reaction temperature and reaction time. The chemorheological model[2] can predict the viscosity variation at different cure cycles. It is not possible to simulate the cure cycle for thermosetting processing based only on these two models because the effect of the applied pressure must be considered.

In this article, the third in this series, discussion will focus on the influence of the time of pressure application on the physical properties of composite sheets based on analysis of the viscosity variation.

EXPERIMENTAL

Continuous carbon fiber prepregs used in this work were made from T300–E-PEK–DDS (DDS is 4,4′-diamonodiphenyl sulfone). A novel E-PEK and curing agent DDS have been previously described in the first article of the series.[1] T300 carbon fiber was used as a 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–DDS 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 313 K. The prepregs were stored under 248 K until use to prevent premature curing reaction. Before use, the prepregs were vacuum-dried for four hours (313 K).

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 a 0.5 radian angle was used. The weight of samples used in these tests was about 0.25 g. The density, fiber volume fraction, and void content were measured according to ASTM D792-86, ASTM D3171-76, and ASTM D2734-70, respectively.

RESULTS AND DISCUSSION

There are no reliable criteria for determining the time of pressure application. Therefore, traditionally, it has been determined by experience. Research on the effects of varying processing temperature and pressure has been from many directions. Yokota[5] pointed out that whenever the curing temperature is lower or higher than a critical value, it will result in high void content. This is because the laminates cannot be degassed completely due to high resin viscosity at low temperature, and the resin will gel too rapidly to flow if the temperature is very high. Similarly, there is also a critical value for the applied pressure. Some authors suggested[6,7] that the fiber volume fraction of a composite does not increase with the applied pressure if the pressure is higher than the critical value and distortion and breakage of fiber occur. Harper et al.[4] studied the effects of varying processing temperature and pressure on the physical properties of composites; and an optimal range of curing pressure and temperature, which was defined as a processing window, was proposed. They found that the density of a composite increases with curing temperature to a maximum value then decreases. The flow of the matrix resin will be inhibited at low temperature due to high viscosity, resulting in laminates with lower fiber volume fraction, lower density, and higher void content. Similar phenomena occur at higher temperatures because there is not enough time to permit resin flow before gelation. There are linear relationships between density, fiber volume fraction, void content, and curing pressure.

In fact, appropriate resin flow is very important in the processing of a composite because the physical properties of the composite, such as fiber volume fraction, void content, and density, are very sensitive to the resin flow. The variations in these physical properties have significant influence on the mechanical properties of the composite. Most of the previous reports just focused on the effects of varying temperature and pressure during pure isothermal or nonisothermal curing processes. In most cases, actually, the pressure cannot be widely adjusted for industrial production. The time of pressure application, which is called the applying pressure window, is one of the most im-

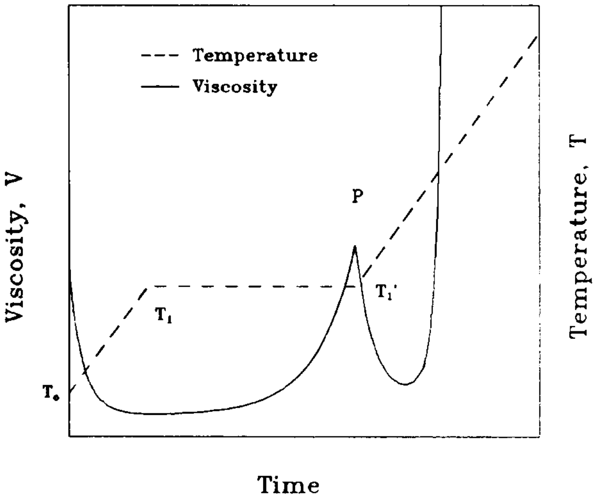

Figure 1 A typical schematic cure cycle of fiber-reinforced thermosetting composite.

portant processing parameters of the cure cycle. However, there is no detailed discussion on this parameter from the point of viscosity. The term applying pressure window means the most suitable viscosity range to apply pressure during a curing process. The resin flow is dependent mainly on the resin viscosity if the pressure is not changed. Therefore, determination of the time of pressure application has to rely on analysis of the resin viscosity variation during the cure process. The main target of this article is to investigate the range of viscosity value suitable to apply pressure.

For a low viscosity system, a so-called stepwise temperature cure cycle is widely used. Figure 1 shows a typical schematic stepwise temperature cure cycle, in which there are two isothermal processes. The viscosity variation during such cure cycle for the E-PEK–DDS system measured by a cone and plate rheometer is shown in Figure 1. The time of applying pressure in such a complex process is very important because the resin viscosity changes continuously. Whenever the pressure is applied at either too low or too high a viscosity, the manufactured composite will not be the best one. There are two viscosity valleys associated with temperature in the case of E-PEK/DDS. The first one is the result of competition between viscosity reduction, due to resin melting, and viscosity increase, due to advancing cure. Although this first viscosity valley could be considered as an opportunity to apply pressure, the relatively rapid increase in viscosity around this valley narrows the processing window. The second viscosity valley arises from the second nonisothermal process and is also due to the competition between the viscosity declining with temperature increase and the viscosity increase with cure. The width and the lowest point (V_L) of the second viscosity valley can be manipulated through controlling the preceding isothermal process. Therefore, the width-adjustable second viscosity valley supplies a suitable pressing window, and it is usual to apply pressure at the point p, as shown in Figure 1.

The fiber volume fraction, void content, and density of composite sheets, fabricated according to arbitrarily selected cure cycles, were chosen as reference criteria to evaluate the influence of the time of pressure application because these physical properties depend mainly upon the resin flow.

All laminate specimens 50 by 60 mm were prepared by stacking 10 layers of the prepregs together. Laminates were placed in a mold positioned between heated platens of a compression molding press, then cured with six different cure cycles. The cure cycles are shown in Figure 2. Considering the requirements in industry, the heating rate at the dynamic step of the cure cycles was chosen as 2.5 K·min^{-1}, and the chosen pressure applied was 0.6 MPa.

The resin fluidity at the second viscosity valley decreases with holding time (t_1) in the first isothermal process (423 K). The density of the composite decreases with increasing holding time at T_1 (Fig. 3). This is because the longer the isothermal holding time, the higher the resin viscosity. It is found that a higher fiber volume fraction would be obtained if the isothermal holding time

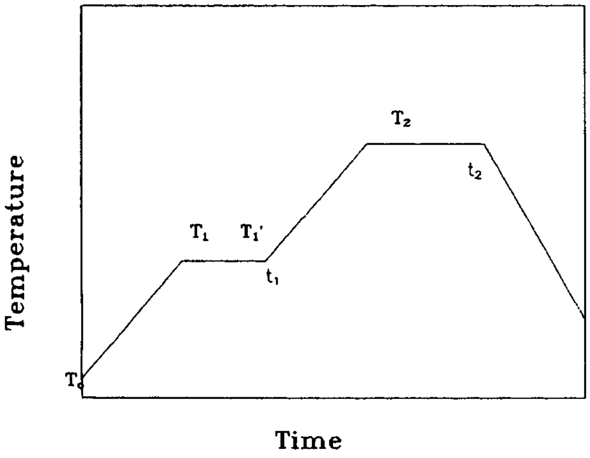

Figure 2 Cure cycle used in this work: T_0 = 298 K, T_1 = 423 K, T_2 = 473 K; t_1 = 15, 30, 45, 60, 75, 90 min. Heating rate at dynamic process is 2.5 K·min^{-1}.

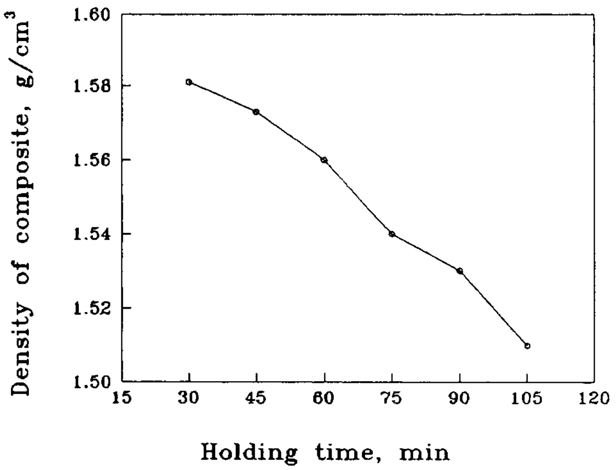

Figure 3 The relationship between the composite density and the holding time at the first isothermal process of cure cycle.

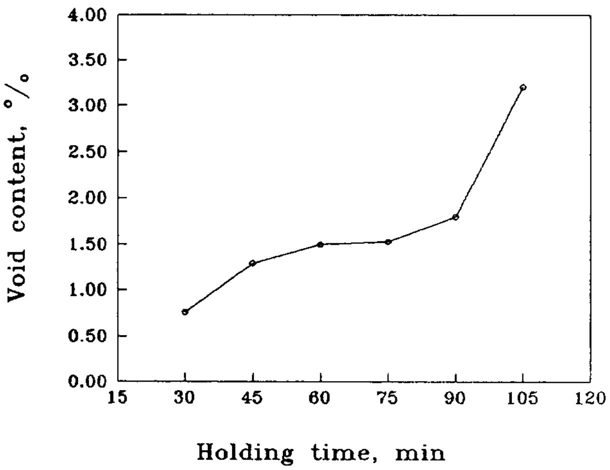

Figure 5 The relationship between the void content of composite and the holding time at the first isothermal process of cure cycle.

at the first isothermal process at 423 K is shorter than 45 min. This means that too much resin was squeezed out. On the contrary, lower fiber volume fraction is obtained when the isothermal holding time (t_1) is much longer than 45 min because the viscosity of the resin becomes so high that not enough resin flow takes place, resulting in higher resin content.

The change in fiber volume fraction has a similar relationship to the change in density (Fig. 4). As shown in Figure 5, however, the density decreases more quickly than that of the fiber volume fraction when the holding time (t_1) is longer than 45 min. This indicates that the density of the composite is affected more significantly by void content when the time of pressure application was set in the higher resin viscosity range. However, the relationship between void content and isothermal holding time (Fig. 6) is not similar to that between the density (or fiber volume fraction) and isothermal holding time. The reason is that there is not enough resin flow due to the viscosity increase, and less trapped gas bubbles off.

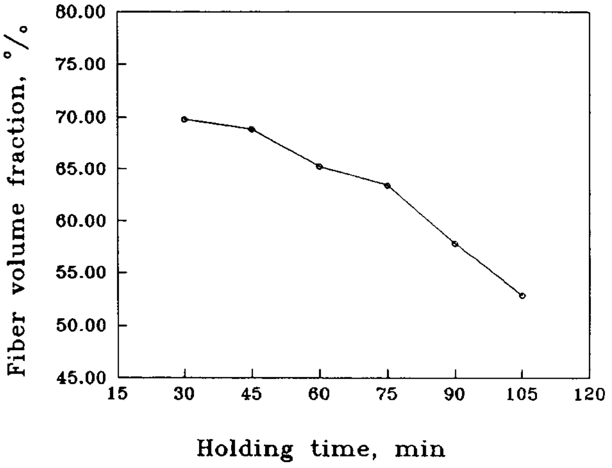

Figure 4 The relationship between the fiber volume fraction of composite and the holding time at the first isothermal process of cure cycle.

It is well known that the fiber volume fraction and void content have significant influence on the mechanical properties of composite. The optimal fiber volume fraction ranges from 57–63%, and the acceptable void content is lower than 2%. The relationships of fiber volume fraction and void content with isothermal holding time are compared in Figure 7. The dashed line area (Fig. 7) parallel to the X axis corresponds to the fiber volume fraction, ranging from 57–63%, and void content lower than 2%. It is found through comparison of Figures 4 and 6 that the optimal fiber volume fraction and the acceptable void content match as shown by the dark area in Figure 7. The viscosity range, associated with the holding time, and corresponding to the dark area, provides a good opportunity to determine the pressing window. Some of the experimentally measured viscosity profiles during different cure cycles are displayed in Figure 8. Figure 9 shows the relationship between the lowest point viscosity (V_L) of the second valley in the viscosity curve and the holding time at the first isothermal step. It is evident from Figures 7 and 9 that the optimal viscos-

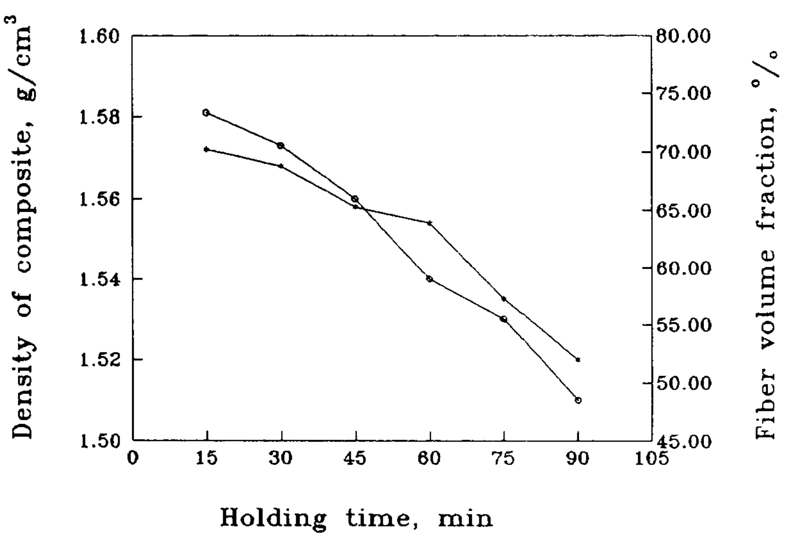

Figure 6 Comparison of the density with the fiber volume fraction of composite prepared from different cure cycles.

ity range for applying pressure is between 400 and 1200 Pa·s for the carbon-fiber-reinforced E-PEK. The viscosity range from 400 to 1200 gives a quantitative parameter, which is a very useful reference criterion for determining the time of pressure application.

CONCLUSIONS

The determination of the time of pressure application for the curing of thermosetting composites has to rely on the analysis of the resin viscosity variation associated with curing temperature. It is found that a stepwise temperature cure cycle is more suitable for the manufacture of carbon-fiber-reinforced epoxy-terminated poly(phenylene ether ketone). In the stepwise temperature cure cycle actually used, there are two viscosity valleys associated with temperature in the viscosity curve. The first one is the result of competition between viscosity reduction due to resin melting and viscosity increase due to the crosslinking reaction. Although this first viscosity valley could be considered as the point of pressure application, the relatively quick increase in viscosity around this valley narrows the processing window. The second viscosity valley arises from a second dynamic process. Width of the second valley can be

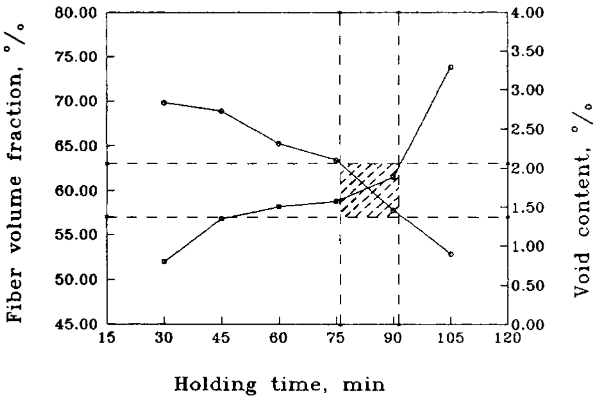

Figure 7 Comparison of the fiber volume fraction with the void content of composite. The dark area corresponds to the optimal range of fiber volume fraction and the acceptable void content.

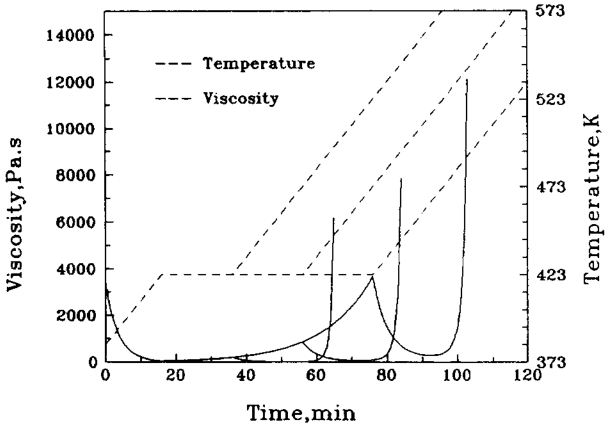

Figure 8 Some of the experimental measured viscosity profiles during cure cycles.

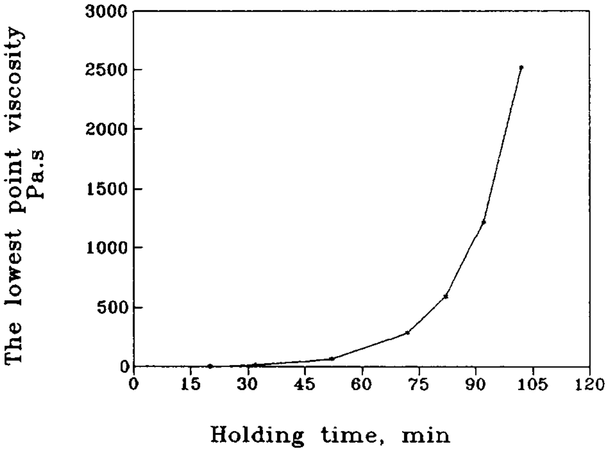

Figure 9 The relationship between the lowest viscosity during the second dynamic process and the holding time at the first isothermal step.

manipulated through controlling the preceding isothermal process. Therefore, the width-adjustable second viscosity valley provides a suitable processing window. Analysis on the effect of fiber volume fraction, void content, and density on composite sheet quality indicates that viscosity ranging from 400 to 1200 Pa · s at the second viscosity valley (V_L) is an acceptable range to apply pressure.

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