

Differential Scanning Calorimetry Cure Studies on the Effect of Addition of Epoxy Diluents to Tetrafunctional Epoxy Resins

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Synopsis

The effect of the addition of *p*-aminophenol and aniline-based epoxy diluents on the curing behavior of highly viscous tetraglycidyl diamino diphenyl methane resin with diamino diphenyl sulfone hardener have been investigated kinetically by differential scanning calorimetry. Dynamic scans were carried out over a temperature range 30–300°C for different resin formulations. Isothermal scans at four different temperatures have also been carried out for the evaluation of kinetic parameters. Heat flow measurements at different heating rates have indicated the evidence of autocatalytic behavior of curing reaction following a simple *n*th-order kinetics.

INTRODUCTION

The use of tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) as the main constituent of the resin matrix in high performance composites employed in aircraft and spacecraft industries has generated considerable interest. The study of curing characteristics of TGDDM with different types of hardeners is a matter of great significance to understand the kinetic behaviour of resin reactions. The addition of diluent modifiers to epoxy systems continued to offer the possibility of obtaining good resin formulation systems to improve the overall properties of composite material.

Differential scanning calorimetry (DSC) is a valuable technique for investigating the kinetic parameters of curing reaction of thermosetting polymers.¹ The cure kinetics of TGDDM/DDS system using DSC has been reported by Barton.² It is also reported that the addition of epoxy diluent to a conventional epoxy resin-curing agent formulation improves certain properties and lowers the cure temperature.^{3,4}

As part of our composite research programme, we have described in this paper the application of DSC techniques for kinetic investigation of TGDDM/DDS system with two epoxy diluents, namely triglycidyl-*p*-aminophenol (TGPAP) and diglycidylaniline (DGA).

EXPERIMENTAL

Materials

The epoxy resins TGDDM, TGPAP, and DGA were synthesized in our laboratory. The synthetic procedure adopted has shown the least reaction time of

3–4 h between the reactants.⁵ Diaminodiphenyl methane (Fluka) and *p*-aminophenol (Fluka) were used after sublimation. Analytical grade aniline was used after distillation. Epichlorohydrin was freshly distilled each time before use. Diaminodiphenyl sulfone (DDS) from Fluka was used without further purification.

The epoxide equivalents of TGDDM, TGPAP, and DGA were found to be 117.5, 104.4, and 116.8 g mol⁻¹, respectively. The corresponding theoretical epoxide equivalents are 105.6, 92.33, and 102.5. The functionality of about 3.6 for TGDDM, 2.7 for TGPAP, and 1.8 for DGA have shown a comparable degree of purity of resins. A slightly higher values of epoxide equivalents in the synthesised resins are likely to be due to the presence of chlorinated, hydroxylated, and oligomeric compounds.

Techniques

The calorimetric measurements were made with a Dupont 9900 computer/thermal analyzer with 910 DSC module. The temperature scale of the instrument was calibrated with high purity indium while the heat flow calibration was done with high purity alpha alumina disc.

The samples for DSC studies have been prepared as follows. An exact weight of about 2.0 g of resin (with or without the diluents) was taken in a small capsule and the required amount of DDS was mixed thoroughly with it. The mixture was heated at 130°C for 10 min to ensure the complete mixing of components. They were stored in a sealed container at about -10°C. The resin systems thus obtained was used for DSC runs. Two to 10 mg were taken in aluminium pans for dynamic (constant temperature) DSC studies. An empty pan was used as the reference for measuring the heat flow. The dynamic scans were taken up to 300°C at varying heating rates ranging from 5 to 20°C/min. For isothermal measurements, the instrument was first calibrated for three different temperatures and then the sample pan was inserted. The DSC runs were made in duplicate and the reproducibility of kinetic data was found to be 98–99%. The kinetic parameters were computed for each run and the values were averaged and reported with analytical variations.

RESULTS AND DISCUSSION

Figure 1 shows a typical plot of selected dynamic runs carried out at a heating rate of 10°C/min, in the temperature range 30–300°C, for different stoichiometric resin mixtures. The weight ratio of 30% DDS was used for obtaining the above thermograms. From the characteristic DSC scans the temperatures at which the curing reaction started (T_i), attained the maximum (T_p), and completed (T_f), the cure range, and the cure time for different compositions are presented in Table I. The reactivities of the diluents with curing agent depend upon the location of epoxy group in the molecule. It was observed that the gelation time for TGDDM : TGPAP formulation was higher than TGDDM : DGA formulation.

The reaction mechanism for the addition of primary or secondary amine to epoxide, which takes into account the phenomenon of catalysis by hydrogen bond donors was proposed by Horie et al.⁶ The generation of catalytic hydroxyl

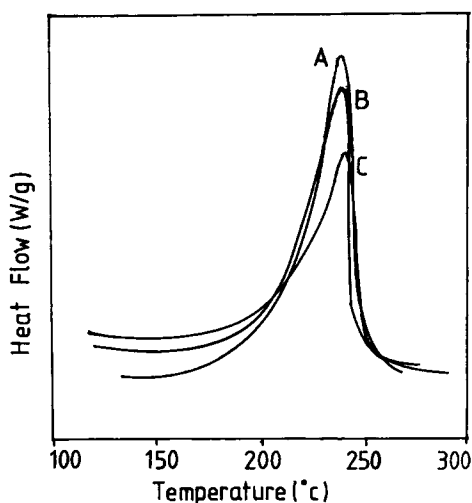


Fig. 1. Dynamic scans at 10°C/min for the stoichiometric mixture of (A) TGDDM, (B) TGDDM-TGPAP (80 : 20), (C) TGDDM-DGA with 30% DDS.

groups by the amine-epoxide addition reaction explained the autocatalytic features of the overall reaction.

The general scheme of reaction is shown below:

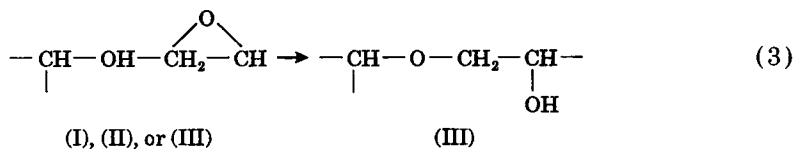
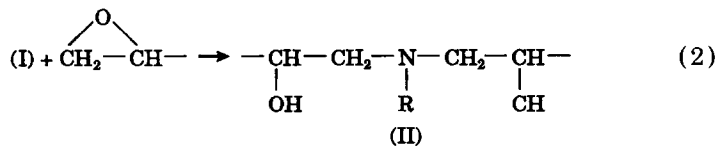
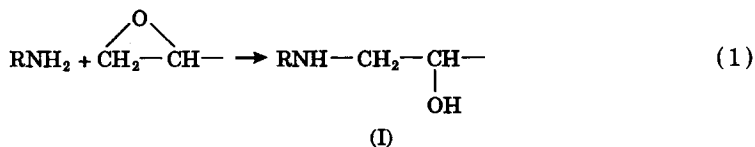


TABLE I

Apparent Rate Constants and Activation Energy from Isothermal Data for the Stoichiometric Resin/DDS Mixture [Composition TGDDM-TGPAP (80 : 20)]

Fitted to Eq. (4) with $m = n = 1$.

Temperature (°C)	K_1 (S ⁻¹)	K_2 (S ⁻¹)	E_1	E_2
			(kJ mol ⁻¹)	
172	0.84	4.38		
186	1.77	7.11	55.02	60.96
202	2.4	13.63		
217	3.6	17.45		

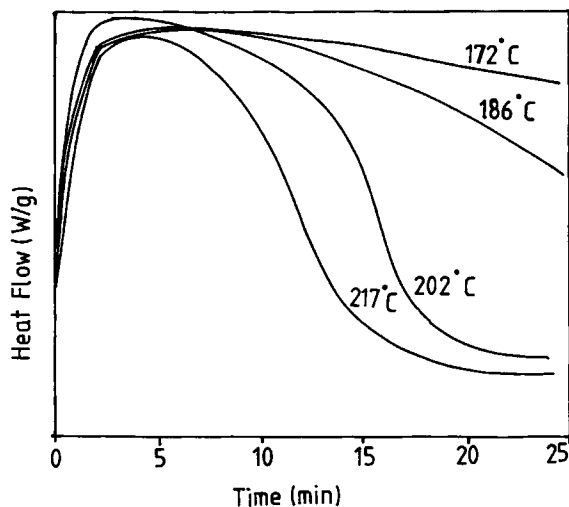


Fig. 2. Isothermal DSC data at 172, 186, 202, and 217°C for the stoichiometric mixture of TGDDM-TGPAP (80 : 20) and DDS.

The interpretation of the kinetics is based on the mechanism proposed by Schnechter et al.⁷ and Smith⁸ for the reaction of secondary amines with epoxides, which was extended by Horie et al.⁶ to include the primary amine reaction. The overall rate equation derived for this mechanism may be expressed in terms of fractional conversion α as

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \quad (4)$$

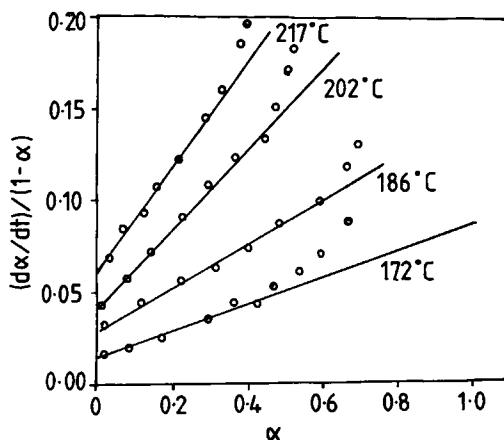


Fig. 3. Isothermal data plotted in the form of eq. (4) $m = n = 1$ for the stoichiometric mixture of TGDDM-TGPAP (80 : 20) and DDS.

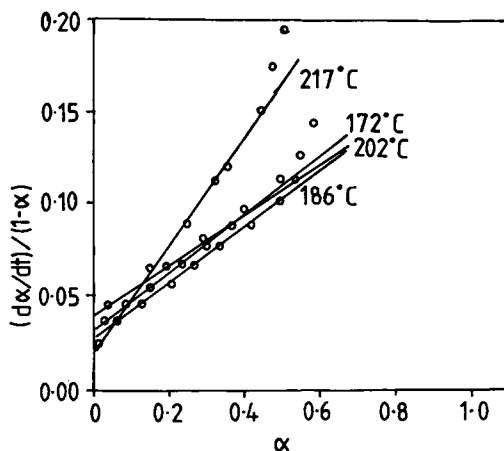


Fig. 4. Isothermal data plotted in the form of eq. (4) $m = n = 1$ for the stoichiometric mixture of TGDDM-DGA (80 : 20) and DDS.

where K_1 refers to the reaction catalysed by proton donors initially resident in the system (m th order) and K_2 is associated with the reaction catalyzed by hydroxyl groups formed in the amine-epoxide addition (n th order).

Isothermal DSC scans were made on resin formulations to study the behavior of curing reaction with the help of eq. (4). Isothermal scans were carried out at 172, 186, 202, and 217°C for 80 : 20 TGDDM : TGPAP and TGDDM : DGA formulations. A representative scan is shown in Figure 2. The thermograms were then analyzed for fractional conversion α as the ratio of partial heat of reaction, q , at a given time t , to the overall heat reaction Q obtained from the total peak area. The present isothermal data are shown as plots of $(d\alpha/dt)/(1-\alpha)$ vs. α , in Figures 3 and 4. Linearity of these plots have indicated a good fit to eq. (4) for $m = n = 1$ and has strengthened the autocatalytic behavior of the reaction. The intercepts and initial slopes of the plots in Figures 3 and 4 were determined by linear regression and the values of the corresponding apparent rate constants K_1 and K_2 are given in Table II. But the observed data have indicated a bimolecular rate determining step ($n = 2$) between hydroxylic and either amine or a rapidly formed amine-epoxide adduct as shown by a plot of $(d\alpha/dt)/(1-\alpha)^2$ vs. α in Figure 5 for TGDDM : TGPAP formulation. Both K_1 and K_2 are Arrhenius functions of temperature as shown by the linearity of plots of $\ln K$ against reciprocal temperature in Figure 6.

TABLE II
Curing Characteristics of Epoxy Resins with 30% DDS

Epoxy system	Proportion (% w/w)	T_i (°C)	T_p (°C)	T_f (°C)	Curing temp range (°C)	Curing time (min)
TGDDM	—	175.91	241.1	249.26	73.35	7.5
TGDDM-TGPAP	80 : 20	172.43	243.36	254.19	81.71	8.42
TGDDM-DGA	80 : 20	179.42	242.44	252.21	72.79	7.82

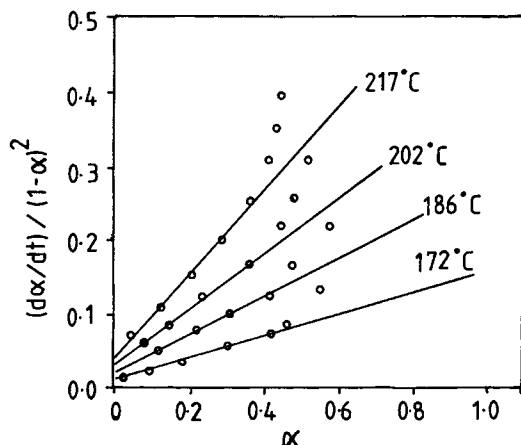


Fig. 5. Isothermal DSC data for the stoichiometric mixture of TGDDM-TGPAP (80 : 20) and DDS.

The peak exotherm temperature (T_p) varied in a predictable manner with the heating rate (ϕ). Figures 7 and 8 show the variation of heat flow at 5, 10, and 20°C/min heating rate for 80 : 20 TGDDM : TGPAP and TGDDM : DGA. Even for autocatalysed reactions, the dynamic DSC scans gives an accurate measure of the activation energy and preexponential factor.¹ A simple and accurate relationship between activation energy E , heating rate ϕ , and peak exotherm temperature T_p was given by Ozawa^{9,10} in the form of

$$E = \frac{-R}{1.052} \cdot \frac{\Delta \ln \phi}{\Delta(1/T_p)} \quad (5)$$

Preexponential factor $\ln A$ and E were determined by the Kissinger equation

$$-\ln(\phi/T_p^2) = \frac{E}{RT_p} - \ln\left(\frac{AR}{E}\right) \quad (6)$$

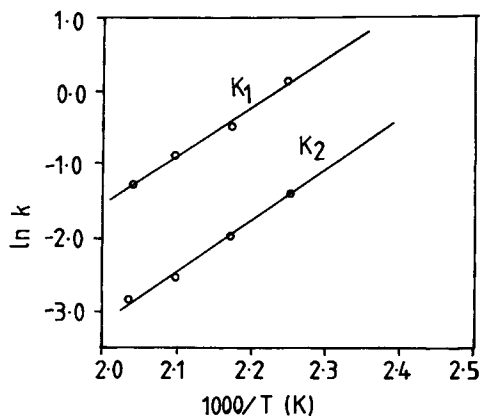


Fig. 6. Temperature dependence of rate constants.

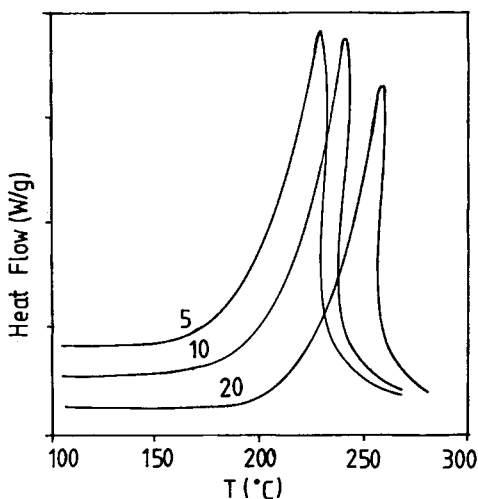


Fig. 7. DSC scans at different heating rates (5, 10, and 20°C/min) for 80 : 20 TGDDM-TGPAP with 30% DDS.

The values obtained from the above equations are comparable and are presented in Table III.

CONCLUSIONS

Cure kinetics of two resin formulations consisting of trifunctional and di-functional diluent in a tetrafunctional matrix resin were investigated by differential scanning calorimetry. Isothermal experiments carried out on the resin

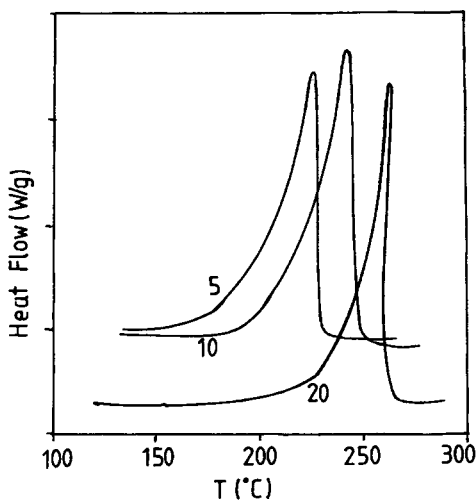


Fig. 8. DSC scans at different heating rates (5, 10, and 20°C/min) for 80 : 20 TGDDM-DGA with 30% DDS.

TABLE III
Kinetic Parameters Obtained from Eqs. (5) and (6)

System	Proportion (w/w)	E_a , energy of activation (kJ mol ⁻¹)		ln A, frequency factor (min ⁻¹)	
		(5)	(6)	(5)	(6)
TGDDM	—	83.07	82.2	18.48	18.283
TGDDM-TGPAP	80 : 20	92.53	92.38	20.7	20.62
TGDDM-DGA	80 : 20	78.7	77.75	17.586	17.249

formulations have strengthened the autocatalytic behavior of the curing reaction. The data from DSC scans may be described as a good approximation for a simple n th-order reaction.

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