

# Cure Kinetics of Neat and Graphite-Fiber-Reinforced Epoxy Formulations

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## Synopsis

An investigation was carried out into the cure kinetics of neat and graphite fiber-reinforced epoxy formulation, composed of tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) resin and diaminodiphenyl sulfone (DDS) curing agent. Two experimental techniques were employed: isothermal differential scanning calorimetry (IDSC) and dynamic differential scanning calorimetry (DDSC). An autocatalytic mechanism with the overall reaction rate order of 2 was found to describe adequately the cure kinetics, of the neat resin and the composite. All kinetic parameters, including reaction rate constants, activation energies and preexponential factors, were calculated and reported. The presence of graphite fibers in the composite had only a very small initial effect on the kinetics of cure.

## INTRODUCTION

A comprehensive research program in advanced composites is currently underway at Polytechnic University, a part of which is aimed at fundamental modeling of processing of fiber-reinforced polymer-matrix composites.<sup>1-3</sup> An essential ingredient of such models is the information on the kinetics of cure, i.e., the rate of conversion of liquid prepolymer into a 3-dimensional thermoset network. In this study, we investigated the kinetics of an epoxy formulation based on tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and diaminodiphenyl sulfone (DDS), commonly used as the matrix material in advanced composites employed in the aerospace industry. Both neat and graphite fiber-reinforced formulations were studied and compared.

An excellent chronological review of the studies on thermoset cure kinetics was written by Prime, several years ago.<sup>4</sup> The majority of the subsequent research activity in the field of cure of epoxy resins has been cited in several recent publications by our group<sup>5-7</sup> and will not be reviewed here. But, despite the ongoing studies, the following two questions regarding epoxy cure have not been fully answered: (1) the exact mechanism of cure of the TGDDM/DDS formulation and (2) the effect of presence of graphite fibers on the rate of reactions in the matrix. This article addresses the latter question.

More specifically, the objectives of this study were: (1) to compare the results of the neat resin kinetics obtained from isothermal (IDSC) and

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dynamic differential scanning calorimetry (DDSC); (2) to provide a direct comparison of cure kinetics of neat resin versus composite and thence elucidate the effect of fibers (if any) on the rate of cure; and (3) to develop models that describe cure kinetics of the neat resin formulation and its graphite composite.

## EXPERIMENTAL

### Materials

The matrix formulation used in this study was composed of an epoxy resin (MY720 from Ciba-Geigy Co.) which contains mainly the tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) molecules, and 4,4'-diaminodiphenyl sulfone (DDS) as the curing agent. Their molecular structures are shown in Figure 1. The formulation contained 33 parts (25 wt %) of curing agent per hundred parts of resin (phr). The epoxy-amine mixtures were prepared by heating the resin to 120°C, adding the curing agent and stirring continuously until a clear mixture was obtained (in approximately 15 min). The homogeneous mixture was then degassed under a 25 in. Hg vacuum at 100°C for 20 min. The fiber selected for reinforcement was the Celion 6000 graphite fiber, which is a continuous, high-strength, polyacrylonitrile (PAN)-based fiber, used in 6000 (6K) filament-count tows. The fibers were surface treated to promote adhesion to epoxy compounds.

### Characterization

The incoming epoxy resin was characterized by infrared spectroscopy (IR) and nuclear magnetic resonance (NMR). The epoxy equivalent weight (EEW)

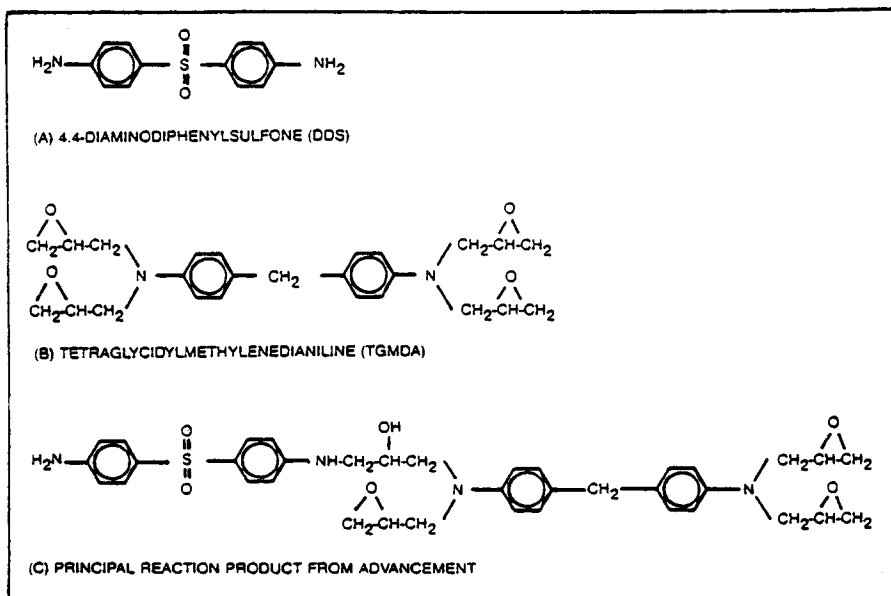


Fig. 1. Chemical composition of the resin.

was determined by dissolving a known amount of the resin in chlorobenzene and titrating it with HBr/AcOH 0.1*N* using crystal violet indicator solution (0.1%); the acid solution was standardized against potassium acid phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ). The titration was carried out according to the ASTM method 1652-73. The theoretical EEW value of TGDDM resin is 107; however, the calculated value of EEW of the received MY720 resin was 131, which is within the reported range of 126-133.

### Fabrication of the Prepreg Tape

The first step in the production of composites is the preparation of a unidirectional, resin-impregnated tape commonly referred to as "prepreg." The process used to manufacture Gr/Ep prepreg tape was divided into two stages: (I) coating of the formulated epoxy resin on the release paper and (II) preimpregnation of the aligned fibers. The details of our process have been described in the literature<sup>8</sup> and will not be repeated here.

For the study of kinetics of composite, the samples were obtained by cutting the Gr/Ep prepreg. The resin content in the prepreg was 48% by weight, and the prepreg pieces were cut to less than 0.5 mm in length. Samples weighing between 5 and 15 mg were then placed in hermetically sealed aluminum pans and tested.

### Techniques

#### *Isothermal Differential Scanning Calorimetry (IDSC)*

The calorimetric measurements were made with a Perkin-Elmer DSC-7. The heat of reaction was determined by carrying the reaction isothermally to completion at the following temperatures: 155, 167, 177, and 187°C. Thermal equilibrium of the sample and the reference holder was achieved in less than 30 s and nitrogen gas was introduced into the DSC cell. A continuous curve was obtained, showing the rate of heat generation for a given weight of sample as a function of cure time. The reaction was considered complete when the rate curve leveled off to a baseline. The total area under the exotherm curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure ( $H_I$ ) at a given temperature.

After the isothermal cure was completed, the sample was cooled rapidly in the DSC to 30°C. It was then heated at 10°C/min from 30 to 280°C in order to determine the residual heat of reaction ( $H_R$ ). The sum of the isothermal heat and the residual heat was taken to represent the ultimate heat of cure ( $H_{\text{ult}}$ ). The reaction rate was determined directly from the DSC thermograms according to the following equation:

$$\frac{d\alpha}{dt} = \frac{1}{H_{\text{ult}}} \frac{dH}{dt} \quad (1)$$

To express the experimental results in terms of the extent of reaction ( $\alpha$ ), the DSC curves were integrated, and the partial areas, as a function of time, were normalized with respect to  $H_{\text{ult}}$  and sample weight.

*Dynamic Differential Scanning Calorimetry (DDSC)*

A dynamic scan of an "as-prepared" sample was run yielding the reference value of the total heat of reaction,  $H_T$ . Other samples were then cured at different temperatures isothermally, in an oven or the DSC itself, for various periods of time. At desired time intervals, samples were removed from the isothermal cure environment and quenched. A dynamic scan (10°C/min) was then applied to these partially cured samples, and the residual heat of reaction  $H_R$  was recorded. The difference of  $H_T$  and  $H_R$  was taken as the heat of reaction during the elapsed period at a given temperature. The degree of conversion for DDSC was calculated from

$$\alpha = \frac{H_T - H_R}{H_T} \quad (2)$$

**RESULTS AND DISCUSSION****Cure Kinetics of the Neat Resin***Isothermal Differential Scanning Calorimetry (IDSC)*

The values of  $H_I$ ,  $H_R$ , and  $H_{ult}$  were calculated as a function of isothermal curing temperature according to the procedure described in experimental section, and are plotted in Figure 2. We found that, as the cure temperature is increased, the isothermal heat of reaction increases, while the residual heat of reaction decreases. However, the ultimate heat of reaction remains almost constant, at least within the temperature range used in this study.

To express the experimental results in terms of the extent of reaction ( $\alpha$ ), the DSC curves were integrated using eq. (1), and the partial areas as a function of time were normalized with respect to  $H_{ult}$  and the sample weight. The solid curves in Figure 3 represent the degree of conversion as a function of time with cure temperature as a parameter. Gupta et al.<sup>9</sup> also studied the MY720/DDS epoxy formulation, and found that the total heat of reaction obtained from DSC thermograms was 143 cal/g (597 J/g), which compares very well with the result of this work ( $H_t = 145$  cal/g). At each cure temperature, the extent of reaction levels off before reaching the fully cured state (100%). This result can be interpreted by invoking the concept of vitrification, whereby due to the growth of the thermoset network the glass transition of the polymer exceeds the curing temperature and the polymer network vitrifies. Naturally, further curing in the glassy state, albeit conceivable, is extremely slow. The onset of vitrification causes a shift from the chemical control to the diffusion control of cure reactions. The entire concept of vitrification, which is out of the scope of this study, has been described in a series of fine papers by Gillham and co-workers.<sup>10,11</sup>

*Dynamic Differential Scanning Calorimetry (DDSC)*

This method of kinetic analysis is generally preferred when the rate of heat evolution is too small for detection by the IDSC method or very long times are required, which is particularly true at low temperatures. A shortcoming of

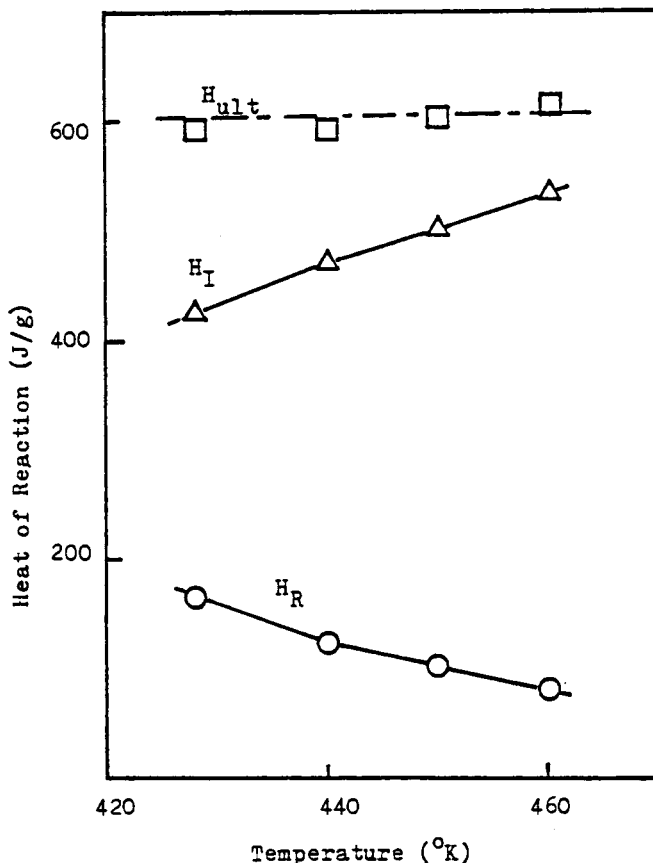


Fig. 2. Isothermal ( $H_I$ ), residual ( $H_R$ ), and ultimate ( $H_{ult}$ ) heat of reaction as a function of curing temperature for neat resin.

this method is the lack of a direct measure of the reaction rate; however, reaction rates can be estimated from tangents to the conversion vs. cure time curves. Fava<sup>12</sup> showed the equivalency of IDSC and DDSC methods for epoxy-anhydride systems. In our study, the results calculated from eq. 2 are shown as the open symbols in Figure 3.

### Cure Kinetics of the Composite

In the next set of experiments, the DSC studies were performed on the prepreg. The total heat of reaction of 72 cal/g (302 J/g) was calculated from a dynamic scan (30–280°C at 10°C/min) of the prepreg sample. Since the resin content of the prepreg was 48% by weight, the calculated heat of reaction of the prepreg based upon the previously obtained value for neat resin should be 145 cal/g  $\times$  48% = 70 cal/g (the heat of reaction of neat resin was 145 cal/g). This result suggests that the preimpregnation process did not produce further cure in the prepreg.

The reaction rate and degree of cure of prepreg were calculated by the DDSC method and are plotted in Figure 4. For a better understanding of the

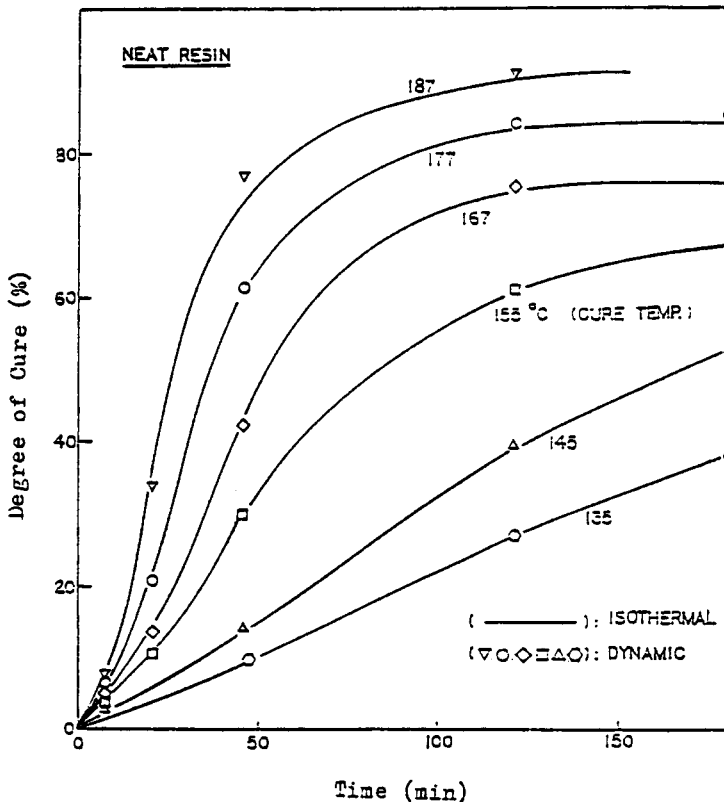


Fig. 3. Degree of cure as a function of time with cure temperature as a parameter. Comparison of isothermal (—) and dynamic ( $\nabla$ ,  $\circ$ ,  $\diamond$ ,  $\square$ ,  $\triangle$ ,  $\circ$ ) DSC data for neat resin.

kinetics of cure of the prepreg, conversions in the neat resin and the prepreg are compared in Figure 5. As seen in that figure, the initial reaction rates (the tangent of each curve) of prepreg were only slightly higher than those of neat resin; however, the final conversions of both are identical. The observed difference is not significant and could possibly result from the presence of the surface treatment of graphite fibers. The surface of graphite fiber used in this study was treated with an epoxy compatible material, which may have contributed to the slight increase in the initial reaction rate.

### Modeling of Cure Kinetics of Neat Resin and Composite

Thermoset cure is a complex process which begins by formation and linear growth of chains that soon begin to branch and then crosslink. In the past, both mechanistic and phenomenological approaches have been undertaken to describe the kinetics of cure of thermosets. The former approach relies upon the knowledge of the exact reaction mechanism, leading to the development of structural models via statistical analysis.<sup>13-16</sup> The latter treatment involves monitoring of a global change of characteristic parameters during cure without the precise understanding of events on the molecular level.

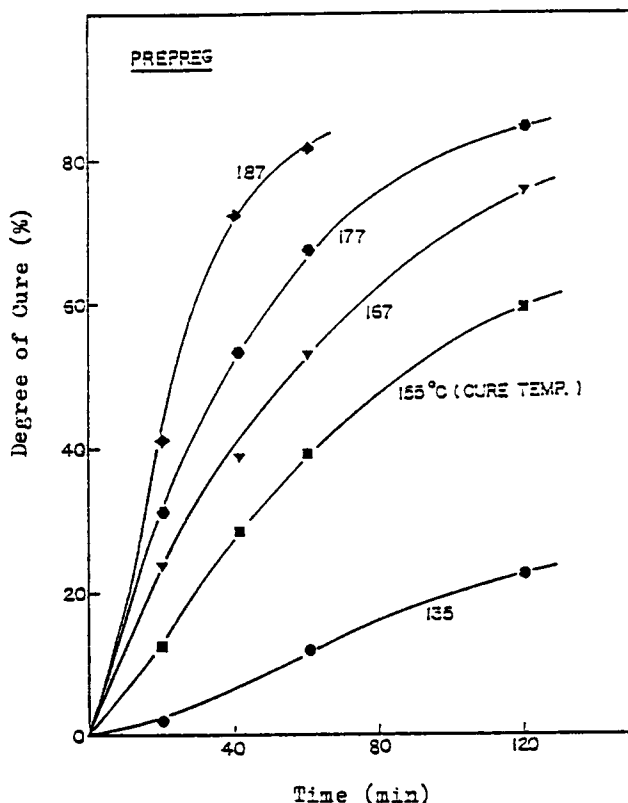


Fig. 4. Degree of cure as a function of time with cure temperature as a parameter. DSC data for composite.

In amine-cured epoxy resins, it is generally accepted that the primary amine-epoxide reaction starts first and proceeds at the highest rate. The possible subsequent reactions include the secondary amine-epoxide, the hydroxyl-epoxide, and the epoxide-epoxide reactions. This holds true for both bifunctional and multifunctional epoxies, although from the studies of reaction mechanisms of the latter group, a more complex picture has emerged. For instance, there is no consensus of opinion in the literature with respect to relative rates and importance of various reactions in TGDDM/DDS formulations.<sup>17-24</sup>

In an early study by Shechter et al.<sup>25</sup> the chemistry of cure of bifunctional epoxy resins by amine hardeners was investigated using model compound reactions. They found that combination of epoxide and primary amine leads to two principal reactions: (1) primary amine + epoxide = secondary amine and (2) secondary amine + epoxide = tertiary amine. They also found that hydroxyl groups generated during the reaction or provided by the addition of solvent (plus other catalysts, including moisture) accelerated the amine-glycidyl ether reaction markedly. In all cases, the hydroxyl group served only as a catalyst for the reaction and not as a contender for epoxide in competition with amine. According to the mechanism proposed by Shechter, hydroxyl group aids in the opening of the epoxide ring by hydrogen bonding

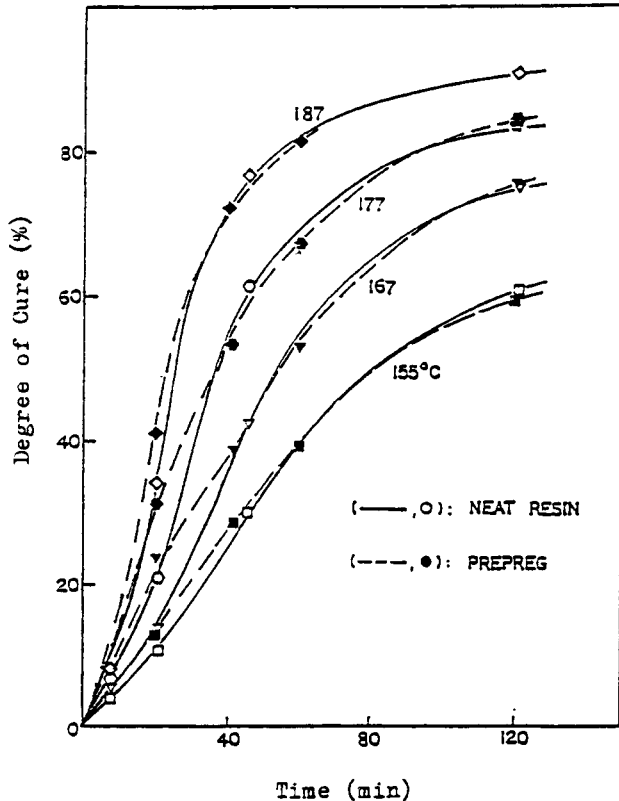


Fig. 5. Degree of cure as a function of time with cure temperature as a parameter. Comparison of DSC data for neat resin and composite: (—, ○) neat resin; (---, ●) prepreg.

in the transition state. Further support for this concept was later provided by Dusek and Bleha.<sup>26</sup> Smith<sup>27</sup> assumed that this mechanism is the rate-controlling step for the overall reaction between a secondary amine and epoxide and proposed a third-order kinetic expression which was consistent with the results of Shechter. Horie et al.<sup>28</sup> assumed that external catalysts or impurities, initially present in the system, as well as the reaction products containing hydroxyl groups, act as true catalysts and are not consumed in any side reactions. The following kinetic expression was derived:

$$d\alpha/dt = (k_1 + k_2\alpha)(1 - \alpha)(B - \alpha) \quad (3)$$

where  $\alpha$  is the degree of cure,  $k_1$  and  $k_2$  are rate constants, and  $B$  is the initial ratio of amine hydrogen equivalents to epoxide equivalents. This equation has been used by Horie<sup>28</sup> and was later modified empirically by Sourour and Kamal<sup>29</sup> in the study of amine-bifunctional epoxide reactions by differential scanning calorimetry. Subsequently, several authors<sup>30-36</sup> used the following modified form of eq. (3) to describe cure of both bifunctional and multifunctional epoxy resins:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (4)$$



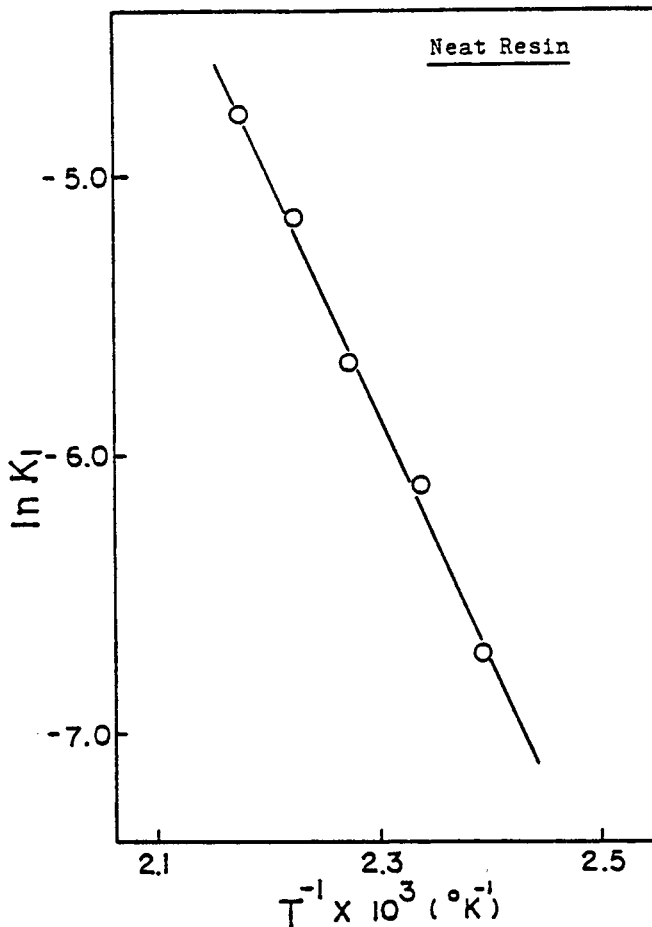


Fig. 6. Reaction rate constant  $k_1$  as a function of temperature for neat resin.

where the sum of  $m$  and  $n$  represent the overall reaction rate order. Equation (4) is an empirical equation which nevertheless adequately describes the autocatalytic cure kinetics of most amine-cured epoxy resins. The overall reaction order ( $m + n$ ) was assumed to be 2, and the validity of this assumption has been confirmed elsewhere.<sup>5</sup> The details of determination of  $k_1$ ,  $k_2$ , and  $m$ , together with references to all previous pertinent kinetic information, were included in our recent publications.<sup>5-7</sup> The reaction rate constants  $k_1$  and  $k_2$  of the neat resin, and the composite are plotted as a function of temperature in Figures 6-9. The activation energies calculated from these rate constants are summarized in Table I.

We have previously reported<sup>5</sup> that the activation energies for the MY720/DDS (19% by weight DDS) system were  $E_{r1} = 21.7$  kcal/mol and  $E_{r2} = 15.9$  kcal/mol. Lee et al.<sup>38</sup> used eq. (4) as their kinetic model and found  $E_{r1} = 19.3$  kcal/mol and  $E_{r2} = 18.6$  kcal/mol, respectively. Dusi et al.<sup>39</sup> assumed a different mechanistic kinetic model and determined  $E_k$  to be 16.1 kcal/mol for the boron trifluoride monoethylamine ( $\text{BF}_3\text{MEA}$ )-accelerated TGDDM/DDS system as 17.5 kcal/mol for the nonaccelerated system. A

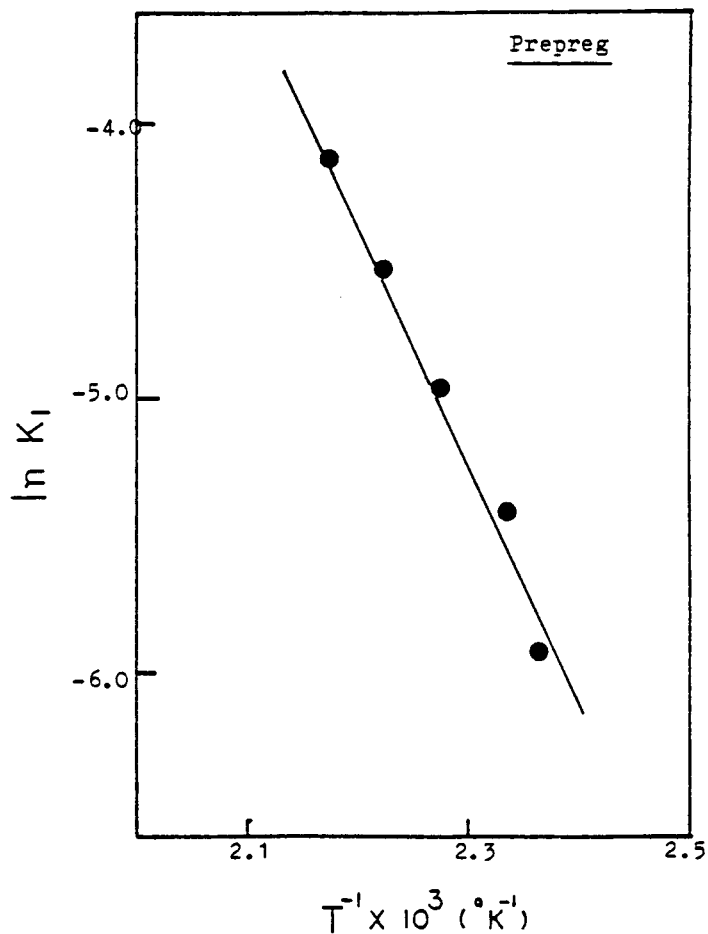


Fig. 7. Reaction rate constant  $k_1$  as a function of temperature for composite.

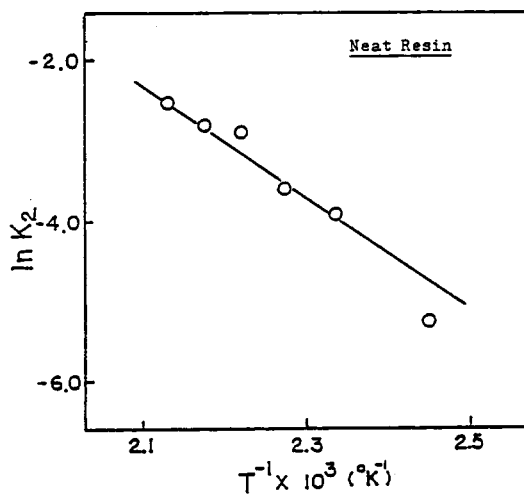


Fig. 8. Reaction rate constant  $k_2$  as a function of temperature for neat resin.

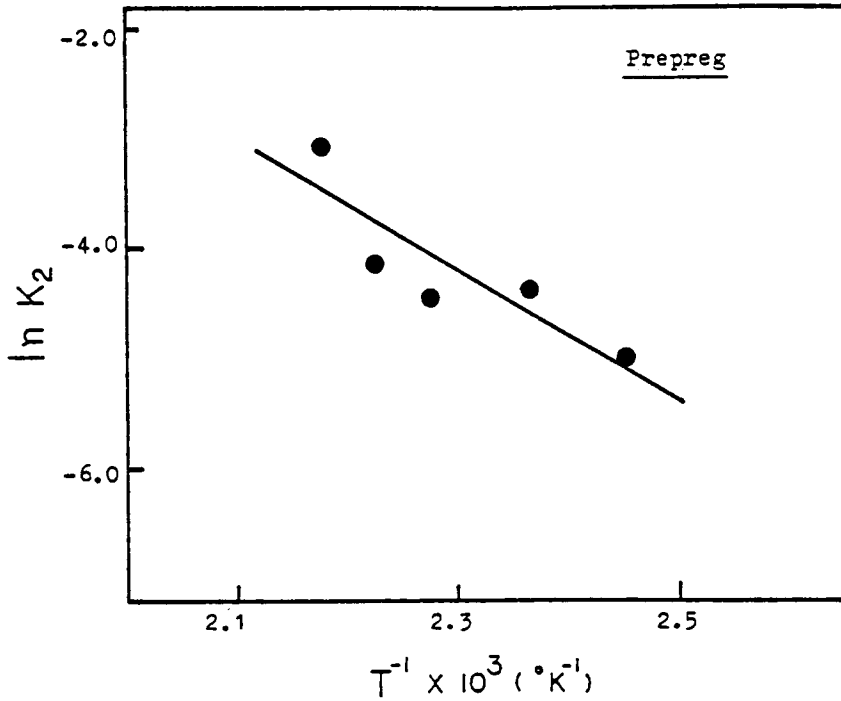


Fig. 9. Reaction rate constant  $k_2$  as a function of temperature for composite.

TABLE I  
Summary of Kinetic Parameters

(A) Neat resin	
$k_1$ ( $\text{min}^{-1}$ )	$1.58 \times 10^6 \exp(-17.4 \text{ kcal/gmol/RT})$
$k_2$	$2.21 \times 10^5 \exp(-13.9 \text{ kcal/gmol/RT})$
$E_{r1}$	17.4 kcal/mol
$E_{r2}$	14.0 kcal/gmol
(B) Composite	
$k_1$ ( $\text{min}^{-1}$ )	$9.43 \times 10^6 \exp(-18.5 \text{ kcal/gmol/RT})$
$k_2$	$1.47 \times 10^5 \exp(-13.9 \text{ kcal/gmol/RT})$
$E_{p1}$	18.5 kcal/mol
$E_{p2}$	13.9 kcal/mol

value of 12–13 kcal/mol was obtained from a dielectric study of cure.<sup>40</sup> Our experimental data fall within the range of the reported results.<sup>37-40</sup>

The herein developed autocatalytic kinetic model is further used in the modeling studies of composites processing. The reaction rate expression is substituted into an energy balance equation, which is then solved for the temperature distribution during cure as a function of time and location within the laminate. This topic is discussed in our recent publication.<sup>3</sup>

### CONCLUSIONS

We have completed an investigation of the cure kinetics of a neat epoxy formulation and its graphite fiber composite. The formulation studied was

comprised of a tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) epoxy resin and diaminodiphenyl sulfone (DDS) as the curing agent. Experimental results were generated by isothermal and dynamic differential scanning calorimetry. An autocatalytic reaction rate expression was found to describe well the kinetics of both the neat resin and the composite. Plots of extent of reaction as a function of cure time had a characteristic "S" shape, while the reaction rate constants followed the Arrhenius dependence on temperature. The presence of fibers in the composite caused only a slight initial increase in the reaction rate but the final extent of reaction remained unaffected.

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