Equivalent Processing Time Analysis of Glass Transition Development In Epoxy/Carbon Fiber Composite Systems

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ABSTRACT: The cure kinetics and glass transition development of a commercially available epoxy/carbon fiber prepreg system, DMS 2224 (Hexel F584), was investigated by isothermal and dynamic-heating experiments. The curing kinetics of the model prepreg system exhibited a limited degree of cure as a function of isothermal curing temperatures seemingly due to the rate-determining diffusion of growing polymer chains. Incorporating the obtained maximum degree of cure to the kinetic model development, the developed kinetic equation accurately described both isothermal and dynamic-heating behavior of the model prepreg system. The glass transition temperature was also described by a modified DiBeneditto equation as a function of degree of cure. Finally, the equivalent processing time (*EPT*) was used to investigate the development of glass transition temperature for various curing conditions envisioning the internal stress buildup during curing and cooling stages of epoxy-based composite processing. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 144–154, 2002; DOI 10.1002/app.10282

Key words: epoxy; carbon fiber; composite; glass transition temperature; residual stress; equivalent time; curing kinetics

INTRODUCTION

The kinetic characterization of thermoset resins is usually required to understand structure–property–processing relationships for high performance composite manufacturing and utilization. In particular, the cure kinetics of commercialized B-staged resins and prepregs are usually required for their process and quality control purposes. However, it should be mentioned that the quantitative kinetic descriptions of commercial prepreg systems are not very well predicted from the chemical nature of the resin and functional constituents usually due to various side and coupled reactions. Curing reactions of thermosetting polymers are often so complex that detailed kinetic information is collectively obtained by incorporating various analysis techniques such as differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and Fourier transform infrared (FTIR).[1–8] For general purposes of thermoset polymer utilization, the DSC kinetic analysis has been efficiently utilized in both isothermal and dynamic-heating conditions for quick screening tests of material performance and durability as well as in determining processing windows of reacting systems.[5,9–12]

In the curing of thermosetting resins, two different rate-determining stages are often ob-

served.[5,9] In the early stage of reactions, the reaction rate is often chemically controlled and thus depends on the concentration of unreacted monomers. As the polymer chain grows longer, the rate of curing reaction is increasingly affected by the diffusion rate of unreacted monomers and/or unreacted functional groups attached to growing polymer chains. This diffusion control typically becomes dominant near the glass state of polymers as T_g approaches T_{cure} with the progress of cure reactions. When $T_g \approx T_{cure}$, the polymer chains are subsequently vitrified and the diffusion rate becomes all but negligible.[13–15]

According to Matsuoka et al., the diffusion-limited processes may affect the cure kinetics as well as ultimate properties of cured thermosetting polymers.[16] Specifically, the ultimate properties of thermosetting polymers are mainly attained in the final stage of cure when the crosslinking reaction rates are limited by the diffusion of the molecular species in the resin systems. To optimize the processing conditions, it is of practical importance to quantitatively describe the cure-dependent diffusion phenomena.[17] Several kinetic models have been developed to incorporate both kinetic-controlled and diffusion-controlled stages of thermoset cures.[7,16–18] In particular, Kenny et al. (1991) has presented a phenomenological approach for modeling the diffusion-rate controlled curing of epoxies, and this model was adopted in this study through appropriate modifications for the prediction of the kinetic behavior of our model epoxy prepreg system.[9]

As with most thermoset systems, the internal stresses of high performance epoxy-based composites are usually evolved during curing as well as cooling stages, which often result in part warpage, void formation, and interply delamination. During curing by dynamic-heating and isothermal holding stages, the internal stresses are induced by matrix cure shrinkage in the geometrically constrained conditions by fibers, inserts, and tool surfaces.[19–22] In addition, internal stresses are known to develop during cooling stages due to the thermal shrinkage and thermal expansion mismatch of the anisotropic and heterogeneous constituents of composite laminates as well as among the part and the tooling materials. During the composite curing process, the glass transition temperature (T_g) increases by the progress of resin curing as a function of temperature (T_{cure}) and time. The thermal history of the difference between cure temperature and glass transition temperatures ($T_{cure} - T_g$) may be regarded as a significant factor in determining the residual stresses and consequently the final structural stability of the cured laminate parts.

The epoxy-based systems may be cured far above or close to the glass transition temperature resulting in different states of residual stress residing in the final structural part. When T_{cure} is maintained far higher than the glass transition temperature (T_g) during epoxy cure, it may be reasonable to consider that the internal stress developed by cure shrinkage could be easily released because the mobility of the growing polymer chain is maintained high. In this case, the resulting internal stress seems to be mostly developed during cooling stage, where the operating temperature (T^{cure}) becomes lower than the ultimate glass transition temperature. On the other hand, when T_{cure} is controlled to be close or below T_g during curing reactions, the curing epoxy may incidentally be gelled and vitrified during cure processing, and thus the internal stress may be fixed in the laminates due to the limited mobility of frozen polymer chains. Even in this case the internal stress is also evolved during the cooling stage, when T_{cure} decreases to be lower than $T_{g\infty}$. Overall, the internal stress is closely related to the difference between T_g and T_{cure} during curing as well as cooling stages. Consequently, it may be important to estimate the development of the glass transition in correlation to the curing conditions of temperature and time, which subsequently results in the residing internal stress distribution of the final structure. It should also be mentioned that the development of T_g as a function of T_{cure} usually depends on kinetic characteristics, thermodynamic nature, and specific curing conditions, which are usually composed of several dynamic heating, cooling and isothermal-holding conditions.

In this study, a commercially important epoxy/carbon fiber composite prepreg system, DMS 2224, was chosen as a model system for the study of the diffusion-controlled cure kinetics and the development of glass transition temperature in dynamic/isothermal heating conditions. The equivalent processing time (EPT) was used to investigate the deviation of the glass transition temperature from curing temperature for various curing conditions envisioning the internal stress buildup during curing as well as cooling stages of epoxy-based composite processing.

EXPERIMENTAL

The material investigated in this study was a widely used commercial prepreg system, woven Hexel W3L282/F584 (DMS 2224), which is a 350°F-curable high performance composite prepreg system.[23] The basic formulation of the matrix resin contains popular 350°F curable triglycidyl diaminodiphenyl methane (TGDDM)/diaminodiphenyl sulfone (DDS) with 41% resin content and 193 g/m^2 fiber areal weight. The prepreg is very commonly used for both primary and secondary structural applications in commercial airplanes. Further details on this prepreg system may be found elsewhere.[23]

DSC experiments were performed by TA Instruments DSC 910. Isothermal and dynamic-heating experiments were conducted in a flowing N$_2$ environment using prepreg samples of 7.0 ± 1.0 mg size. For isothermal experiments, the DSC cell was preheated to the experimental temperatures (cure temperature) at 155, 160, 170, 180, 190, and 200°C. Then the sample pan was quickly placed in the DSC cell. Dynamic-heating experiments were performed at various heating rates at 1, 2, 5, 10, and 20°C/min from 25 to 350°C.

The glass transition temperature of the partially cured samples at different isothermal condition was determined under a constant heating rate of 10°C/min. For the specimens over 60% of conversion, the glass transition was obliterated by the exothermic peak of cure. In this case, the glass transition temperature was measured by TA Instruments Modulated DSC (MDSC), which is an extension of conventional DSC and provides information about the reversing and nonreversing characteristics of thermal events.[24] In the MDSC, a rapid heating-rate oscillation was added to a conventional linear temperature ramp or timed isothermal period. A Fourier transform deconvolution process is then used to separate the resultant total heat flow signal into reversing, nonreversing and heat capacity components. This additional information desirably aids interpretation of such systems as our curing thermosets in the vicinity of glass transition. The MDSC experiments were performed at a heating rate 5°C/min.

RESULTS AND DISCUSSION

Isothermal Kinetic Analysis

The reaction rate of thermoset polymers may be expressed as a function of conversion (α) and temperature (T) in a separable form, viz.,[5,10–12,25,26]

Table I   Heat of Reaction and Maximum Degree of Cure Obtained in Isothermal Cure Conditions

Temp. (°C)	$H(t)$ (J/g)	Maximum Degree of Cure (α_m)[a]
155	78.08	0.5185
160	98.51	0.6541
170	123.2	0.8183
180	126.3	0.8765
190	138.8	0.9220
200	148.4	0.9858

[a] Based on $H_T = 150.6$ J/g obtained by dynamic heating at 10°C/min.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (1)$$

where $f(\alpha)$ is a conversion-dependent function and $k(T)$ is rate constant as defined by the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \qquad (2)$$

where A is the preexponential constant, E is activation energy, and R is gas constant.

The total heat of reaction and the maximum degree of cure obtained at various isothermal temperatures are summarized in Table I. The area under the DSC cure corresponds to the total heat of reaction at the isothermal reaction temperatures. The heat of curing distinctively increases with the curing temperature, which should be accounted for in modeling cure kinetics and glass transition development. In this isothermal curing, the conversion (degree of cure) may be defined as the heat of generation normalized by the total heat of reaction up to a specific time, viz.,

$$\alpha = \frac{H(t)}{H_T} \qquad (3)$$

where $H(t)$ is heat of reaction as a function of time and H_T is total heat of cure. The reaction may be regarded as being finished when the exothermic curve levels off to the baseline. The total heat of cure (H_T) used for the normalization of isothermal heat of cure was $H_T = 150.8$ J/g obtained from the total area under the dynamic heating DSC curve at a heating rate of 10°C/min.
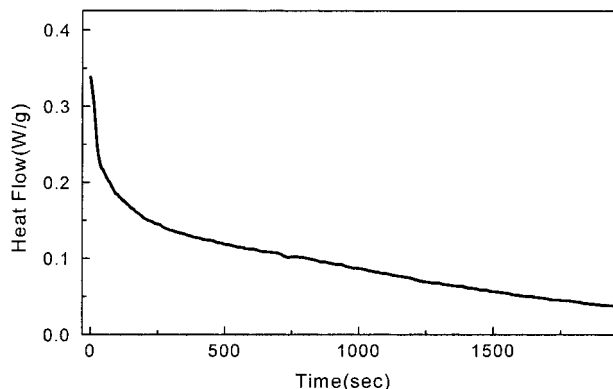
Figure 1 Isothermal DSC thermogram of epoxy/carbon fiber DMS 2224 prepreg at 190°C.

Figure 1 shows an isothermal DSC thermogram expressed showing the rate of heat generation as a function of time at 190°C. As can be seen, the rate of heat generation exhibits a maximum at the beginning of reaction, i.e., at $t = 0$, and gradually decreases with time. Such a decelerating-rate characteristic of exothermic reaction may be expressed by an nth-order reaction, viz.,

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \qquad (4)$$

where n is reaction order. Complete reviews on the kinetic characterization of epoxy systems by using different models and techniques can be found elsewhere.[5,10–12]

As also seen in Figure 2, the maximum degree of cure, which can be attained at each isothermal temperature, increases and tends to approach 1.0 as the isothermal cure temperature increases. As mentioned earlier, isothermal curing of thermoset systems may go through two curing stages affected by chemical activity of reacting groups and physical mobility of polymer chains. In most thermosetting systems, the curing reaction proceeds in liquid state when the T_g of the B-staged system is usually lower than the curing temperature (T_{cure}). In this stage, the apparent reaction rate is determined by the reactivity of unreacted monomers until the T_g approaches T_{cure}. When $T_g \approx T_{cure}$, the second stage of curing may be considered to commence. In this temperature region, the polymer chains vitrify and the reaction rates decrease considerably due to the fact that mobility of the reacting groups becomes very restricted.[5] The reaction time to reach $T_g \approx T_{cure}$ is often called the vitrification of thermoset systems.[3,5]

When the system reaches the glass state by vitrification, the overall reaction rate is considered to be controlled by the diffusion rate of unreacted groups in polymer chains. The slow segmental motions caused by the structural relaxation of polymer chains are the only ones permitted in glass-state polymers, and the degree of cure often tends to exhibit a practically constant limiting value, thus preventing the full conversion of cure reaction.[27,28]

As shown in Figure 2, it seems evident that the curing reactions are restricted by the mobility of polymer chains in isothermal conditions. There have been several modifications of kinetic models in order to express the diffusion limitation of reacting polymer chains. For example, the reaction constants have been assumed as a function of conversion and temperature, and then the overall reaction rate has been expressed as[17,27,29]

$$\frac{1}{k_a(\alpha, T)} = \frac{1}{k_T(T)} + \frac{1}{k_d(\alpha, T)} \qquad (5)$$

where k_a is the overall rate constant, k_T is the Arrhenius rate constant of the chemical reaction, and k_d is the diffusion-controlled rate constant. Consequently, the overall rate constant (k_a) and the diffusion-controlled rate constant (k_d) are assumed to be functions of both temperature and conversion, whereas the chemically controlled Arrhenius rate constant is the function of temperature only.

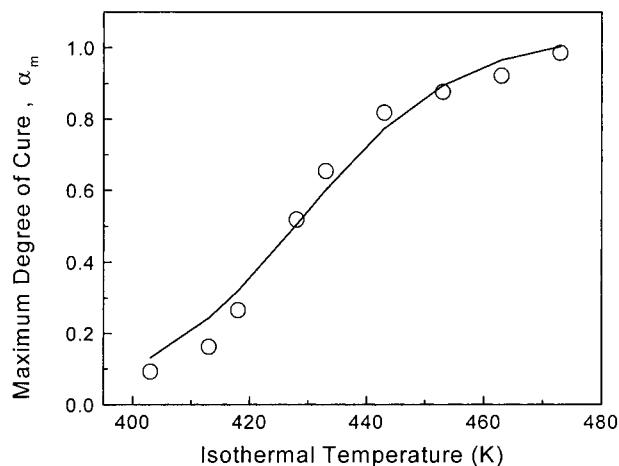As an analogous approach, Wisanrakkit et al. has used a modified form of the Williams–Lan-

Figure 2 Maximun degree of cure of DMS 2224 system plotted as a function of isothermal cure temperature.

Table II   Estimated Parameters of Modified Kinetic Model Using Isothermal DSC Data

	Cure Temperature (°C)					
	155	160	170	180	190	200
$k(\times 10^{-4}$ $\text{s}^{-1})$	1.99	3.60	4.90	6.87	14.2	17.0
A (s^{-1})			8.733×10^5			
E (kJ/mol)			78.434			
n			1			
a			1.04			
b			9.26×10^{13}			
k_m			0.075			

del–Ferry (WLF) equation to calculate k_a both above and below T_g. In this approach, the rate constant (k_d) of curing reaction is expressed by the temperature dependence of diffusion constant, i.e., WLF equation,[27]

$$\ln[k_d(T)] = \ln[k_g(T_g)] + \frac{2.303\, C_1(T - T_g)}{C_2 + |T - T_g|} \quad (6)$$

where C_1 and C_2 are constants.

In another approach, a phenomenological kinetic model has been derived by Kenny, et al. incorporating the diffusion-rate control into the reaction-kinetic expression by using the maximum degree of conversion (α_m) achieved by isothermal curing.[9] However, it should be mentioned that a linear relationship was assumed in this approach between α_m and T_{cure}, which subsequently led to an infinite value of α_m with increasing temperature.

As seen in Figure 2, the maximum conversion seems to approach 1.0, which corresponds to the fully cured state of the model system in dynamic-heating conditions, with the increasing curing temperature. Therefore, we may express the maximum degree of cure shown in Figure 2 quantitatively by using an empirical equation in the form of rational functions:

$$\alpha_m(T) = \frac{a}{1 + b\, \exp(-k_m T)} \quad (7)$$

The values of fitting parameters a, b, and k_m obtained by a curve fitting method are given in Table II. As can be seen in eq. (7), the conversion approaches 1.0 with curing temperature, which desirably results in a limiting value of glass tem-

perature ($T_{g\infty}$). Incorporating the maximum degree of cure represented by eq. (7) into eq. (4), the model equation may be expressed as

$$\frac{d\alpha}{dt} = k(T)\left(1 - \frac{\alpha}{\alpha_m(T)}\right)^n \quad (8)$$

It is likely that the term of $\alpha/\alpha_m(T)$ expresses a relative conversion that can be achieved in each isothermal cure temperature. Equation (8) expresses characteristic features of isothermal curing behavior, where the reaction rate approaches zero as the degree of cure approaches α_m.

In isothermal conditions, the model eq. (8) may also be expressed as an explicit form of α as a function time by separating variables and simply integrating it with respect to time and conversion. As a result, the integrated form of eq. (8) becomes

$$\alpha = \alpha_m[1 - \exp\{-\alpha_m(T)k(T)t\}]$$
$$\text{when} \quad n = 1 \quad (9)$$

$$\alpha = \alpha_m[1 - (\alpha_m(T)k(T)t/(n - 1)\}]^{1/1-n}$$
$$\text{when} \quad n \neq 1 \quad (10)$$

The reaction order, n, is often determined by comparing the relation between the conversion-dependent function and the apparent reaction rate. If the reaction order is correctly determined, according to eq. (8), the reaction rate ($d\alpha/dt$) should give a linear relation with the conversion-dependent function providing the reaction rate constants from the slope of the relation.[10,11] For the model system in this study, the reaction order was determined as 1.0. Subsequently, the activation energy (E) and preexponential factor (A) were determined by plotting the reaction constant vs inverse temperature according to the Arrhenius expression. Figure 3 shows $E = 78.4$ kJ/mol and $A = 8.733 \times 10^5$ s^{-1} determined from the isothermal curing experiments. Taking the activation energy determined in Figure 3 as a representative value of the model prepreg system, all the kinetic parameters of the model equation can be determined and the obtained values are summarized in Table II.

Using the model eq. (9) and parameters in Table II, Figure 4 compares the experimental data and kinetic model prediction for several isothermal cure temperatures. As can be seen, the modified kinetic model compares well with the progress of curing reactions as well as the conver-
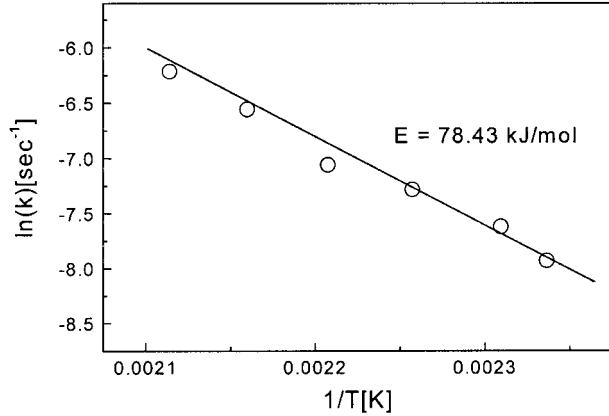
Figure 3 Activation energy of DMS 2224 systems obtained from isothermal cure experiments.

Figure 5 Activation energies obtained by Flynn–Wall and Kissinger methods in dynamic-heating conditions.

sion at equilibrium seemingly resulting from the diffusion-controlled rates of epoxy cure. It demonstrates the validity of modeling methodology, which is capable of described such phenomenological results of cure reactions as thermally limited to a partial degree of cure in isothermal conditions.

Dynamic-Heating Kinetic Analysis

For dynamic-heating analysis, two kinetic methods were utilized in this study: Kissinger method and Flynn–Wall method,[30,31] both of which use multiple heating rates to determine kinetic parameters. According to the Kissinger method, the activation energy is obtained from the maximum reaction rate, where $d(d\alpha/dt)$ is analytically zero under a constant-heating rate condition. The Arrhenius-type kinetic expression gives the following relation when the maximum reaction appears:
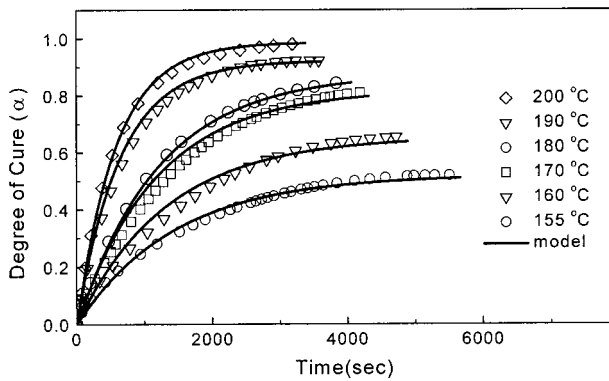

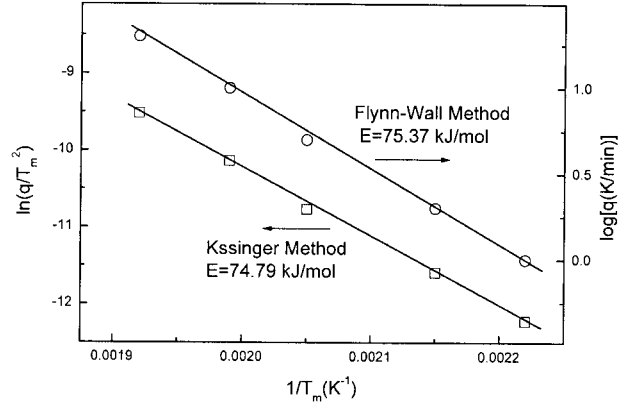**Figure 4** Model comparison of degree of cure at different isothermal cure temperatures.

$$\frac{d[\ln(q/T_m^2)]}{d(1/T_m)} = -\frac{E}{R} \qquad (11)$$

where T_m is the maximum-rate temperature and q is a constant heating rate. Accordingly, a plot of $\ln (q/T_m{}^2)$ vs $1/T_m$ gives the activation energy without a specific assumption of the conversion-dependent function.

Based on the Doyle's approximation, an alternative method was developed by Flynn and Wall for the calculation of activation energy, viz.,[32]

$$\log[g(\alpha)] = \log\left(\frac{AE}{R}\right) - \log q - 2.315$$

$$- 0.4567 \frac{E}{RT_m} \quad (12)$$

where $g(\alpha)$ is the integral of the inverse of conversion-dependent function with respect to conversion, i.e., $g(\alpha) = \int d\alpha/f(\alpha)$. Starting with eq. (12), a more accurate value of activation energy may be obtained by an iterative calculation by ASTM D698 in order to improve the linear approximation on the integration term.

These two methods were applied to the dynamic-heating experimental data obtained at several heating rates between 1.0 and 20.0°C/min. The Flynn–Wall method can provide activation energies at different conversion levels, but in this study it was only applied to the maximum-reaction rate where the DSC peak appears.

Applying the Flynn–Wall and Kissinger methods to the maximum reaction rates, the activation energies were determined by the slopes of the

Table III   **Heat of Reaction and Activation Energy Calculation in Dynamic-Heating Experiments**

Heating Rate (K/min)	$T_{\max}$ (°C)	$\ln(q/T_{\max}^2)$	$\log(q)$	H_T (J/g)
1	178.1	-12.223	0	132.9
2	192.5	-11.593	0.301	132.1
5	214.6	-10.770	0.699	144.2
10	230.1	-10.139	1.000	150.6
20	248.9	-9.519	1.301	133.5

linear relation in Figure 5. The calculation procedure and the data used to obtain this figure are summarized in Table III. The determined activation energies are 75.4 and 74.8 kJ/mol for Flynn–Wall and Kissinger methods, respectively, which are favorably compared with the activation energy 78.4 kJ/mole obtained from isothermal kinetic analyses.

For the model prediction in dynamic-heating conditions, eq. (8) may be integrated numerically, for example, by using the Runge–Kutta method. The experimental and the predicted degrees of cure are presented in Figure 6 as a function of temperature in dynamic-heating conditions and a good agreement can be observed between them. It additionally demonstrates the validity of our modeling methodology describing the kinetic behavior of thermoset systems both in isothermal and dynamic-heating conditions. It should be mentioned that the parameters used the model predictions in Figures 4 and 6 are the same as those in Table II.
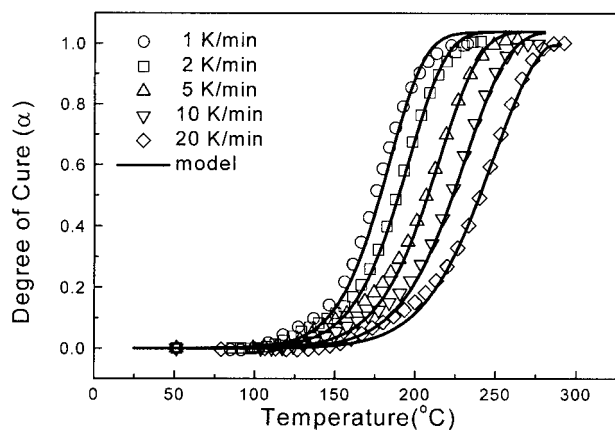
Figure 6   Model comparison of cure for dynamic-heating cure at different heating rates.
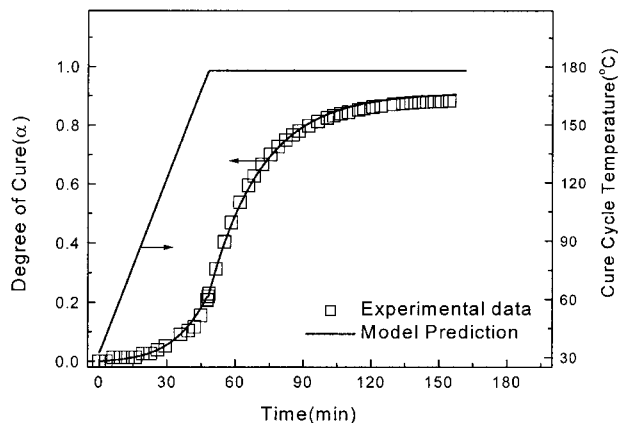
Figure 7   Model comparison of degree of cure for standard cure cycle composed of dynamic-heating and isothermal holding segments.

Standard Cure Cycle Analysis

Finally, the developed model should be tested for a standard cure cycle of high performance composite materials in order to be practically used for various manufacturing conditions. The curing condition of high performance composite is generally composed of dynamic heating and isothermal holding segments usually up to 177°C (350 F) in a continuous manner. In this study, a typical standard cure cycle shown in Figure 7 was used for the validation of the developed model. The proposed model equation was numerically solved by using the model parameters in Table II, and the predicted conversion is compared with the experimental data in Figure 7. As can be seen, the model prediction is in good agreement with the experimental result for the standard cure cycle: a constant heating at 2.7°C/min (5°F/min) from room temperature to 177°C (350°F), an isothermal holding at 177°C for 2 h, and a cooling at 2.7°C/min from 177°C to room temperature. It demonstrates that the developed model is capable of predicting the cure behavior at such curing cycles as composed of both isothermal and dynamic-heating conditions. The model parameters used in this prediction are the same as those previously determined in isothermal kinetic analyses in Table II.

Glass Transition Temperature Development

The physical and chemical properties of thermosetting polymers are usually dependent upon the degree of conversion, which subsequently has a strong dependence on the glass transition tem-
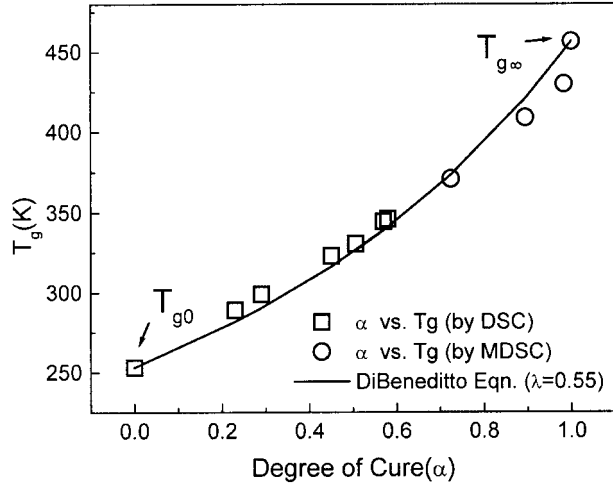
Figure 8 Glass transition temperature as a function of degree of cure compared with modified DiBeneditto equation ($\lambda = 0.55$).

perature of the polymer. As the conversion increases during the cure of thermosetting materials, the glass transition temperature also increases due to chain growth and molecular weight increment. It has been reported that there may be an intimate relation between the onset of the diffusion control regime and the glass transition.[28,29,33,34] DiBeneditto has derived a T_g conversion relation through an entropic consideration of idealized simple systems consisting of a mixture of fully cured network and monomer.[13,14] The simplified form of the DiBeneditto equation including the adjustable parameter (λ) becomes

$$T_g = T_{g0} + \frac{(T_{g0} - T_{g\infty})\lambda\alpha}{1 - (1 - \lambda)\alpha} \qquad (13)$$

where T_{g0} is the T_g of the "uncured" monomer, $T_{g\infty}$ is the highest T_g of the "fully cured" material, and λ is a structure-dependent parameter. This relationship compares well with the glass transition temperature of our model system as a function of conversion in Figure 8. The maximum glass transition temperature ($T_{g\infty}$) of our model system is 183.2°C and the T_g of the uncured prepreg (T_{g0}) is −20°C. Although it is not shown here, a plot of $(T_g - T_{g0})/(T_{g\infty} - T_{g0})$ vs α shows that the modified DiBeneditto equation describes the characteristic shape of T_g dependence on the progress of cure reactions. In this analysis, λ was treated as an adjustable parameter and determined as 0.55.

Figure 9 shows the calculated conversion and $T_{cure} - T_g$ as a function of a standard one-step

cure cycle, which is composed of constant heating (2.7°C/min), isothermal holding (177°C for 2 h), and constant cooling (2.7°C/min) steps. The value of $T_{cure} - T_g$ shows a maximum, and it decreases to lower than 30°C in the middle of isothermal holding. Finally, the glass transition temperature becomes higher than the curing temperature during cooling stage giving negative values of $T_{cure} - T_g$. As mentioned earlier, the residual stress may be closely related to the deviation of these two temperatures. For example, the residual stress may permanently be fixed in the laminate during the "cooling" stage when $T_{cure} - T_g$ becomes below zero due to polymer vitrification. However, depending on the status of mobility and the volumetric shrinkage of the curing matrix system, the residual stress may be generated during "isothermal holding," where T_g approaches to T_{cure} close enough for partial vitrification of the polymer chain.[35] Although it is out of the scope of this study identifying the details of residual stress development during composite cure, it should be mentioned that the value of $(T_{cure} - T_g)$ be one of the most significant factors to be considered in analyzing residual stress development in composite manufacturing and utilization.

Equivalent Processing Time via Glass Transition Temperature

The value of $T_{cure} - T_g$ usually depends on the curing kinetics of the matrix system and thermal processing conditions. For example, the value of $T_{cure} - T_g$ may remain small during processing for the matrix polymer chains to be partially vit-

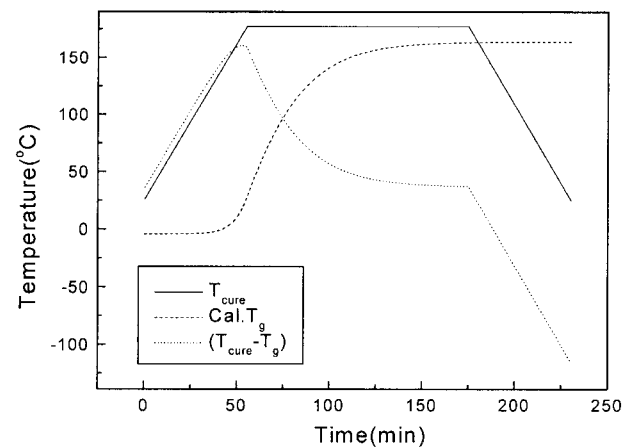**Figure 9** Development of glass transition temperature and $T_{cure} - T_g$ calculated by the development model during standard cure-cycle curing process.

rified, and thus the residual stress may be developed during the laminate cure. For example, if an extremely slow heating rate is used, the vitrification may occur during the heating stage because the heating rate is slow enough for the growing polymer chain to approach the diffusion-controlled limit. Otherwise, the residual stress may be reasonably assumed to build up during isothermal holding and/or cooling stages where T_g approaches T_{cure}. Accordingly, it may be desired to examine a property-related quantity, e.g., $T_{\mathrm{cure}} - T_g$, in various processing conditions to identify the optimal property-related processing conditions minimizing the residual stress of laminates.

When it is desirable to compare the property-related quantity as a function of various processing conditions, the equivalent time methodology has been successfully applied to degradation and cure kinetic processes.[36–38] As with most epoxy systems, the residual-stress property of our model prepreg system is likely to depend on such processing conditions as heating/cooling rates, isothermal times, and temperatures as well as cure kinetics of the matrix material. Relating the residual stress development to the property-related property of $T_{\mathrm{cure}} - T_g$, various processing conditions may be collectively compared by using the equivalent time methodology. In this methodology, the reaction kinetic theory is used to estimate an equivalent processing time (EPT), which is the time for the same conversion to be obtained in various thermal conditions.

For instance, the epoxy system is heated at the heating rate of q_{RC} from the room temperature (T_R) to the curing temperature (T_C), and held at T_C for Δt_C. Then, the part is cooled to T_C at a cooling rate of q_{CR}. Incorporating these processing variables through the kinetic analysis, the different thermal steps may be expressed by the EPT in a continuous fashion, and subsequently the development of the property-related processing quantities may well be compared with respect to EPT.

According to this methodology, the EPT in dynamic heating or cooling stages (EPT_{dyn}) may be defined as the isothermal reaction time (at a certain T) required to obtain the same conversion that can be obtained by the dynamic-heating or cooling conditions. In addition, the EPT in isothermal condition (EPT_{iso}) may also be defined by the isothermal reaction time required to obtain the same conversion (at a certain T) that could be obtained at a different isothermal temperature

T_C. The detail derivation of the equivalent processing time is described elsewhere.[36–38]

The resulting EPT_{dyn} (at T) for a dynamic heating from T_R to T_C at a constant heating rate, q_{RC}, may be expressed as

$$EPT_{\mathrm{dyn}}(T_R \rightarrow T_C, q_{RC}) = \frac{E}{q_{RC}R} \exp\left(\frac{E}{RT}\right)$$
$$\times \{p(E/RT_C) - p(E/RT_R)\} \quad (14)$$

where $p(x) = \int_x^\infty [\exp(-x)/x^2\}$ and $x = E/RT$.

Similarly, the EPT_{dyn} (at T) for a cooling stage at a cooling rate of q_{CR} from T_C to T_R may be written as

$$EPT_{\mathrm{dyn}}(T_C \rightarrow T_R, q_{CR}) = \frac{E}{q_{CR}R} \exp\left(\frac{E}{RT}\right)$$
$$\times \{p(E/RT_R) - p(E/RT_C)\} \quad (15)$$

In addition, when the prepreg is cured at T_C for an isothermal curing time (Δt_{iso}), it may be converted to an EPT_{iso} at T corresponding to the same conversion to be achieved.

$$EPT_{\mathrm{iso}}(T_C) = \Delta t_{\mathrm{iso}}\exp\left\{\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_C}\right)\right\} \quad (16)$$

Therefore, eqs. (14)–(16) provide EPTs (at a certain T), which leads us to compare the property-related quantities in various processing conditions. In other words, the processing condition at a certain time and temperature can be converted to an EPT by adding the EPTs in eqs. (14)–(16), providing the equivalent property-related quantity compared at the same level of conversion. At a certain value of EPT, the same cured state of polymer matrix can be represented for different processing conditions. In this study, $T_{\mathrm{cure}} - T_g$ was taken as a property-related property to be examined as a function of EPT in order to compare the cure processing conditions in light of residual stress development.

In this study, the reference temperature appearing as T in eqs. (14)–(16) was fixed at $T = T_c = 177°C$. In this case, it can be easily realized $EPT_{\mathrm{iso}} = \Delta t_{\mathrm{iso}}$ at 177°C in eq. (16). The activation energy used in this study was 78.43 kJ/mol, $\Delta t_{\mathrm{iso}} = 120$ min, $q_{CR} = -2.75°C/min$, $T_C = 177°C$, and $T_R = 20°C$. Using these values in eqs. (14)–(16), the EPT can be calculated as a function of any processing conditions and subsequently related to the calculated glass transition tempera-
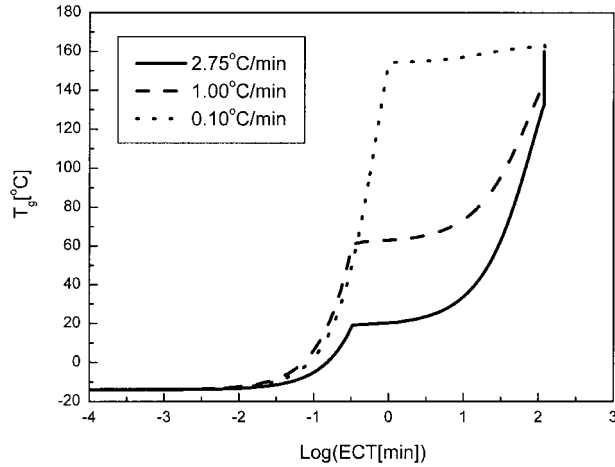
Figure 10 Development of glass transition temperature plotted as a function of *EPT* comparing various heating rates in standard cure cycle.

ture and $T_{\text{cure}} - T_g$. In this study, three different heating rates were investigated: $q_{RC} = 0.1, 1.0$, and 2.75°C/min. Figure 10 compares the glass transition temperatures calculated as a function of *EPT* at three different heating rates. There can be seen two distinct steps in the characteristic shape of the glass transition temperature. The first accelerating increase of T_g corresponds to a constant heating rate at q_{RC}. As can be seen, the glass transition temperature reaches at 150 and 20°C in the first stage when being heated at 0.1 and 2.75°C/min, respectively. The next acceleration of the glass transition corresponds to the isothermal holding at $T_{\text{cure}} = 177$°C. In this isothermal stage, the glass transition temperature increases from 150°C to 160°C at 0.1°C/min of heating, but from 20 to 160°C at 2.75°C/min of heating. In other words, the glass transition temperature at a slow heating rate reaches close to the cure temperature during the heating stage of curing, but at a fast heating rate during the isothermal holding stage of curing. Plotted as a function of *EPT*, the glass transition temperature development can be clearly compared in various curing conditions of time and temperature.

Regarded as an important property-related quantity in the development of residual stresses, $T_{\text{cure}} - T_g$ may be plotted as a function of *EPT* comparing different curing conditions consisting of different heating rates. In Figure 11, the characteristic shape of the curves exhibits three stages of curing conditions: heating from room temperature to 177°C, isothermal holding at 177°C, and cooling from 177°C to room tempera-

ture. In the first stage of heating, $T_{\text{cure}} - T_g$ shows a maximum. When the temperature is maintained isothermally at 177°C, the value of $T_{\text{cure}} - T_g$ gradually decreases. Finally, $T_{\text{cure}} - T_g$ decreases almost vertically in the cooling state at $\log(EPT) \approx 2.1$ for all the three cases resulting in negative values. At a slow heating rate, for example at 0.1°C/min, $T_{\text{cure}} - T_g$ reaches almost zero before the isothermal holding starts. In the case of the fast heating at 2.75°C/min, however, the cure temperature is much higher than the glass transition temperature and thus $T_{\text{cure}} - T_g$ is still maintained at around 150°C in the vicinity of isothermal holding stage.

It should be mentioned that the absolute value of the residual stress created by the volume shrinkage of the matrix material during dynamic heating and isothermal holding may be smaller than those created during cooling. However, it should be mentioned that the modulus and strength of the matrix in the middle of heating or isothermal holding may also be lower than the fully cured state of composite laminate. Therefore, the cure-induced volumetric shrinkage in the middle of curing may be enough to create microvoids, cracks, and/or delamination.[35] In this sense, the changing value of $T_{\text{cure}} - T_g$ during the curing process should be cautiously examined in relation to the changing modulus, strength, and volumetric shrinkage values. When those properties are quantitatively correlated, for example, with $T_{\text{cure}} - T_g$, various processing conditions may well be compared to minimize the internal stress distribution as well as the final performance of the integrated part of composite lami-
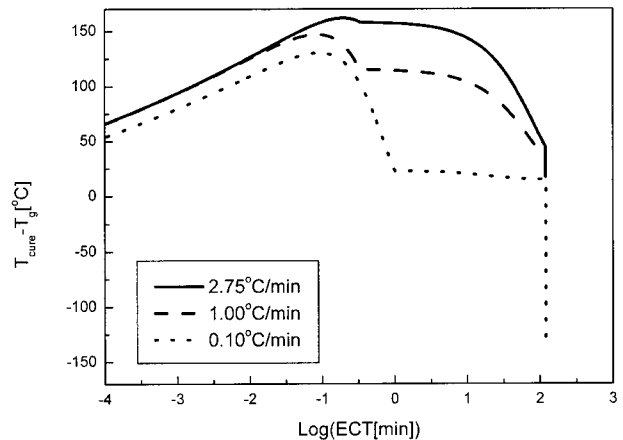

Figure 11 Development of $T_{\text{cure}} - T_g$ plotted as a function of *EPT* comparing various heating rates in standard cure cycle.

nates. Overall, it is demonstrated that the developed *EPT* may be used to analyze the property-related processing conditions systematically combining chemical reaction kinetics and physical performance characteristics.

CONCLUSIONS

The cure kinetics and glass transition development of a commercially available epoxy/carbon fiber prepreg system, DMS 2224 (Hexel F584), was investigated by isothermal and dynamic-heating experiments. A kinetic model was developed to describe a limited degree of cure as a function of isothermal curing temperatures seemingly caused by the rate-determining diffusion of growing polymer chains. Incorporating the obtained maximum degree of cure to the kinetic model development, the developed kinetic equation accurately described both isothermal and dynamic-heating behavior of the model prepreg system. Finally, the *EPT* was used to investigate the development of glass transition temperature for various curing conditions envisioning the internal stress buildup during curing and cooling stages of epoxy-based composite processing.

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