

## STOICHIOMETRIC AND HEATING-RATE EFFECTS ON DSC-EVALUATED KINETICS FOR A HIGH-PERFORMANCE EPOXY SYSTEM

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(Received 28 December 1983)

### ABSTRACT

Dynamic DSC experiments on a high-performance amine-cured epoxy system have shown that the kinetic parameters determined assuming an overall reaction for the system are dependent on the heating rate of the scan. The high-performance system examined in this investigation is the TGDDM–DDS epoxy system. Changes in the number, location, and magnitude of the transitions in the thermograms which occur with changes in the heating rate were interpreted through the definition of two reaction regimes: one in which the primary-amine addition reaction predominates; and the other in which the secondary-amine addition, hydroxyl–epoxide, and homopolymerization reactions become significant. To elucidate these regimes, three compositions were examined: epoxy alone; excess epoxy; and excess amine. The activation energies for the two reaction regimes were determined to be 16.7 and 42.3 kcal mol<sup>-1</sup>, respectively. A model proposed by Prime for the heating rate dependence of the kinetic parameters as determined by DSC is also analyzed for its applicability for the kinetic analysis of this reaction system. Further, analysis of isothermal data is considered as an integral part of the kinetic analysis for this system.

### INTRODUCTION

Composite materials are being utilized in increasing amounts for the construction of commercial aircraft, and their use in load-bearing applications is expected to expand appreciably in the near future. Carbon-fiber reinforced epoxy composites presently constitute the most widely employed systems in the aerospace industry thus placing major emphasis on understanding the kinetic behavior of the epoxy matrix systems both for quality control purposes and for the determination of processing and property

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characteristics. The epoxy component utilized in most high performance matrix formulations is the tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) which is cured in the presence of an amine, usually 4,4'-diaminodiphenylsulfone (DDS). To these basic multifunctional components, others are incorporated in the manufacture of commercial formulations for ease of processing and matrix-dominated property improvements. Accordingly, the work of Seferis and co-workers has been focused on TGDDM-DDS systems consisting of excess amounts of epoxies and containing various amounts of polyglycidyl ether of Bisphenol-A Novalac [1-4] and boron trifluoride-monoethylamine ( $\text{BF}_3\text{-MEA}$ ) as a catalyst [5,6], approximating commercial systems such as Narmco 5208 and Fiberite 934, respectively.

Nicolais and co-workers [7] as well as other investigators [8] have focused their efforts on the TGDDM-DDS and DGEBA-TETA systems emphasizing stoichiometric formulations with excess amounts of amine. Combined efforts by both groups have led to an understanding on a fundamental basis of the dynamic and static moisture behavior of these systems based on structural and polymer network descriptors [9,10]. Network descriptors, even for the complex commercial epoxy systems, have proved to be the key in model development for property and processing understanding [2].

In order to provide details about the network structure, the reaction kinetics and types of the curing reaction must be investigated so that the types of linkages and network density may be identified. In general, differential scanning calorimetry (DSC) has been shown to be a valuable tool in studying reaction kinetics and is thus utilized in the present investigation. However, the interpretation of the data obtained by this technique has been the source of considerable discussion [11-13]. Of particular interest to this analysis is the dependence of the kinetic parameters determined by DSC on the heating rate of the scan. In two communications, Prime put forth a model which, unlike previous experimenters, incorporated the heating rate as a parameter in the kinetic analysis [14,15]. This model assumes that the activation energy, apparent order of reaction, and pre-exponential factor are all independent of temperature which means that only a single reaction with a single mechanism is being considered.

Morgan et al. [16] and Tanaka and Mika [17] have studied epoxy resins including the TGDDM-DDS system by spectroscopic and other techniques and have shown the existence of multiple reactions. Of the possible reactions in this epoxy system, the amine-epoxide addition reactions (both primary and secondary) and the hydroxyl-epoxide/homopolymerization reactions are of primary interest. In general, the identification of individual reactions within the overall cure mechanism is difficult using DSC since each reaction contributes, to a varying extent, to the overall heat of reaction. However, by adjusting the stoichiometry of the reacting mixture, the reaction regime of interest may be driven such that it is the only one of significance.

The present investigation was focused on the reaction kinetics determined

by DSC for the TGDDM–DDS epoxy system and how they are influenced by the heating rate of the experiment. In addition, the different possible reaction regimes occurring during the curing process may be separated and analyzed individually by altering the stoichiometry of the reacting mixture. By reacting TGDDM alone the kinetics of the hydroxyl–epoxide/homopolymerization reactions of the second regime were investigated while the stoichiometric composition for primary–amine addition (100 PHR DDS) was utilized to study that reaction regime. The theoretical derivation of Prime [14,15] is also investigated to determine its applicability to the data obtained. In order to simplify the analysis, the second resin, Novalac, was not included in this study. However, its effect on the kinetics of the curing reactions for the complete system, i.e., TGDDM–Novalac–DDS, has been previously reported [3].

## EXPERIMENTAL

The samples used in this study were a mixture of tetraglycidyl-4,4'-diaminodiphenylmethane (MY720) and 4,4'-diaminodiphenylsulfone. Two specific compositions utilizing 35 and 100 parts of DDS per 100 parts of epoxy (PHR) in the TGDDM were investigated. Considering that stoichiometrically for the amine–epoxide reaction 56 PHR DDS is required, the compositions examined provided two systems, one with excess epoxide groups and one with excess amino hydrogens.

The samples were prepared by dissolving the DDS in the TGDDM using 9 ml reagent grade acetone. Heating the mixture to 40–45°C facilitated the mixing procedure. A mixing time of 10–15 min was sufficient for the DDS to dissolve. Upon dissolution, the samples were placed in a vacuum oven at 60°C and 0 cm Hg absolute to remove the solvent. This procedure required approximately 4 h. After removal from the oven the beakers were sealed with a paraffin film and placed in a freezer at –10°C until required.

Prior to performing the experiment the beaker was removed from the freezer and allowed to equilibrate to room temperature, then a portion of the sample was placed in an aluminum sample pan and weighed. The weight of the samples used in these experiments was  $10.0 \pm 0.2$  mg. The lids were then placed on the pans and the pans were non-hermetically sealed. In order to achieve acceptable scans for the TGDDM alone a weight of between 2 and 3 mg was required due to the sensitivity of the instrument and the great exothermicity of the hydroxyl–epoxide reaction.

Reaction data and analyses were conducted with the DuPont 910 differential scanning calorimeter attached to the 1090 thermal analyzer. The DSC runs were performed in both isothermal and dynamic modes. The isothermal runs were done at three temperatures: 140, 160, and 180°C. The duration of these tests was extended until a stable baseline in the thermograms was

achieved. The dynamic experiments were performed at five different heating rates: 0.2, 2, 10, 20, and 50°C min<sup>-1</sup>. The tests started at about 30°C and finished after the exotherm was complete. The end temperature varied with the heating rate from 60°C for the 0.2°C min<sup>-1</sup> run to 400°C for the 50°C min<sup>-1</sup> run.

## RESULTS AND DISCUSSION

The DSC thermograms for the TGDDM-35 PHR DDS system at various heating rates are given in Fig. 1. At the slower heating rates (0.2 and 2°C min<sup>-1</sup>) multiple transitions may be distinguished, whereas at the faster heating rates (10, 20, and 50°C min<sup>-1</sup>) only a single peak is observed. With an increase in the heating rate the first peak may be seen to diminish while the second becomes the dominant peak. The slower heating rates also display a broadly-based and rounded peak while the others are more sharp and narrow. For all scans the overall heat of reaction was approximately the same for each case as can be seen from the values reported in Table 1.

If a standard Arrhenius expression is utilized to determine the kinetic parameters, i.e., activation energy, apparent order of reaction, and pre-exponential factor, a significant variation in these parameters is found with variations in the heating rate. In order to account for this apparent depend-

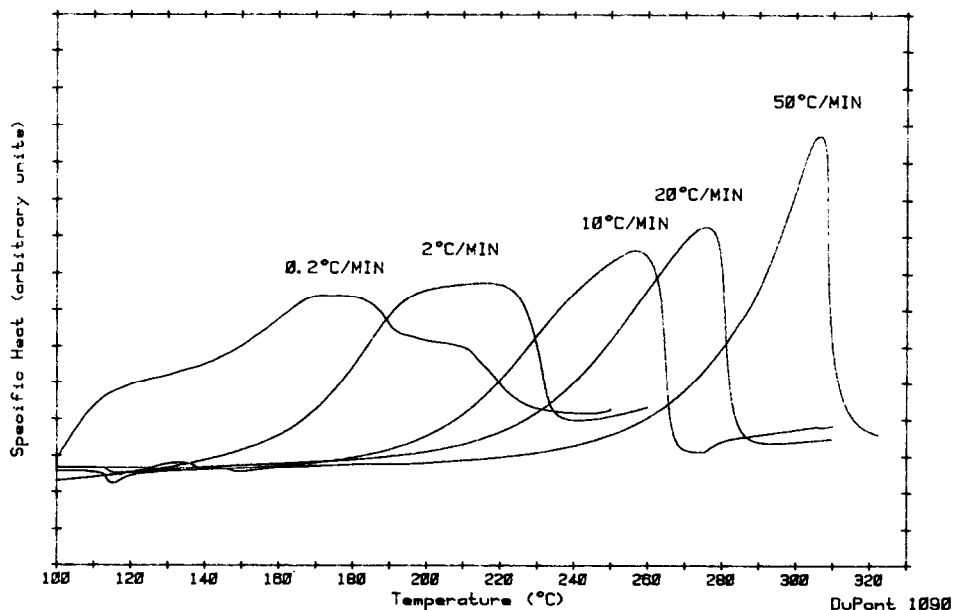


Fig. 1. DSC thermograms for the TGDDM-35 PHR DDS epoxy system at five distinct heating rates.

TABLE 1

The heat of reaction for the curing reaction of the TGDDM-35 PHR DDS epoxy system at different heating rates

Heating rate (°C min <sup>-1</sup> )	Heat of reaction (kcal mol <sup>-1</sup> )
0.2	161.0
2	162.2
10	187.3
20	176.3
50	163.1

ency of the kinetic parameters on the scanning rate, the model developed by Prime was utilized to analyze the data [14,15].

The model by Prime is derived from the observation that the extent of reaction,  $\alpha$ , is a function of both time,  $t$ , and temperature,  $T$ , and, therefore, the rate at which the extent of reaction changes with time,  $d\alpha/dt$ , can be expressed by the following equation

$$\frac{d\alpha}{dt} = \left(\frac{\partial\alpha}{\partial t}\right)_T + \left(\frac{\partial\alpha}{\partial T}\right)_t \left(\frac{dT}{dt}\right) \quad (1)$$

The expression given by Prime for the heating-rate dependence of the reaction rate is as follows [14,15]

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n \exp\left(\frac{-E}{RT}\right) Z \quad (2)$$

where

$$Z = \left(1 + \frac{Et\phi}{RT^2}\right) = \left(1 + \frac{E\Delta T}{RT^2}\right) \quad (3)$$

and  $A$  is the pre-exponential factor,  $n$  is the apparent order of reaction,  $E$  is the activation energy,  $\phi$  is the heating rate ( $dT/dt$ ), and  $\Delta T$  is the difference between the initial reaction temperature, which must be clearly defined by the investigator, and the instantaneous temperature at time  $t$ . This equation was obtained by integrating the rate of change in the extent of reaction at constant temperature,  $(\partial\alpha/\partial t)_T$ , expressed in the form of a general Arrhenius equation with respect to time. The equation is then differentiated with respect to temperature to obtain the expression for  $(\partial\alpha/\partial T)_t$ , as shown by eqn. (4), which is obtained if it is assumed that the activation energy, apparent reaction order, and pre-exponential factor are constant with respect to time and temperature [14,15]

$$\left(\frac{\partial\alpha}{\partial T}\right)_t = A(1 - \alpha)^n \exp\left(\frac{-E}{RT}\right) \left(\frac{tE}{RT^2}\right) \quad (4)$$

The expression for the reaction rate determined from DSC thermograms developed by Borchardt and Daniels was utilized for the model [18]. The equation for the change in the extent of reaction with time states that the reaction rate is equal to the height of the DSC thermogram at time  $t$  divided by the total area under the curve. For the value of the apparent reaction order, Prime utilized an extended version of an equation originally developed by Kissinger [19]. As is shown in eqn. (5) below, this equation is evaluated at the peak of the thermogram as is denoted by the subscript  $p$

$$n \cong \frac{E(1 - \alpha)_p}{RT_p^2 \left( \frac{d\alpha}{dt} \right)_p} \quad (5)$$

According to the derivation, eqn. (2), along with the associated relationships (eqns. 3–5), now gives expressions for the isothermal activation energy, apparent reaction order, and pre-exponential factor as a function of the heating rate. By analyzing the data with these expressions kinetic parameters independent of the scanning rate and corresponding to isothermal results should be obtained. However, the values of  $Z$  as calculated from eqn. (3) depend on the temperature difference from the initial to final reaction temperatures or the heating rate of the scan multiplied by the time from the initial reaction temperature. The initial reaction temperature (or time) is defined at the value of zero conversion,  $\alpha \cong 0$ , prior to the exotherm. The result of the analysis should not be influenced by selecting different initial temperatures since before the exotherm the conversion is near zero. However, the results were found to depend upon the selection of the initial time (or temperature). For this analysis, the initial temperature was selected as the point of departure from the initial linear portion of the DSC trace in order to maintain consistency.

Another model which also tries to account for the heating-rate dependence of the kinetic parameters determined by DSC has been developed by Rogers and Smith [20]. As is found in other models, the curve height and area are utilized. However, in this technique the slope of the curve is also incorporated. Because of this feature, analysis of the present experimental results with this method produced widely scattered values for the kinetic parameters and therefore will not be discussed here.

In general, for all currently available models, a major assumption inherent in both models is that the kinetic parameters of the system are constant with respect to both time and temperature. In the event of a multiple reaction-mechanism system, the values for the activation energy, apparent reaction order, and pre-exponential factor would become functions of temperature making these models invalid. For example, a single reaction occurring by two competitive mechanisms which are differently activated will show different apparent activation energies from the DSC analysis depending on the temperature, i.e., the heating rate. In addition, the isothermal case of an

autocatalyzed reaction may not be simply described by  $d\alpha/dt = K(1 - \alpha)^n$ . This possibility may apply to the TGDDM-DDS system examined here since the primary amines which react with the epoxide groups form hydroxyl groups which, in turn, may catalyze the homopolymerization reaction [17].

In Table 2, the results of the calculations for the kinetic parameters for various heating rates and compositions can be seen. As is demonstrated by these results, a dependence of the kinetic parameters on the heating rate used occurs in addition to that described by the model. One probable explanation which can be provided is the possibility of four separate reactions occurring. For all of the scans, if more than one reaction is occurring then all of the reactions involved contribute to the overall heat of reaction, i.e., total area under the curve. The effect of using such a heat of reaction in the analysis is to "average" the kinetic parameters to some intermediate value between the limiting cases. At slow heating rates, the sample spends more time at lower temperatures, while at fast heating rates more time is spent at higher temperatures. Additionally, this means that the lower-activated reaction will predominate at low heating rates, and the higher-activated reaction will become more significant at higher heating rates.

Another problem arises from the multiplicity of peaks at the lower scanning rates, which follows from the multiplicity of the reactions occurring. The choice of the peak is important due to the need to evaluate certain values at the peak of the exotherm in order to apply the Prime analysis. For the 0.2 and 2°C min<sup>-1</sup> cases, the first peak predominates, and, therefore, the values for the activation energy, apparent reaction order, and pre-exponential factor were evaluated using the first peak. For the 10, 20, and 50°C min<sup>-1</sup> cases, the second peak is predominant and was utilized for the analysis. This change in dominance of the peaks identifies two reaction regimes, one identified by lower heating rates (0.2 and 2°C min<sup>-1</sup>), and another regime identified by higher heating rates (10, 20, and 50°C min<sup>-1</sup>).

The first of the reaction regimes is characterized by a lower activation energy and, therefore, occurs at lower temperatures or equivalently lower heating rates. This regime is dominated by the primary-amine addition reaction, which has been identified by many investigators as the primary

TABLE 2

Kinetic parameters for the TGDDM-35 PHR DDS epoxy system determined from DSC experiments run at various heating rates using the method of Prime

Heating rate (°C min <sup>-1</sup> )	Activation energy <i>E</i> (kcal mol <sup>-1</sup> )	Pre-exponential factor ln <i>A</i>	Reaction order <i>n</i>
0.2	20.6	19.0	1.49
2	22.7	19.8	1.06
10	21.6	18.1	0.32
20	23.7	20.0	0.22
50	31.0	26.0	0.21

reaction of this epoxy system [2,5–8,16,17]. The reaction between the epoxide groups and the primary amino hydrogens has been shown to occur readily in this system. The other reaction regime is characterized by a higher activation energy and, therefore, becomes significant at higher temperatures or equivalently higher heating rates. The reactions between the epoxide and hydroxyl groups, the epoxide groups with themselves, and the secondary amino hydrogens and the epoxide groups are included in this reaction regime. The hydroxyl–epoxide and homopolymerization reactions have both been shown to be highly activated due to the nature of the bonding present, while the secondary-amine addition reaction is hypothesized to be highly sterically hindered and therefore highly activated as well.

With this identification of two reaction regimes, a linear dependence of activation energy as a function of the heating rate is observed. A similar linear dependence is observed between the natural logarithm of the pre-exponential factor and the heating rate. These empirical relations are useful for providing rational modifications of the analytical description of the heating-rate dependence discussed earlier, which assumed the kinetic parameters to be constant with respect to time and temperature. These modifications of the expressions provided earlier involve integrating and differentiating the standard expression of Borchardt and Daniels [18]

$$\left(\frac{d\alpha}{dt}\right)_T = A(1 - \alpha)^n \exp\left(\frac{-E}{RT}\right) \quad (6)$$

where  $A$ ,  $n$ , and  $E$  are now all functions of temperature and, as before in Prime's analysis,  $\alpha$  is a function of time and temperature. First, integration with respect to time at constant temperature is performed to obtain eqns. (7) and (8)

$$[(1 - \alpha)^{-n} d\alpha]_T = \left[ A \exp\left(\frac{-E}{RT}\right) dt \right]_T \quad (7)$$

$$\left. \begin{array}{l} \text{for } n = 0 \quad \alpha + C \\ \text{for } n = 1 \quad \ln(1 - \alpha) + C \\ \text{for all other } n \quad \frac{1}{n-1}(1 - \alpha)^{(1-n)} + C \end{array} \right\} = A t \exp\left(\frac{-E}{RT}\right) \quad (8)$$

Since only  $\alpha$  is a function of time, the integration only adds a factor of time to the right-hand side of the equality. Differentiation with respect to temperature at constant time is then performed, keeping in mind the dependence of the kinetic parameters on temperature, obtaining eqns. (9) and (10)

$$\frac{\partial}{\partial T} \left\{ \begin{array}{l} n = 0 \quad (\alpha + C) \\ n = 1 \quad [\ln(1 - \alpha) + C] \\ \text{all other} \quad n \left( \frac{1}{n-1} (1 - \alpha)^{(1-n)} + C \right) \end{array} \right\}_t = \frac{\partial}{\partial T} \left[ A t \exp\left(\frac{-E}{RT}\right) \right]_t \quad (9)$$



$$\begin{aligned}
& (1 - \alpha)^{-n} \left( \frac{\partial \alpha}{\partial T} \right)_t - \left[ \frac{1}{n-1} + \ln(1 - \alpha) \right] \frac{(1 - \alpha)^{1-n}}{n-1} \left( \frac{\partial n}{\partial T} \right)_t \\
& = t \exp \left( \frac{-E}{RT} \right) \left( \frac{AE}{RT^2} \right) - \frac{A}{RT} \left( \frac{\partial E}{\partial T} \right)_t + \left( \frac{\partial A}{\partial T} \right)_t
\end{aligned} \tag{10}$$

If the kinetic parameters ( $n$ ,  $A$ , and  $E$ ) are all independent of temperature, the Prime expression is recovered, but if not, the dependence of these factors on temperature are incorporated into eqn. (10). One possible simplification of this expression could be to assume that the kinetic parameters are only constant for a certain temperature range where the other reaction mechanisms are insignificant, i.e.

$$\left. \begin{aligned}
E &= E_m = f(T) \\
A &= A_m = g(T) \\
n &= n_m = h(T)
\end{aligned} \right\} \text{ for } T_m < T < T_{m+1} \tag{11}$$

where  $m$  refers to an indexing number for the corresponding reaction regime. Since the values have now been assumed to be constant, their derivatives are equal to zero and the simplified model may be applied for a particular mechanism.

In Fig. 2, the thermograms for isothermal experiments at 140, 160, and 180°C appear for the TGDDM-35 PHR DDS system. The appearance of a maximum provides further evidence from kinetic considerations of the existence of an overall autocatalytic reaction mechanism. These curves exhibit the same problem for analysis as the dynamic scans in that the overall area under the curve corresponds to a heat of reaction with contributions from multiple reactions.

A diagram of the experimental conversion with respect to the overall heat of reaction as a function of time is also shown in Fig. 3. The conversion was determined by subtracting the partial heat of reaction/overall heat of reaction ratio from 1. As can be seen from the figure, the conversion begins slowly, then accelerates, and finally slows to an asymptotic value. This phenomenon occurs in a progressively shorter period of time as the temperature is increased. The asymptotic value reached at the completion of the scan was not equal to 1. This is due to the system becoming glassy and restricting species from reacting. To check for the appearance of any residual heat of reaction due to the presence of additional curing, dynamic scans were performed at a heating rate of 10°C min<sup>-1</sup>. Figure 4 shows the thermograms for the residual heat of reaction which occurred after isothermal curing at 140, 160, and 180°C for various periods of time.

It is hypothesized that the faster and lower activated reaction regime is the addition of the primary amine to the epoxy, and the slower and more highly activated reactions are the homopolymerization of the epoxy, secondary-amine addition, and hydroxyl-epoxide reactions. In order to study the single

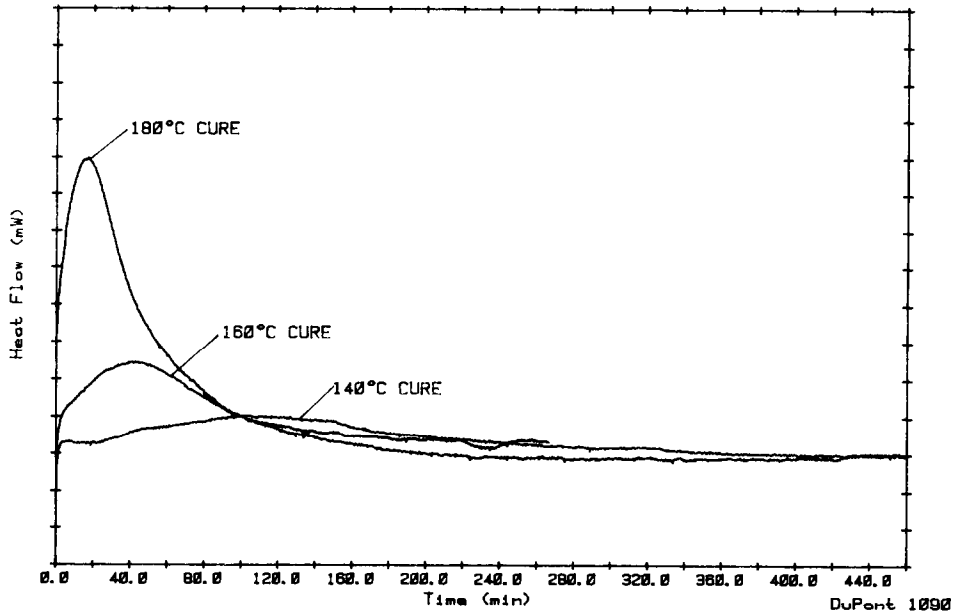


Fig. 2. DSC thermograms for the TGDDM-35 PHR DDS epoxy system at three isothermal temperatures.

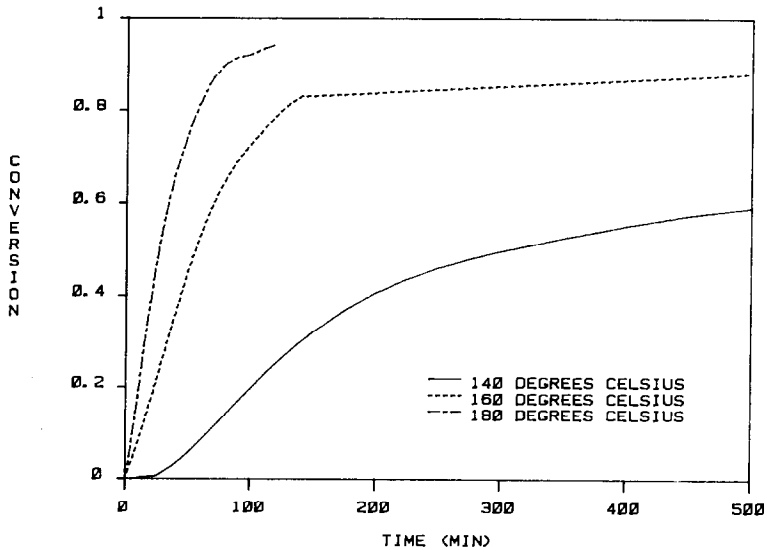


Fig. 3. Fractional conversion as a function of time curves for the TGDDM-35 PHR DDS epoxy system as determined from the isothermal and residual heats of reaction.

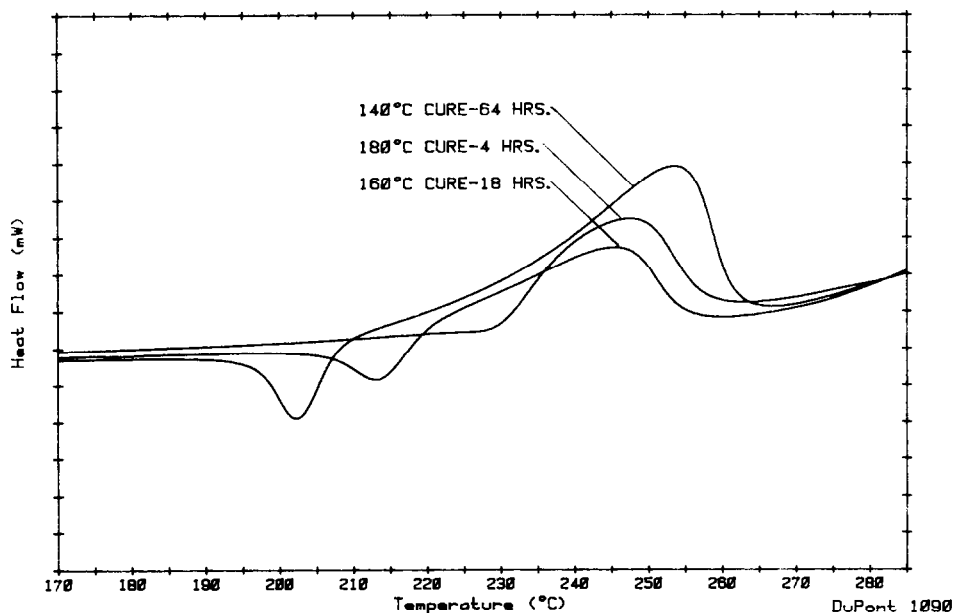


Fig. 4. Dynamic ( $10^{\circ}\text{C min}^{-1}$ ) DSC thermograms of the residual heat of reaction for the TGDDM-DDS epoxy system after the isothermal runs of different duration ensuring constant baseline.

reaction of the primary-amine addition separately, the stoichiometric composition for primary-amine addition of 100 PHR DDS with TGDDM was used. The reactions of homopolymerization of the TGDDM and hydroxyl-epoxide were separated by studying TGDDM alone. For these systems, DSC scans were performed at different heating rates and can be seen in Figs. 5 and 6. Now, considering that in each case only a single regime is activated, the simplified model may be applied. As can be seen in Tables 3 and 4, the values for the activation energy for each reaction regime considered remain constant with the heating rate. The values of the activation energy for the primary-amine addition and homopolymerization regimes were found to be  $16.7$  and  $42.3 \text{ kcal mol}^{-1}$ , respectively. Thus, the simplified analysis has been found to be adequate to describe the single regime and was used for these calculations.

The values for TGDDM alone varied more than expected based on this analysis. This was probably due to the difficulty in analyzing the thermograms for this system. The problems arose due to the highly exothermic nature of the homopolymerization/hydroxyl-epoxide reaction. This made integration of the peak area most difficult, and thus gave rise to this phenomenon.

The results reported in Table 3 also indicate that even though the activation energy and pre-exponential factor may be essentially constant for the TGDDM-100 PHR DDS case, another reaction may be occurring. This

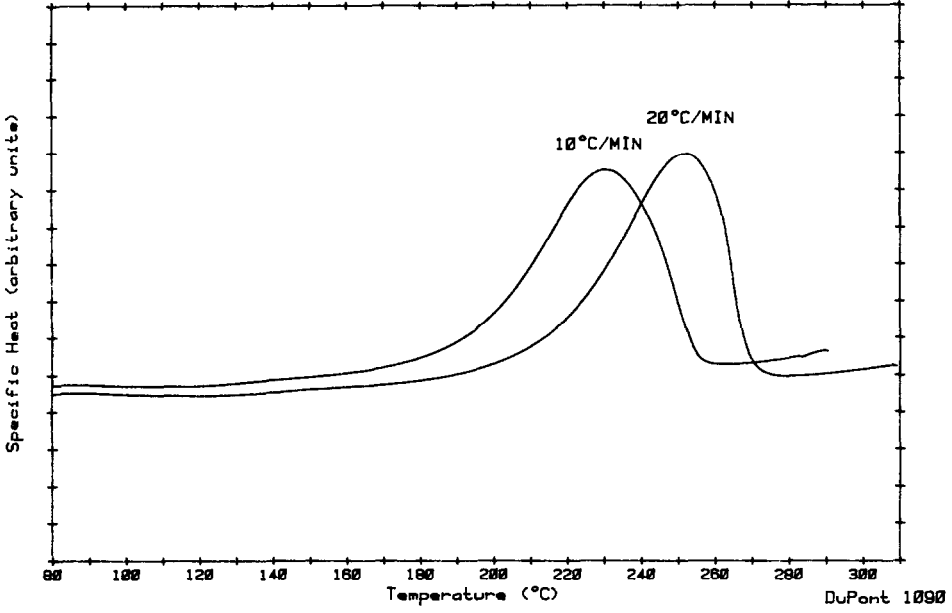


Fig. 5. DSC thermograms for the TGDDM-100 PHR DDS epoxy system at two characteristic heating rates.

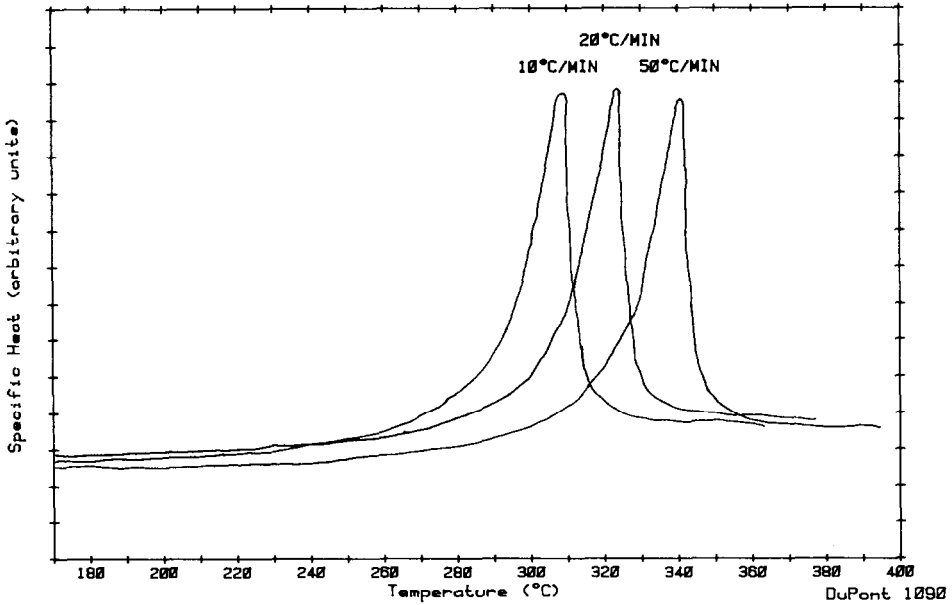


Fig. 6. DSC thermograms for TGDDM alone at three characteristic heating rates.

TABLE 3

Kinetic parameters for the TGDDM-100 PHR DDS epoxy system at various heating rates as determined by the methods of Prime

Heating rate (°C min <sup>-1</sup> )	Activation energy <i>E</i> (kcal mol <sup>-1</sup> )	Pre-exponential factor ln <i>A</i>	Reaction order <i>n</i>
10	16.8	13.9	0.54
20	16.5	13.6	0.38

TABLE 4

Kinetic parameters of TGDDM alone at various heating rates as determined by the method of Prime

Heating rate (°C min <sup>-1</sup> )	Activation energy <i>E</i> (kcal mol <sup>-1</sup> )	Pre-exponential factor ln <i>A</i>	Reaction order <i>n</i>
10	46.0	37.8	0.01
20	41.2	33.0	0.04
50	39.6	31.2	0.07

TABLE 5

Comparison of the rate constants for the primary amine addition and hydroxyl-epoxide reactions based upon the kinetic parameters obtained from DSC thermograms as determined utilizing the method of Prime

Temperature	<i>k</i> <sub>pa</sub>	<i>k</i> <sub>homo</sub>	Relative rate $\left(\frac{k_{pa}}{k_{homo}}\right)$
140°C	$1.45 \times 10^{-3}$	$2.50 \times 10^{-8}$	58 000
180°C	$8.75 \times 10^{-3}$	$2.36 \times 10^{-6}$	3 700
220°C	$3.93 \times 10^{-2}$	$1.06 \times 10^{-4}$	400

is demonstrated by the significant variation in the order of reaction with the heating rate suggesting that another reaction such as the secondary-amine addition, homopolymerization, or hydroxyl-epoxide reaction is taking place.

The values of the activation energy obtained assuming an overall reaction for the TGDDM-35 PHR DDS system were thus heating-rate dependent since the values of the kinetic parameters approach the limiting cases of the first reaction regime as the heating rate gets very small and the higher activated regime as the heating rate becomes larger. The rate constants calculated from the results of the dynamic tests at 140, 180, and 220°C are shown in Table 5. The results indicate that the first reaction regime in which the primary-amine addition reaction may be assumed to dominate is significantly faster at temperatures up to and including the curing temperature, while at the higher temperature regime the homopolymerization, hydroxyl-epoxide, and secondary-amine addition reactions become significant.

## CONCLUSIONS

Based on the analysis of both the dynamic and isothermal scans for the TGDDM–DDS system, it can be concluded that multiple reactions are occurring and that the system is autocatalyzed. Direct application of such techniques as the simple Arrhenius equation and the methods of Prime and Rogers and Smith for the determination of the kinetic parameters are not valid for this type of reaction mechanism. However, this system may be analyzed by defining two reaction regimes; one representing the primary amine–epoxide dominated reaction mechanism, and the other where the hydroxyl–epoxide, homopolymerization and/or secondary-amine addition reactions may become significant. The kinetic parameters obtained from the stoichiometric primary-amine composition approximate the first reaction regime parameters, while when the TGDDM component alone was tested the expected homopolymerization reaction parameters approximated the second, highly activated reaction regime for the mixed TGDDM–35 PHR DDS system.

The Prime model may be successfully applied due to the relatively constant nature of the kinetic parameters for the overall reaction occurring in each regime. The value of the activation energy for the kinetic regime corresponding to the primary amine–epoxide reaction was calculated to be  $16.7 \text{ kcal mol}^{-1}$  while for the second regime describing the homopolymerization, secondary amine–epoxide, and hydroxyl–epoxide reactions the value was found to be about  $42.3 \text{ kcal mol}^{-1}$ . These values represent the limiting cases for the results of the dynamic DSC scans and may be utilized in the formulation of a kinetic model for this high-performance, amine-cured epoxy system.

Overall, this study has demonstrated that well-established methods for DSC kinetic analysis may be extended to account for different mechanisms which may be activated during a dynamic scan.

## ACKNOWLEDGMENTS

The authors express their appreciation for the financial and instrumentation support given for this investigation by the DuPont Company's Analytical Instrument's Division and the Boeing Commercial Airplane Company, through the Polymeric Composites Laboratory of the University of Washington. Special thanks are also extended to CNR and Aeritalia of Italy for their support of this research through the Polymer Engineering Laboratory of the University of Naples.

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