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EFFECTS OF REACTIVE DILUENT DIEPOXIDIZED CARDANOL AND EPOXY FORTIFIER ON CURING KINETICS OF EPOXY RESIN

M. B. Patel, R. G. Patel and *V. S. Patel*

DEPARTMENT OF CHEMISTRY, SARDAR PATEL UNIVERSITY,
VALLABH VIDYANAGAR, 388120, INDIA

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Different formulations, composed of the diglycidyl ether of bisphenol-A, diepoxidized cardanol as reactive diluent, an anhydride as curing agent, and a tertiary amine as curing catalyst, with/without the use of an epoxy fortifier, were analysed. The effect of the fortifier on the diluent was also observed. The overall kinetics of curing was observed to follow a simple Arrhenius-type temperaturedependence, with an activation energy in the range 54–120 kJ/mol, with first-order kinetics up to 85% conversion. An increase in activation energy was observed with an increase of diluent content. The curing reaction was found to follow a three-step mechanism, involving a nucleophilic bimolecular displacement reaction, for which an explanation was offered. Incorporation of the fortifier lowers the curing temperature, but does not alter the final degree of reaction.

The mechanical and electrical properties of cured epoxy resins are strongly dependent upon the degree of curing. The curing reaction is a highly exothermic process, and control of heat generation during curing is often a key point for optimization of the properties. Calorimetric techniques have become one of the most effective methods of obtaining complete quantitative information on the curing process of thermosets [1, 2]. An important reason is that DSC may be used to determine the rate of polymerization directly, continuously and even in a gel or solid state.

The curing kinetics of liquid DGEBA with different anhydrides as curing agent with/without accelerator has been studied extensively by several workers [3, 4]. To achieve modifications, attempts have been made to cure liquid DGEBA together with reactive diluents such as epoxidized Mowrah oil, epoxidized safflower oil, epoxidized CNSL, etc. [5–7]. All the above reactive diluents are prepared by carrying out epoxidation at the olefinic double bonds in their structures.

In the present investigation we used diepoxidized cardanol; this has two epoxide groups, one of which is of glycidyl type, introduced by reaction of a hydroxy group

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present in cardanol with epichlorohydrin, while the other is produced by epoxidation at the olefinic double bond using preformed peroxyacid. The primary objective of this work was to investigate the curing behaviour of the liquid diglycidyl ether of bisphenol-A (DGEBA), with diepoxidized cardanol (DEC) as reactive diluent, with different anhydrides as curing agent, and with triethylamine as curing catalyst, by applying the DSC technique [8]. The effects of fortifiers on the curing characteristics of the epoxy resin-diluent system and on those of the reactive diluent alone have been also investigated.

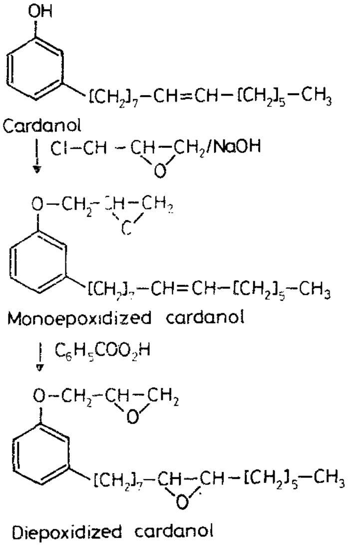
Experimental

Materials

A general purpose DGEBA-type commercial epoxy resin was prepared [9] and used in this investigation without further purification; it had an epoxy equivalent weight (EEW) of 190 g eq.$^{-1}$ [10].

Cardanol, the basic raw material required for epoxidation, was obtained by vacuum distillation (246–247°/2 mm) of technical grade Cashew Nut Shell Liquid (CNSL).

The diepoxidized cardanol (DEC), a reactive diluent with an EEW of 284.3 g eq.$^{-1}$, was prepared following the reported method [11].



The epoxy fortifiers VCDHA and VCDAA, the condensation products of one mole of vinylcyclohexane dioxide (VCD) with 2 moles of 4-hydroxyacetanilide (HA) or 2 moles of acetoacetanilide (AA), respectively, and also PGEHA and PGEAA, the condensation products of one mole of phenyl glycidyl ether (PGE) with one mole of HA or one mole of AA, respectively, were prepared by heating the starting materials at 160° for 2 h with 0.1% (w/w) diethylamine hydrochloride as catalyst [12].

The curing agents phthalic anhydride (PA), nadic methyl anhydride (NMA) and dodecyl succinic anhydride (DSA), and the curing catalyst triethylamine (TEA), were laboratory reagents and were used without further purification.

Methods

The calorimetric measurements were carried out with a DuPont 900 thermal analyzer at a single heating rate of 10 deg $\min^{-1}$ in the temperature range 30–230°. The system was calibrated with a sample of known heat of fusion, to make the data as accurate as possible. For each experiment, approximately 5 g of reaction mixture was prepared previously by mixing DGEBA and an anhydride in the stoichiometric amount with/without the use of DEC (in stoichiometric amount) as well as fortifier (20 phr) using 1% w/w TEA.

The required amount of the sample (~5–8 mg) was weighed in an open aluminium pan, which was sealed just before each scan, an empty pan being taken as the reference. The weight of the pan with sample was measured before and after the scan to make sure that there was no weight loss during the DSC measurements. The baseline in the DSC scan was taken as the slanted line joining the curve extremities.

The heat released during curing in the DSC, measured as functions of time and temperature, was assumed to be directly proportional to the rate of reaction:

$$\alpha' = \mathrm{d}\alpha/\mathrm{d}t = (1/Q_{\mathrm{ult}})(\mathrm{d}\alpha/\mathrm{d}t)$$

The degree of reaction α was taken as the heat evolved at a certain time (Q_t) divided by the heat of reaction (Q_{ult}):

$$\alpha = \frac{Q_t}{Q_{\mathrm{ult}}}$$

Measurement of the heat of reaction in a sample whose temperature is scanned should give useful information on the reaction kinetics, if it is assumed that the heat of reaction is directly proportional to the degree of reaction.

Kinetic parameters, such as activation energy (E), order of reaction (n) and frequency factor ($\ln A$), were calculated by using two computational methods:

(i) Barrett relation [13]:

$$K=\frac{\mathrm{d}\alpha/\mathrm{d}t}{A-a}=\frac{\mathrm{d}H/\mathrm{d}t}{A-a}$$

where α is the degree of reaction, and A and a are the total area and the area at a particular temperature T, respectively.

When this relation is used, it is assumed that the reaction can be described by a simple n^{th} order Arrhenius-type temperature-dependence.

(ii) Freeman–Carroll relation [14]:

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

The terms involved in this have the usual significance as described in the literature.

Results and discussion

The present work deals with the study of DSC curing kinetics of various epoxy resin formulations to examine the effects of (1) diluent, (2) fortifier and (3) structure of anhydride.

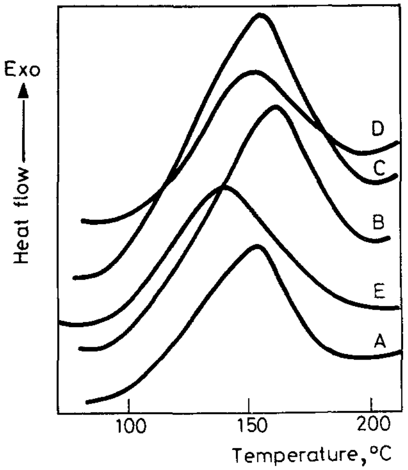


Fig. 1 Typical results of dynamic DSC scans for different epoxy resin formulations: [A] DGEBA, [B] DGEBA : DEC (70 : 30), [C] DGEBA-DEC-VCDHA, (70 : 30) : 20, [D] DEC, [E] DEC : VCDHA

Typical results of selected dynamic scans are shown in Fig. 1. Curing characteristics such as the temperatures of onset of curing (T_i), peak exotherm (T_p) and completion of curing (T_f), obtained from the exotherms in the DSC scans, are presented in Tables 1, 3 and 5.

With the Barrett relation, rate constant K was estimated at different temperatures, and kinetic parameters E and $\ln A$ were determined. For this, Arrhenius plots of $\ln K$ *vs.* $1/T$ (Fig. 2) were drawn, which were very good straight lines up to about 85% conversion. The data presented in Tables 2, 4 and 6, together with the regression coefficients (r), were obtained from regression plots.

Table 1 Curing characteristics of various epoxy systems with PA as catalyst and TEA as curing catalyst

Resin system	Proportions	Curing characteristics, °C		
		T_i	T_p	T_f
DGEBA	+	95	153	190
DGEBA–DEC	90:10	95	155	190
DGEBA–DEC–VCDHA*	(90:10):20	90	145	195
DGEBA–DEC	80:20	98	158	205
DGEBA–DEC–VCDHA*	(80:20):20	85	140	185
DGEBA–DEC	70:30	100	160	200
DGEBA–DEC–VCDHA*	(70:30):20	95	155	200

* VCDHA used as 20 phr.

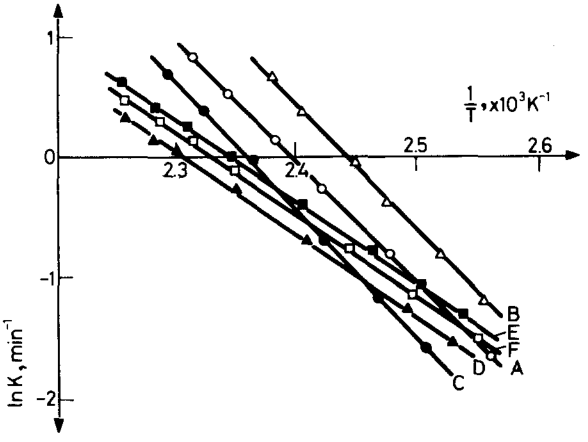


Fig. 2 Arrhenius plots of $\ln k$ *vs.* $1/T$ for different DGEBA : DEC molar ratios and DEC-fortifier system DGEBA : DEC: [A] 90:10 (○), [B] 80:20 (△), [C] 70:30 (●), [D] 0:100 (▲), DEC-fortifier [E] VCDAA [■), [F] VCDHA [□)

Table 2 Kinetic parameters derived using relation (1)* and relation (2)** for different epoxy resin systems

Ratio (DGEBA : DEC) : VCDHA	Relation 1			Relation 2		
	$E \pm 2$ kJ/mol	$\ln A \pm 1$ min^{-1}	r	$E \pm 2$ kJ/mol	n	r
(100: 0):0	78.6	21.4	0.99	78.6	1.10	0.99
(90:10):0	81.8	22.3	0.99	82.8	0.92	0.99
(90:10):20	65.4	17.8	0.98	66.2	1.15	0.97
(80:20):0	84.4	23.0	0.99	85.5	0.96	0.98
(80:20):20	70.1	19.1	0.96	72.3	1.38	0.99
(70:30):0	87.9	29.2	0.98	89.4	1.08	0.97
(70:30):20	76.7	25.5	0.99	74.6	0.95	0.98

* Relation 1 – Barrett relation

** Relation 2 – Freeman–Carroll relation

Table 3 Curing characteristics of DGEBA–DEC (80:20)-anhydride composition with TEA as catalyst

Anhydride	Curing characteristics, °C		
	T_i	T_p	T_f
PA	95	158	205
PA–VCDHA*	85	140	185
DSA	100	165	205
DSA–VCDHA*	90	160	205
NMA	125	170	205
NMA–VCDHA*	110	165	200

* VCDHA used as 20 phr

Table 4 Kinetic parameters derived using relation (1)* and relation (2)** for DGEBA : DEC (80 : 20)-anhydride-TEA resin system with/without fortifier

Anhydride	Relation 1			Relation 2		
	$E \pm 2$ kJ/mol	$\ln A \pm 1$ min^{-1}	r	$E \pm 2$ kJ/mol	n	r
PA	84.4	23.0	0.98	85.5	0.96	0.98
PA–VCDHA***	70.1	19.1	0.99	92.3	1.38	0.99
DSA	111.4	30.6	0.98	115.2	1.25	0.94
DSA–VCDHA***	100.1	27.3	0.99	99.8	1.15	0.97
NMA	120.2	32.7	0.96	118.3	1.32	0.99
NMA–VCDHA***	106.0	29.0	0.99	110.7	1.17	0.99

*, ** as described in Table 2

*** VCDHA used as 20 phr

Table 5 Comparative data for diluent-fortifier* system with PA as curing agent and TEA as curing catalyst

Resin system	Curing characteristics, °C		
	T_i	T_p	T_f
DEC	105	150	200
DEC–VCDHA	95	145	205
DEC–VCDAA	95	145	195
DEC–PGEHA	100	147	205
DEC–PGEAA	95	147	205

* All fortifiers used as 20 phr

Table 6 Kinetic parameters derived using relation (1)* and relation (2)** for DEC–PA–TEA resin system with different fortifiers***

Resin system	Relation 1			Relation 2		
	$E \pm 2$ kJ/mol	$\ln A \pm 1$ min^{-1}	r	$E \pm 2$ kJ/mol	n	r
DEC	58.5	15.7	0.92	60.1	1.025	0.98
DEC : VCDHA	54.2	14.8	0.97	58.3	1.34	0.98
DEC : VCDAA	55.8	15.3	0.98	54.6	1.07	0.99
DEC : VCDHA	54.6	14.5	0.99	58.4	1.00	0.97
DEC : PGEAA	56.5	15.2	0.97	56.1	1.03	0.98

*, ** as described in Table 2
*** fortifiers used as 20 phr

The Freeman–Carroll relation was used to determine the kinetic parameters E and n. Tables 2, 4 and 6 show data derived from these. Selected plots are drawn in Fig. 3. The results obtained from the two relations are in good agreement with each other.

Effect of diluent

To observe the diluent effect, the diluent DEC was incorporated with DGEBA in three different ratios, viz. DGEBA : DEC = (i) 90 : 10, (ii) 80 : 20, and (iii) 70 : 30, the anhydride (PA) and amine (TEA) being kept fixed. The curing characteristics listed in Table 1 show that the temperature of onset of the curing exotherm (T_i) increases with increase of the diluent content. The activation energy obtained from the Arrhenius plots (Fig. 2) for these systems reveals the dependence of the curing rate on the amount of diluent (Table 2).

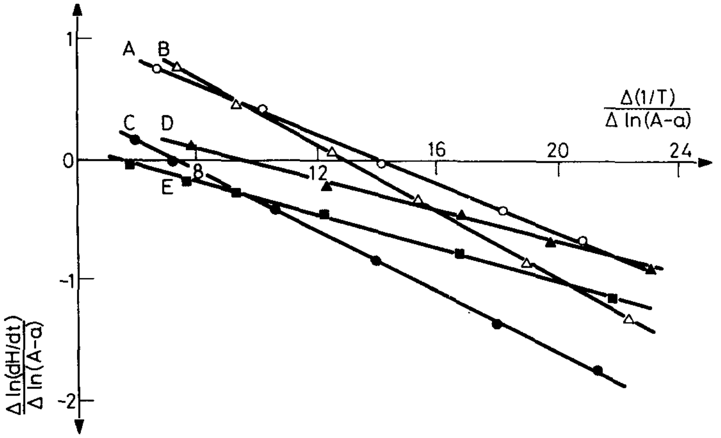


Fig. 3 Freeman–Carroll plots for different anhydride system and DEC-fortifier system: [A] PA (○), [B] DSA (△), [C] NMA (●), [D] DEC–PGEHA (▲), [E] DEC–PGEAA (■)

The present work shows that the incorporation of DEC is a decisive factor in the curing of the DEC-incorporated DGEBA resin system. The higher the amount of DEC, the lower the curing rate and the lower the finally attainable degree of reaction of the epoxide group. It is therefore quite conceivable that in the DEC : DGEBA resin system the reaction first occurs by the diluent DEC (Table 5) forming an intermediate product layer, which then diffuses out to contribute to the chain growth and cross-linking of the epoxy resin. It would then follow that the curing rate should be proportional to the amount of DEC.

Effect of fortifier

An epoxy fortifier is an additive which, when mixed with the resin-curing agent system prior to curing, results in an increase in the strength and modulus of the cured product.

In the present investigation, four different fortifiers (VCDHA, VCDAA, PGEHA and PGEAA) were used with the DEC-curing agent system, while VCDHA was used with the DGEBA : DEC (80 : 20) curing agent system, the curing catalyst being TEA in both systems. The curing characteristics of these systems are shown in Tables 1, 3 and 5.

In separate experiments, the curing of the five systems described in Table 5 was performed isothermally in a paraffin bath at 135°. The curing process was monitored by measuring the EEW of all the systems at a particular time, following the method described earlier. In the DEC–PA–TEA system, about 20% (considering EEW at the start to be 100%) of the epoxy groups were unreacted after

20 min at 135°. For the identical experiment containing 20 phr fortifiers, less than 8–12% of the epoxy groups were unreacted in the four different systems. To achieve a similar degree of curing, the DEC–PA–TEA system requires 35 min. Therefore, it can be said that fortifiers accelerate the curing process but do not alter the final degree of reaction. They also lower the starting curing temperature (T_i) (Table 5). When the fortifier (VCDHA) was mixed with the DGEBA : DEC resin system, a similar type of behaviour was observed (Tables 1 and 3). The tabulated kinetic parameters are in good agreement with the observed curing characteristics (Tables 2, 4 and 6). Patel et al. [15] suggested that the hydroxy group present in the fortifier structure might be the factor responsible for catalysis of the reaction.

In the DEC–PA-fortifier resin system, the fortifier VCDHA proved to be superior to the other fortifiers (Table 6). However, no difference was observed between the reactivities of VCDHA and VCDAA. This may indicate that the bifunctionality of both fortifiers played a major role in the reaction. The lower reactivities of PGEHA and PGEAA might be due to the monofunctional nature. However, the behaviour of epoxy fortifiers is more complex because of the thermosetting nature of the resin system, in which so many chemical and physical changes occur during the curing reaction. The kinetic parameters presented in Table 6 reveal the same trend.

Effects of structure of anhydride

The effect of the anhydride structure on the curing kinetics of the DGEBA : DEC (80 : 20) system were observed in the case of three anhydrides: PA, NMA and DSA. These were chosen because of their high commercial purity, their application, their structural complexity and their long alkyl chain length. The reactivities of the three anhydrides were compared via the characteristic temperatures (Table 3) and kinetic parameters (Table 4).

An acid anhydride with a lower T_i under a given set of curing conditions is more reactive towards the epoxy resin utilized. Of these three anhydrides, the maximum reactivity was displayed by PA and the minimum reactivity by NMA. The initial reaction rate in epoxy formulation is reported [16] to be proportional to the concentration of the catalyst. Subsequently, a nucleophilic biomolecular displacement reaction takes place with the acid anhydride. In this way, it can be considered that the higher reactivity of PA is due to the planarity in the structure, which facilitates the nucleophilic biomolecular displacement reaction. The long alkyl chain length in the DSA structure makes its acidity lower, which is confirmed by its higher activation energy. The activation energy of NMA is highest due to the steric hindrance generated by the bicyclic structure.

Conclusions

From the DSC data obtained in the curing of the DGEBA–DEC-acid anhydride-TEA resin system with/without fortifiers, it is observed that the incorporation of DEC with DGEBA epoxy resin lowers the reactivity of the overall resin system. Use of a fortifier enhances the curing process. The reactivities of the anhydrides towards curing depends upon their chemical structures.

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Zusammenfassung — Es wurden verschiedene Ausgangsgemische, bestehend aus dem Diglyzidyläther von Bisphenol A, diepoxydiertem Kardanol als reaktives Streckmittel, einem Anhydrid als Vernetzungsmittel und einem tertiären Amin als Vernetzungskatalysator mit bzw. ohne Anwendung eines Fortifyers untersucht. Der Einfluss des Fortifyers auf das Streckmittel wurde ebenfalls untersucht. Die Bruttokinetik der Vernetzung zeigt eine Temperaturabhängigkeit einfachen Arrhenius-Types mit einer Aktivierungsenergie im Bereich von 54–120 kJ/mol sowie einen Reaktionstyp erster Ordnung mit einer Konversionsrate von 85%. Ein steigender Streckmittelgehalt bewirkt ein Anwachsen der Aktivierungsenergie. Der Vernetzungsreaktion liegt ein Dreistufenmechanismus zu Grunde, der unter anderem auch eine nukleofile bimolekulare Substitutionsreaktion beinhaltet. Der Einsatz eines Fortifyers senkt zwar die Vernetzungstemperatur, verändert aber nicht die Endkonversionsrate.

Резюме — Исследованы различные композиции, состоящие из диглицидного эфира бисфенола-А, диэпоксидированного карданола, как разбавителя реакции, ангидрида, как вулканизирующего агента, и третичного амина, как катализатора реакции отверждения, с или без использования эпоксизакрепителя. Установлено влияние закрепителя на разбавитель.

Найдено, что общая кинетика реакции отверждения подчиняется простой температурной зависимости аррениусовского типа с энергией активации 54–120 кдж · моль$^{-1}$ и реакцией первого порядка с 85% превращением. Наблюдалось увеличение энергии активации с увеличением содержания разбавителя. Найдено, что реакция отверждения следует трехступенчатому механизму, включающему реакцию нуклеофильного бимолекулярного смерения, для которой и предложено объяснение. Введение закрепителя понижает температуру отверждения, но не затрагивает конечную степень реакции.