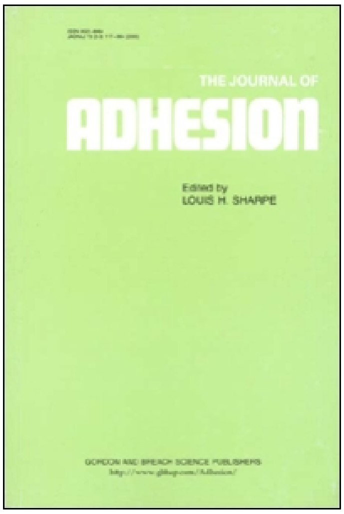

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Characterization of Epoxy Prepreg Curing Process

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Characterization of Epoxy Prepreg Curing Process

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The isothermal and dynamic curing process of epoxy composite was studied using differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and other techniques. The variation of degree of curing with time and temperature was analyzed. The degree of curing was limited at any particular temperature because of the diffusion control in isothermal curing process. Half-life and maximum cure time were discussed in the analysis of the isothermal curing process. The modeling result from isothermal curing process indicated that degree of curing calculated with diffusion control agreed well with experimental data. The degree of curing calculated by two methods for dynamic curing process had a deviation with experimental data in either earlier or later cure stages. The relationship between T_g *and the degree of curing was described by two models. Both models agreed well with the experimental* T_g*. The isothermal curing diagrams of time–temperature–transformation (TTT) and conversion–temperature–transformation (CTT) were constructed. Each region in TTT and CTT diagrams corresponded to the phase state of the curing process, so that the curing mechanism was clearly reflected in diagrams. The thermal stability analysis indicated the epoxy resin system was very thermally stable under temperature of 300°C.*

Keywords: Adhesion; Composites; Curing; Epoxy; Phase diagrams; Thermal analysis

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1. INTRODUCTION

The curing process determines the degree of curing of an epoxy prepreg and has important effects on the mechanical properties of the final products. Optimal curing schedules are the keys to achieve efficiently the desired properties of the cured materials. Although suppliers of commercial epoxy prepreg resins usually suggest curing cycles for the customers, these curing cycles may not be the optimal ones for a particular application. The aim of the present study was to find the optimal curing cycles for application of epoxy prepregs to composite joints in pipe systems. The isothermal and dynamic modelings of curing kinetics help elucidate the details of the curing process. By determining the kinetic parameters, such as the rate constant and the activation energy, the degree of curing and the curing rate can be predicted.

Besides the kinetics of the curing process, the changes of thermal characteristics during curing, such as the glass transition temperature, T_g, of the resin should also be considered. T_g is the temperature where an amorphous polymer changes either from a glassy to a rubbery state or from a rubbery to a glassy state. It is an important characteristic because the application temperature range of the polymer depends on its T_g.

The isothermal curing process of thermosetting polymers often involves the appearance of gelation and vitrification. For a given epoxy prepreg system, the gelation occurs at a special conversion point [1,2] where the polymer changes from a viscous liquid state to a rubbery state. However, the vitrification is closely related to T_g. When T_g is lower than the isothermal curing temperature, the curing process is controlled kinetically. The T_g increases from T_{g0} with the advancement of curing. When it reaches the isothermal curing temperature, the vitrification occurs, and the polymer changes to a glassy state. The curing rate becomes slower after vitrification and eventually the process stops. A new reaction might be triggered when the curing temperature increases.

Gelation and vitrification involve phase transitions during the curing process. These transitions can be described by a time–temperature–transformation (TTT) isothermal curing diagram [3,4] or by a conversion–temperature–transformation (CTT) diagram [5,6]. Both the TTT and CTT diagrams are divided into several regions, such as solid glass, liquid, solid/gelled rubber, solid/gelled glass, gelled rubber, gelled glass, and char. The diagrams show clearly the possible phase changes during the isothermal curing process.

An array of methods might be used to analyze the curing of an epoxy prepreg. Differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and a rotational rheometer were used in this work. The DSC analysis is based on the specific heat change of the epoxy prepreg while the sample is cured. The kinetic parameters of curing reactions may be obtained from DSC data. TGA data express the thermal stability of the sample from which an eventual weight loss can be determined while the sample is heated isothermally or dynamically.

2. EXPERIMENTAL

2.1. Materials

A commercial epoxy prepreg 8552 Epoxy Matrix sample from Hexcel Corporation, Pleasanton, California, USA, was used in this work. The sample was an amine-catalyzed multifunctional epoxy resin system with reinforcement of carbon fiber, containing 33% (by weight) resin and the curing agent. The epoxy prepreg samples with different degrees of cure were prepared in a specially designed oven by curing the samples from room temperature to a series of preset temperatures at a heating rate of 5°C/min with a constant flow of nitrogen.

2.2. Methods

The isothermal and the dynamic DSC curing measurements were performed in an inert atmosphere (nitrogen) using a Seiko DSC 6200 instrument (Seiko Instruments Inc., Chiba, Japan) and a Modulated DSC unit from TA Instruments (New Castle, DE, USA), respectively. Samples of 7–10 mg were prepared and sealed in aluminum pans. An empty aluminum pan was used as a reference. The sampling time for isothermal curing measurements was set to 6 s (3 s for the isothermal curing temperatures of 210°C and 220°C). The sampling time for all dynamic measurements was set to 1 s. A Thermal Gravimeter Analyzer from TA Instruments was used to study the thermal stability of the epoxy prepreg during the dynamic scanning. An uncured prepreg sample (16 mg) and a fully cured prepreg sample (11 mg) were analyzed from room temperature to 600°C at a heating rate of 5°C/min. The rheology of the curing process of epoxy prepreg resins was investigated by means of a stress-driven Bohlin VOR rheometer (Bohlin Instruments, Inc., East Brungwick, NJ, USA) using parallel plates.

3. RESULTS AND DISCUSSION

3.1. DSC Thermal Analysis and Degree of Curing

DSC thermal curing analysis is based on the peak of heat flow curve from the epoxy prepreg sample. The peak is caused by the cure reaction, which is an exothermal process. From the DSC heat flow curve, the partial and total cure reaction heats can be calculated.

For the isothermal curing time, the transient degree of curing at each isothermal temperature calculated from cure reaction heat is a function of time. Degree of curing increases with increment of cure time until it reaches its maximum. The maximum degree of curing changes with isothermal cure temperature. Its relationship to the isothermal cure temperature is shown in Figure 1. Note that the maximum degree of curing increases linearly with the increment of the cure temperature until it rises to 1, the degree of curing for the fully cured epoxy prepreg sample. This is similar to the results reported by Kenny *et al.* [7] and Lee and Wei [8]. At lower isothermal cure temperatures, the cure reaction stops at a lower degree of curing because of diffusion control. Increasing the cure temperature shifts the diffusion control to the kinetic control and the cure reaction stops at a higher degree of curing, so the maximum degree of curing increases at the higher temperatures.

A maximum cure time exists corresponding to the maximum degree of curing at each isothermal cure temperature. The values for the maximum cure time at different isothermal cure temperatures are

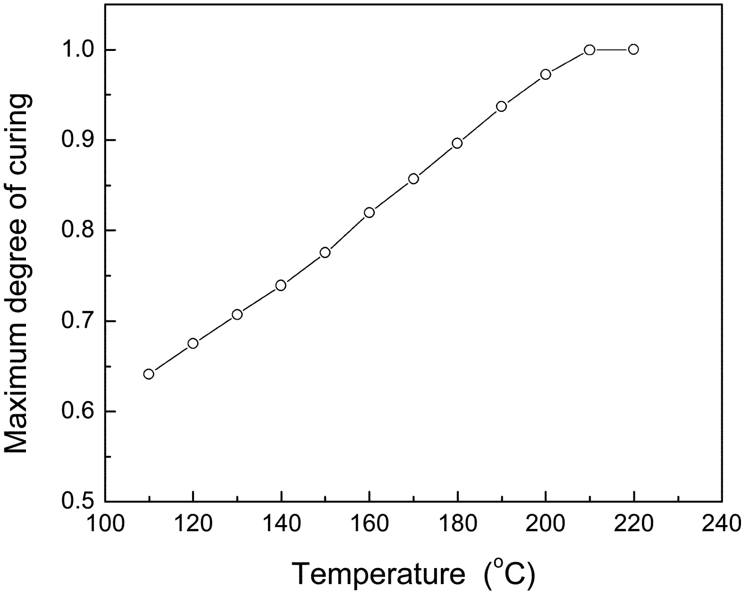

FIGURE 1 Maximum degree of curing as a function of isothermal cure temperature.

very different. The relationship between the maximum cure time and the isothermal cure temperature is given in Figure 2. Half-life is another important parameter for the isothermal curing time. It is the time required to reach 50% conversion at a certain cure temperature. The relationship between the half-life and isothermal cure temperature is also given in Figure 2. It is actually an iso-conversional plot of cure time *vs*. temperature at a degree of curing of 0.5. By comparison, it is clear that half-life is much smaller than the maximum cure time at the same isothermal temperature. This is not difficult to understand. At the same temperatures, the cure rate in the later cure stage becomes much smaller, so it needs much more time in the late cure stage than in the early cure stage to increase the same value of degree of curing. The curves suggest that both the maximum cure time and half-life decay exponentially with respect to the isothermal cure temperature. So, increasing cure temperature can significantly decrease cure time. From Figure 2, the 60-min half-life temperature was determined, which was 142°C.

Half-life temperature is very useful to verify DSC thermal cure results. The following experiments were designed based on the conventional 60-min half-life temperature. An uncured sample was

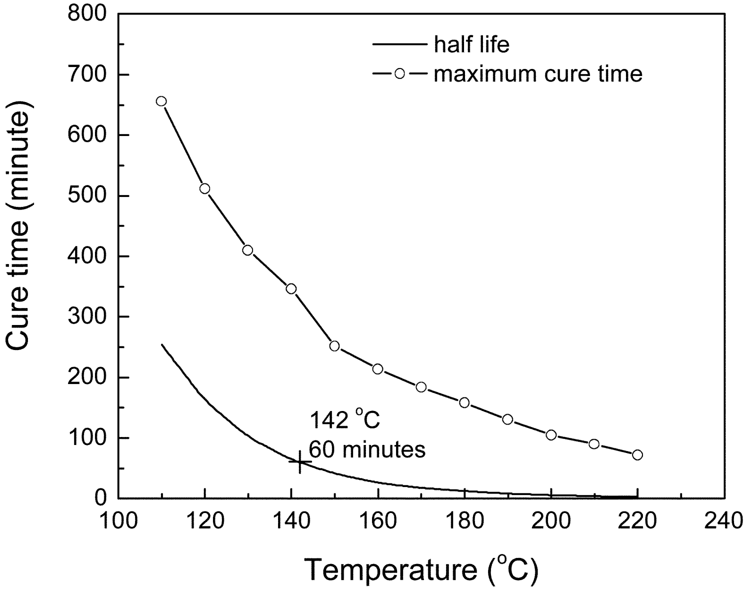

FIGURE 2 Half-life and the maximum cure time for the isothermal curing process as a function of isothermal cure temperature.

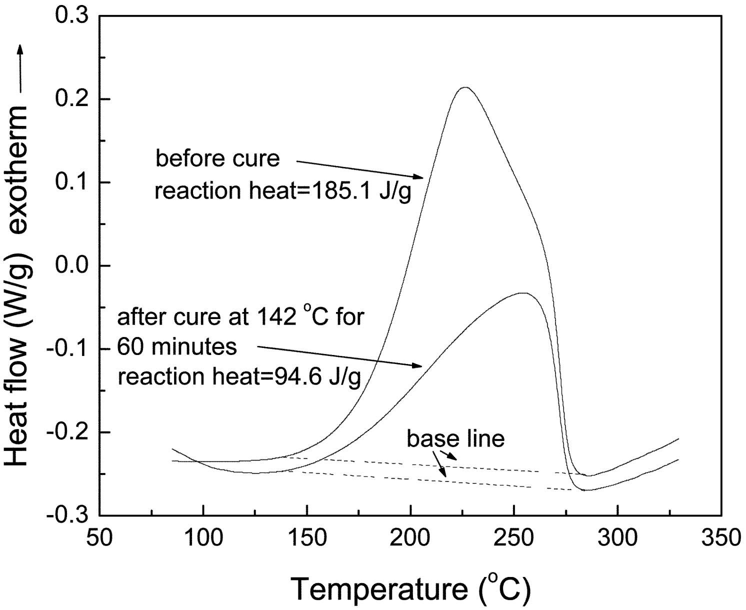

FIGURE 3 Comparison of dynamic cure heats between the fresh and partially cured samples at a heating rate of 10°C/min. The ratio of the reaction heat of the cured sample to the reaction heat of the fresh sample is 0.51.

scanned with DSC at a heating rate of 10°C/min. Its heat flow and dynamic cure heat are shown in Figure 3. Another uncured sample was aged at 142°C for 60 min and then quickly moved from the instrument chamber to a container held below 0°C. After the aged sample was cooled and the instrument was ready, the aged sampled was scanned with DSC, at the same heating rate of 10°C/min. The heat flow and the residual heat of the partially aged sample are also shown in Figure 3. The dynamic cure heat of the partially aged sample should be close to half of the dynamic cure heat of the uncured sample. The data in Figure 3 shows that the ratio of the cure heat for the sample cured at 142°C for 60 min to the cure heat of the uncured sample is 0.51, which is close to 0.5. So, the experimental results discussed earlier are also confirmed to be reasonable by the half-life temperature.

As discussed earlier, the time to achieve 50% of the degree of curing decreases with the increment of isothermal cure temperature. For the same degree of curing, the required cure time changes with the different isothermal temperatures. The iso-conversional plots of $1/T$ *vs.* $\log t$ under various constant degrees of curing are shown in Figure 4. For curves with degrees of cure from 0.1 to 0.6, an almost linear relationship

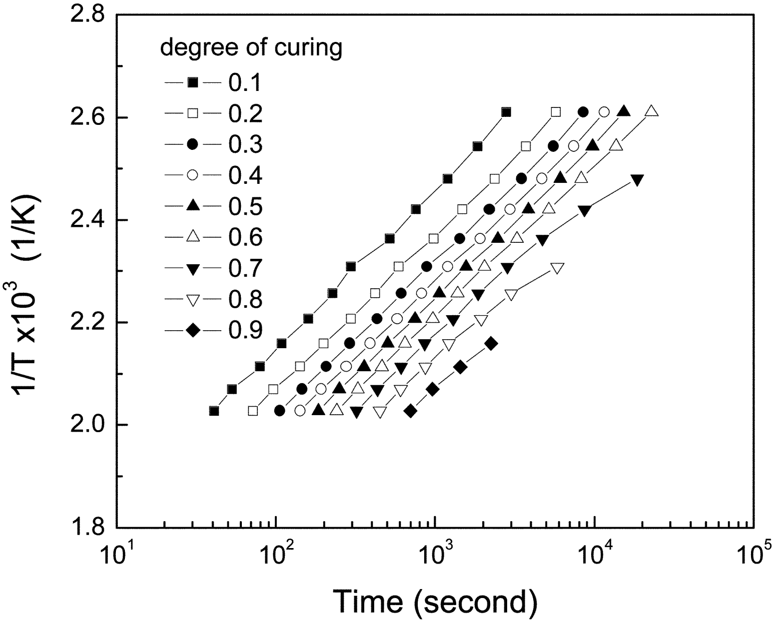

FIGURE 4 Iso-conversional plots of *1/T vs.* logarithmic time for epoxy prepreg.

between the reciprocal of the absolute cure temperature and logarithmic cure time is observed over the isothermal temperature range of 110 to 220°C. This linear relationship means that the curing process in this region is controlled by the curing kinetics. For curves with degrees of cure from 0.7 to 0.9, a nonlinear relationship is observed. With the increment of degree of curing, the nonlinear part of the curve shifts to a higher isothermal cure temperature. This means that the curing process in this region is not controlled by kinetics but rather by diffusion. The region controlled by diffusion shifts to a higher temperature at the higher degree of curing. It was suggested that this region is the onset of vitrification [9]. The details of phase transition of the curing time are discussed later.

3.2. Modeling of the Curing Process

The autocatalytic four-parameter model without diffusion control [10] was considered for the isothermal curing reaction as follows:

$$r = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{1}$$

where r is the curing rate, α is the degree of curing, m and n are the orders of the curing reaction, and k_1 and k_2 are the rate constants.

To account for the effect of the diffusion on the rate of the curing reaction, the autocatalytic four-parameter model was modified by including a diffusion factor [11]:

$$r = \frac{1}{1 + \exp(C(\alpha - \alpha_c))}(k_1 + k_2\alpha^m)(1-\alpha)^n \tag{2}$$

where C and α_c are temperature-dependent empirical constants. The constant α_c is called the critical degree of curing.

All the parameters in Equations (1) and (2) were determined by nonlinear least squares curve fitting to experimental data. The details were reported elsewhere [12]. The curing degree for a resin cured isothermally at 160°C, calculated using the model with or without diffusion, respectively, is compared in Figure 5 with the experimental value determined from DSC data. It appears that both models agree well with the experimental values when the curing degree is less than 0.75. However, for a degree of curing higher than 0.75, the model without diffusion deviates gradually from the experimental plot, whereas

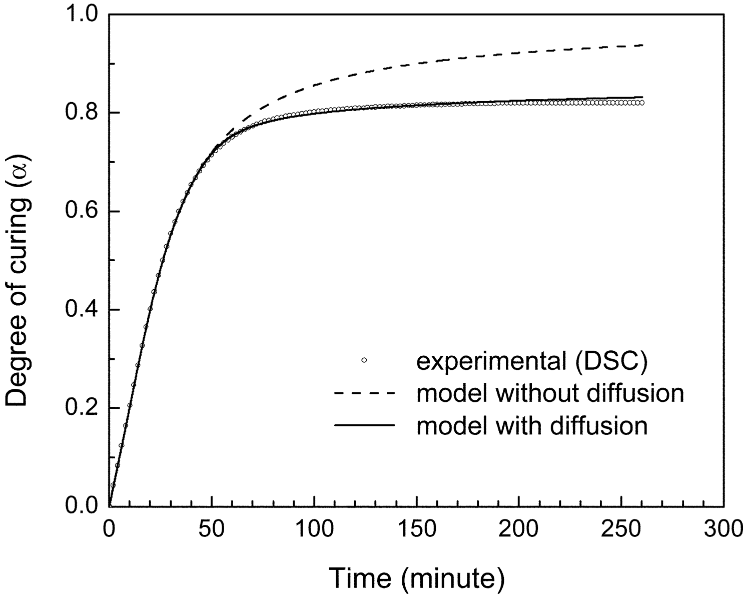

FIGURE 5 Degree of curing as a function of time for a sample isothermally cured at 160°C calculated using the autocatalytic model without and with diffusion control, respectively, and its comparison with the experimental value.

the model with diffusion continues to agree very well with it. The degree of curing calculated from the model without consideration of diffusion control is higher than the experimental data because it is based on pure kinetics. During the curing process, the glass transition temperature of the system gradually increases. When the isothermal cure reaction reaches a certain stage (*e.g.*, degree of curing of 0.75 at 160°C), the T_g of the system (around 160°C) changes from below the cure temperature to equal or above the cure temperature, and vitrification (glassy state) occurs. At this stage, the mobility of the system decreases dramatically; therefore, the rate of the curing reaction undergoes a significant decrease and falls below the kinetic rate as the curing reaction becomes diffusion controlled. Accordingly, the degree of curing increases very little in the glassy state. The region of the glass state is discussed later in a CTT phase diagram.

Unlike the isothermal curing process studied previously, the dynamic curing process shows no diffusion control in the later cure stage [13] because the cure temperature (increasing at a constant heating rate) is always higher than the T_g of the curing system, and, thus, no glassy state occurs. The kinetic rate of the curing reaction can be used to express the total rate of the dynamic curing process. For a dynamic curing proceeding at a constant heating rate, the kinetic rate of the curing reaction is not only a function of the degree of curing, but also a function of curing temperature. The autocatalytic model for the curing reaction can be expressed in this case as in Equation [13]:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}}\alpha^m(1-\alpha)^n \tag{3}$$

where A is the preexponential factor, E_a is the activation energy, R is the gas constant, and T is the temperature.

The parameters in Equation (3) were determined by two methods. The first method was based on the kinetic model described by Kissinger [14] and Ozawa [15]. By transformation of Equation (3), the heating rate was expressed as a function of the exothermic peak temperature. In this method, the parameters are obtained from several DSC runs at different heating rates. The relative shift in exothermic peak is a function of heating rate. A linear relationship exists between the peak temperature and the heating rate. The activation energy was assumed to be the same at different heating rates and was determined from the slope of the curve. The preexponential factor and the orders of the curing reaction at each heating rate were determined by a multiple nonlinear least-squares regression. The second method was based on the approach of Borchardt and Daniels [16]. In this method, the parameters were obtained from only a single DSC run. By taking the logarithm of both sides of Equation (3), a linear expression for the logarithm of the curing rate can be obtained. The parameters in Equation (3) were then determined by a multiple linear regression analysis. Details regarding the use of these two methods were reported elsewhere [13]. The degree of curing calculated by the two methods and the experimental data collected for a heating rate of 5°C/min are plotted in Figure 6. It seems that the degree of curing modeled according to the Kissinger and Ozawa approach agrees well with the experimental data in the late stages of the curing reaction, whereas the degree of curing determined by the Borchardt and Daniels approach agrees well with the experimental data in the early stages of the dynamic curing process. The Kissinger and Ozawa method could be used for an exothermic curve with multiple peaks and shoulders and, therefore, more than one cure reaction was involved in the curing process. In this method, parameters were obtained by fitting the peaks of the exothermic curve using multiple nonlinear least-squares regression analysis. This method usually produces accurate results

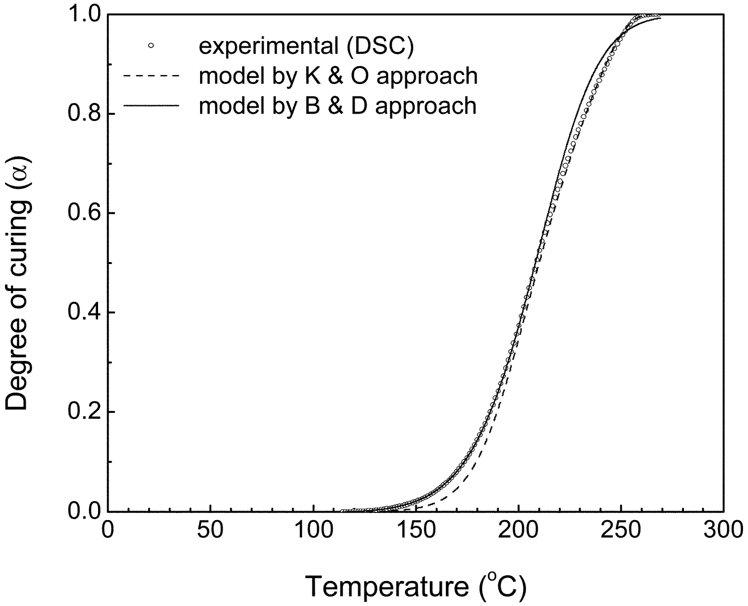

FIGURE 6 Plots of the degree of curing of the epoxy prepreg sample dynamically cured at a heating rate of 5°C/min calculated using the method based on the Kissinger and Ozawa approach and the Borchardt and Daniels approach, respectively, and the plot of experimental values determined from DSC data.

in the center region of the peak but may be in error in the tail region. The degree of curing by the Kissinger and Ozawa method differed from the experimental data in the early stages of the curing reaction. The Borchardt and Daniels method required one well-shaped exothermic peak to get a linear relationship between the logarithm of the curing rate and the reciprocal of the cure temperature. For curing processes where an additional shoulder appeared in the exothermic curve in the later cure stage, the linear relationship did not exist and, therefore, results based on the Borchardt and Daniels method were in error.

3.3. Glass Transition Temperature

For an epoxy prepreg system, T_g can be related to the progress of the curing process; *viz.*, the T_g increases with the degree of curing. There is a unique relationship between the T_g and the curing degree, regardless of the curing temperature and the reaction path [17–25]. A theoretical equation relating T_g to the degree of curing was proposed by DiBenedetto [24]:

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{(\varepsilon_x/\varepsilon_m - F_x/F_m)\alpha}{1 - (1 - F_x/F_m)\alpha} \tag{4}$$

where T_{g0} is the glass transition temperature of the uncrosslinked polymers, α is the fractional conversion of the reaction, ε_x and ε_m are the lattice energies for crosslinked and uncrosslinked polymers, respectively, and F_x and F_m are the corresponding segmental mobilities.

The DiBenedetto equation cannot be applied to some polymer systems, especially if they are highly crosslinked [19,26]. Pascault and Williams [27] modified the DiBenedetto equation by introducing the maximum glass transition temperature, $T_{g\infty}$, to get

$$T_g = \frac{(1 - \alpha)T_{g0} + \lambda\alpha T_{g\infty}}{(1 - \alpha) + \lambda\alpha} \tag{5}$$

where λ is an adjustable structure-dependent parameter with values between 0 and 1. Equation (5) can be applied to polymer systems at higher reaction extents [20].

On the other hand, Venditt and Gillham [28] derived a relation for thermosetting systems, similar to Equation (5), which considered the entropy of mixed systems:

$$T_g = \exp\left(\frac{(1 - \alpha)\ln(T_{g0}) + (\Delta c_{p\infty}/\Delta c_{p0})\alpha \ln(T_{g\infty})}{(1 - \alpha) + (\Delta c_{p\infty}/\Delta c_{p0})\alpha}\right) \tag{6}$$

where Δc_{p0} and $\Delta c_{p\infty}$ are the heat-capacity differences between the liquid/rubbery state and the glassy state for the uncured and fully cured systems, respectively.

The measurements of T_g for all the prepared samples were conducted through the modulated DSC mode. The underlying heating rate was set to 5°C/min with the temperature amplitude of 2°C. The actual modulated temperature changes at a rate greater or less than the underlying heating rate.

In the modulated DSC mode, the total heat flow through the prepreg sample could be divided into a reversible heat flow and a nonreversible heat flow. The reversible heat flow is related to the transition of the resin into a glassy state. It can be used to detect T_g. The nonreversible heat flow is related to the exothermic effect of the curing process. The exothermic reaction heat can be considered as the residual heat of the partially cured sample. Consequently, the degree of curing of the sample can be calculated using the residual heat [29]. Figure 7 depicts the reversible and the nonreversible heat flows for the uncured prepreg sample. From the dependence of the reversible heat flow upon the temperature, the T_g was observed at 1.4°C. It was taken as the middle of the inflection in the lower-temperature transition region. Integration of the area corresponding to the exothermic deflection of the nonreversible heat flow curve at higher temperatures gave the

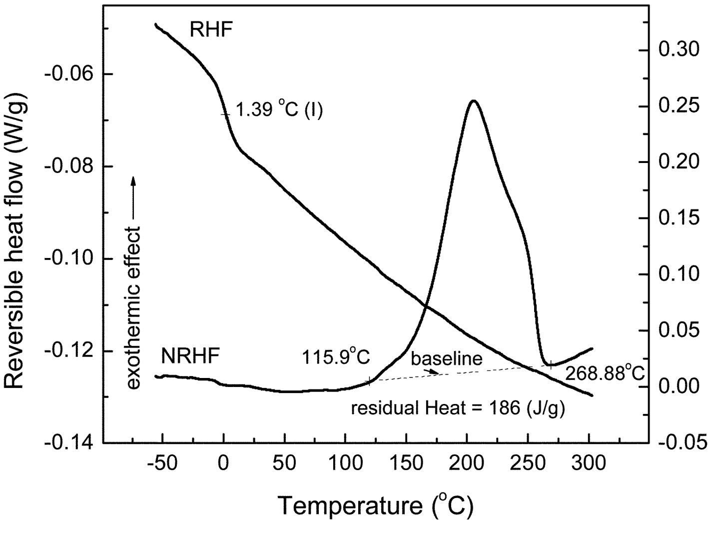

FIGURE 7 Reversible and nonreversible heat flows for dynamic curing of fresh prepreg with a heating rate of 5°C/min.

amount of the residual heat. The glass transition and the residual heat for all other samples were determined in the same way as described. The highest T_g value was observed for the fully cured epoxy prepreg resin (231.5°C). The dependence of the experimental glass transition upon the degree of curing is shown in Figure 8. The relationship between these two parameters was found to be nonlinear. As discussed earlier, it was assumed that the glass transition temperature of epoxy prepreg systems is dependent only upon the degree of curing, regardless of the curing cycle or curing history. Therefore, the T_g can be thought of as an index for the degree of curing [17,18]. Both the Pascault and Williams Equation (5) and the Venditt and Gillham Equation (6) were used to fit the experimental glass transition data *versus* the degree of curing. The modeled curves are compared with experimental values in Figure 8. It has been found that both equations fit the experimental results very well.

The structure-related parameter, λ, and $\Delta c_{p\infty}/\Delta c_{p0}$ were determined by nonlinear least-squares regression analysis. The values for λ and $\Delta c_{p\infty}/\Delta c_{p0}$ were 0.64 and 0.87, respectively. Materials with different structures may have different λ values. The reported values of λ and $\Delta c_{p\infty}/\Delta c_{p0}$ for epoxy systems range from 0.16 to 0.69 [19,20,28].

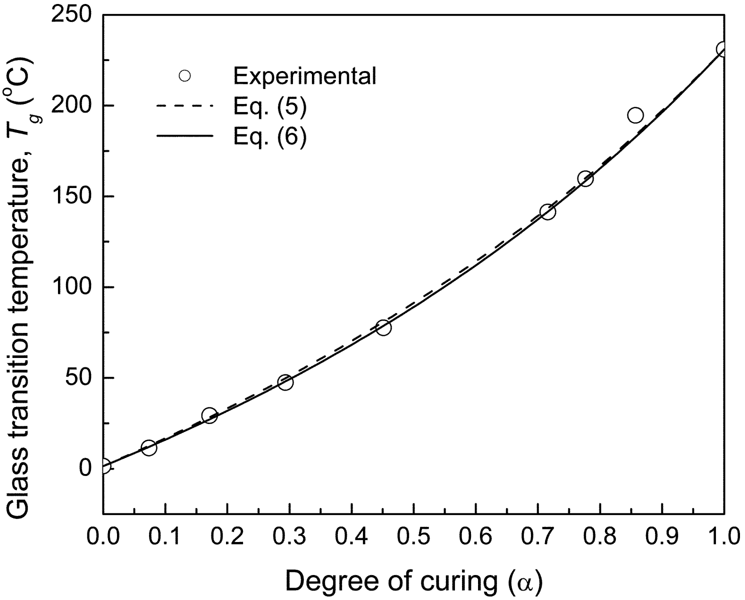

FIGURE 8 Dependence of T_g upon the degree of curing.

The curvature of the T_g plot *versus* the degree of curing is affected by the value of λ [19,27]. A smaller value of λ will result in a larger curvature. This means that T_g increases faster at a higher degree of curing.

3.4. Isothermal TTT Curing Diagram and CTT Curing Diagram

The dependence of the degree of curing of an epoxy prepreg resin upon time has been investigated in isothermal conditions [12]. The relationship between T_g and the isothermal cure time can be found only if the glass transition temperature depends solely upon the degree of curing, being independent of the curing temperature. In other words, only in these conditions can the cure time required for T_g to rise to the isothermal curing temperature be determined. This relationship can be represented by the vitrification curve.

The gel time can be determined by dynamic rheology analysis using different criteria [30,31]. In the present investigation, the gel time of the isothermal curing process was considered as the time required for the storage modulus G′ to equal the loss modulus G″. The relationship between isothermal curing temperature and the gel time is represented by the gelation curve. As shown in Figure 9, the isothermal

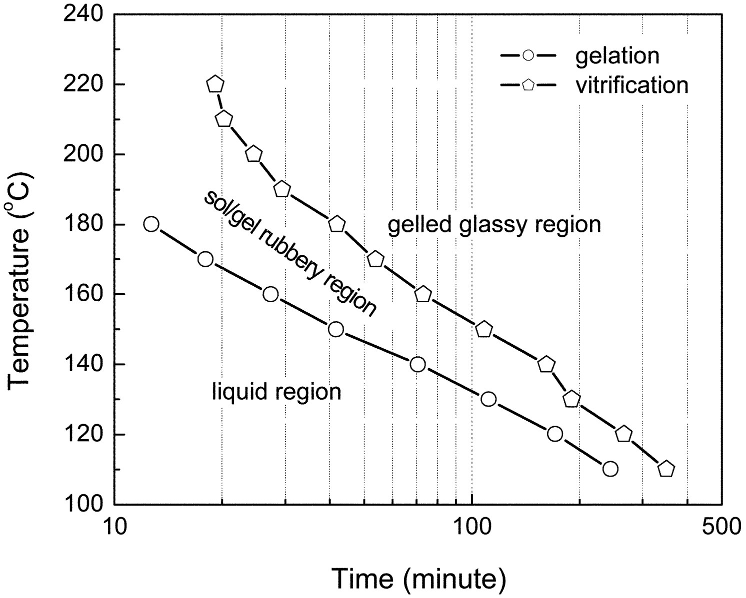

FIGURE 9 TTT diagram of isothermal curing for the epoxy prepreg system.

TTT curing diagram can be constructed by plotting both the vitrification and the gelation curve in the same graph. Depending upon the isothermal curing path with respect to temperature and time, the curing process is controlled by kinetics in the liquid and rubbery regions and by diffusion in the glassy region of the resin.

The CTT phase diagram for curing the epoxy prepreg system is shown in Figure 10. For the isothermal curing temperatures considered, the degree of curing at the gel time ranged from 0.49 to 0.53, with an average value of 0.513. This value was used to draw the straight gelation line in Figure 10. The vitrification curve was obtained from the relationship of T_g *versus* the degree of curing. As shown in Figure 10, the glass transition temperature at the gel point, ${}_{\mathrm{gel}}T_g$, read at the intersection of the gelation line with the vitrification curve, was 93.4°C. For a given degree of curing and a curing temperature, the CTT diagram can tell whether the curing of epoxy resins is controlled kinetically (reaction rate) or by a diffusion process. In an example of an isothermal curing process at 160°C, when the degree of curing increased to about 0.51, the epoxy resin system reached the state of gelation. It is the onset of a crosslinked network. This was the upper limit point for the epoxy resin system to be processable because it lost its ability to flow. However, the reaction rate remained

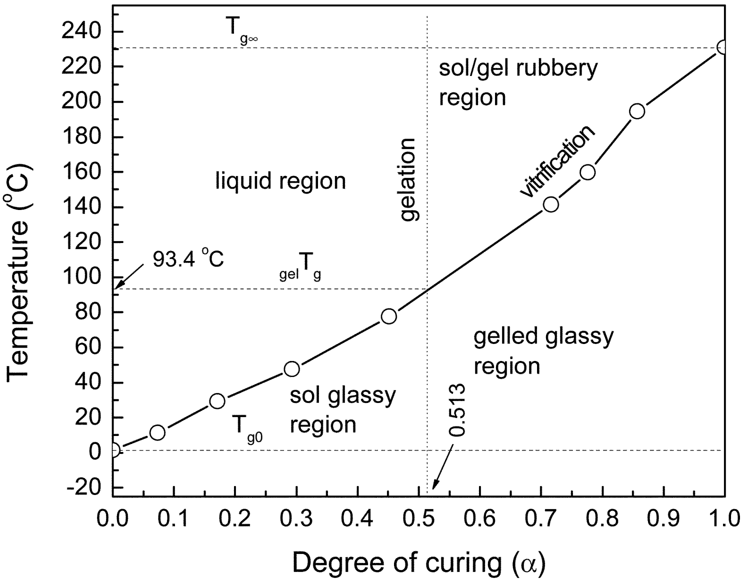

FIGURE 10 CTT phase diagram for curing of the epoxy prepreg system.

unchanged (kinetically controlled) at this point. The degree of curing continued to increase. The epoxy resin system reached a glassy state at a degree of curing of about 0.75. At this point, the curing process became diffusion controlled. The cure reaction rate decreased dramatically, and the degree of curing increased very slowly. Raising the cure temperature to a higher level (*e.g.*, 180°C) would change the epoxy resin system from a glassy state to a gel state. The curing process once again became kinetically controlled until it reached a new glass transition point at a degree of curing of about 0.82.

As reported earlier in Figure 4, for the degree of curing from 0.1 to 0.6, there was an almost linear relationship between the reciprocal of cure temperature and logarithmic cure time, indicating the curing process was kinetically controlled. For the degree of curing from 0.7 to 0.9, the relationship was nonlinear, indicating the curing process was diffusion controlled. This phenomenon can be explained by the CTT phase diagram. For the epoxy resin system with degree of curing of 0.6, its T_g was about 110°C. So, all the isothermal cure temperatures (except 110°C) were higher than T_g. The epoxy resin system was in either a liquid or gel state. So, diffusion was not a problem to the curing process and, thus, a linear relationship was observed. For the epoxy resin system with a degree of curing of 0.7, its T_g was 137°C. Two isothermal cure temperatures (110 and 120°C) were far below the T_g; so, the epoxy resin system was in the glassy state. The curing process was dominated by diffusion and, therefore, a nonlinear relationship was observed.

3.5. Thermal Stability

The thermal stability might affect both the curing process of epoxy prepregs and the mechanical properties of the cured material. TGA is capable of detecting very small weight differences owing to the loss of volatile components present in the composition or resulting from the thermal degradation of the material. A fresh prepreg sample of size 15.688 mg was scanned with TGA from 25 to 600°C, heating at 5°C/min. Figure 11 shows the variation of the weight percent and its derivative with temperature. The volatile content in the epoxy prepreg sample was very small, about 0.2%. The sample was very stable over a wide range temperature, from room temperature up to 300°C, where the weight loss was only 1%. The study of the cure reaction analysis should be limited to this temperature range to prevent the effect of thermal degradation on the DSC heat flow. The onset of degradation occurred at 330°C (the intersection of the two dashed tangent lines). Above this temperature, the weight loss of sample increased

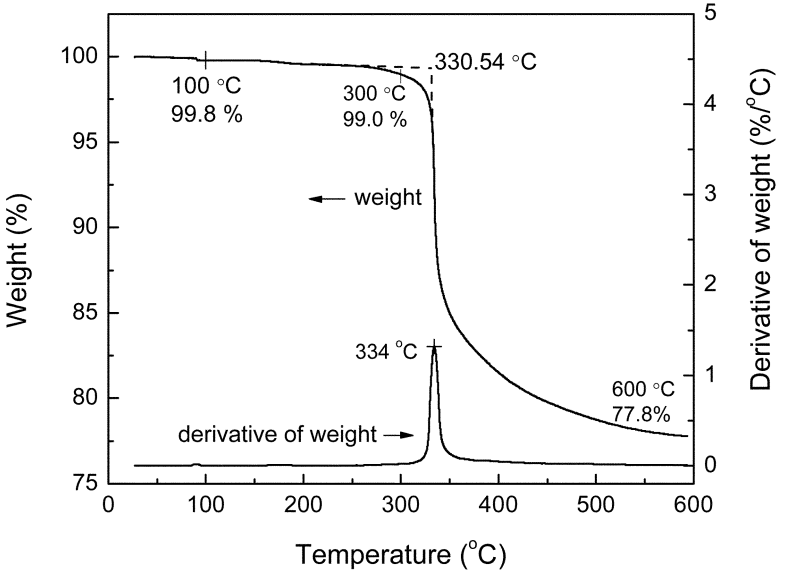

FIGURE 11 TGA curves of epoxy prepreg samples. Numerical data correspond to the uncured epoxy prepreg sample.

dramatically. The maximum rate of thermal degradation, as given by the derivative of the weight loss curve, occurred at 334°C (peak temperature). The weight loss at 600°C was about 22%. Considering that the prepreg contained 33% (w/w) epoxy resin, about 67% of the cured resin decomposed.

4. CONCLUSIONS

The maximum degree of curing in the isothermal curing process increased with the increment of isothermal cure temperature. Both the maximum cure time and half-life decay exponentially with respect to the isothermal cure temperature. When the degree of curing reached a certain value, the curing process became diffusion controlled. The autocatalytic four-parameter model without diffusion control deviated largely from actual data in the late stages of the isothermal curing process. However, the autocatalytic six-parameter model with diffusion control agreed very well with experimental data over the whole isothermal curing process. For the dynamic curing process, the degree of curing given by the Kissinger and Ozawa approach agreed well with experimental data in the late curing stages, whereas the degree of curing calculated by Borchardt and Daniels approach agreed well with the experimental values in the early curing stages.

The glass transition temperature increased nonlinearly with the degree of curing. The T_g values for the uncured and fully cured epoxy prepregs were 1.4 and 231.0°C, respectively. The unique relationship between T_g and the degree of curing can be modeled by the modified DiBenedetto equation and by the equation proposed by Venditt and Gillham. Both equations agreed well with the experimental T_g values.

The isothermal TTT and CTT curing diagrams are very useful for the selection of curing cycles. The appearance of gelation and vitrification closely relates to the phase transition. The different phase states were clearly represented in different regions of TTT and CTT diagrams. The TTT and CTT diagrams were able to predict when and where the curing process was kinetically controlled or was controlled by diffusion.

Thermogravimetric analysis indicated that the epoxy resin system was very thermally stable over a temperature range from room temperature to 300°C. The onset thermal degradation temperature was 334°C, at a heating rate of 5°C/min. The maximum rate of degradation was recorded at 334°C, and about 67% of the epoxy resin system degraded at 600°C.

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