Cure Kinetics of Epoxy Formulations of the Type Used in Advanced Composites

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Synopsis

An analysis of the cure kinetics of three different formulations composed of tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) epoxy resin and diaminodiphenyl sulfone (DDS) was performed. A series of isothermal tests was run, and the experimentally obtained results were checked against the proposed kinetic model. An autocatalyzed mechanism with the overall reaction order of 2 was found to adequately describe the cure kinetics. An increase in reaction rate was observed at higher temperature and higher DDS concentration. For a given formulation, the extent of reaction corresponding to the maximum reaction rate was independent of temperature. A secondary exotherm was detected, particularly in formulations with low DDS concentration, at approximately 40% conversion. At that point, the rate of primary amine–epoxide reaction decreases, and other reactions dominate the curing process. Such a mechanism is likely to cause a formation of an inhomogeneous thermoset morphology.

INTRODUCTION

Linear epoxy resins (liquid or solid) are converted into 3-dimensional thermoset network via the process known as curing. Chemical reactions that take place during cure determine the resin morphology which, in turn, determines the physical/mechanical properties of the cured thermoset. The understanding of the mechanism and rate (kinetics) of cure is the first essential step in the process of evaluation of processing–morphology–property–durability relationships in neat thermosets and their composites.

An excellent review of the kinetics of thermoset cure has been recently written by Prime.[1] However, in spite of considerable current research activity in the field of cure of epoxy resins, numerous questions are yet to be answered. This is particularly true for the case of tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) epoxy resins cured with diaminodiphenyl sulfone (DDS), which are commonly used as the polymeric matrix in high-performance composites employed in aircraft and spacecraft industries. Nonetheless, it is perhaps surprising to note that, in spite of the vigorous research activity, the information about the cure kinetics of neat TGDDM/DDS systems is only now becoming available in the literature, although mostly in the preprint form.[2-8] Some of the major questions associated with the cure of TGDDM/DDS formulations include: (i) elucidation of types and relative rates of chemical reactions occurring during cure; (ii) formulation of the corresponding kinetic models; and (iii) understanding of the formation of inhomogeneous network morphology during cure and its effect

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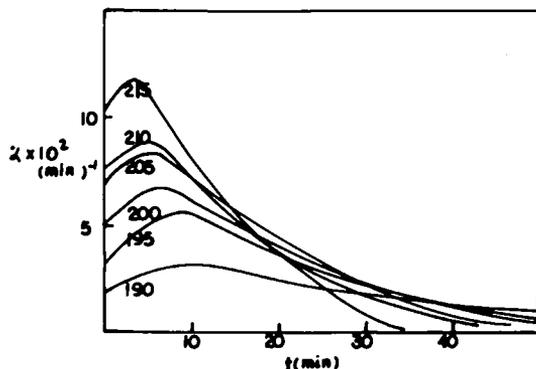
Fig. 1. Reaction rate as a function of time with temperature (°C) as a parameter for formulation 3.

on the physical/mechanical properties of thermosets. Some aspects of these questions are briefly discussed below.

It is generally accepted that, in amine-cured epoxy resins, 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. However, there is no agreement in the literature with respect to the relative rates and importance of those reactions.[2-8]

On the other hand, the concept of inhomogeneous thermoset morphology still remains incompletely understood. It is generally recognized today that the model of coexisting regions of higher and lower crosslink density adequately describes the morphology of highly crosslined thermosets.[9] It should be pointed out, however, that the origin, size and distribution of inhomogeneities, reported in various epoxy resins, were found to depend on the type of the resin(s)/curing agents(s)/catalyst(s) formulation and the curing conditions. The likelihood of formation of inhomogeneous morphology is expected to be high in the commercially available high-temperature epoxy formulations which, in addition to the tetraglycidyl molecules, are known to contain various impurities.[10]

At the present time, a comprehensive research program is unfolding in our laboratories, aimed towards understanding of the processing–morphology–property–durability relationships in neat thermosets and composites. The objective of this study was to analyze the cure kinetics of several TGDDM/DDS formulations by differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

The formulations used in this study were composed of Ciba-Geigy's MY720 epoxy resin, which contains basically the TGDDM molecules, and HT967 hardener (DDS). The three formulations investigated contained 23, 28, and 37 parts of curing agent per hundred parts of resin (phr), by weight, respectively. Hereafter, the three formulations used will be referred to as formulation 1 (23
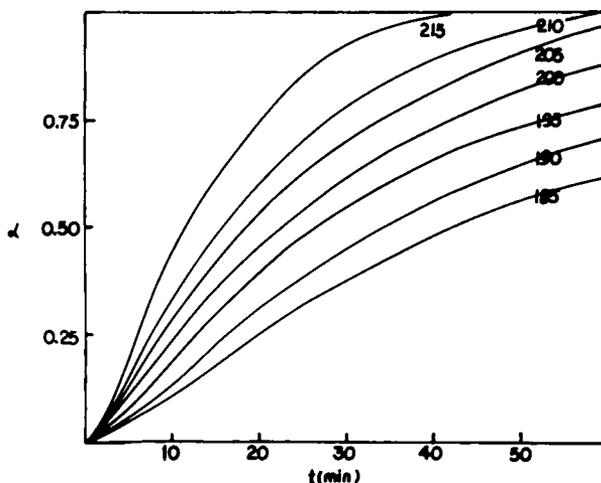
Fig. 2. Extent of reaction as a function of time with temperature (°C) as a parameter for formulation 1.

phr DDS), formulation 2 (28 phr DDS), and formulation 3 (37 phr DDS). The corresponding amine-to-epoxy ratios are; 0.44 for formulation 1, 0.54 for formulation 2, and 0.71 for formulation 3. The epoxy–amine mixtures were prepared by heating the resin to 125°C and adding the curing agent with continuous stirring until a clear mixture was obtained (in approximately 2 min). Mixing was done in an oil bath where the temperature was maintained at 125 ± 1°C. Reactions during mixing were negligible as confirmed by an uneventful 2-h isothermal (130°C) DSC thermogram. The mixture was then either tested immediately or stored in the refrigerator. If not used within a week, the mixture was discarded and a fresh one prepared.

Techniques

Samples were removed from the refrigerator and allowed to warm to 20°C. Small sample quantities (5–15 mg) were then placed in hermetically sealed aluminum pans. The calorimetric measurements were made with a DuPont 910 DSC. The thermogram data were stored in DuPont 1091 Disk Memory and calculated by DuPont 1090 Thermal Analyzer. The DSC was calibrated with high purity indium (Fisher Thermetric Standards). A steady isothermal baseline was established at the preset cure temperature using two empty sample pans. The data acquisition system was then initiated, and the sample was introduced into the DSC cell. The heat of reaction was determined by carrying the reaction isothermally to completion at the following temperatures; 185°C, 190°C, 195°C, 200°C, 205°C, 210°C, and 215°C. Thermal equilibrium of the sample and the reference holders was achieved in less than 1 min, 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 the sample as a function of time. The reaction was considered complete when the rate curve leveled off to the baseline. The total area under the exotherm curve, based one the extrapolated baseline
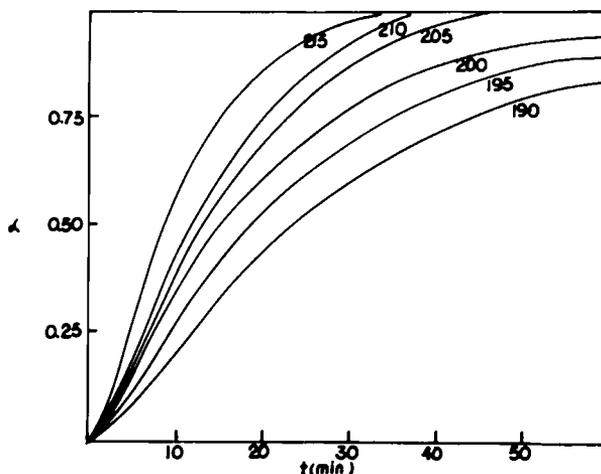
Fig. 3. Extent of reaction as a function of time with temperature (°C) as a parameter for formulation 2.

at the end of the reaction, was used to calculate the isothermal heat of cure, H_T, at a given temperature.

After the isothermal cure was completed, the sample was cooled rapidly in the DSC to 150°C. It was then heated at 10°C min^{-1} from 150°C to 300°C in order to determine the residual heat of reaction, H_R. The sum of the isothermal heat (H_T) and the residual heat (H_R) was taken to represent the ultimate heat of cure (Hult). Finally, the samples were weighed again and compared to the initial weight. Weight losses were negligible in all cases.

The exact value of the glass transition (T_g) of the fully cured system was difficult to detect. The exotherm due to the residual heat levels off in the vicinity of 260°C indicating that the $T_{g\infty}$ is in that temperature range. However, the T_g endotherm is hard to determine partly due to an insufficient sensitivity of the DSC and partly due to the fact that the onset of degradation (exotherm) occurs in the same temperature range.

RESULTS AND DISCUSSION

In all DSC thermograms, the rate of heat generation (dH/dt) was found to exhibit a maximum when plotted as a function time. Consequently, the reaction rate, which is proportional to the rate of heat generation, also passes through a maximum and then decreases with time. Such behavior is characteristic of chemical reactions in which products act as catalysts for the reaction and which are referred to as the autocatalytic reactions. A general description of autocatalysis[11] and the application of autocatalytic kinetics to thermoset cure have been considered elsewhere.[12-16] It is worth noting here that the initial rate of autocatalytic reactions is not necessarily zero, for there is a possibility that reactants can be converted into products via alternative paths, only one of which is autocatalytic. The reaction rate equation used in this study was[16]

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{1}$$
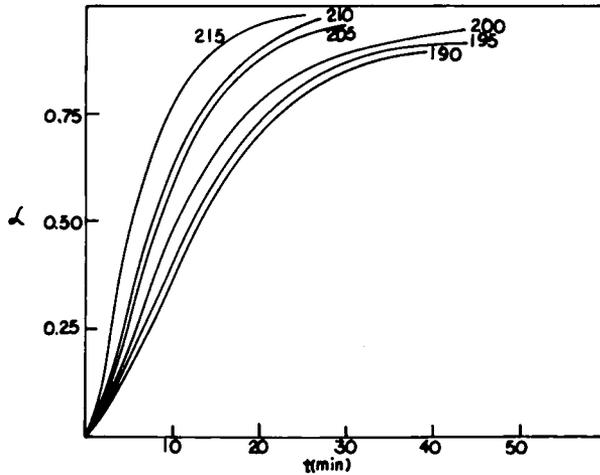
Fig. 4. Extent of reaction as a function of time with temperature (°C) as a parameter for formulation 3.

where α is the extent of reaction, k_1 and k_2 reaction rate constants, and $(m + n)$ the overall reaction order. The overall reaction order $(m + n)$ was assumed to be two, and the validity of this assumption was confirmed as described later in the text. This equation has been used in the kinetic studies of cure of several polyester and epoxy formulations, but not for the neat TGDDM/DDS system. The reaction rate was determined directly from the DSC thermograms according to

$$\frac{d\alpha}{dt} = \frac{1}{H_{\text{ult}}} \frac{dH}{dt} \tag{2}$$

where H_{ult} is the ultimate heat of cure, i.e., the sum of isothermal heat of cure and the residual heat obtained in the subsequent dynamic test. Hence, to express the experimental results in terms of the extent of reaction (α), the DSC curves were integrated and the partial areas as a function of time were normalized
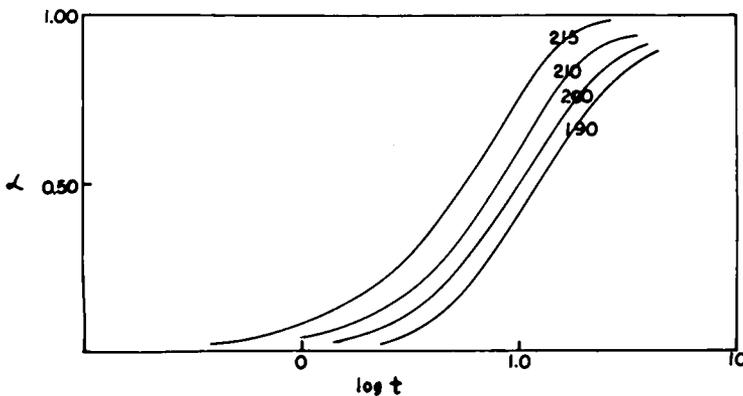
Fig. 5. Extent of reaction as a function of log time with temperature (°C) as a parameter for formulation 3.
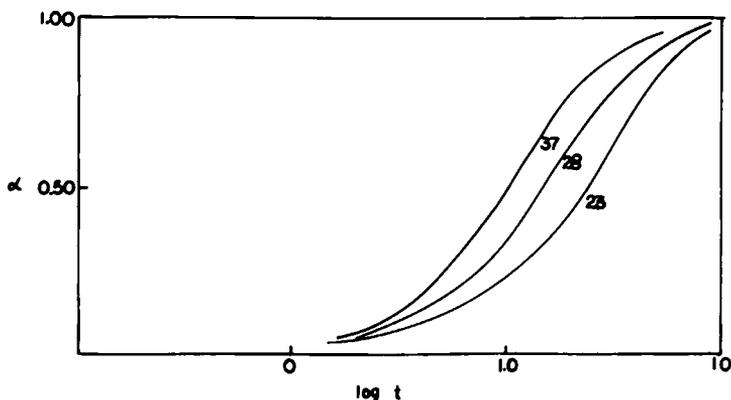
Fig. 6. Extent of reaction as a function of log time with DDS concentration (phr) as a parameter for isothermal cure at 200°C.

with respect to H_{ult} and sample weight. Numerical integration of the kinetic data was performed using the trapezoidal rule on an HP-85 microcomputer.

A series of isothermal reaction rate curves for the formulation 3 (containing 37 phr DDS) are shown in Figure 1. With a decrease in cure temperature, a decrease in the peak value of reaction rate ($\dot{\alpha}_p$) and its shift to longer times were observed. Analogous results were obtained with the other two formulations. Plots of extent of reaction as a function of time for formulations 1–3 are shown in Figures 2–4, respectively. At any given time, the extent of reaction is seen to increase as both temperature and the concentration of DDS are increased. The extent of reaction was next plotted as a function of log time, and the resulting curves for formulation 3 (37 phr DDS) are shown in Figure 5. All the curves had the same shape but were shifted along the log time axis in accordance with the cure temperature. Furthermore, the slopes of these curves were essentially identical over the intermediate range of conversion, suggesting that the same overall cure mechanism prevails in the temperature range investigated in this study.

It is further seen in Figure 6 that at a given temperature the slopes of the extent of reaction curves for formulations 1–3 are also similar in the intermediate con-
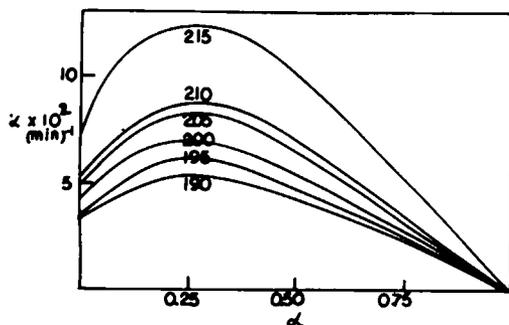
Fig. 7. Reaction rate as a function of extent of reaction with temperature (°C) as a parameter for formulation 3.
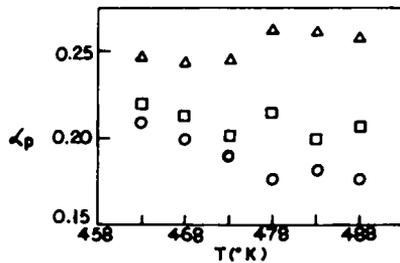
Fig. 8. Extent of reaction at peak as a function of curing temperature for formulations 1 (O), 2 (□), and 3 (△).

version range. At any given time, however, the highest extent of reaction is obtained with the highest concentration of DDS.

The rate of reaction as a function of the extent of reaction for formulation 3 is shown in Figure 7. Although the value of reaction rate at the peak ($\dot{\alpha}_p$) increases as a function of temperature, the extent of cure at the peak (α_p), for a given formulation, is only slightly affected by changes in temperature. Curves of the type shown in Figure 7 were also obtained for formulations 1 and 2 but are not shown here. Instead, plots of the extent of cure at the peak as a function of cure temperature for all three formulations are shown in Figure 8. These results suggest that, for a given formulation, the extent of cure at peak is independent of the cure temperature. On the other hand, at any given temperature the value of α_p increases with an increase in DDS concentration. It is further seen in Figure 8 that the maximum reaction rate occurs (depending on DDS concentration) between 17–26% conversion. The autocatalyzed reactions are generally characterized by the maximum rate at approximately 30–40% conversion (1), although values lower than 20% have been reported, e.g., for the autocatalytic cure of an unsaturated polyester.[14] This number, however, is a function of the composition of curing formulation, as clearly seen in Figure 8.

The maximum reaction rate ($\dot{\alpha}_p$) and the time required to reach that peak (t_p)
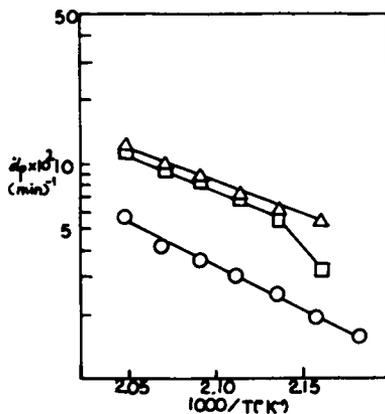
Fig. 9. Reaction rate at peak as a function of curing temperature for formulations 1 (O), 2 (□), and 3 (△).
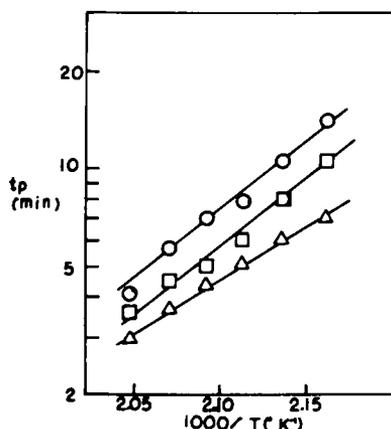
Fig. 10. Time to peak as a function of curing temperature for formulations 1 (O), 2 (□), and 3 (△).

as a function of temperature are shown in Figures 9 and 10, respectively. As expected, the maximum rate increases with increasing temperature. A linear relationship was observed for all formulations. The time required to reach the peak (t_p) was found to decrease with increasing temperature, again in a linear fashion for all formulations.

The kinetic rate constant k_1, which describes the initial reaction rate at a given temperature, was determined directly from the DSC thermogram and was normalized with respect to the sample weight. The temperature dependence of k_1 for formulations 1 and 3 is shown in Figure 11. In spite of the meticulous experimentation and numerous reruns, which have led to the highest obtainable accuracy, there were fluctuations in the values of the point of initiation of reaction. Such fluctuations are believed to be responsible for the oberved deviations from the Arrhenius relation, as shown in Figure 11.
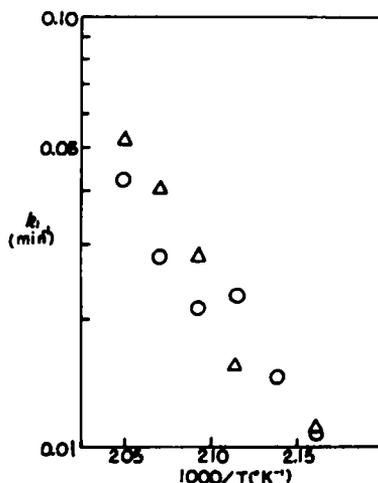
Fig. 11. Initial reaction rate constant (k_1) as a function of temperature for formulations 1 (O) and 3 (△).
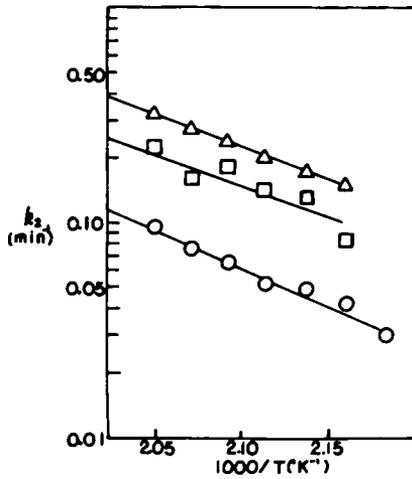
Fig. 12. Reaction rate constant (k_2) as a function of temperature for formulations 1 (O), 2 (□), and 3 (△).

On the other hand, the temperature dependence of the reaction rate constant k_2 fits well the classical Arrhenius form, as shown in Figure 12. Some scatter of data, however, was observed with formulation 2. The energy of activation based on the rate constant k_2 and the temperature dependence of k_1 and k_2 for formulations 1 and 3 only are summarized in Table I. The energy of activation was within the range reported in the literature for different epoxy formulations (1).

As previously stated the overall order of reaction, $m + n$, was assumed to be two. Values of m were calculated from

$$m = \frac{\ln \dfrac{\dot{\alpha}_p/(1 - \alpha_p)^n - k_1}{nk_1\alpha_p^{1-m}/[m - (m + n)\alpha_p]}}{\ln \alpha_p} \tag{3}$$

This computation was done using the Pegasus root-finding method.[17] For all formulations, the value of m appears to increase with increasing temperature as seen in Figures 13–15. Although the scatter of data is noticeable, particularly for formulations 1 and 3, the value of m was found to be between 0.5 and 0.7. In earlier studies of other epoxies and polyesters, the value of m was reported to

TABLE I
Summary of Kinetic Parameters for Formulations 1 and 3

	Formulation 1 (23 phr DDS)	Formulation 3 (37 phr DDS)
k_1	$2.22 \times 10^8 \exp\left(-\dfrac{9.11 \times 10^7 \text{ J/kg·mol}}{RT}\right)$	$9.77 \times 10^{12} \exp\left(-\dfrac{13.3 \times 10^7 \text{ J/kg·mol}}{RT}\right)$
k_2	$1.21 \times 10^6 \exp\left(-\dfrac{6.64 \times 10^7 \text{ J/kg·mol}}{RT}\right)$	$6.13 \times 10^4 \exp\left(-\dfrac{4.97 \times 10^7 \text{ J/kg·mol}}{RT}\right)$
Ea$_2$ (kcal/g· mol)	15.9	11.9
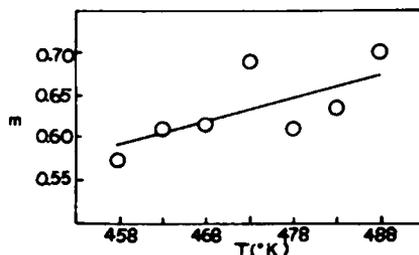
Fig. 13. Kinetic parameter m as a function of curing temperature for formulation 1.

change as a function of the type (chemistry) of the formulations.[14,18] For a given formulation, however, the value of m was reported by these authors to be independent of temperature. Other researchers have observed a decrease in m with increasing temperature (16). The constancy of $m + n = 2$ was assumed in all these studies. In order to determine the validity of the assumed overall reaction order of 2, a routine was constructed to minimize the error between the predicted values of the rate and those obtained from the data. This was accomplished by varying the value of $m + n$ using the method of Powell.[19] From the complete analysis of all data, it was found that the error was minimized when the value of $m + n$ was about 2. Thus, the assumption of second overall order for the TGDDM/DDS formulations studied in this work was confirmed at least from the mathematical standpoint.

An interesting phenomenon was observed in the reaction rate vs. the extent of reaction curves of formulation 1 (23 phr DDS). As shown in Figure 16, another reaction exotherm peak seems to appear about approximately 40% conversion. Unfortunately, the overlap of exotherms due to various possible reactions, precludes the isolation and quantitative analysis of any single reaction from a DSC thermogram. The presence of an overlapping exotherm is detected by considering the deviation of the experimentally obtained rates from the results calculated from the rate equation [eq. (1)] at extent of reaction greater than 0.4. This discrepancy is clearly seen in Figure 17, where the error in the calculated reaction rate was seen to become pronounced at higher α. It is possible that the second exotherm reflects changes in cure chemistry upon the completion of primary amine–epoxide reactions. As the concentration of primary amines is increased (formulations 2 and 3), the primary amine–epoxide reaction is carried out to higher α and the intensity of secondary exotherm becomes diminished. An
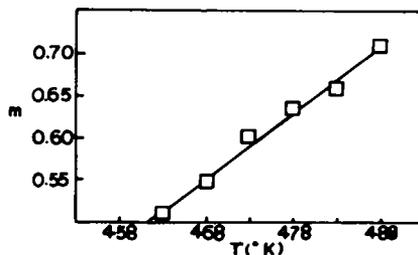
Fig. 14. Kinetic parameter m as a function of curing temperature for formulation 2.
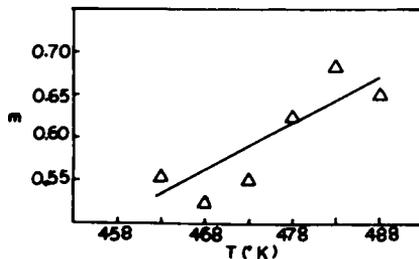
Fig. 15. Kinetic parameter m as a function of curing temperature for formulation 3.

elaborate FTIR study of the types and relative rates of various chemical reactions occurring in TGDDM/DDS formulations, has been recently reported by Morgan et al.[8] They have shown that (in the formulation containing 25 wt % DDS) the rate of consumption of epoxy groups by the primary amine–epoxide reaction decays to zero above 40% conversion. Simultaneously, the secondary amine–epoxide and hydroxyl epoxide reactions accelerate and continue to occur at similar rates. At least qualitatively, their results appear to agree with our observation of the secondary exotherm. Furthermore, in a recent study of a TGDDM/DDS (28 phr) system, it was suggested that the primary amine–epoxide reaction dominates the first 60–90 min of cure at 177°C.[6] This reaction, according to these authors, is followed by the epoxide–hydroxyl reaction (etherification) which was said to result in 50% conversion of all epoxide groups, as determined by the FTIR analysis. Other researchers, however, have reported that the primary amine–epoxide and the homopolymerization of epoxide groups are the predominant reactions during cure of TGDDM/DDS systems.[3] In yet another study of two epoxy formulations cured with dicyandiamide, the activation energies for the primary amine-epoxide and hydroxyl-epoxide reactions were reported to be very close.[20] Although a unifying concept of the chemistry of cure of TGDDM type epoxies is lacking, it is apparent that more than one type of reactions occur and that further research in this area is needed.

The values of the ultimate heat of cure (Hult) are shown in Table II as a function of cure temperature and curing agent concentration. Interestingly, as the curing agent concentration was increased from 23 to 28 to 37 phr, the av-
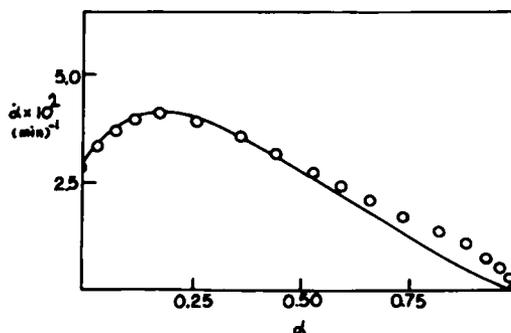
Fig. 16. Reaction rate as a function of extent of reaction for formulation 1 cured at 210°C. Note the onset of overlapping exotherm at approximately 40% conversion.
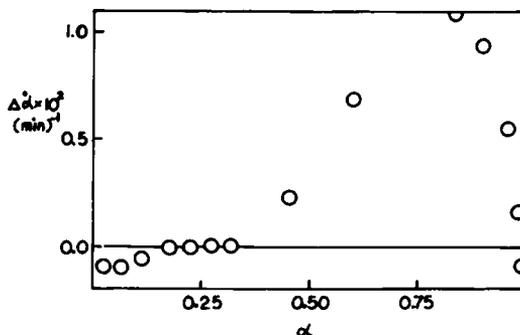
Fig. 17. Error (discrepancy) between the experiment and the curve-fit kinetic equation as a function of extent of reaction. Note the onset of relatively large deviation at about 40% conversion.

erage value of Hult was found to decrease from 718 to 647 to 581 J/g. These values are approximately double the typical values of the heat of reaction reported for the stoichiometric DGEBA/DDS system.[21] One must recall, however, that a *tetra*-functional epoxy resin has been used in this study. The observed decrease in the ultimate heat of reaction as the concentration of curing agent is increased is of considerable interest. Apparently, the extent of consumption of epoxy groups by reactions other than primary amine–epoxide is larger in the amine deficient formulations. Furthermore, the occurrence of different chemical reactions during cure is apt to lead to the formation of inhomogeneous network morphology which is also a function of curing agent concentration. Variations in morphology (within the same system), in turn, would result in the local differences in physical/mechanical properties and durability of thermosets. An inhomogeneous morphology has been correlated to physical/mechanical properties of amine cured-DGEBA type epoxies.[9,22] However, a unifying concept of direct quantitative relationships between cure kinetics and the corresponding morphology has not been advanced. In one recent study, it was suggested that, as a consequence of different reactions during cure of TGDDM/DDS systems, an inhomogeneous thermoset network would be formed, characterized by two or more values of M_c and/or T_g.[6] Similar suggestion has been put forward in another study, based upon a probabilistic model formulation for TGDDM/DDS/Novolac systems.[23] The subject of processing (cure)–morphology–property–durability relationships in TGDDM type epoxy resins is currently under active investigation in our laboratories.

CONCLUSIONS

A DSC study of cure kinetics of three different TGDDM/DDS formulations was performed. An autocatalytic kinetic equation was found to compare well with the experimentally obtained results. The assumption of the overall reaction order of 2, was shown to be valid. Higher cure temperature and higher DDS concentration led to an increase in the reaction rate. The extent of reaction at the highest (peak) value of reaction rate, for a given formulation, was independent of temperature. The maximum reaction rate was observed between 17–26%

TABLE II
The Ultimate Heat of Cure (J/g) as a Function of Formulation and Cure Temperature

T^a (°C) \ Formulation	1 (23 phr)	2 (28 phr)	3 (37 phr)
185	744	—	—
190	740	624	595
195	712	651	583
200	714	650	563
205	731	637	579
210	738	670	599
215	692	659	566

[a] Each isothermal DSC run was followed by a dynamic DSC run.

conversion, depending on the amount of DDS in the formulation. At approximately 40% conversion in formulation 1, there were signs of additional exothermic reactions, suggesting a multiplicity of chemical reactions during cure. It was concluded that the correlation between the cure kinetics and the ensuing network morphology must be elucidated.

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