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KINETIC STUDY ON THE EFFECT OF ADDITION OF EPOXY DILUENTS AND/OR FORTIFIER ON THE CURING CHARACTERISTICS OF DGEBA BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract—The effects of the addition of diluents and/or fortifier (PGEHA), synthesized by condensing phenylglycidyl ether (PGE) and 4-hydroxy acetanilide (HA) using 0.1 wt % diethylamine hydrochloride as catalyst, on the epoxy resin have been investigated kinetically by differential scanning calorimetry. The rate of reaction was followed dynamically over the range 25–300°C. The activation energy for the various epoxy systems, as determined using four different computational methods, is in the range of 51–97 kJ mol^{-1} and the order of the reaction is ~2.0.

INTRODUCTION

Differential scanning calorimetry (DSC) is a valuable technique for investigating parameters of the curing reaction of thermosetting polymers [1]. Acitelli *et al.* [2] reported the kinetics of the system bisphenol-A diglycidyl ether and *m*-phenylene diamine as curing agent using DSC. It is also reported that the addition of epoxy fortifier to a conventional epoxy resin-curing agent formulation improves certain properties and lowers the cure temperatures [3, 4]. The effect of the diluent content on epoxy–anhydride systems has also been reviewed [4–7]. However no systematic efforts have been made to study the cure kinetics of such systems with fortifier.

In the present work, the DSC technique is applied to the cure kinetics of various epoxy resin systems using phthalic anhydride (PA) as the curing agent and diamino-diphenylmethane (DDM) as catalyst. The overall kinetic parameters of the curing reactions are estimated using four different relations [8–11] based on a single dynamic scan. The effects of addition of diluents such as epoxidized 2,2,6,6-tetramethylol cyclohexanol (ETMC), 1,4-butandiol diglycidyl ether (BDDE), epoxidized mowrah oil (EMO), epoxidized cashew-nut-shell liquid (ECNSL) and/or the fortifier (PGEHA) on the characteristic parameters are investigated.

EXPERIMENTAL

Materials

The resin diglycidylether of bisphenol-A (DGEBA) was prepared according to the published method [12].

Synthesis of fortifier

The reagents required for the preparation of fortifier; (i) phenylglycidyl ether (PGE) was prepared by the published method [13] and (ii) 4-hydroxy acetanilide (HA) was a pharmaceutical grade chemical which was recrystallized from distilled water. The epoxy fortifier (PGEHA) was prepared by condensing PGE and HA using 0.1 wt % diethylamine hydrochloride as catalyst and purified by recrystallization from acetone (m.p. 128°) [14].

Synthesis of diluents

2,2,6,6-Tetramethylol cyclohexanol (TMC) was prepared by hydroxymethylation with simultaneous Cannizzaro reaction proposed by Roach and Witcoff [15].

Mowrah oil (iodine value, 62.2) and CNSL (iodine value, 88.3) were epoxidized by the *in situ* technique [16] using 30% H_2O_2, acetic acid and conc. H_2SO_4 as catalysts. The epoxy equivalents (EE) and EMO and ECNSL were determined by the hydrochlorination method [17].

1,4-Butandiol diglycidyl ether (BDDE) was a laboratory grade (Aldrich Chemical Company, Inc.) chemical and 1,4-diamino-diphenyl methane used as catalyst was a laboratory grade reagent recrystallized from benzene (m.p. 92–93°). Reagent grade phthalic anhydride (PA) was purified before use, m.p. 130–131°C. Its purity by the esterification method, was 99.5%.

Measurements

The epoxy equivalents of DGEBA, PGEHA, ETMC, EMO and ECNSL were determined as 190.0, 0.0, 132.0, 500 and 465 $\text{g}\cdot\text{eq.}^{-1}$ respectively. The number-average molecular weights, by vapour pressure osmometry, are 380, 300, 444, 464 and 424 for DGEBA, PGEHA, ETMC, EMO and ECNSL respectively.

DATA ANALYSIS AND RESULTS

Scanning experiments

A Du Pont-900 differential scanning calorimeter was used for a dynamic scan at a heating rate of $10°\text{C min}^{-1}$. The DSC cell was calibrated with samples of known heat of fusion according to the instrumental manual. The samples of the resin systems (~2 g) for DSC scan were prepared by thorough mixing of the required components just before the starting of the scan in small capsules. About 2–5 mg of the sample was taken in the DSC cell and cured in the DSC using an empty cell as a reference.

The exothermic peak obtained in the scan was analyzed to give heat flow as a function of temperature and time. The heat flow data, relative to the baseline, were processed further to obtain the fractional conversion and the rate of reaction. The base lines under the exotherm were drawn manually by

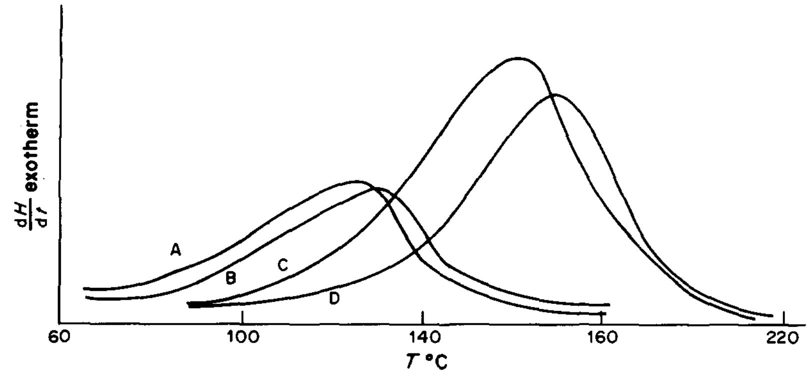

Fig. 1. DSC curves for (A) DGEBA, (B) DGEBA–PGEHA, (C) DGEBA–EMO and (D) DGEBA–EMO–PGEHA using PA as curing agent and 1% DDM as catalyst.

joining the regions before the start and after completion of the exothermic transition. The overall rate constant, k, was estimated using the Barrett relation, Eqn 1, at different temperatures assuming that the rate constant k has Arrhenius-type temperature dependence; activation energy E_a and the frequency factor $\ln A$ were computed [8].

The Barrett relation can be described as

$$k = \frac{\mathrm{d}\alpha/\mathrm{d}t}{A-a} = \frac{\mathrm{d}H/\mathrm{d}t}{A-a} \tag{1}$$

where α is the fractional conversion, and A and a are total area and area at a particular temperature t respectively.

In order to estimate both E and n, three different relations viz. Freeman–Carrol relation Eqn 2 [9], Ellerstein relation Eqn 3 [10] and Kay–Westwood relation Eqn 4 [11] were used. Using relations (2), (3) and (4) and drawing appropriate regression plots, both E and n were evaluated:

$$\frac{\ln(\mathrm{d}H/\mathrm{d}t)}{\ln(A\text{–}a)} = n - \frac{(\mathrm{E/R})\Delta(1/T)}{\Delta\ln(A\text{–}a)} \tag{2}$$

$$T^2(\mathrm{s/h}) = (\mathrm{E/R}) - nT^2(\mathrm{h/r}) \tag{3}$$

$$\frac{\left(1-\dfrac{H}{H_T}\right)\dfrac{\mathrm{d}}{\mathrm{d}t}\left(\dfrac{\mathrm{d}H}{\mathrm{d}t}\right)}{\beta\left(\dfrac{\mathrm{d}H}{\mathrm{d}t}\right)^2} = \mathrm{E/R}\,\frac{\left(1-\dfrac{H}{H_T}\right)}{\dfrac{\mathrm{d}H}{\mathrm{d}t}\cdot T^2} - \frac{n}{H_T\cdot\beta} \tag{4}$$

In all four relations, the various terms have the usual significance reported in the literature [7–10].

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 25–300°C. From the characteristic DSC scan, 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 the various epoxy resin systems are presented in Table 1. The area under the curve and the heat flow, $\mathrm{d}H/\mathrm{d}t$ measured from the height of the curve at different temperature intervals were obtained and the data were fitted to four different relations. In using these analyses, it was assumed that the reactions can be described as a simple nth order, Arrhenius type temperature dependent as the reactions appeared to follow the simple Arrhenius kinetics up to at least 75% of completion. This has been revealed from very good linear plots of $\ln k$ vs $1/T$, shown in Fig. 2.

The values of activation energy E and the frequency factor $\ln A$ obtained from the regression plots (Fig. 2) of the data fitted to Eqn 1 are listed in Table 2, along with the least square regression coefficients. The data were also fitted to Eqn (2)–(4) to evaluate E and n simultaneously. The values estimated by regression analysis for E and n are listed in Table 3. The selected plots drawn using these relations are shown in Figs 3–5.

The data listed in Table 1 show characteristics of the curing of systems with different diluents. The reactivities of the diluents with curing agent depend upon the location of the epoxy group in the molecule. Diluents containing glycidyl ether groups are quite

Table 1. Curing characteristics of epoxy-PA (1:1) system with 1% DDM

Epoxy system	Proportion (% w/w)	T_i (°C)	T_p (°C)	T_f (°C)	Cure range (°C)	Cure time (min)
DGEBA	—	76	130	160	84	9.45
DGEBA–PGEHA	(80:20)	75	127	158	81	8.59
DGEBA–ETMC	(80:20)	218	253	294	76	11.34
DGEBA–BDDE	(80:20)	83	156	214	131	9.52
DGEBA–EMO	(80:20)	97	168	217	120	11.32
DGEBA–ECNSL	(80:20)	124	176	288	164	10.58
DGEBA–ETMC–PGEHA	(80:20)-20	215	250	288	73	10.26
DGEBA–BDDE–PGEHA	(80:20)-20	80	155	210	130	8.47
DGEBA–EMO–PGEHA	(80:20)-20	95	165	214	119	9.38
DGEBA–ECNSL–PGEHA	(80:20)-20	120	170	281	161	8.33

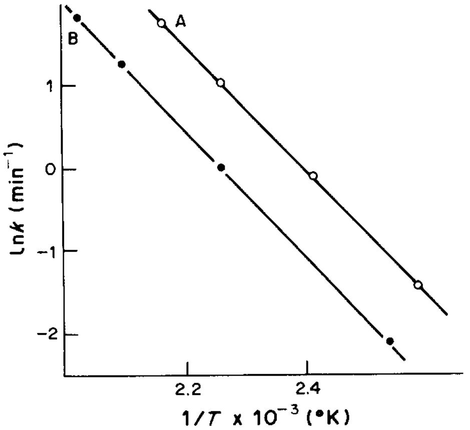

Fig. 2. Plot of ln$k$ vs $1/T$ for system (A) DGEBA–EMO and (B) DGEBA–EMO–PGEHA.

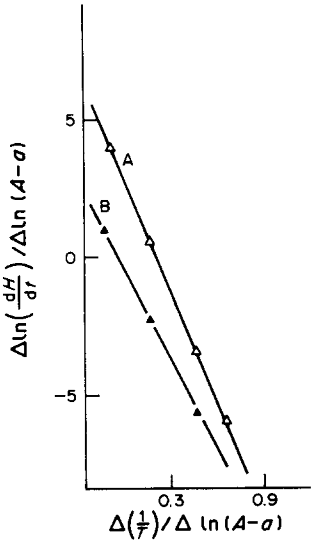

Fig. 3. Freeman–Carrol plot for (A) DGEBA–EMO and (B) DGEBA–EMO–PGEHA.

reactive with amines, whereas diluents containing internal epoxides or ring-situated epoxides are more reactive towards anhydrides and acids. It was observed that the gel time of the systems increased due to the effect of diluents, but the peak exotherm temperatures and the extent of reaction of the curing system decreased [16].

Considering these facts, diluents EMO and ECNSL have been used as they provide viscosity reduction as well as modification in the properties of cured systems. They are also considered as diluents which can be employed to modify the heat deflection temperature, chemical resistancy and to some extent, to change physical properties. ETMC increases the functionality which results in the extended pot life of the system with increased activation energy and the curing temperature, which may be due to the steric hindrance.

The addition of the fortifier PGEHA to the resin–diluent system lowers the curing temperature at the start and at the completion (Fig. 1). The cure time decreases up to ~2 min on using the fortifier. The effect of fortifier to lower the cure temperature and to speed up the curing is expected as the hydroxyl group present in the fortifier may be responsible for catalyzing the reaction. Shachter *et al.* [18] have observed similar behaviour in the reaction of epoxide and amine using some hydrogen donors in the system.

Table 2. Data evaluated using Barrett relation [1]

System	Proportion (% w/w)	E ± 2, Energy of activation (kJ mol⁻¹)	ln*A* ± 1 Frequency factor (min⁻¹)	Regression coefficient
DGEBA	—	53.2	15.5	0.997
DGEBA-PGEHA	(80:20)	51.3	14.8	0.995
DGEBA-ETMC	(80:20)	94.6	27.4	0.979
DGEBA-BDDE	(80:20)	52.8	15.2	0.981
DGEBA-EMO	(80:20)	84.2	24.3	0.993
DGEBA-ECNSL	(80:20)	93.6	34.2	0.986
DGEBA-ETMC-PGEHA	(80:20)-20	88.6	29.2	0.992
DGEBA-BDDE-PGEHA	(80:20)-20	50.7	14.5	0.983
DGEBA-EMO-PGEHA	(80:20)-20	82.6	24.3	0.975
DGEBA-ECNSL-PGEHA	(80:20)-20	77.9	22.1	0.953

Table 3. Kinetic parameters obtained using relations (2)–(4)

System	Proportion (% w/w)	E ± 2 Energy of activation (kJ mol⁻¹) (2)	(3)	(4)	*n* Order of reaction (2)	(3)	(4)
DGEBA	—	54.1	54.4	53.9	1.95	1.90	1.94
DGEBA-PGEHA	(80:20)	52.2	52.7	51.6	1.98	1.91	1.98
DGEBA-ETMC	(80:20)	96.8	96.9	95.5	1.90	1.93	1.91
DGEBA-BDDE	(80:20)	53.4	53.9	52.7	1.97	1.92	1.94
DGEBA-EMO	(80:20)	86.7	87.1	85.5	1.93	1.92	1.99
DGEBA-ECNSL	(80:20)	94.2	94.9	93.9	1.97	1.96	1.93
DGEBA-ETMC-PGEHA	(80:20)-20	75.6	75.1	74.8	1.90	1.93	1.99
DGEBA-BDDE-PGEHA	(80:20)-20	52.4	52.9	51.8	1.96	1.99	1.98
DGEBA-EMO-PGEHA	(80:20)-20	83.9	84.1	82.9	1.91	1.99	1.97
DGEBA-ECNSL-PGEHA	(80:20)-20	78.9	79.2	77.81	1.94	1.98	1.96

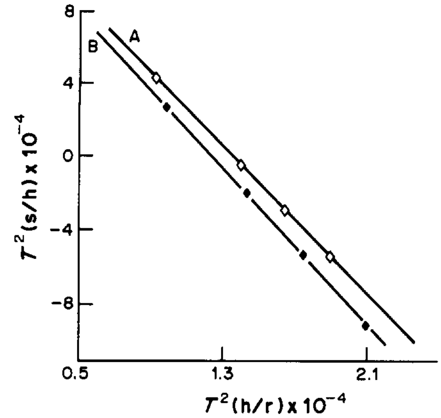

Fig. 4. Ellerstein plot for (A) DGEBA–EMO and (B) DGEBA–EMO–PGEHA.

The effect of the higher functionality and the addition of fortifier to the epoxy–anhydride system is also evident from the values of the kinetic parameters (Tables 2 and 3). The energy of activation and the frequency factor decrease on using the fortifier.

The trend in the characteristic parameters may be regarded as very good guides for the use of diluents and fortifier in the epoxy systems to improve the properties.

In the present case, the data are treated assuming a simple *n*th order Arrhenius-type kinetics. The kinetic parameters obtained also support the assumption giving the activation energy in the range 51–97 kJ mol^{-1} in good agreement with the reported values for various epoxy–anhydride systems [19].

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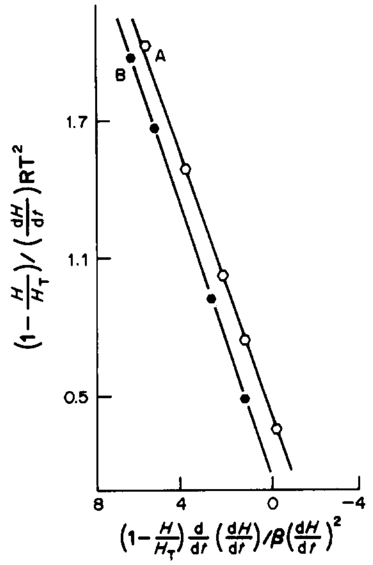

Fig. 5. Kay–Westwood plot for (A) DGEBA–EMO and (B) DGEBA–EMO–PGEHA.

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