

Cure Kinetics of Neat Versus Reinforced Epoxies

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Synopsis

An investigation was carried out into the cure kinetics of neat vs reinforced epoxy systems. The formulations were composed of tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) epoxy resin and diaminodiphenyl sulfone (DDS). Glass was used as reinforcement. A series of isothermal differential scanning calorimetry (DSC) thermograms were run and analyzed by the proposed autocatalytic kinetic model. An increase in reaction rate was observed at higher temperature and higher DDS concentration in both neat and reinforced formulations. The presence of reinforcement had an effect on the cure kinetics. The observed effect, however, was not very pronounced. Slightly lower values of the reaction rate constant and longer times needed to reach the maximum reaction rate were recorded in reinforced systems. After reaching the peak value, the rate of reaction dropped off faster in reinforced formulations, resulting in lower average value of H_{ult} , the ultimate heat of reaction. It was suggested that the reinforcement imposes restrictions on the molecular mobility of reactive species.

INTRODUCTION

As a result of a multitude of chemical reactions during curing, linear epoxy resins are converted into three-dimensional thermoset networks. The rate and the mechanism of those reactions dictate the processing conditions and influence the network morphology. The latter, in turn, determines the properties and durability of cured thermosets.

An excellent review of numerous studies of thermoset cure kinetics has been written by Prime.¹ Most recently, however, considerable interest has been generated in the studies of epoxy resins based on tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and cured with diaminodiphenyl sulfone (DDS), which are commonly used as the polymeric matrix in high-performance composites employed in aircraft and spacecraft industries. We have recently reported the result of one such study of cure kinetics for various neat resin formulations.²

As a continuation of our comprehensive research program in the area of processing-morphology-property-durability relationships in neat thermosets and composites, we have undertaken a study of cure kinetics of the same epoxy formulations,² but in the presence of reinforcement. The objective of this work is to provide a direct comparison of cure kinetics of neat vs reinforced TGDDM/DDS formulations, cured under otherwise identical conditions.

EXPERIMENTAL

Materials

The formulations used in this study were composed of Ciba-Geigy's MY720 epoxy resin, which contains basically the TGDDM molecules, HT967 hard-

ener (DDS), and glass microspheres as reinforcement (40% by wt). The glass microspheres (#3000-CP02) were supplied by Potters Industries, Inc., and were treated with a coupling agent recommended for use with epoxy resins. The two formulations investigated contained 23 and 37 parts of curing agent per hundred parts of resin (phr), by weight, respectively. Hereafter, the two formulations used will be referred to as formulation 1 (23 phr DDS) and formulation 2 (37 phr DDS). The corresponding amine/epoxy ratios were 0.44 for formulation 1 and 0.71 for formulation 2. The epoxy-amine mixtures were prepared by heating the resin and reinforcement 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 $125 \pm 1^\circ\text{C}$. Reactions during mixing were negligible, as confirmed by an uneventful 2-h isothermal (130°C) differential scanning calorimetry (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 by means of 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: 190, 195, 200, 205, and 210°C. Thermal equilibrium of the sample and of 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 on the extrapolated baseline 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 $10^\circ\text{C min}^{-1}$ from 150 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 (H_{ult}). 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 because the DSC

is insufficiently sensitive and partly because the onset of degradation (exotherm) occurs in the same temperature range.

RESULTS AND DISCUSSION

A series of isothermal DSC thermograms were obtained on reinforced systems and are shown, for formulation 2, in Figure 1. The reaction rate, which is proportional to the rate of heat generation, passes through a maximum and then decreases as a function of curing time. Also, with a decrease in cure temperature, the peak value of reaction rate ($\dot{\alpha}_p$) decreases and shifts to a longer curing time. Such behavior is typical of the autocatalytic reactions and is analogous to that observed and reported in the neat resin.² The reaction rate equation used to describe the cure kinetics is:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \quad (1)$$

where α is the extent of reaction, k_1 and k_2 are reaction rate constants, and $(m + n)$ is the overall reaction order, which was previously shown to be 2 for the neat resin.² The reaction rate was determined from the DSC trace, via the expression:

$$\frac{d\alpha}{dt} = \frac{1}{H_{\text{ult}}} \frac{dH}{dt} \quad (2)$$

H_{ult} , the ultimate heat of cure, is the sum of the isothermal heat of cure

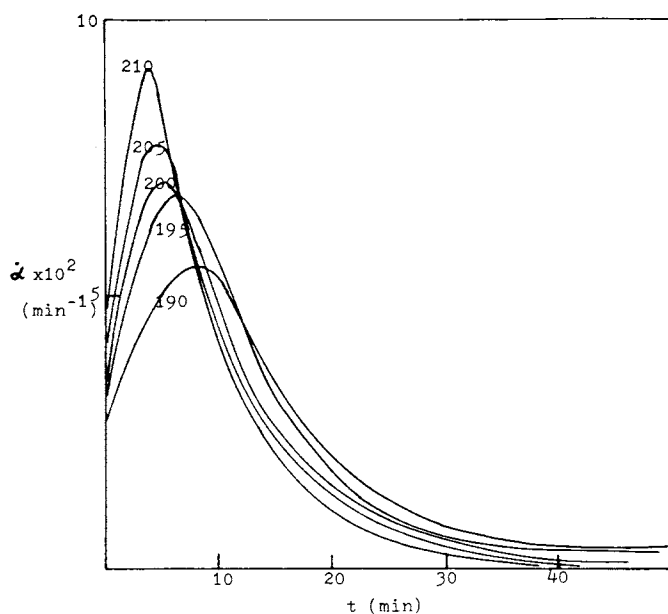


Fig. 1. Reaction rate as a function of time with temperature ($^{\circ}\text{C}$) as a parameter for reinforced formulation 2.

(H_T) and the residual heat (H_R) obtained in the subsequent dynamic DSC run. To calculate the extent of reaction (α), the DSC curves were integrated and normalized with respect to H_{ult} and sample weight. We also note that the calculations of heats of reaction (H_T and H_R) in reinforced systems were normalized with respect to the mass of epoxy formulation.

Values of the ultimate heat of cure, for both neat and reinforced formulations cured at different temperatures, are summarized in Table I. Interestingly, as the curing agent concentration was increased, the average value of H_{ult} was found to decrease for both neat and reinforced formulations. Apparently, the extent of consumption of epoxy groups by reactions other than primary amine-epoxide is enhanced in the amine-deficient formulations. Moreover, for a given formulation, the average value of H_{ult} was higher for the neat than for the reinforced resin. It appears then that the presence of reinforcement contributes to a decrease in the overall number of chemical reactions and hence a lower value of H_{ult} . After reaching the peak value, the reaction rate falls off to the baseline faster in reinforced formulations.

Plots of the extent of reaction as a function of time for reinforced formulations 1 and 2 are shown in Figures 2 and 3, respectively. The extent of reaction increased with both temperature and the concentration of DDS. A direct comparison with the behavior of neat formulations 1 and 2 revealed a slight difference, in that the curves for reinforced formulations were somewhat below the corresponding isotherms for neat formulations. The same held true for the dependence of the extent of reaction as a function of log time, which is shown in Figure 4 for reinforced formulation 2.

The reaction rate was analyzed next. Reaction rate as a function of extent of reaction, with temperature as a parameter, is shown in Figure 5. Once again, the observed dependence was very similar to that reported for the neat resin.² Although the peak value of reaction rate ($\dot{\alpha}_p$) increased with increasing temperature, the peak value of the extent of reaction (α_p) remained virtually unaffected by changes in temperature. A direct comparison of the dependence of α_p on temperature, in neat vs reinforced formulations, is shown in Figure 6. The maximum reaction rate for neat formulations occurred between 17% and 26% conversion. The maximum reaction rate for the reinforced formulation 1 was also in that range, where-

TABLE I
The Ultimate Heat of Cure as a Function of Formulation and Cure Temperature

Temperature (°C) ^a	1 (23 phr)		2 (37 phr)	
	Neat	Reinforced	Neat	Reinforced
190	740 ^b	655	595	512
195	712	658	583	581
200	714	683	563	536
205	731	727	579	552
210	738	742	599	635

^a Each isothermal DSC run was followed by a dynamic DSC run.

^b In joules per gram.

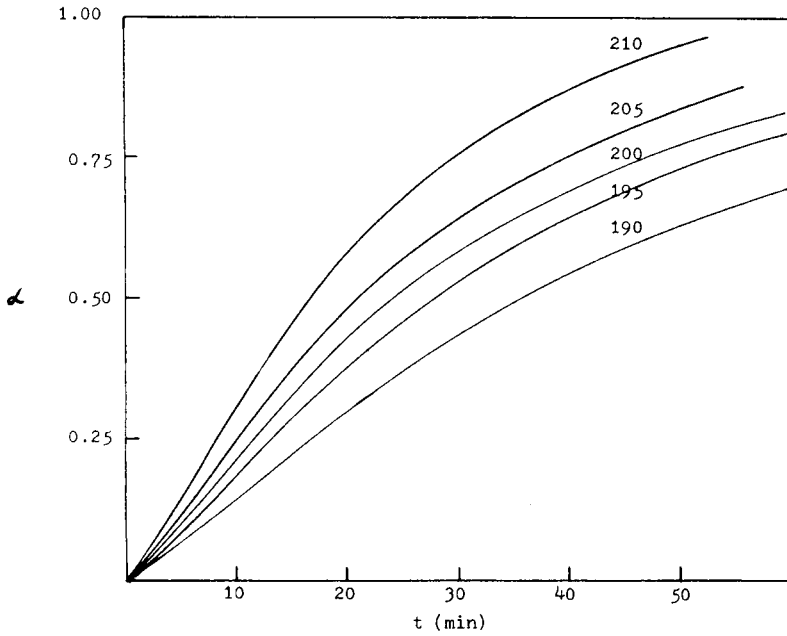


Fig. 2. Extent of reaction as a function of time with temperature ($^{\circ}\text{C}$) as a parameter for reinforced formulation 1.

as for reinforced formulation 2 the maximum rate was located between 28 and 34% conversion. In general, autocatalytic reactions are characterized by maximum rates between 30% and 40% conversion. The reinforced formulation 2 was in that range, although this is clearly a function of the type

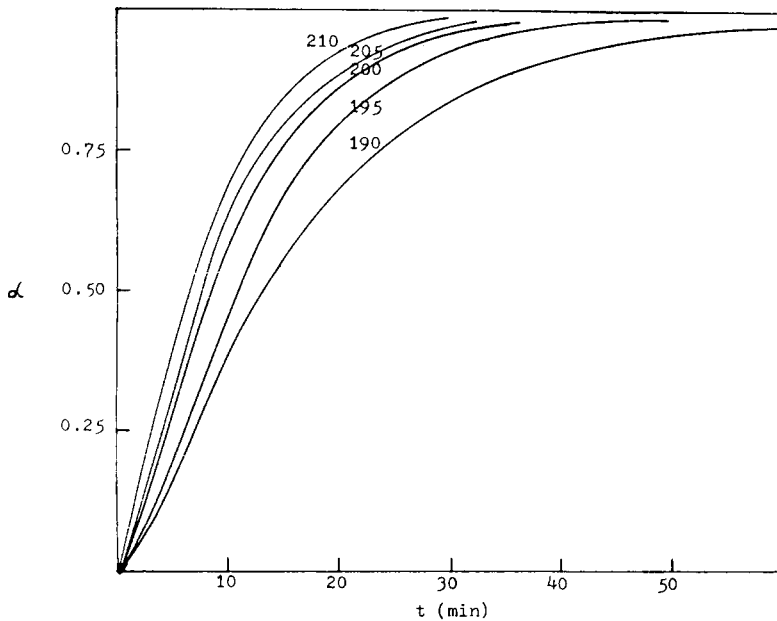


Fig. 3. Extent of reaction as a function of time with temperature ($^{\circ}\text{C}$) as a parameter for reinforced formulation 2.

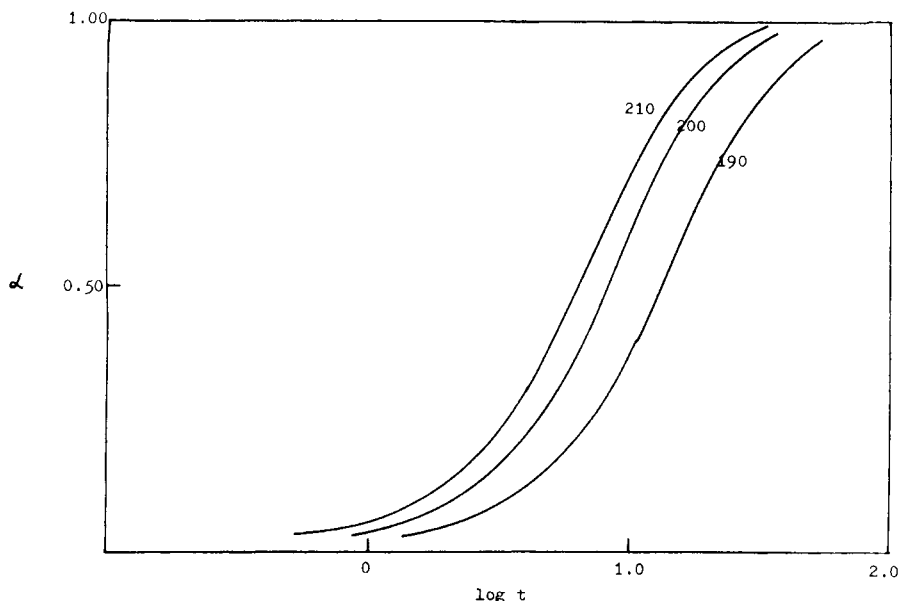


Fig. 4. Extent of reaction as a function of log time with temperature ($^{\circ}\text{C}$) as a parameter for reinforced formulation 2.

of curing formulation, as exemplified by values lower than 20% reported elsewhere.³

The maximum reaction rate ($\dot{\alpha}_p$) and the time required to reach that peak (t_p) as a function of temperature are plotted in Figures 7 and 8, respectively. Again, data for both neat and reinforced formulations are shown. The maximum reaction rate increased linearly with temperature at a similar rate for all formulations (almost identical slope). Interestingly, the curves for two reinforced formulations were found to lie slightly beneath the corresponding curves for neat formulations. Thus at any given temperature, the value of $\dot{\alpha}_p$ was lower for the reinforced formulation.

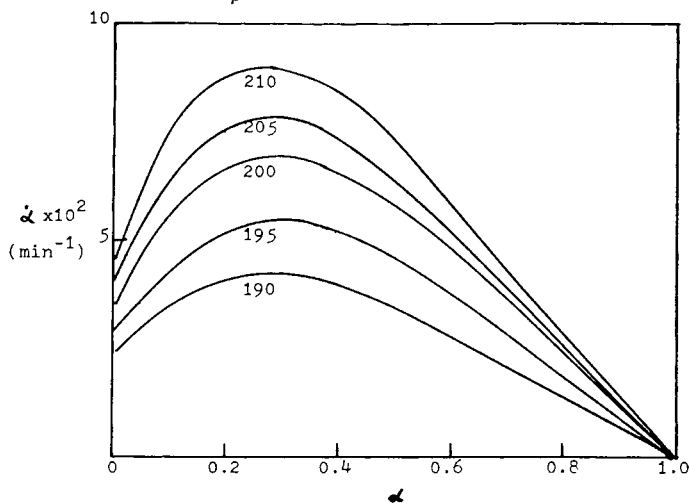


Fig. 5. Reaction rate as a function of extent of reaction with temperature ($^{\circ}\text{C}$) as a parameter for reinforced formulation 2.

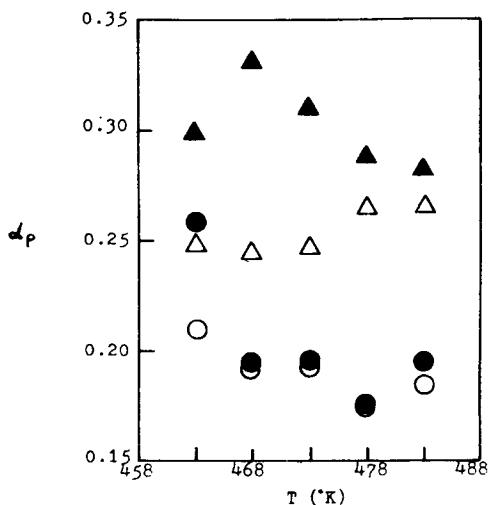


Fig. 6. Extent of reaction at peak as a function of curing temperature for neat formulations 1(○) and 2(△), and reinforced formulations 1(●) and 2(▲).

As expected, the time required to reach the peak (t_p) was found to decrease with increasing temperature, again in a linear fashion for all formulations, as seen in Figure 8. It is interesting to note, however, that the curves for the reinforced formulations lie above those of neat formulations. Hence at a given temperature, it took a little longer to reach the maximum rate peak (t_p) in the presence of reinforcement.

The kinetic rate constant k_1 , which describes the initial reaction rate at a given temperature, was read off the original DSC trace and was normalized with respect to the sample weight. The temperature dependence of k_1 for both neat and reinforced formulations is depicted in Figure 9. Slight fluctuations in the accuracy of determination of the onset of reactions are believed responsible for the observed deviations from the Arrhenius expression seen in the neat formulations.

The temperature dependence of the reaction rate constant k_2 for both

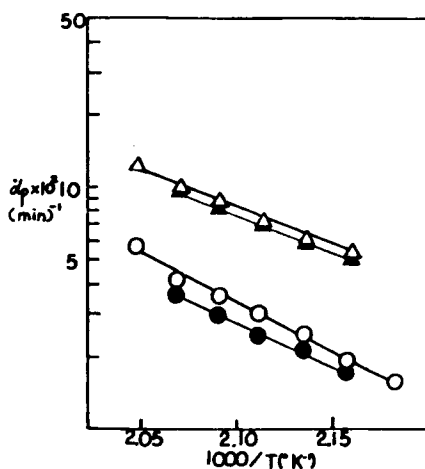


Fig. 7. Reaction rate at peak as a function of curing temperature for neat formulations 1(○) and 2(△), and reinforced formulations 1(●) and 2(▲).

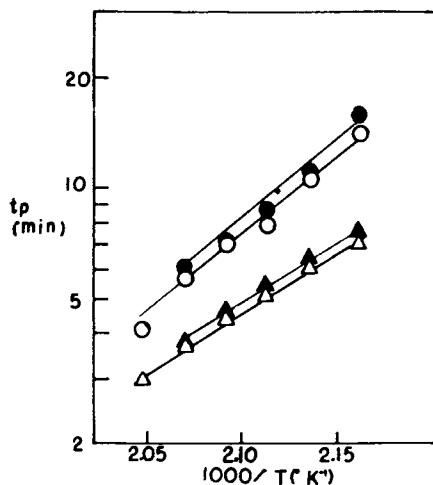


Fig. 8. Time to peak as a function of curing temperature for neat formulations 1(○) and 2(△), and for reinforced formulations 1(●) and 2(▲).

neat and reinforced formulations is presented in the Arrhenius form in Figure 10. A summary of the corresponding kinetic parameters is given in Table II. The energies of activation fell within the range reported in the literature for various epoxies. At any given temperature, the kinetic rate constant was higher in the formulation containing a higher concentration of DDS (formulation 2). It was also observed that the k_2 values for neat formulations were above those of the corresponding reinforced formulations.

The overall reaction rate order ($m+n$), was assumed to be 2. The validity of that assumption was previously confirmed, and the values of m were calculated as described.² Figures 11 and 12 summarize the m values of all

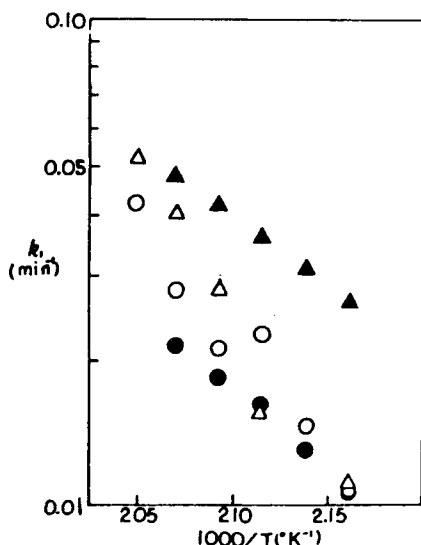


Fig. 9. Initial reaction rate constant (k_1) as a function of temperature for neat formulations 1(○) and 2(△), and reinforced formulations 1(●) and 2(▲).

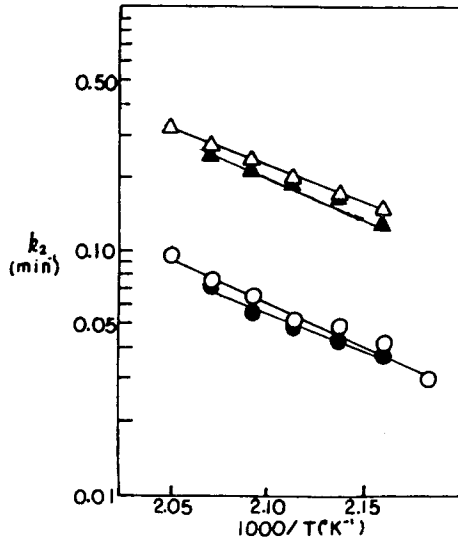


Fig. 10. Reaction rate constant (k_2) as a function of temperature for neat formulations 1(○) and 2(△), and reinforced formulations 1(●) and 2(▲).

TABLE II
Summary of Kinetic Parameters

	Neat	Reinforced
Formulation:		
k_1	2.22×10^8 exp($9.11 \times 10^7 \text{ J/kgmolRT}$)	1.34×10^5 exp($6.27 \times 10^7 \text{ J/kg-molRT}$)
k_2	1.21×10^6 exp($6.64 \times 10^7 \text{ J/kgmolRT}$)	2.41×10^4 exp($5.14 \times 10^7 \text{ J/kg-molRT}$)
Ea_2 (kcal/gmol)	15.9	12.3
Formulation 2:		
k_1	9.77×10^{12} exp($13.3 \times 10^7 \text{ J/kgmolRT}$)	9.70×10^{12} exp($5.43 \times 10^7 \text{ J/kgmolRT}$)
k_2	6.13×10^4 exp($4.97 \times 10^7 \text{ J/kgmolRT}$)	4.88×10^5 exp($5.81 \times 10^7 \text{ J/kgmolRT}$)
Ea_2 (kcal/gmol)	11.9	13.9

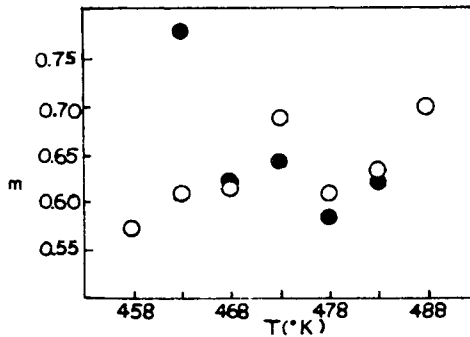


Fig. 11. Kinetic parameter m as a function of curing temperature for neat (○) and reinforced (●) formulation 1.

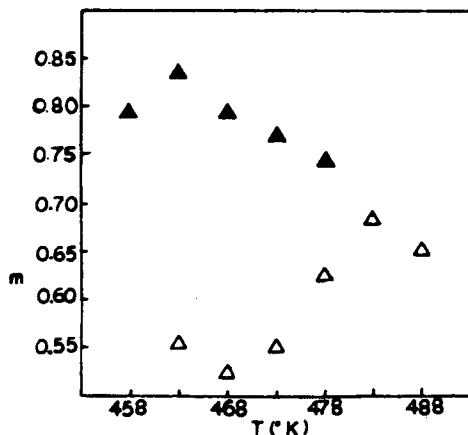


Fig. 12. Kinetic parameter m as a function of curing temperature for neat (Δ) and reinforced (\blacktriangle) formulation 2.

formulations. A data scatter of up to $\pm 10\%$ was recorded, and hence no definite trends were established as a function of the type of formulation. For a given formulation, the value of m was reported to be independent of temperature,^{3,4} and, in another study, to decrease with increasing temperature.⁵ Although the scatter of our data was noticeable, the value of m was found to remain mostly between 0.5 and 0.7. Somewhat higher m values, between 0.75 and 0.83, were recorded with reinforced formulation 2, as seen in Figure 12.

Although the effect of the reinforcement on cure kinetics was not very pronounced, there are several points that should be emphasized. As one would expect, a higher cure temperature and a higher DDS concentration resulted in an increase in the reaction rate in both neat and reinforced formulations. The lower value of H_{ult} in reinforced formulations suggests the role of reinforcement in restricting the molecular mobility of reactive species. This could then account for, e.g., the observed longer time to peak (Fig. 8) and the slightly lower values of k_2 for the reinforced formulations (Fig. 10). The restrictions to molecular mobility imposed by the reinforcement are envisioned to become more pronounced as the reactions proceed, because of the concomitant increase in viscosity. As the diffusion control becomes progressively more important, the molecules in the vicinity of reinforcement are "shielded" (by the reinforcement) and hence are increasingly less likely to encounter a reactive species than the molecules in the bulk. That could be the reason why the reaction rate, after going through the maximum, falls off to the baseline noticeably faster in the reinforced formulations. Is it then possible that the reaction rate in reinforced systems may vary as a function of the distance from reinforcement? We believe that to be true, although more definitive proof is needed. We have recently investigated the nature of the reinforcement-matrix boundary region in graphite/epoxy composites and found that it differs from the bulk resin.⁶ We are presently working to establish whether the morphological character of the reinforcement-matrix boundary region is determined primarily during cure (chemical reactions) or during the final stage of the processing sequence: cooling.⁷

CONCLUSIONS

Cure kinetics of two neat vs reinforced epoxy formulations were investigated by differential scanning calorimetry. Experimental results were described well by an autocatalytic kinetic equation. In all formulations, higher cure temperature and higher DDS concentration led to an increase in the reaction rate. The extent of reaction at the maximum rate of reaction was independent of temperature but took a longer time to attain in reinforced formulations. Values of the reaction rate constant, k_2 , were slightly lower for the reinforced formulations. Also, the values of H_{ult} were lower for reinforced formulations. An explanation was offered in terms of the restrictions to molecular mobility imposed by the reinforcement. It was concluded that the correlation between the cure kinetics and the ensuing network morphology in neat vs reinforced systems should be further investigated.

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