

A Unified Treatment of Cure and Degradation Through the Composite Methodology

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SYNOPSIS

The *composite methodology*, developed by Seferis and coworkers, was used to describe the kinetics for both a commercial and a model controlled-flow epoxy-based resin system throughout cure and degradation. By utilizing this previously developed generalized methodology, capable of describing two or more kinetic mechanisms acting in series or parallel, a fundamental understanding of the kinetic behavior of a prepreg system from cure through degradation was established. Differential scanning calorimetry (DSC), and simultaneous differential thermal analysis–thermogravimetric analysis (SDT) were utilized to provide the experimental kinetic information. Two approaches were used to determine the activation energies for each of the resin systems, and a comparison is made between these approaches and the two thermoanalytical techniques. Using the determined kinetic parameters, the kinetic model was compared with experimental kinetics throughout cure and degradation at heating rates from 2–20°C/min. The results show that the kinetic model fits the experimental data well. In addition, the results demonstrate that the same weighting factors are applicable to both the model and commercial controlled-flow resins. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Controlled-flow resin prepreg systems are important in the processing of honeycomb structures in the aircraft industry.^{1,2} One requirement of these systems is that they demonstrate a much higher minimum viscosity during cure than an unmodified prepreg resin. The controlled flow characteristic of these resin systems allows the resin to remain in the prepreg skins, and not bleed into the honeycomb core while the honeycomb structure is being cured.²

A commercially available controlled-flow epoxy-based prepreg system, presently qualified to Boeing Material Specification, BMS 8-256, was modeled with the use of thermal analysis.³ The controlled flow model prepreg system was developed so the kinetic and rheological requirements of such systems can be investigated as they relate to processing and

properties. More specific to this study is the development of a kinetic model that describes the experimental kinetics of both the model and commercial controlled-flow prepreg resin systems throughout cure and degradation.

The *composite methodology* has been used in the past to model either cure or degradation mechanisms, with multiple reactions, of neat polymers and composites.^{4–6} A unifying extension of this model is developed here to describe the kinetic mechanisms from cure through degradation. Cure and degradation reactions are typically analyzed as separate entities. Cure is classically discussed in terms of conversion, where reactants are converted to the desired product(s). On the other hand, degradation occurs due to the transformation of products into typically undesired substances such as gases and/or char. The combination of these reactions is necessary for a complete understanding of the kinetics of multiple reaction systems so that the relative contribution of each reaction can be identified. As a result, the onset of these reactions, as they relate to cure and deg-

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radation, can be identified. For such systems, this can be accomplished by distinguishing the heat of reaction supplied by each of the cure and degradation reaction mechanisms. Usefulness of this type of model may be easily related to carbon-carbon technology where, as the curing reaction progresses, the viscoelastic resin/fiber precursor becomes more elastic, acting totally elastic when fully carbonized (e.g., totally degraded).⁷ Due to the different mechanisms of cure and degradation, the model developed here describes this complete process as the "percent reacted" from cure through degradation.

EXPERIMENTAL

Materials

The materials used in this study were a commercial controlled-flow resin prepreg system presently qualified to Boeing Commercial Airplane Material Specification BMS 8-256, and a model controlled-flow system. The model system components are included to show the complexity of the reacting system.³

The epoxy resins utilized in the controlled-flow model formulation were a combination of a difunctional and tetrafunctional epoxy manufactured by Shell Chemical Co. The difunctional epoxy used was Epon 8280, a low-molecular weight liquid of diglycidyl ether of bisphenol-A (DGEBA), which has a degassing agent added. The tetrafunctional epoxy used was Epon HPT 1077, which is tetraglycidylether of methylenedianiline (TGMDA). Bisphenol-A (BPA) was also used from Aldrich Chemical Co.

Elastomers used in the formulation are a combination of liquid and solid carboxyl-modified copolymers of butadiene and acrylonitrile. The liquid low-molecular weight carboxyl-terminated butadiene acrylonitrile (CTBN) elastomer, Hycar 1300*13, was obtained from B. F. Goodrich Co. The solid high-molecular weight carboxyl-modified elastomer used was Nipol 1472 (CMBN), from Zeon Chemical Co., which has randomly distributed pendant carboxyl groups on the copolymer of butadiene/acrylonitrile.

Two different amine curing agents were used in this formulation. The main curing agent used was diaminodiphenyl sulfone (DDS), HT 976, provided by Ciba-Geigy. The co-curing agent used was dicyandiamide (DICY), Amicure CG-1200, from Pacific Anchor Chemical Co.

Several processing solvents were used including acetone, methanol, and dimethylformamide.

The components were as follows: 225 g TGMDA, 75 g DGEBA, 30 g BPA, 7 g CMBN, 12 g CTBN, 45 g DDS, 6 g DICY.

Analysis

Differential scanning calorimetry (DSC) and simultaneous differential thermal analysis-thermogravimetric analysis (DTA-TGA) were utilized to generate both dynamic and isothermal kinetic data. Experiments were performed dynamically at heating rates of 2, 5, 7, 10, and 20°C/min to 400°C in N₂. Experiments were performed isothermally for 2 h at temperatures of 160, 165, 170, 175, and 180°C in N₂. DSC data were generated with a TA Instruments 912 DSC interfaced to a Thermal Analyst 2000 controller. DTA-TGA data were generated with a TA Instruments SDT 2960 interfaced to a Thermal Analyst 2100 controller. These experiments were performed on both the commercial and model controlled-flow resin systems.

Background

If the total heat of reaction for complete cure is ΔH_∞ , then the extent of reaction or conversion (α) at any time during an experiment can be found by

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_\infty} \quad (1)$$

The rate of conversion in a dynamic DSC experiment at a constant heating rate can be expressed as

$$\frac{d\alpha}{dt} = q \left(\frac{d\alpha}{dT} \right) = k(T) f(\alpha) \quad (2)$$

where q is the heating rate (dT/dt), $k(T)$ is the rate constant, and $f(\alpha)$ is the conversion-dependent function.

The temperature dependence of the rate constant, $k(T)$, may be described by the Arrhenius expression.

$$k(T) = A \exp(-E/RT) \quad (3)$$

Autocatalytic and n th order kinetics are the two general categories that can describe most thermoset curing mechanisms.⁸ If the rate of conversion is proportional to the concentration of unreacted material, then n th order kinetics can be assumed

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

where α is the degree of conversion and n is the reaction order.⁸

Combining eqs. (2) through (4), the following relation can be derived.

$$\frac{d\alpha}{dt} = q \left(\frac{d\alpha}{dT} \right) = A(1 - \alpha)^n \exp\left(-\frac{E}{RT}\right) \quad (5)$$

When equation (5) is integrated with respect to temperature and conversion, an integrated form is obtained:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{AE}{qR} \int_\infty^x \frac{\exp(-x)}{x^2} dx = \frac{AE}{qR} p(x) \quad (6)$$

where

$$p(x) = \int_\infty^x \frac{\exp(-x)}{x^2} dx \quad (7)$$

and $x = E/RT$. Many techniques, utilizing different approaches, have been developed for estimating the $p(x)$ integral.⁹⁻¹³ The technique used in this study for approximating $p(x)$ is an experimental formula developed to give extremely accurate results for a large range of $p(x)$.^{14,15} This formula is believed to give $p(x)$ errors less than 0.5% for the region $1.6 < x$, which is not observed by most other techniques.¹⁴ The empirical formula is

$$p(x) \approx \frac{e^{-x}}{(x - d)(x + 2)} \quad (8)$$

where the following expression has been found for the experimental parameter d .¹⁴

$$d = \frac{16}{x^2 - 4x + 84} \quad (9)$$

The two techniques used for determining the activation energy, E_a , and pre-exponential constant, A , were developed by Kissinger,¹¹ and Ozawa.^{16,17} Kissinger's technique assumes the maximum reaction rate occurs when $d^2\alpha(t)/dt^2 = 0$, which corresponds to the peak exotherm temperature(s). Therefore, differentiation of eq. (5) with respect to time and setting the resulting expression equal to zero gives

$$\frac{qE}{RT_m^2} = An(1 - \alpha)_m^{n-1} \exp\left(-\frac{E}{RT_m}\right) \quad (10)$$

where T_m is the maximum-rate (peak exotherm) temperature. This technique assumes that the product $n(1 - \alpha)_m^{n-1}$ is independent of the heating rate, q , which allows the activation energy to be found by a plot of $\ln(q/T_m^2)$ vs. $1/T_m$. This method was originally developed for DTA; however, it has been shown to be more accurate for DSC.¹⁸

Ozawa utilized Doyle's approximation¹⁹ to develop a relationship between activation energy (E_a), heating rate (q), and peak exotherm temperature (T_m) shown in eq. (11). It is assumed that the extent of reaction at the peak exotherm is constant and independent of heating rate. By using the following approximate relationship

$$\log q = C - 0.4567E_a/RT_m \quad (11)$$

the activation energy can be obtained from the peak exotherm temperature (T_m) as a function of heating rate (q).

The appropriate conversion-dependent function, $f(\alpha)$, is generally determined by assuming a hypothetical reaction mechanism and comparing the model results with the experimental data. However, the curing of a thermoset can be extremely complicated and may follow many independent reaction paths, not to mention the difficulties that arise when more than one curing agent is utilized to complete the cure. When several independent and/or competing reactions take place, the total reaction can be approximated by the composite methodology with appropriate weighting factors.⁴ Therefore, weighting factor(s) may be introduced to describe the relative contribution of each cure and degradation reaction mechanism, using

$$f(\alpha) = \sum_i y_i f_i(\alpha) \quad (12)$$

where the expressions used for $f_i(\alpha)$ are generally n th order or autocatalytic or a combination of both, and

$$\sum_i y_i = 1.0 \quad (13)$$

Specific forms of $f_i(\alpha)$ can be determined for a reacting system by understanding the physical and chemical nature of the formulation and performing isothermal and dynamic DSC and SDT experiments.

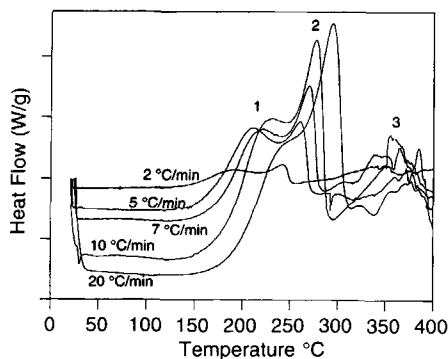


Figure 1 Dynamic DSC thermograms of the model controlled-flow resin performed at 5 different dynamic heating rates in N_2 .

RESULTS AND DISCUSSION

Dynamic kinetic experiments are more useful than isothermal kinetic experiments when multiple reaction exotherms, partially reacted systems, and/or difficult baseline determinations are observed.⁸ Each of these are possible in any thermoset reaction, but are more common with complex curing and degradation reactions. An example of this behavior is observed for both resin systems under investigation in which two curing exotherms and one degradation exotherm are seen when heated dynamically using DSC and SDT. Figure 1 demonstrates this phenomenon and the effect of heating rate on the model resin using DSC for the analysis. This figure shows that as the heating rate is increased from 2 °C/min to 20 °C/min, the peak temperatures associated with each cure and degradation exotherm increase, due to a decrease in residence time. The same experiments were performed on the commercial controlled-flow resin system, which show similar dynamic DSC and DTA thermograms. Figure 2 shows a DSC overlay of the two resin systems performed at 10 °C/min. This figure shows similar reaction exotherms, including reaction onset and peak temperatures for the two resin systems, as do comparisons at other heating rates. Using the corresponding peak temperatures associated with each cure and degradation exotherm at the heating rates of 2–20 °C/min, the necessary kinetic parameters were determined.

By using simple relationships between activation energy (E_a), heating rate (q), and the peak exotherm temperatures (T_m), the necessary kinetic parameters were determined for use in the kinetic model. Kissinger's method was used in addition to Ozawa's method to determine the activation energies (E_a) and the pre-exponential constants (A) for both resin

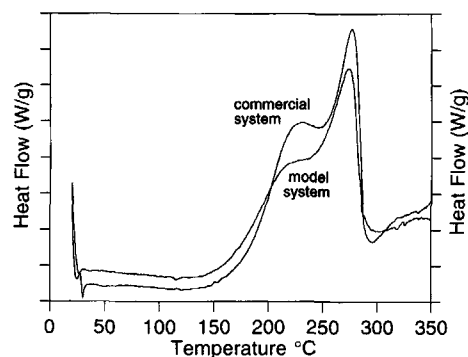


Figure 2 DSC comparison of the commercial and model controlled-flow resin, performed dynamically at 10 °C/min in N_2 .

systems. In these plots, activation energies were determined by the slope of the lines, and the pre-exponential constants were determined from the y intercepts. The equations used and the underlying assumptions for using these methods were discussed previously. Figure 3 demonstrates a plot of Kissinger's method used to determine the kinetic parameters of the model controlled-flow resin from cure through degradation. For this figure, the three peak temperatures were determined from DSC. The first two peak temperatures are associated with cure, and the third peak with degradation, as can be seen in Figure 1. The usefulness of this technique, as well as Ozawa's technique, is that the activation energy (E_a) can be determined without a specific assumption of the conversion-dependent function, $f(\alpha)$. Figure 4 demonstrates a plot of Ozawa's method used to determine the kinetic parameters of the model controlled-flow resin from cure through degradation. For this figure, the peak temperatures were determined from SDT to illustrate the other method of

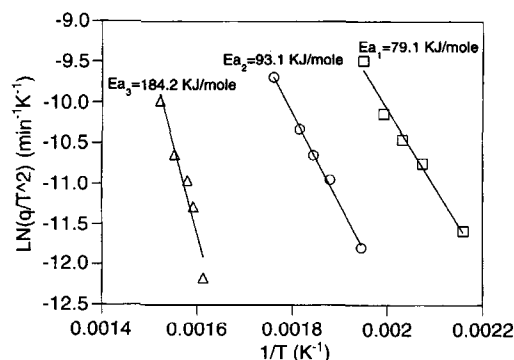


Figure 3 Kissinger's method used to determine the cure and degradation activation energies from the peak temperatures obtained by dynamic DSC experiments.

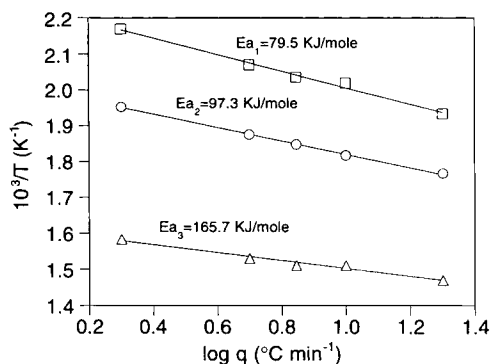


Figure 4 Ozawa's method used to determine the cure and degradation activation energies from the peak temperatures obtained by dynamic SDT experiments.

kinetic parameter analysis used. Table 1 shows the activation energies for the two resins determined from Kissinger's and Ozawa's methods using experimental information from the two thermoanalytical techniques. Again, the two cure exotherms are associated with one and two, and the degradation exotherm with three. This table shows that there is little variation in the activation energies determined by Kissinger's and Ozawa's methods. A comparison between DSC and DTA shows similar activation energies for the curing reactions, but large variations for the degradation activation energies. For the commercial resin, the results from DTA show higher degradation activation energies than DSC. This phenomenon is reversed for the model resin. The large experimental differences in degradation activation energies seen when comparing results from DSC and DTA can be attributed to the unclearly

defined degradation exotherm peaks for DTA. Therefore, DSC experimental results were used in the kinetic model.

Due to the proprietary nature of the commercial system components, only the model resin components will be discussed. The possible curing reactions associated with the various components in the model formulation were minimized by adducting the reactive rubber with the epoxy. Therefore, curing agent selectivity was not a problem, and only epoxy/curing agent reactions were assumed to occur.²⁰ A combination of two curing agents, dicyandiamide (DICY) and diaminodiphenyl sulfone (DDS), are used in the model formulation to provide the required kinetics and final properties. The activation temperature for the co-curing agent, DICY, is lower than that of DDS. Therefore, the first exotherm and the resulting activation energy of the model resin are attributed to the DICY/epoxy reaction. The activation energy determined for this reaction for the model resin was found to correspond to the literature values reported for the reaction of DICY and difunctional resins (DGEBA). The literature values ranged from approximately 52–96 kJ/mol depending on the DICY particle size.²¹ In resin formulations, many variables affect activation energies including epoxy resin selection, stoichiometric ratio of curing agent to epoxy, as well as the chemical and physical nature of the curing agent used, and the method of incorporation in the formulation. This reaction has been regarded as very complex, as described by many investigators.^{22–26} Even though the reaction is complex, previous investigators have used *n*th order kinetics to describe this reaction.²¹ Hence, the first reaction

Table I Activation Energies of the Cure and Degradation Reactions for the Commercial and Model Resin

Resin	Analysis Technique	Exotherm	E_{act} Kissinger's (kJ/mol)	E_{act} Ozawa's (kJ/mol)
BMS 8-256	DSC	1	63.1	67.9
		2	100.2	104
		3	137.6	149.9
	SDT	1	67.5	72.3
		2	98.4	102.2
		3	177	183.5
Model Controlled-Resin	DSC	1	79.1	83.9
		2	93.1	97.3
		3	184.2	195.8
	SDT	1	74.8	79.5
		2	93.3	97.3
		3	158.6	165.7

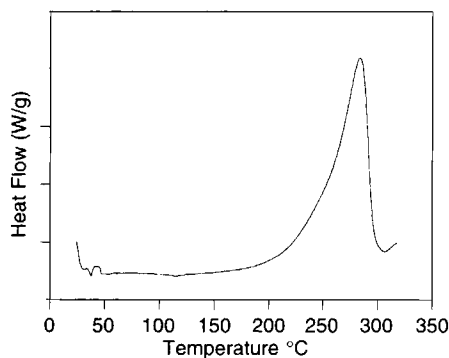


Figure 5 DSC thermogram of a modified model controlled-flow resin where only DDS is used as the curing agent, performed dynamically at 10°C/min in N₂.

exotherm resulting from the DICY/epoxy reaction was assumed to follow n th order kinetics. This assumption is verified later by isothermal experiments.

The reaction of epoxy with DDS, used to complete the cure in the model resin system, is well established in the literature.²⁷⁻³⁰ The DDS/epoxy reaction produced the second curing exotherm in the model system, and therefore the resulting second activation energy. This was determined by performing thermal analysis experiments on a modified model resin system where the components were the same, except only DDS (no DICY) was used as the curing agent. Figure 5 shows the results of a DSC experiment performed at 10°C/min to 350°C in N₂ on the modified model resin system. When this figure is compared with Figure 2, it is obvious by the higher activation temperature and peak exotherm temperature that this exotherm is responsible for the second activation energy. The activation energy for the DDS/epoxy reaction of the model system corresponds to the literature values. The values are reported to be between 69.7 and 99.1 kJ/mol depending on the stoichiometric ratio of epoxy to curing agent.¹⁷ Previous work by Nam and Seferis⁵ modeled the curing reaction of TGMDA/DDS as a combination of both n th order and autocatalytic kinetics, using the composite methodology. As a result, the curing reaction due to DDS in the model controlled-flow resin could be regarded as similar to that of the TGMDA/DDS reaction with the exception that the epoxy/DICY reactions have already occurred. Due to this previous reaction, the resulting conversion-dependent function $f(\alpha)$ could be assumed to follow either autocatalytic, n th order or a combination of the two for this reaction. For simplicity, the second reaction exotherm, resulting from the epoxy/DDS reaction, was assumed to follow n th order kinetics, which was

verified by isothermal experiments, which are described later. In addition, the degradation reaction exotherm was also assumed to follow n th order kinetics.

The conversion-dependent functions $f(\alpha)$ used to describe the reaction mechanisms of these two resin systems were assumed to be n th order for the curing and degradation reactions. This assumption was validated for the curing reactions by performing isothermal DSC and SDT experiments. Figure 6 shows an overlay plot of isothermal DSC experiments performed on the commercial resin. The reaction rate reaches a maximum at time zero, which is characteristic of an n th order reaction. Consequently, both resin systems demonstrate this isothermal behavior.

For the kinetic model developed in this paper, each reaction stage was assumed to follow n th order kinetics. More specifically, each reaction stage in the process was considered to follow first-order kinetics and proved later by model fitting. It was also assumed that each reaction occurs without significant competing reactions from the other curing agent. Thus, the kinetics of each reaction can be determined separately. Therefore, for a first-order reaction, the conversion or percent reacted can be obtained from eq. (6) as

$$\alpha = 1 - \exp\left(\frac{-AE_a p(x)}{Rq}\right) \quad (14)$$

where A and E_a are determined from the methods described previously. For the model predictions, the activation energies (E_a) and pre-exponential constants (A) were selected from Kissinger's method of analysis using DSC as the thermal technique.

The weighting factors for each of the reactions were determined experimentally for both the model

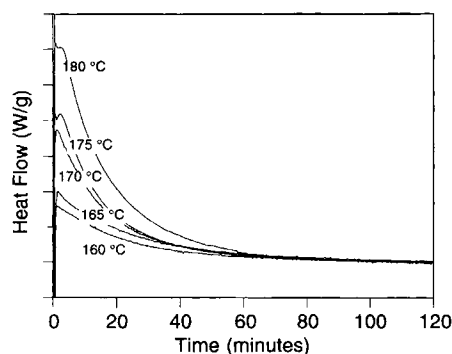


Figure 6 Isothermal DSC thermograms of the commercial resin system performed at five different isothermal temperatures in N₂.

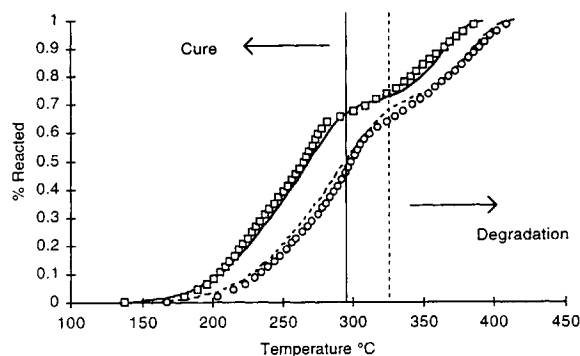


Figure 7 A plot of percent reacted vs. temperature comparing the experimental and model predictions of the model controlled-flow resin system for the heating rates of 7 (□) and 20°C/min (○).

and commercial resin system. First, the total heat of reaction for the combined cure and degradation exotherms was determined. Once this was accomplished, the separate heats of reaction were determined for each reaction, which allowed computation of the fractional contribution of each reaction. The experimental percentages determined for the commercial and model resin by this method are: peak one, 20–30%; peak two, 40–60%; peak three, 20–30%. The percentages are not exact due to differences in the two resin systems as well as the variability between repeated experiments. From a material balance, the total reacted can be simply derived as

$$\alpha = \sum_i y_i \alpha_i \quad (15)$$

where $\sum_i y_i$ must always equal one. The resulting expression was finalized by model fitting and determined to be

$$\alpha = 0.2\alpha_1 + 0.5\alpha_2 + 0.3\alpha_3 \quad (16)$$

which is applicable to both resin systems. This expression, used with eq. (14) and their respective determined kinetic parameters E_a , A , $p(x)$, predicts the experimental data very well for the 2–20°C/min heating rates from cure through degradation. Experimental data were determined by integrating cure through degradation of the DSC thermograms performed at the different heating rates. The parameters determined from Kissinger's method and DSC were used in the kinetic model results because this combination was found to predict the experimental data the best for both resin systems. Figure 7 shows a plot of the percent reacted vs. temperature of the

model controlled-flow resin system for the heating rates of 7 and 20°C/min. Clearly, it is seen that cure and degradation occur at lower temperatures for the 7°C/min heating rate as compared to the 20°C/min heating rate. The solid and dashed lines, which are model fits, are seen to predict the experimental data very well. Also in this plot, a solid line is drawn to distinguish cure from degradation for the 7°C/min heating rate, and a dashed line is drawn to distinguish cure from degradation for the 20°C/min heating rate. It should be noted that the cure reaction is distinguished from the degradation reaction, and the y axis is labeled "percent reacted" to include both cure conversion and degradation. This nomenclature is used because we cannot talk in terms of classical conversion if both cure and degradation are included in the same model. Also it is important to note that the "percent reacted" is a calorimetric percent, not a mole, weight, or volume percent. Figure 8 is a plot of the percent reacted vs. temperature of the commercial system for the heating rates of 7 and 20°C/min. Again, on this plot, a solid line is drawn to distinguish cure from degradation for the 7°C/min heating rate, and a dashed line is drawn to distinguish cure from degradation for the 20°C/min heating rate. The commercial system uses the same weighting factors as the model system in which only E_a and A are different.

Small deviations were observed when comparing the model fit to experimental data at 2°C/min heating rates. Figure 9 demonstrates this phenomenon. This figure shows the percent reacted vs. temperature of the model controlled-flow system performed at a heating rate of 2°C/min. A solid line is drawn to distinguish cure from degradation, at which a discontinuity is seen in the experimental data. This

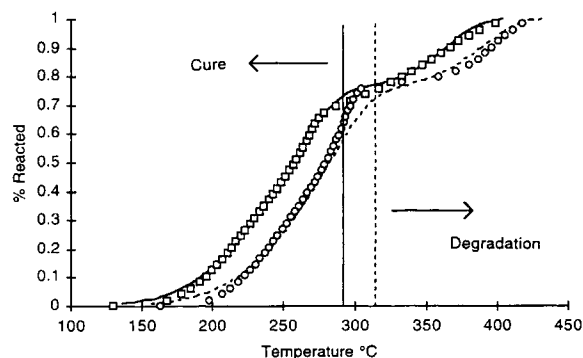


Figure 8 A plot of percent reacted vs. temperature comparing the experimental and model predictions of the commercial controlled-flow resin for the heating rates of 7 (□) and 20°C/min (○).

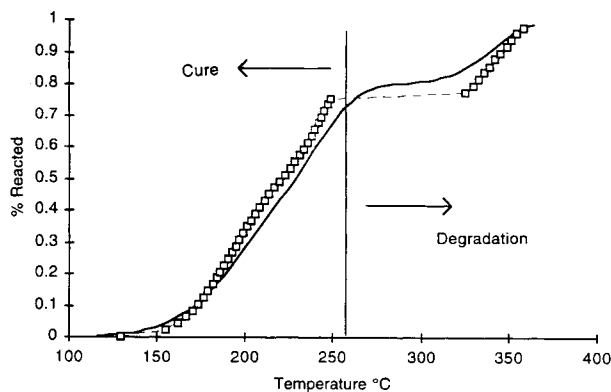


Figure 9 A plot of percent reacted vs. temperature comparing the experimental and model predictions of the model controlled-flow resin system performed at a heating rate of $2^{\circ}\text{C}/\text{min}$.

discontinuity is due to the insensitivity of the integration program where a gradual slope is observed during the transition to degradation. The small deviations of the model fit in this figure can be attributed to the increased sensitivity of the material components to a lower heating rate. Additionally, the peak temperatures and exotherms had significant variability between repeated experiments, which causes a difference in the activation energies. Furthermore, since the DSC and DTA thermograms changed slightly between repeated experiments, the experimental kinetics were changed. These differences, although slight, can cause the model to not fit as accurately as possible. However, for the heating rates investigated, the model predicted the experimental data very well.

Plots can also be created for percent reacted vs. time with the same modeling methodology. These plots are similar to the percent reacted vs. temperature plots because the heating rates are constant.

CONCLUSIONS

The *composite methodology* has previously been applied to either curing or degradation reactions. A unified treatment of the *composite methodology* was developed to describe cure through degradation using both a model controlled-flow epoxy-based resin and a commercially available controlled-flow resin system. DSC and SDT experimental results used in accordance with Kissinger's and Ozawa's method provided the kinetic parameters used in the model. The combination of DSC and Kissinger's method

provided the best parameters for the closest model fit for both systems examined.

Weighting factors for the kinetic model were determined from a balance of experimental results and model fit predictions. The kinetic expression developed from these weighting factors was found to be applicable to both the commercial and model controlled-flow resin systems.

By using the unified *composite methodology*, the relative contribution of each reaction can be identified whether the reaction is associated with cure or degradation. Consequently, two or more reaction mechanisms can be combined so the total reaction can be described in great detail. This work demonstrates that the *composite methodology*, previously developed for cure and degradation processes, can be unified to include cure through degradation, which is essential for complete kinetic characterization of composite system.

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