

INVESTIGATION OF KINETICS OF CURING OF TRIGLYCIDYL-*p*-AMINOPHENOL WITH AROMATIC DIAMINES BY DIFFERENTIAL SCANNING CALORIMETRY

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The kinetics of curing of triglycidyl-*p*-aminophenol with four different diamines in stoichiometric amounts were investigated by means of differential scanning calorimetry. The results indicated that the curing reaction follows first-order Arrhenius kinetics with an activation energy in the range 40–70 kJ·mol⁻¹. The effect of the structure of the curing agent on the curing characteristics is discussed on the basis of the curing characteristics and the kinetic parameters. An epoxy fortifier was observed to lower the curing temperature of an epoxy-amine system when incorporated prior to curing.

The reactivity and the exothermic nature of thermosetting materials calls for the basic study of their curing reactions. The curing characteristics include the degree of curing, the temperature, the duration of curing and the variability of the heat of reaction. Differential scanning calorimetry (DSC) permits a relatively quick and precise determination not only of the temperature range, but also of the heat of reaction of a given exothermic transition [1]. This technique has been applied for evaluation of the curing characteristics for different types of thermosetting materials, such as phenolics [2], unsaturated polyesters [3] and epoxy resins [4–7].

The kinetics of the curing reactions of epoxy resins with diamines has been analysed by several researchers [5, 7]. The literature reveals several applications of epoxies cured with amines, but detailed information is not available regarding the curing kinetics of triglycidyl-*p*-aminophenol (TGAP), which is being used increasingly in adhesives and composites for high-temperature applications and also in aircraft compositions [8], as the trifunctionality of the resin results in a three-dimensionally tightly crosslinked structure with improved thermal stability relative to other types of epoxy resins.

The present investigation reports on the curing kinetics of TGAP, with different diamines in stoichiometric amounts as curing agents, with respect to how the

chemical structure of the reactants determines the properties of the cured materials and affects the curing characteristics. The overall kinetic parameters of the curing reactions were estimated by using the relations reported to be applicable for dynamic DSC scans. On the basis of the evaluated data, the effects of an epoxy fortifier which is known to lower the cure temperature [5] and improve the strength of the cured composition [9] were investigated.

Experimental

The epoxy resin system used for the study was a stoichiometric mixture of triglycidyl-p-aminophenol (TGAP) with m-phenylenediamine (MPD), 4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenyl ether (DDE) and 4,4'-diaminodiphenyl sulfone (DDS). TGAP was prepared via the method reported in the literature [10]. The brown resin had an epoxy equivalent weight of 103.9, as estimated by hydrochlorination [11]. The number average molecular weight determined by vapour pressure osmometry was about 300. Infrared analysis on a Perkin-Elmer-983 spectrophotometer showed typical epoxy absorptions at 910 cm^{-1} and 860 cm^{-1} .

The epoxy fortifier PGEHA [9], the condensation product of phenyl glycidyl ether (PGE) and 4-hydroxyacetanilide (HA), was prepared and characterized as described previously [5].

All the diamines were used after recrystallization from the appropriate solvents.

Differential scanning calorimetry

A DuPont-900 differential scanning calorimeter was used for the dynamic scans, at three different heating rates, 5, 10 and 20 deg/min^{-1} . Prior to scanning, the DSC cell was calibrated with samples with known heats of fusion and melting points. The samples for DSC scans ($\sim 5\text{ g}$) were prepared just before the start of the experiment, by mixing the stoichiometric amounts of resin and a curing agent and in some selected experiments 20 PHR epoxy fortifier. About 10 mg of the sample was taken in an aluminium pan, placed in the DSC cell and the scan was run with an empty pan as reference for each scan.

Analysis of the DSC scan

Scans using a resin-curing agent composition with or without fortifier showed a broad exotherm in the temperature range $60\text{--}235^\circ$, but no exotherms were detected in the DSC scans of a resin alone or in the scans of cured resins, indicating that the exotherms are due to the exothermic curing reactions. The exotherms obtained were analysed to obtain two basic parameters, the peak height dH/dt and the area a

under the exotherm, and some characteristic temperatures such as the temperature of initiation of curing (T_i), the peak maximum temperature (T_p) and the temperature of the completion of curing (T_f). The parameters dH/dt and a , determined at a series of temperatures, together with the peak temperatures at different heating rates, were used to evaluate the kinetic constants. The kinetic constants were calculated by assuming that the peak maximum represents a point of constant conversion for each heating rate and that the curing reaction obeys Arrhenius-type kinetics.

A simple yet accurate relationship (Eq. 1) between the activation energy E , the heating rate φ and the peak exotherm temperature T_p , based on the work of Ozawa [12], was used to calculate E :

$$E = \frac{RA \log \varphi}{0.4567 \Delta(1/T_p)} \quad (1)$$

A similar type of relation (Eq. 2), the well-known Kissinger relation [13], was used to estimate the activation energy:

$$\frac{d[\ln(\varphi/T_p^2)]}{d(1/T_p)} = -\frac{E}{R} \quad (2)$$

where φ is the heating rate, T_p is the temperature maximum (K), R is the gas constant and E is the activation energy.

One more relation [14] involving the term $(dH/dt)_{\max}$, useful for deriving the ratio of the activation energy to the order of reaction, was employed to evaluate E/n (Eq. 3):

$$E/n = \frac{RT^2}{(H_T - H) \cdot \varphi} X \left(\frac{dH}{dt} \right) \left(\frac{dH}{dt} \right)_{\max} \quad (3)$$

The Freeman–Carroll (FC) relation [15] permits the determination of the activation energy and the reaction order simultaneously from a single dynamic DSC scan. The form of the FC relation used in the present analysis was

$$\frac{\Delta \ln(dH/dt)}{\Delta \ln H_r} = \frac{(E/R)\Delta(1/T)}{\Delta \ln H_r} + n \quad (4)$$

In Eqs 3 and 4, E is the Arrhenius activation energy, n is the order of the reaction, R is the gas constant, T is temperature (K), dH/dt is the rate of heat generation, $H_r = H - H_T$, where H is the total heat of reaction and H_T is the heat of reaction at a particular temperature, and φ is the heating rate.

Results and discussion

Some selected DSC curves at three different heating rates for the TGAP-DDM system are reproduced in Fig. 1. For each of the systems studied, the exothermic transition was observed in some specific temperature range, depending upon the curing agent used. Table 1 lists some of the temperature data, viz. the temperatures at which the curing reaction started, peaked and completed, along with the total exothermic heat of curing ΔH for all the DSC scans. It is evident from the data in Table 1 that the peak temperature shifts to higher temperature with increasing scan rate. The values of ΔH as estimated from the area under the exotherm are also found to vary to a slight extent with the scan rate. Such variations in the peak temperature and in ΔH with the scan rate were also observed by Fava [4].

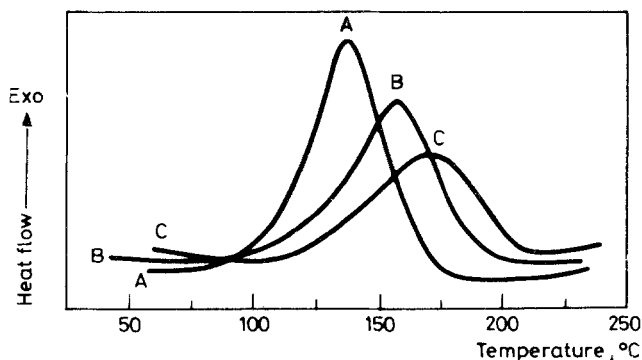


Fig. 1 DSC traces for TGAP-DDM system at three scan rates. A: 5 deg min⁻¹, B: 10 deg min⁻¹, C: 20 deg min⁻¹

A comparison of the curing behaviours of different epoxy systems at a particular DSC scan rate reveals that the values of T_i , T_p and T_f depend upon the curing agent. The values are the lowest for MPD and the highest for DDS. This indicates that the rate of curing for TGAP-MPD is the highest among the systems used. The trend revealed for the ease of curing for the varying epoxy systems is as follows:

TGAP-MPD > TGAP-DDM > TGAP-DDE > TGAP-DDS

An identical trend of the reactivity of the diamines can be observed from Fig. 2, in which the fractional conversion (∞) is plotted as a function of temperature for some selected DSC scans taken at a heating rate of 10 deg/min⁻¹. A more reactive system shifts the curve towards a lower temperature than that of a less reactive system.

The ease of curing depends upon the reactivity of the amines, which in turn depends upon the nucleophilicity of the amino group. In p-substituted amines, delocalization of the lone pair of electrons on the nitrogen is possible, while no such

Table 1 Curing characteristics of epoxy-amine systems at different scan rates

System	ϕ , deg min ⁻¹	T_i , °C	T_p , °C	T_f , °C	Curing range, °C	$\Delta H \pm 15$, J g ⁻¹
TGAP-MPD	5	70	110	160	90	465.6
	10	80	130	175	95	447.1
	20	98	149	197	99	422.6
TGAP-DDM	5	85	138	168	83	443.2
	10	95	156	190	95	428.5
	20	102	168	205	103	399.2
TGAP-DDM-PGEHA	5	78	123	162	84	363.7
	10	82	140	180	98	351.3
	20	97	162	199	102	320.2
TGAP-DDE	5	100	149	180	80	382.7
	10	112	169	205	93	335.2
	20	128	184	235	107	318.6
TGAP-DDS	5	110	186	235	125	325.8
	10	115	201	245	130	302.3
	20	130	220	268	138	285.9

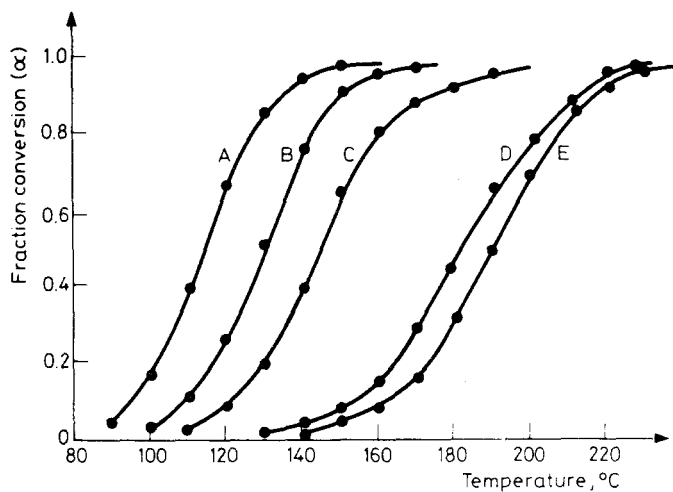


Fig. 2 Plot of fraction of conversion as a function of temperature for the scans at 10 deg min⁻¹
 A: TGAP-MPD, B: TGAP-DDM-PGEHA, C: TGAP-DDM, D: TGAP-DDE,
 E: TGAP-DDS

delocalization of electrons is possible in MPD. As a consequence, MPD is the most reactive diamine. The —O— and —CH₂-linked diamines are more reactive than the —SO₂-linked diamine. A similar reactivity trend has been observed by Dine Hart and Wright [16]. DDS has the lowest reactivity in the series, because of the electron-withdrawing sulfonyl group.

Incorporation of the fortifier in the epoxy system TGAP-DDM lowers the curing temperatures T_i , T_p and T_f , and also the curing time. The effect of lowering the curing temperatures and speeding up the curing is attributed to the catalysing effect of the hydroxyl group present in the fortifier [5]. Similar behaviour was observed by Schechter et al. [17] in the reaction of epoxide and amine with some hydrogen donors in the system.

The effects of the fortifier and the diamine structure on the epoxy-amine curing are also evident from the values of the kinetic parameters.

In order to evaluate the kinetic parameters associated with the curing reaction, the DSC data were treated in terms of four different relations, two based on the scans at different heating rates (Eqs (1) and (2)) and two based on the single dynamic DSC scans. Analyses of the data using Eqs (1) and (2) are illustrated in Figs 3 and 4, respectively. During the analysis using Eqs (1) and (2), the reaction order n was assumed to be one. The energy of activation for various systems determined from regression plots using Eqs (1) and (2) are listed in Table 2.

Data analysis using the maximum points of the DSC curves obtained at various scan rates was employed to evaluate the ratio of the activation energy to the order of reaction using Eq. (3). The results obtained are listed in Table 3.

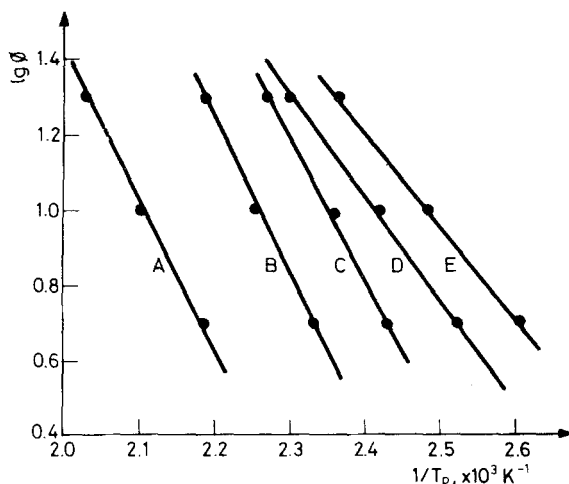


Fig. 3 Data analysis using Ozawa's relation for epoxy systems. A: TGAP-DDS, B: TGAP-DDE, C: TGAP-DDM, D: TGAP-DDM-PGEHA, E: TGAP-MPD

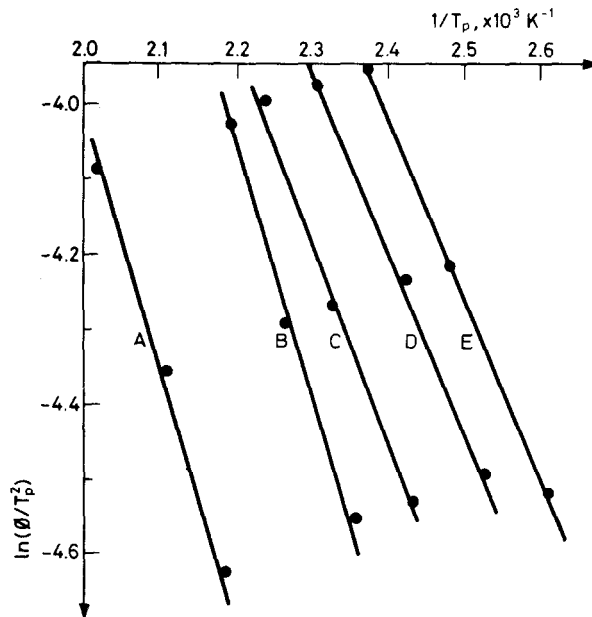


Fig. 4 Data analysis using Kissinger's relation for various epoxy systems: A: TGAP-DDS, B: TGAP-DDE, C: TGAP-DDM, D: TGAP-DDM-PGEHA, E: TGAP-MPD

Table 2 Data for activation energy derived using Eqs (1) and (2)

System	$E \pm 2 \text{ kJ mole}^{-1}$	
	Using Eq. (1)	Using Eq. (2)
TGAP-MPD	44.2	41.0
TGAP-DDM	57.4	56.2
TGAP-DDM-PGEHA	49.8	45.2
TGAP-DDE	62.4	61.9
TGAP-DDS	69.8	67.9

The values of the energy of activation and the order of the reaction using Eq. (4) were derived simultaneously using regression analysis. Selected plots from analysis with the FC relation (Eq. (4)) for selected epoxy systems are shown in Fig. 5. The values of E and n are listed in Table 4, along with the range of fraction reacted (∞) over which the data were linear, and also the regression coefficient (r). The values of E are comparable with those obtained by using Eqs (1) and (2). The values of the order of reaction of around 1 with the FC method and by substituting the values of E from Table 4 in E/n (Table 3) derived with Eq. (3) agree well with the assumption made earlier for the data analysis using Eqs (1) and (2). Further, the linearity of the

Table 3 Kinetic data evaluated using Eq. (3)

System	ϕ , deg min ⁻¹	T_{\max} , °C	α^b at T_{\max}	E/n kJ mole ⁻¹	n^a
TGAP-MPD	5	110	0.49	41.0	0.96
	10	130	0.51	42.0	1.02
	20	149	0.50	43.1	1.06
TGAP-DDM	5	138	0.52	56.7	0.99
	10	156	0.51	55.3	1.02
	20	168	0.48	54.1	0.95
TGAP-DDM-PGEHA	5	123	0.48	47.3	0.98
	10	140	0.50	46.5	0.97
	20	162	0.49	49.2	1.06
TGAP-DDE	5	149	0.52	61.8	0.99
	10	169	0.51	64.1	1.05
	20	184	0.49	62.5	1.01
TGAP-DDS	5	186	0.50	75.4	1.09
	10	201	0.47	69.2	0.99
	20	220	0.47	73.6	1.07

^a Calculated using E/n (column 5) and E (Table 4).

^b α = fraction reacted.

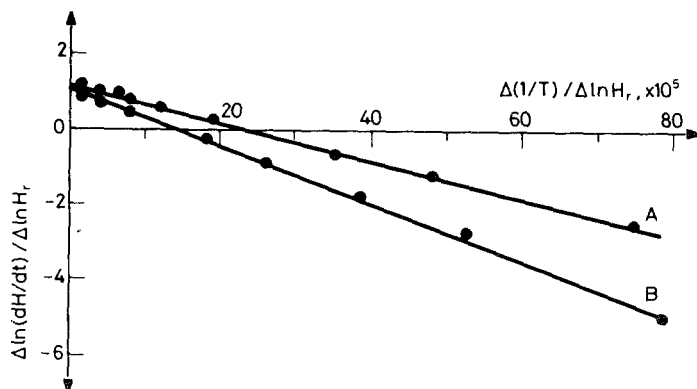


Fig. 5 Freeman-Carroll plots for the scans of selected epoxy systems at 10 deg min⁻¹. A: TGAP-MPD, B: TGAP-DDE

data, as evident from Fig. 2 and the values of the correlation coefficient (~ 0.99), confirms that the curing reaction is a first-order reaction.

The activation energy values for the four epoxy systems differ significantly, indicating the difference in relative reactivities, as also evident from the

Table 4 Kinetic data obtained with FC method

System	φ deg min ⁻¹	$E \pm 2$ kJ mole ⁻¹	n	α^a	r^b
TGAP-MPD	5	42.6	1.08	0.10-0.90	0.998
	10	41.2	1.20	0.12-0.90	0.989
	20	42.4	0.98	0.15-0.89	0.999
TGAP-DDM	5	56.9	1.05	0.12-0.90	0.979
	10	54.4	0.89	0.10-0.95	0.999
	20	56.7	1.10	0.10-0.86	0.995
TGAP-DDM-PGEHA	5	48.2	1.18	0.10-0.82	0.995
	10	47.7	1.12	0.10-0.85	0.978
	20	46.5	1.20	0.15-0.89	0.982
TGAP-DDE	5	62.1	1.02	0.19-0.90	0.992
	10	61.2	0.95	0.08-0.92	1.000
	20	62.0	1.15	0.12-0.78	0.982
TGAP-DDS	5	68.9	1.09	0.15-0.95	0.991
	10	70.1	1.17	0.17-0.92	0.990
	20	69.0	1.12	0.09-0.89	0.987

^a α = fraction reacted.

^b r = regression coefficient.

characteristic temperatures. The energy of activation is lower for a system involving a more reactive diamine than for that of a less reactive diamine.

The kinetics of the epoxy-amine reaction may be rather complex, as both hydrogen atoms of the amino group may take part more or less randomly in the addition reaction with epoxide. However, the rates for the two reactions may be close but not identical, and it can safely be stated that the reactions of primary and secondary hydrogens with epoxide occur simultaneously [1], as revealed by the single DSC peak (Fig. 1). In the present case, the data are consistent with a single activation energy for a particular epoxy-amine system. The kinetic parameters reveal that the reaction obeys first-order Arrhenius kinetics, with an activation energy in the range 40-70 kJ/mole; this is in good agreement with the reported values for the epoxy-amine systems [5-7].

Thus, if the true mechanism of the reaction is so complex that it cannot be described analytically, the process may be characterized in terms of the effective kinetic parameters (E and n), which may be successfully used to obtain useful information on the temperature intervals, the rate and the characteristics of the given reaction. From a practical point of view, a knowledge of qualitative characteristics that allow study and prediction of the curing behaviour under given conditions is of significant importance.

Conclusion

The curing of triglycidyl-p-aminophenol (TGAP) with aromatic diamines obeys first-order kinetics up to at least 80% completion. The scan rate in dynamic DSC mode does not greatly affect the overall kinetics of the uncatalysed curing of TGAP with diamines. Incorporation of the epoxy fortifier PGEHA prior to curing speeds up the curing and lowers the curing temperatures.

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Zusammenfassung — Mittels Differential-Scanning-Kalorimetrie wurde die Kinetik der Vernetzung von Triglycidyl-p-aminophenol mit stöchiometrischen Mengen vier verschiedener Amine untersucht. Laut den Ergebnissen verläuft die Vernetzungsreaktion mit einer Arrhenius-Kinetik erster Ordnung, wobei die Aktivierungsenergie im Bereich von 40–70 kJ/mol liegt. Auf Grundlage der Vernetzungscharakteristika und der kinetischen Parameter wird der Einfluss der Struktur des Vernetzungsreagenz auf die Vernetzungskennndaten beschrieben. Mit einem vor der Vernetzung eingebrachten Epoxyfortifiers konnte die Vernetzungstemperatur eines Epoxy-Amin-Systemes herabgesetzt werden.

Резюме — Методом ДСК исследована кинетика отверждения триглицидил-п-аминофенола с четырьмя различными диаминами, взятых в стехиометрических количествах. Результаты показали, что реакция отверждения подчиняется аррениусовской кинетике первого порядка с энергией активации в интервале 40–70 кдж·моль⁻¹. На основе кинетических параметров обсуждено влияние структуры вулканизирующего агента на характеристики реакции отверждения. Установлено, что эпоксиакрепитель, введенный раньше вулканизирующего агента, понижает температуру отверждения.