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CURING KINETICS OF EPOXY RESIN USING EPOXIDIZED CARDANOL AS DILUENT WITH/WITHOUT FORTIFIER

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ABSTRACT

The curing reactions of diglycidyl ether of bisphenol-A (DGEBA) with different anhydrides as curing agent and triethyl amine as curing catalyst have been studied using mono epoxidized cardanol (MEC) as reactive diluent in different molar ratios with/without the use of epoxy fortifier by differential scanning calorimetry. The overall kinetics of curing follows a simple Arrhenius type temperature dependence with an activation energy range 80–115 kJ mol^{-1}, and first-order kinetics, at least up to 85% conversion. Incorporation of diluent lowers the reactivity of the epoxy system; however addition of epoxy fortifier accelerates the cure process.

INTRODUCTION

Cardanol, the monophenolic component of technical Cashew Nut Shell Liquid (CNSL) because of its phenolic nature and the long alkyl chain with varying degrees of unsaturation, finds many applications in several fields such as coatings [1], adhesives [2], epoxy resins [3,4], laminating resins [5]. There are very few reports in the literature regarding the epoxidation of the phenolic hydroxyl of cardanol with epichlorohydrin [3,6,7]. The kinetics of curing of epoxy resins with anhydrides has been reviewed by several workers [8,9]. However epoxidized cardanol has been studied only for its curing with maleic anhydride and a maleic anhydride–pyromellitic dianhydride mixture [4]. No systematic efforts have been made to study the cure kinetics of diglycidyl ether of bisphenol-A (DGEBA) using mono epoxidized cardanol (MEC) as diluent with different anhydrides as curing agent and triethyl amine as curing catalyst. We studied the kinetics of the epoxy system using differential scanning calorimetry (DSC), which is an important method for thorough understanding of the nature of the curing process in thermosetting resin systems [10]. We also investigated the effect of epoxy fortifier on the curing characteristics.

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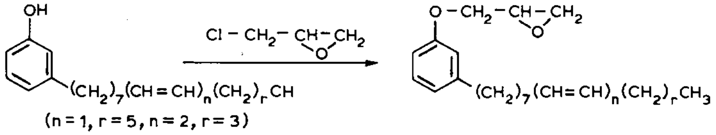
EXPERIMENTAL

Materials

The bisphenol-A type epoxy resin (DGEBA) with epoxy equivalent weight 190 $\mathrm{gm.eq.}^{-1}$ [13] was prepared using the method reported in the literature [11].

The mono epoxidized cardanol (MEC), an epoxy diluent with epoxy equivalent weight 546.3 $\mathrm{gm.eq.}^{-1}$ was prepared following the reported process [3]



The epoxy fortifier (VCDHA), the condensation product of vinyl cyclohexene dioxide (VCD) and 4-hydroxy acetoacetanalide (HA) was prepared using the reported method [12].

The curing agents phthalic anhydride (PA), nadic methyl anhydride (NMA), dodecyl succinic anhydride (DSA) and curing catalyst triethylamine (TEA) were laboratory reagents.

Method

A Du Pont 900 differential scanning calorimeter was used for a dynamic scan at a heating rate of 10 °C min^{-1}. The DSC cell was calibrated with a sample of known heat of fusion, according to the instrument manual. The samples of the resin system (~ 5 g) for the DSC scans were prepared by mixing the resin and the curing agent in the small capsules, using the stoichiometric amount with/without diluent as well as fortifier, using 1% w/w triethylamine as curing catalyst just before the start of the scan. For the experiments using phthalic anhydride as curing agent, the samples prepared were first heated to the melting point of phthalic anhydride and then cooled to room temperature to promote proper mixing of the anhydride. Then a catalytic amount of the amine was added. Samples of the resin system (about 5–8 mg) in open aluminium pans were cured in the DSC under dynamic conditions, using an empty pan as the reference material. The baseline in the DSC scan was drawn manually by joining the points of starting and completion of exothermic transitions in the DSC scan.

Data analysis

DSC gives a measure of the difference in the rates of heat absorption by a sample with respect to an inert reference as the temperature is raised at a constant rate. 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 extent of the reaction. However this assumption is not valid for the complex crosslinking reaction taking place.

Data analysis for the activation energy, reaction order and frequency factor were carried out using two computational methods. For these analyses, it is assumed that the reaction can be described by a simple n-th order, Arrhenius type temperature dependent. The value of the rate constant k at different temperatures was estimated using the Barrett relation (eqn. (1) below) [14], and the kinetic parameters activation energy E and frequency factor ln A were computed. 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, A and a are the total area and area at a particular temperature T, respectively.

In order to estimate E and n (order), the well-known Freeman-Carroll relation (eqn. (2) below) [15] was used. Using this relation and drawing appropriate regression plots, both E and n were evaluated

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

The terms involved in eqn. (2) have the usual meanings.

RESULTS AND DISCUSSION

The present study deals with the DSC investigation of the cure kinetics of various epoxy resin compositions to examine the effect of (i) the diluent (ii) the fortifier, and (iii) the curing agent on the curing characteristics.

Typical results of selected dynamic scans carried out at a heating rate of 10 °C min^{-1} in the range 30–250 °C are shown in Fig. 1. Some cure characteristics such as the temperatures of onset of curing T_i, peak exotherm T_p and completion of curing T_f as well as the cure range obtained from DSC scans are presented in Tables 1 and 3.

From the DSC scans, the area under the curve a and the peak height $\mathrm{d}H/\mathrm{d}t$ were measured at various temperatures T, to determine two basic terms required to solve eqn. (1), and the reaction rate k was obtained. Secondly the fractional conversion was obtained by calculating the partial area to total area ratios at temperature T. Analysing the rate data at different temperatures using the Arrhenius relation, the kinetic parameters E and ln A were determined assuming that the reaction can be described as being simple n-th order Arrhenius-type temperature dependent. The as-

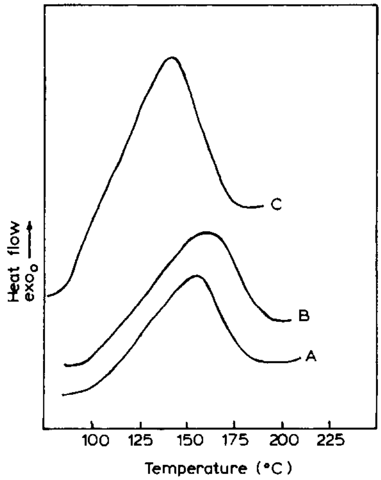


Fig. 1. Typical results of the dynamic DSC scans for different epoxy resin systems. (A) DGEBA; (B) DGEBA : MEC (70 : 30); (C) (DGEBA : MEC)-VCDHA (70 : 30)-20.

sumption is fairly valid as shown by straight line plots of ln k vs. $1/T$ (Fig. 2) up to 85% conversion. The results obtained from the regression plots (Fig. 2) are tabulated in Tables 2 and 4 along with the regression co-efficient r. The results obtained from the regression plots drawn using the Freeman-Carroll relation (eqn. (2)) (Fig. 3) are tabulated in Tables 2 and 4.

Effect of diluent

To observe diluent effect, the diluent MEC was incorporated with DGEBA in three different ratios, viz. DGEBA : MEC (i) 90 : 10, (ii) 80 : 20, and (iii) 70 : 30 keeping anhydrides and amine fixed. The curing characteristics listed

TABLE 1

Comparative data for the curing process of various epoxy systems using phthalic anhydride as curing agent and triethylamine as curing catalyst

Resin system	Proportions	T_i	T_p	T_f
DGEBA	–	95	153	190
DGEBA : MEC	90 : 10	95	154	195
DGEBA : MEC–VCDHA	(90 : 10)–20	90	145	195
DGEBA : MEC	80 : 20	98	155	195
DGEBA : MEC–VCDHA	(80 – 20)–20	85	142	180
DGEBA : MEC	70 : 30	100	158	204
DGEBA : MEC–VCDHA	(70 : 30)–20	85	145	190

Key: DGEBA, diglycidyl ether of bisphenol-A; MEC, mono epoxidized cardanol; VCDHA is the epoxy fortifier; T_i, temperature (°C) of the onset of curing; T_p, temperature (°C) of the peak of the exotherm; T_f, temperature (°C) of completion of curing.

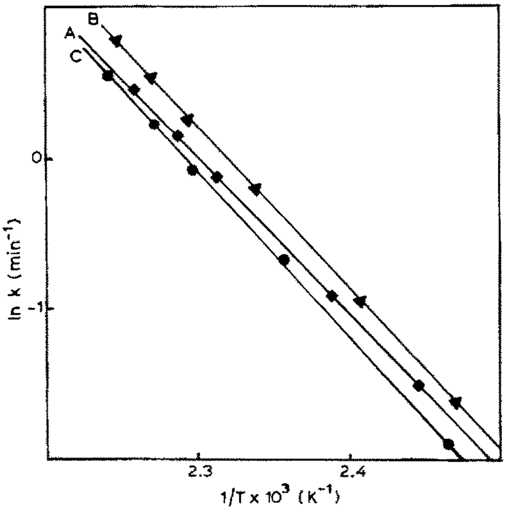


Fig. 2. Arrhenius plots of ln k vs. $1/T$ for different DGEBA:MEC molar ratios. (A) ■, 90:10; (B) ▲, 80:20; (C) ●, 70:30.

in Table 1 show that the exotherm starting temperature (temperature of onset of curing T_i) increases with increasing amount of diluent.

MEC when incorporated with DGEBA lowers the reactivity of the resin system. This is also revealed from the trend of energy of activation and frequency factor (Table 3) which increases with increasing amount of diluent.

TABLE 2

Kinetic parameters derived using the Barrett and Freeman-Carroll relations

Resin system	Proportions	Barrett relation			Freeman-Carroll relation		
		E (±2) (kJ mol^{-1})	ln A (±1) (min^{-1})	r	E (±2) (kJ mol^{-1})	n	r
DGEBA	–	81.8	22.3	0.997	81.80	1.10	0.997
DGEBA:MEC	90:10	83.58	22.94	0.990	82.81	1.017	0.998
DGEBA:MEC –VCDHA	(90:10)–20	68.37	18.50	0.996	66.66	1.21	0.993
DGEBA:MEC	80–20	87.06	23.53	0.997	85.45	1.19	0.999
DGEBA:MEC –VCDHA	(80:20)–20	71.36	19.70	0.980	73.49	1.30	0.998
DGEBA:MEC	70:30	91.41	24.84	0.995	93.65	1.125	0.994
DGEBA:MEC –VCDHA	(70:30)–20	78.92	20.80	0.998	77.29	1.22	0.993

Key: See Table 1 for the meaning of the abbreviations; E, activation energy; A, pre-exponential factor; n, order of the reaction; r, regression coefficient.

TABLE 3

Curing characteristics of DGEBA : MEC (80 : 20)–anhydride system

Anhydride	T_i	T_p	T_f
PA	98	155	195
PA–VCDHA [a]	85	142	180
DSA	110	169	200
DSA–VCDHA [a]	95	167	200
NMA	120	175	205
NMA–VCDHA [a]	95	170	205

[a] VCDHA (epoxy fortifier) used as 20 PHR. Key: PA, phthalic anhydride; DSA, dodecyl succinic anhydride; NMA, nadic methyl anhydride; T_i, temperature (°C) of the onset of curing; T_p, temperature (°C) of the peak of the exotherm; T_f, temperature (°C) of completion of curing.

TABLE 4

Kinetic parameters derived using the Barrett and Freeman-Carroll relations for DGEBA : MEC (80 : 20)–anhydride–NEt_3 resin system

Anhydride	Barrett relation			Freeman-Carroll relation		
	E (±2) (kJ mol^{-1})	ln A (±1) (min^{-1})	r	E (±2) (kJ mol^{-1})	n	r
PA	87.06	25.53	0.997	85.45	1.19	0.999
PA–F [a]	71.36	19.70	0.980	73.49	1.30	0.998
DSA	106.72	28.37	0.991	105.82	1.20	0.999
DSA–F	97.46	27.87	0.994	95.58	0.78	0.994
NMA	114.20	30.81	0.996	116.58	1.014	0.992
NMA–F	101.74	29.36	0.989	105.79	0.89	0.993

[a] F = VCDHA used as 20 PHR. See text for the meaning of the symbols.

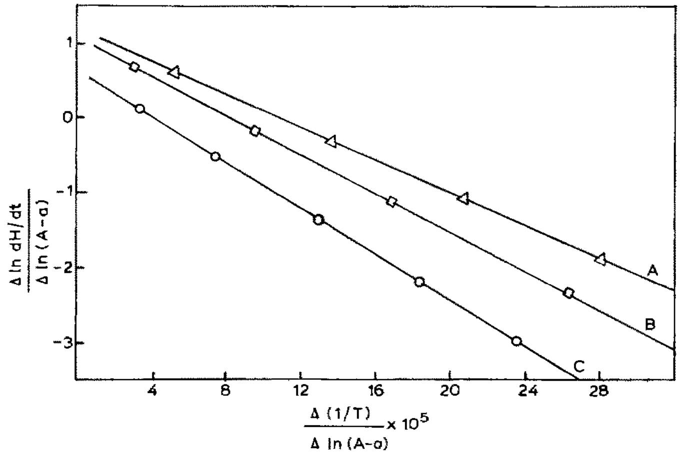


Fig. 3. Freeman-Carroll plots for different anhydride systems. (A) △, PA; (B) □, DSA; (C) ○, NMA.

Effect of fortifier

An epoxy fortifier is an additive which, when mixed with resin-curing agent system prior to curing, results in an increase in strength and modulus of the cured product [6].

In the present investigation we used bifunctional VCDHA as an epoxy fortifier. The addition of VCDHA to the epoxy system DGEBA : MEC (80 : 20) lowers the temperature of onset of curing T_i (Tables 1 and 3) as well as activation energy E (Tables 2 and 4). Incorporation of fortifier not only lowers the cure temperature but also speeds up the cure process. This may be due to the hydroxyl group present in the fortifier responsible for catalyzing the reaction. Similar behaviour was observed by Patel et al. [17].

Effect of anhydride

To observe the effect of the anhydride structure on the curing kinetics of the DGEBA : MEC system, three anhydrides, viz. PA, NMA and DSA are chosen. PA was chosen because of its wide use in commercial applications. NMA and DSA were selected for their structure complexicity and long alkyl chain length respectively.

The data shown in Table 3 indicate that the temperature at onset of curing T_i increases in the order pA < DSA < NMA.

An acid anhydride showing a lower T_i under the same set of curing conditions is more reactive towards the epoxy resin utilized. In this way it can be seen that the higher reactivity of PA is due to the planarity in the structure. The reactivity of DSA lies between PA and NMA. The lower reactivity of DSA over PA may be attributed to the lower acidity, which in turn is due to long alkyl chain present in the structure. The lowest reactivity of NMA may be due to the bicyclic structure, which may make the attack of anhydride to epoxide difficult due to steric hindrance.

It is also evident from the values of the kinetic parameters listed in Table 4 that the greater the reactivity of the anhydride, the lower are the values of the energy of activation and frequency factor.

CONCLUSIONS

The epoxy diluent MEC lowers the reactivity of the epoxy system. However, addition of epoxy fortifier to the resin system accelerates the cure process, which in turn increases the rate of reaction. The anhydride structure influences the reactivity in curing. PA is the most reactive whereas NMA is the least reactive anhydride among the three anhydrides utilized.

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