Effect of Catalyst on the Curing of Tetrafunctional Epoxy Resin Formulations

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SYNOPSIS

Cure kinetics of tetraglycidyl 4,4'-diaminodiphenyl methane resin formulations with diaminodiphenylsulfone as hardener and borontrifluoride-ethylamine adduct as accelerator has been studied by differential scanning calorimetry (DSC) technique both dynamically and isothermally. The DSC scans show multiple exotherm peaks, indicating the complex nature of reaction. The curing exotherms obtained have been analysed to derive the kinetic parameters associated with the curing process. The heat of reaction shows a decreasing trend with increasing catalyst concentration.

INTRODUCTION

The kinetic studies on the curing of thermosetting resins is still an area of great significance because of their extensive applications in preparing advanced composites. The thrust given to such areas of work is related to decrease the total energy consumption without the loss of properties but to improve it further. Even though enough work is carried out on the curing of tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) with different hardeners and catalysts by various workers,[1–4] formulations based on TGDDM continue to offer a lot of scope for making better composites in terms of properties.

In our previous communication,[5] we reported the effect of addition of epoxy diluents on curing of TGDDM. In practice, such formulations often incorporate catalyst to accelerate the thermal curing reaction. Because of low reactivity at ambient temperatures, providing a degree of storage that offers stability to the uncured resins, the borontrifluoride ethylamine (BFE) complexes are found to be particularly suited for curing of matrix resins. The mechanism of catalysis by BFE and related compounds on epoxy curing is still not fully understood. Since BFE complexes have been shown to provide a variety of catalytic species, the curing of epoxies therefore have become more complex. This article describes the study of cure of different epoxy resin formulations with added BFE complexes as catalyst using differential scanning calorimetric (DSC) techniques.

EXPERIMENTAL

The synthesis of epoxy resins based on TGDDM, p-amino phenol (TGPAP), and aniline (DGA) were described in our earlier communications.[5,6] The average epoxide equivalent weights of TGDDM, TGPAP, and DGA were found to be 115.6, 92.33, and 102.5 g mol^{-1} corresponding to tetra-, tri-, and diglycidyl epoxies. BFE adduct was prepared in our laboratory.

The resin formulations were made by mixing different percentages of resins. After mixing the resins, a calculated amount of diaminodiphenyl sulphone (DDS) was added at 130°C over 10 min and the mixture was then cooled to about 85°C. Then BFE adduct was added and dissolved by stirring. About 6–8 mg resin formulation was used for thermal studies.

The techniques for obtaining DSC scans using Dupont 9900 thermal analyzer have also been described previously.[5] The sample was placed in the DSC cell with an empty aluminium pan as the reference. The dynamic DSC scans were taken up to 320°C at varying heating rates ranging from 2–


20°C/min. For isothermal measurements, the instrument was first equilibrated at the required temperature and then the sample pan was inserted. The isothermal runs were conducted at four different temperatures: 128.5, 148.5, 158.5, and 168.5°C. All DSC runs were carried out in triplicate and the reproducibility of kinetic data was found to be 98%.

RESULTS AND DISCUSSION

The curing mechanism for epoxies of the type under consideration is a complex one. The complexity was shown without the addition of catalyst.[5] The effect of addition of BFE adduct has a tremendous effect on exotherm and curing temperature.[2] The strong accelerating effect of the catalyst is shown in Figures 1 and 2 for TGDDM/TGPAP/DDS (80/20/30) and TGDDM/DGA/DDS (80/20/30) systems with 0, 1, and 2% BFE concentration. This plot of fractional conversion against temperature shows that the curing started at around 180°C in the absence of catalyst whereas the commencement of cure temperature lowered with increase in BFE concentration. The observed trend in lowering of heat of reaction with increasing BFE concentration is likely due to the competition between amine addition and cationic polymerisation reaction. This is possibly because of the fact that epoxides are susceptible to polymerisation in the presence of cationic initiator like BF_3^+ to form a polyether that associates with the heat of reaction comparable for amine addition.
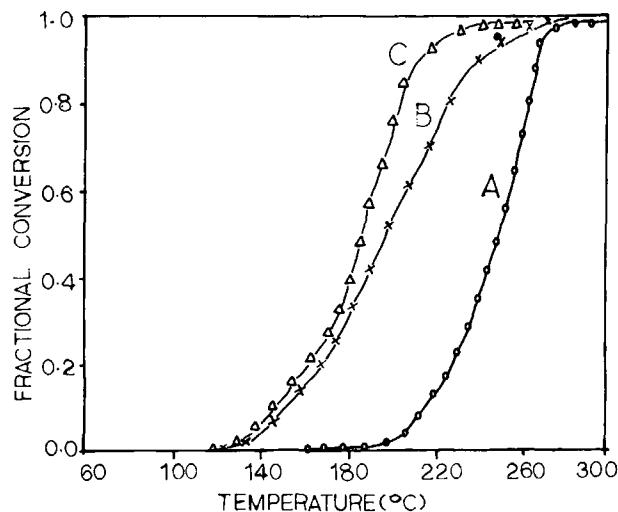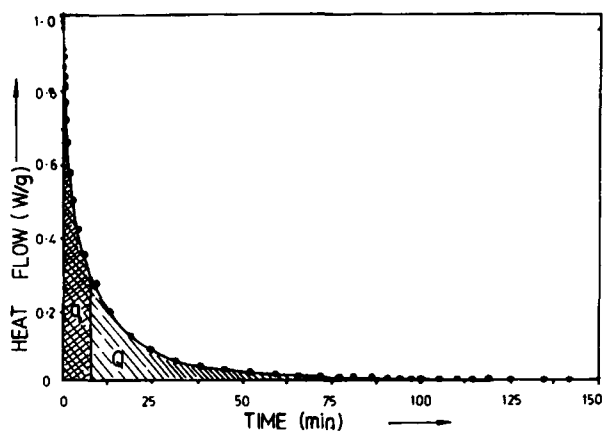

Figure 1 Fractional conversion as a function of temperature, from 10°C/min DSC scans. Resin formulations TGDDM/TGPAP/DDS (80/20/30) and BFE. A, 0% [BFE]; B, 1% [BFE]; C, 2% [BFE].
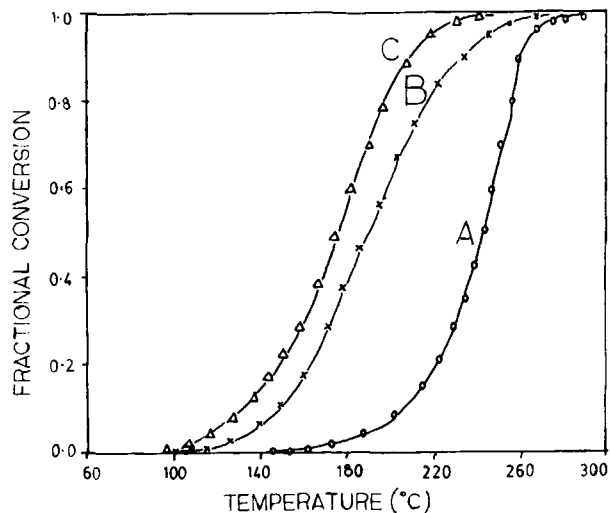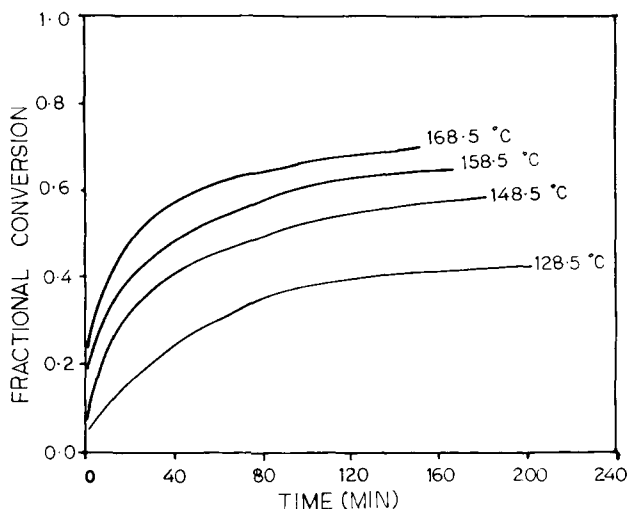

Figure 2 Fractional conversion as a function of temperature, from 10°C/min DSC scans. Resin formulations TGDDM/DGA/DDS (80/20/30) and BFE. A, 0% [BFE]; B, 1% [BFE]; C, 2% [BFE].

The effect of temperature on the curing behaviour of resin catalyst combinations for obtaining kinetic parameters has been carried out by isothermal measurements. A typical plot of heat flow vs. time is shown in Figure 3 for the TGDDM/TGPAP/DDS/ BFE (80/20/30/1) system at 148.5°C. Such isothermal experiments have been conducted at different temperatures, namely, 128.5, 148.5, 158.5, and 168.5°C, for different resin formulations. From these isothermal experiments, fractional conversion was calculated as the ratio of partial heat of reaction q at a given time to the overall heat of reaction Q obtained from the peak area. The total peak area Q was determined by considering the experimentally
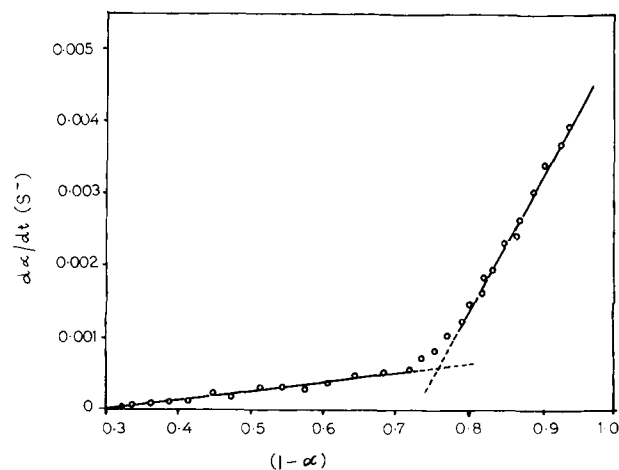

Figure 3 Isothermal heat flow vs. time at 148.5°C for TGDDM/TGPAP/DDS (80/20/30) and 1% BFE.
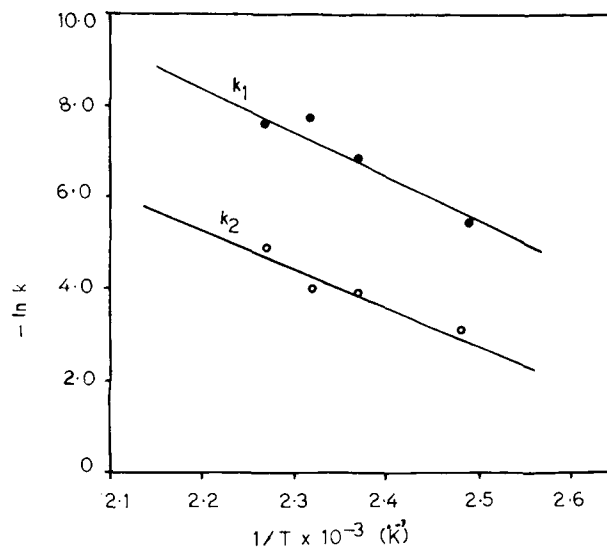
Figure 4   Isothermal fractional conversion vs. time for TGDDM/TGPAP/DDS (80/20/30) and 1% BFE.

Figure 6   Arrhenius plots of apparent first-order rate constants. Initial rate constant (●) and final rate constant (0) for TGDDM/TGPAP/DDS/BFE (80/20/30/1).

determined baseline from which stage onward the heat of reaction is constant, as shown by the darkened area. Figure 4 shows the plot of fractional conversion vs. time for the TGDDM/TGPAP/DDS/BFE (80/20/30/1) system at each temperature. The observed behaviour of rapid initial rise is characteristic of an autocatalysed reaction, in contrast to sigmoidal conversion for an uncatalysed system.

Further, a plot of rate $(d\alpha/dt)$ vs. $(1-\alpha)$ showed the pattern, as indicated in Figure 5. An initial linear region up to about 30% conversion is followed by a region of deaccelaration and again a final linear region. The linear regions correspond to the first-order kinetics with respect to overall conversion. A similar pattern was observed in other cases also. Another

estimate of the initial and final first-order rate constants is by plotting the natural log of the apparent rate constant vs. reciprocal absolute temperature as shown in Figure 6. The linearity of the plot demonstrates the confirmity with Arrhenius equation. The apparent activation energies and preexponential factors determined from isothermal measurements are given in Table I.

A set of heat flow vs. temperature curves from DSC scans at 2, 5, 10, and 20°C/min for resin formulations TGDDM/TGPAP/DDS/BFE and TGDDM/DGA/DDS/BFE (80/20/30/1) are shown in Figures 7 and 8. Both temperatures and the relative height of the component peaks are seen to depend on the heating rate.

A similar observation was made for the system TGDDM/diglycidyl orthpthalate/DDS/BFE (64/11/25/0.4) by Walkup et al.[7] and for TGDDM/DDS/BFE (100/30/1) by Barton.[2] For the present system as illustrated in Figures 7 and 8, the scans at 10°C/min also show peaks at 240, 200, and 160°C

Figure 5   Plot of $d\alpha/dt$ vs. $(1 - \alpha)$ for 148.5°C run.

Table I   Apparent First-Order Kinetic Parameters from Isothermal Data for the Resin System TGDDM/TGPAP/DDS/BFE (80/20/30/1)

Data	Activation Energy $E\alpha$ (KJ/mol)	Frequency Factor ln A (min^{-1})
Initial k	79.0	16.1
Final k	55.0	11.8
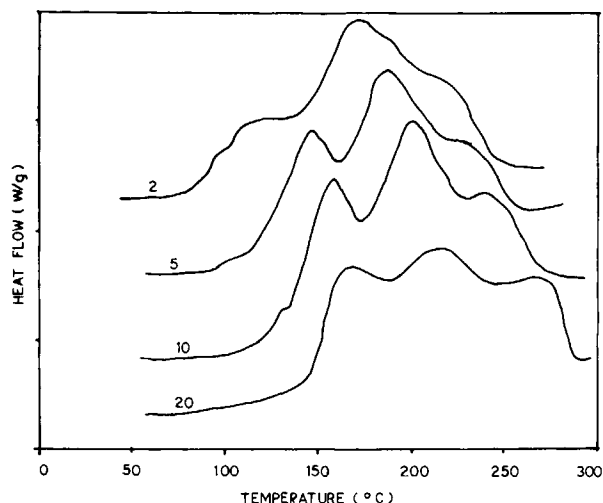
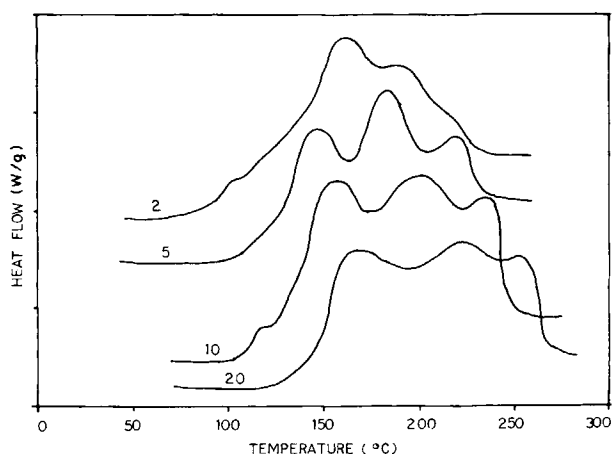**Figure 7** DSC scans at different heating rates for resin TGDDM/TGPAP/DDS (80/20/30) and 1% BFE.

Figure 9 DSC scans at different heating rates for resin TGDDM/TGPAP/DDS (80/20/30) with 2% BFE.
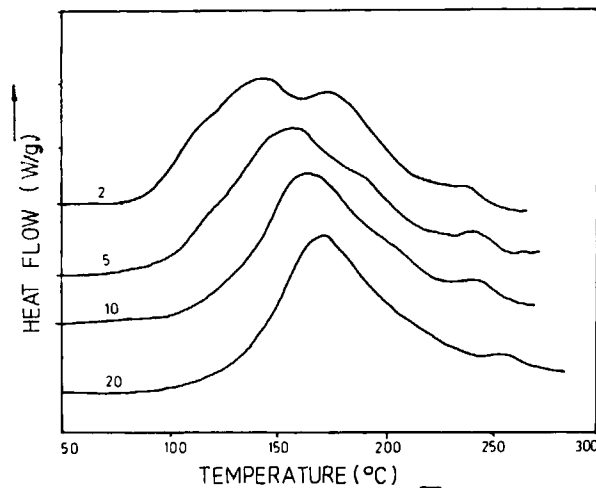
although the order of peak height is different. The addition of TGPAP or DGA into the resin formulation has not remarkably changed the peak pattern of TGDDM/DDS/BFE. With a similar argument proposed by Walkup et al. and Barton, the peak at 240°C is associated with noncatalysed reaction while the other peaks at lower temperatures were associated with reactions involving BFE catalyst. The peak intensity of the uncatalysed reaction decreased with increasing BFE concentration, as shown by the diminished peak intensity illustrated in Figure 9.

The data from dynamic DSC runs were analysed in terms of the kinetic equation:

$$r = \mathrm{d}q/\mathrm{d}t = kf(\alpha), \tag{1}$$

where $f(\alpha)$ is the kinetic function and k the rate constant. For a given value of α it follows that

$$\ln r = A' - (E/RT), \tag{2}$$

where A' = constant, E = activation energy, and R = gas constant. The Ozawa's approximate transformation of eq. (2)[8-10] was also used for evaluation:

$$Ea = \frac{-R}{1.052} \cdot \frac{\Delta \ln \phi}{\Delta(1/T_\alpha)}, \tag{3}$$

where ϕ is the heating rate and T_α is the absolute temperature corresponding to a given degree of conversion. The above models show linear plots of $\ln r$

Figure 8 DSC scans at different heating rates for resin TGDDM/DGA/DDS (80/20/30) and 1% BFE.
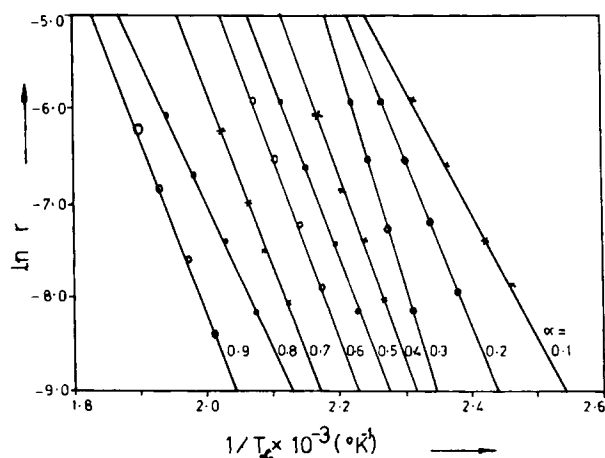
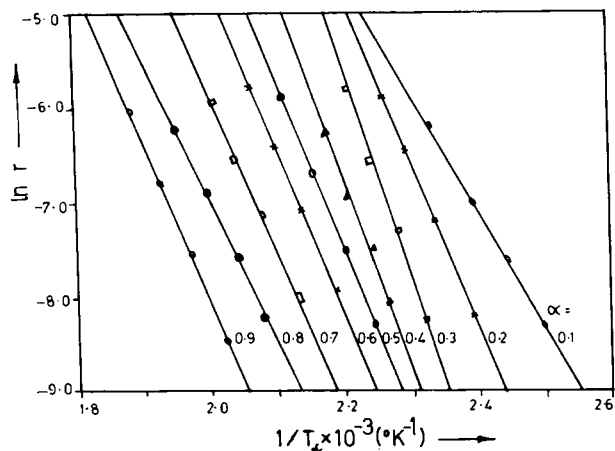**Figure 10** Plot of $\ln r$ against $1/T_\alpha$ from the data of Fig. 7.

Figure 11   Plot of ln r against $1/T_\alpha$ from the data of Fig. 8.

and log ϕ, respectively, against $1/T_\alpha$ as shown in Figures 10–15. A good linearity was observed in all cases over a wide range of conversion. In spite of the addition of epoxy diluents/modifiers (TGPAP/DGA), the complex profiles have shown remarkably linear plots, indicating a good approximation at a given level of conversion. The apparent activation energy as a function of fractional conversion is shown in Figures 16–18. The system TGDDM/TGPAP/DDS/BFE with 2% BFE indicated an increasing trend of E with fractional conversion.
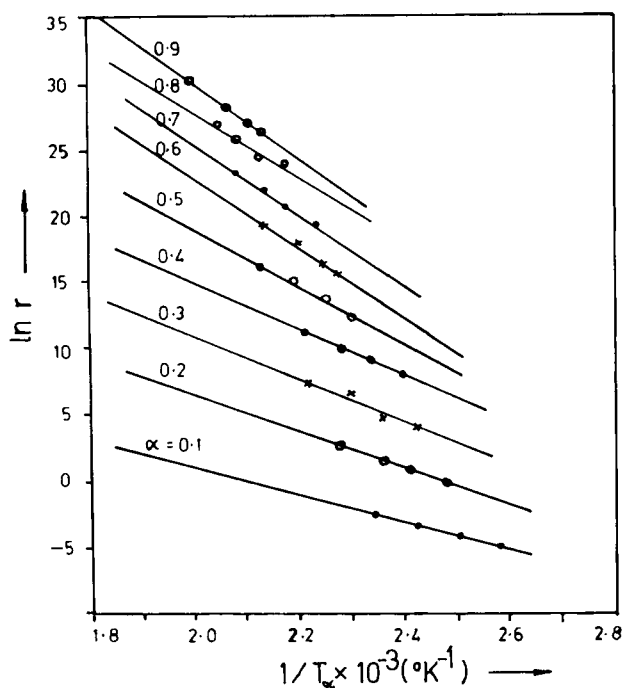

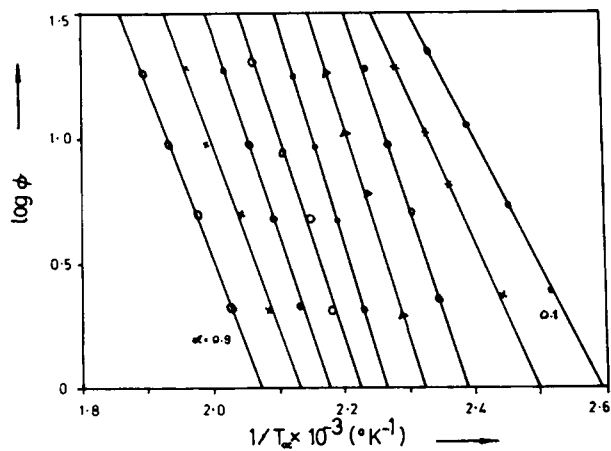**Figure 12**   Plot of ln r against $1/T_\alpha$ from the data of Fig. 9.

Figure 13   Plot of log ϕ against $1/T_\alpha$ for the TGDDM/TGPAP/DDS/BFE (80/20/30/1) system.
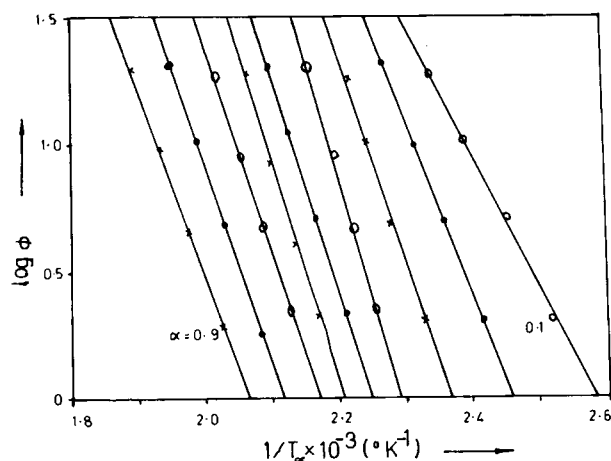

Figure 14   Plot of log ϕ against $1/T_\alpha$ for the TGDDM/DGA/DDS/BFE (80/20/30/1) system.
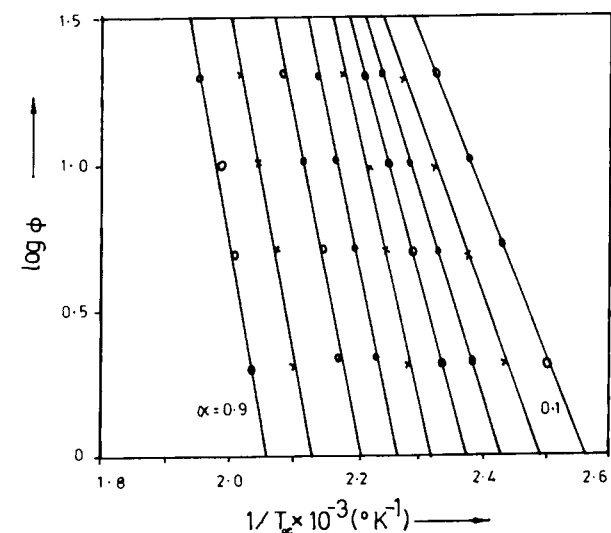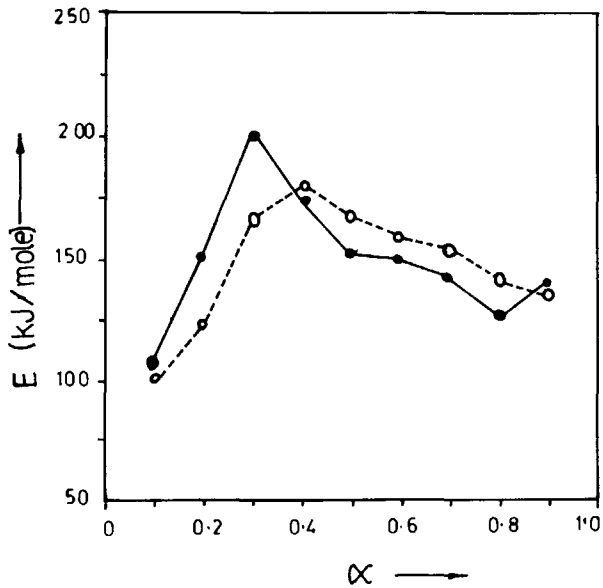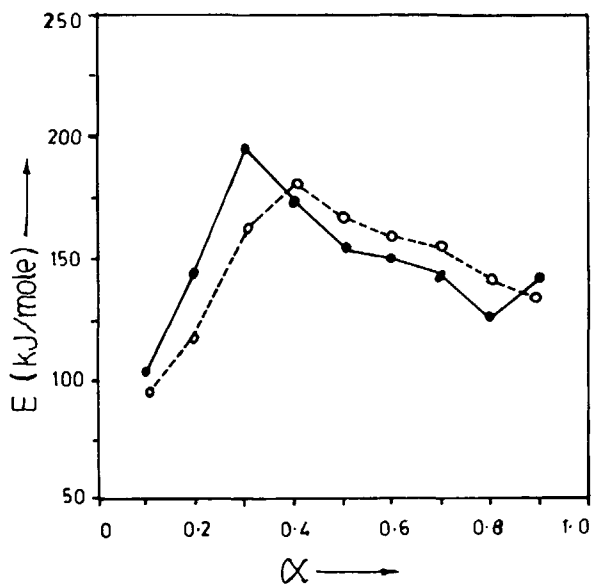

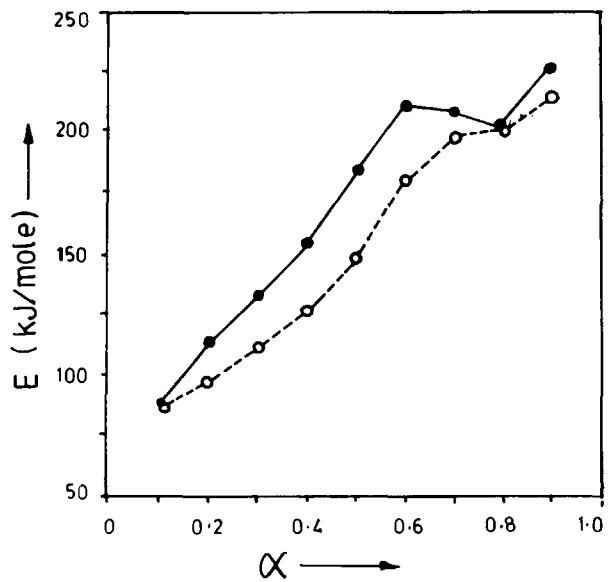**Figure 15**   Plots of log ϕ against $1/T_\alpha$ for the TGDDM/TGPAP/DDS/BFE (80/20/30/2) system.

Figure 16   Dependence of apparent activation energy, E, on conversion for the TGDDM/TGPAP/DDS/BFE (80/20/30/1) system. ●, from eq. (2); ○, from eq. (3).

Figure 18   Dependence of apparent activation energy, E, on conversion for the TGDDM/TGPAP/DDS/BFE (80/20/30/2) mixture. ●, from eq. (2); ○, from eq. (3).

However, maximum E at about 30–40% conversion was observed for the systems TGDDM/TGPAP/DDS/BFE (80/20/30/1) and TGDDM/DGA/DDS/BFE (80/20/30/1). This again coincides with the region of transition to a much slower reaction rate in the isothermal data. These discrepancies between the value of activation energy indi-

cate the complexity of the curing reaction. The complex nature of these reactions has also been demonstrated by other workers.[2,11-16]

Considering this complexity, it is remarkable that the curing of these reactions display good linearity as shown in Figures 10–15. The effect of addition of TGPAP and DGA to TGDDM has clearly indicated

Figure 17   Dependence of apparent activation energy, E, on conversion for the TGDDM/DGA/DDS/BFE (80/20/30/1) system. ●, from eq. (2); ○, from eq. (3).
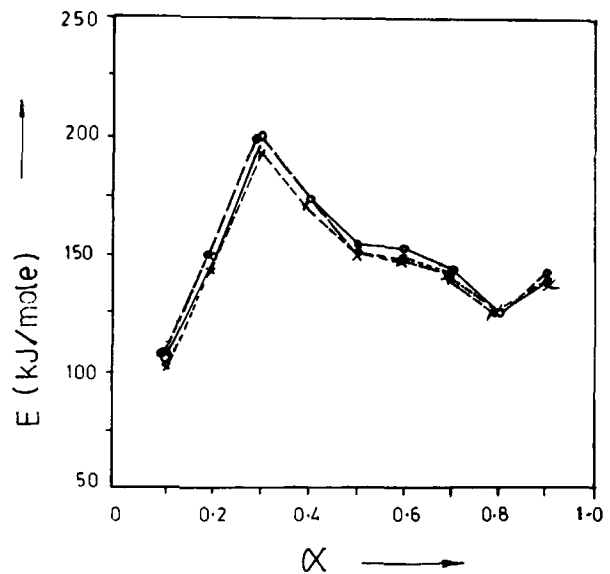
Figure 19   Dependence of apparent activation energy, E, on conversion. ○, TGDDM/DDS/BFE (100/30/1); ●, TGDDM/TGPAP/DDS/BFE (80/20/30/1); ✕, TGDDM/DGA/DDS/BFE (80/20/30/1).

only the decreasing activation energy while maintaining the similar complex behaviour of the reaction. This is illustrated in Figure 19. This is also accountable in terms of reduction in overall functionality to some extent by the addition of epoxy diluents like TGPAP or DGA.

CONCLUSIONS

The addition of BFE as catalyst in TGDDM-based resin formulations indicated the start of curing reaction at a significantly lower temperature. The effect of catalyst on formulations containing epoxy diluents like TGPAP and DGA decreased the apparent activation energy; however, the completion of cure still requires heating up to 250°C. The complex behaviour of the catalysed curing reaction was demonstrated by the presence of multiple peaks in dynamic DSC.

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