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EFFECT OF DIFFERENT EPOXY DILUENTS/FORTIFIER ON THE REACTIVITY IN CURING AND THE THERMAL STABILITY OF EPOXY RESIN USING 2,2-BIS[4-(*p*-AMINOPHENOXY)PHENYL]-PROPANE AS A CURING AGENT

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ABSTRACT

The curing reaction of the diglycidyl ether of bisphenol A with different diglycidyls and triglycidyls (used as diluents) using 2,2-bis[4-(*p*-aminophenoxy)phenyl]propane as a curing agent, with or without fortifier, has been studied by differential scanning calorimetry. The thermal stability of the cured resins has also been discussed. The overall activation energy for the curing reaction is observed to be in the range 48.1–71.4 kJ mol^{-1} and the order of the reaction is found to be $\simeq 1.0$. The activation energy of decomposition of the cured resin falls within the range 48.3–84.5 kJ mol^{-1}.

INTRODUCTION

In the past few years, aromatic amines have attracted widespread interest because of their excellent properties such as high thermal decomposition and high mechanical strength after curing with epoxies. When these amines are cured with epoxy resins, as a result of a multitude of chemical reactions during the curing, the epoxy resins are converted into a three-dimensional thermoset network. These network structures make the epoxies very useful in many fields [1]. Therefore, in this paper, considerable interest has been taken in the study of the curing of the diglycidyl ether of bisphenol A (DGEBA) with a diamine in the presence of various reactive epoxy diluents (diglycidyl and triglycidyl). The purpose of our study was to examine the effect of fortifier and curing agent on the properties of epoxies during curing reactions; therefore, differential scanning calorimetry (DSC) and thermogravimetry (TG) were used for the characterization of the unknown structures. The activation energy of the curing reaction, the kinetic parameters, the thermal stability of the cured resin and the effect of curing agent and fortifier on the thermal stability are discussed in this paper.

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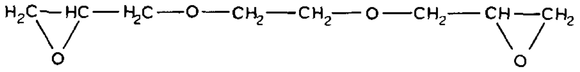
EXPERIMENTAL

Materials

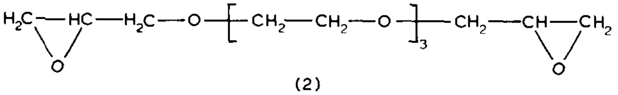
A DGEBA resin was prepared using a method reported in the literature [2]. The epoxy equivalent weight (EEW) of the DGEBA resin was 190 (g equiv.)$^{-1}$.

The following four glycidyls were prepared using a reported method [3]. The structures of these glycidyls are



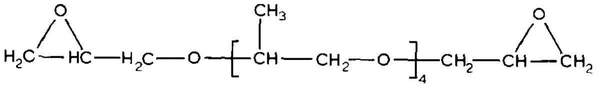
(1)

Diglycidyl ether of ethylene glycol (DGEEG), epoxy equivalent weight 87 (g equiv.)$^{-1}$



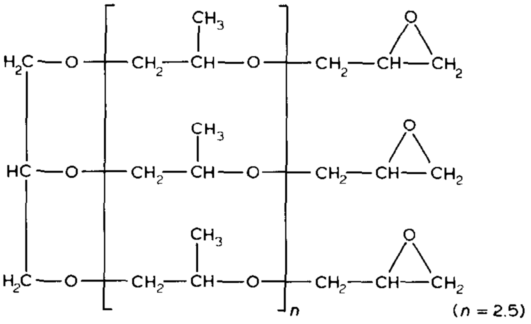
(2)

Diglycidyl ether of triethylene glycol (DGETEG), epoxy equivalent weight 131 (g equiv.)$^{-1}$



(3)

Diglycidyl ether of propylene glycol (DGEPG), epoxy equivalent weight 181 (g equiv.)$^{-1}$

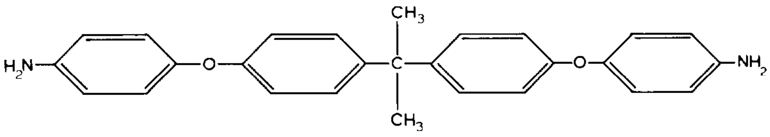


(4)

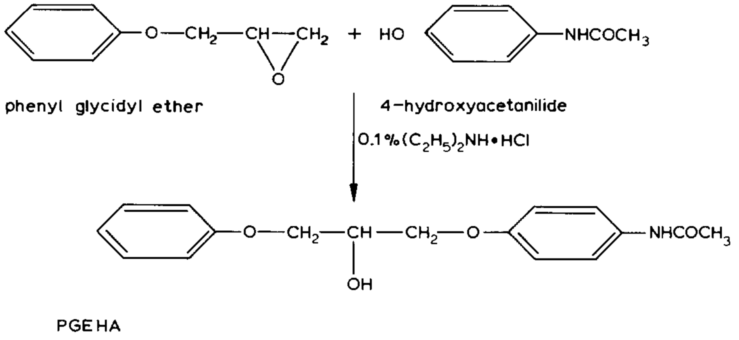
Triglycidyl ether of propoxylated glycerin (TGEPG), epoxy equivalent weight 206 (g equiv.)$^{-1}$.

These glycidyls were used as reactive diluents. The DGEBA : diluent ratio was kept to 80 : 20 throughout the study.

An aromatic diamine, 2,2-bis[4-(*p*-aminophenoxy)phenyl]propane (m.p. 121–122 ° C), used as a curing agent was prepared using the method reported in the literature [4]. The structure of this diamine is



An epoxy fortifier PGEHA was prepared [5] by condensing phenyl glycidyl ether (PGE) with 4-hydroxyacetanilide (HA). The condensation product was used as such for curing purposes. The reaction scheme is



Method

Differential scanning calorimetry

The calorimetric measurements were carried out using a Du Pont 900 differential scanning calorimeter. The instrument was calibrated using standard material of known heat of fusion.

The formulations used in this study were based on a 80 : 20 mixture of a DGEBA resin with different glycidyls. The resin–diluent mixture was heated to 125 ° C, followed by the addition of solid diamine and fortifier.

The mixture was stirred for 2–3 min and degassed under vacuum; the homogeneous material was immediately placed in an aluminium weighing pan and then cured in the differential scanning calorimeter with a heating rate of 10 ° C min^{-1}.

Thermogravimetry

The compounds cured by the above method were kept in a oven (previously heated to 200 ° C) for about 2 hours for complete curing. The products were then powdered, placed under vacuum and analysed using a Du Pont 951 thermogravimetric analyser with a heating rate of 10 °C min^{-1} in a static air atmosphere.

Analysis of DSC and TGA curves

In order to analyse the DSC scan, a linear baseline under the exothermic peak was drawn by joining the initiation and completion points of the exothermic transition. The DSC output was processed further to obtain heat flow data as a function of temperature and time, from which the overall rate constant k was estimated using the Barrett relation (eqn. (1) below). The activation energy E and frequency factor ln A were obtained by assuming that the curing reaction follows a simple Arrhenius-type temperature dependence.

The Barret relation [6] can be described as

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

where A is the total area and a is the area at a particular temperature.

The Freeman–Carroll relation [7] was also used to determine the activation energy E and the reaction order n. The equation is as follows

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

The terms involved in the equations have their usual meanings as described in the literature.

The TG scans were analysed to give the % weight loss as a function of temperature. In order to evaluate the activation energy E for the decomposition of cured samples, it was assumed that the decomposition of epoxies is a first-order reaction and obeys Arrhenius-type kinetics. The Broido relation used to evaluate E is

$$\ln(\ln 1/y) = -(E/R)(1/T) + \text{constant} \tag{3}$$

The terms involved in the above equation have their own significance as reported in the literature [8].

The integral procedure decomposition temperature (IPDT) values were calculated using Doyle's method [9].

RESULTS AND DISCUSSION

In order to study the curing characteristics of different glycidyls, DSC curves were obtained from blends of glycidyls with DGEBA resin. The effect of the curing agent (the diamine) and fortifier were also studied. Relative data of cure characteristics, such as temperature onset of curing T_i,

TABLE 1

Curing characteristics and kinetic parameters of epoxy–amine systems

Epoxy system	Proportions	T_i (°C)	T_p (°C)	Barrett relation		Freeman–Carroll relation	
				$E \pm 2$ (kJ mol^{-1})	$\ln A \pm 2$	$E \pm 2$ (kJ mol^{-1})	n
DGEBA	–	80	165	60.0	17.1	69.7	1.2
DGEBA–PGEHA	–	60	135	52.1	18.1	54.8	1.1
DGEBA–DGEEG	80:20	85	150	46.1	13.5	55.5	1.1
DGEBA–DGEEG–PGEHA	80:20:20	55	145	39.4	13.1	39.5	0.95
DGEBA–DGETEG	80:20	95	160	66.4	19.6	71.4	1.6
DGEBA–DGETEG–PGEHA	80:20:20	75	140	59.3	14.2	62.3	1.2
DGEBA–DGEPG	80:20	95	165	64.1	18.8	76.0	0.90
DGEBA–DGEPG–PGEHA	80:20:20	80	150	53.2	16.7	63.9	1.2
DGEBA–TGEPG	80:20	80	170	48.5	12.2	48.1	0.95
DGEBA–TGEPG–PGEHA	80:20:20	70	145	42.1	10.5	45.1	1.3

Key: DGEBA, diglycidyl ether of bisphenol A; PGEHA, epoxy fortifier; DGEEG, diglycidyl ether of ethylene glycol; DGETEG, diglycidyl ether of triethylene glycol; DGEPG, diglycidyl ether of propylene glycol; TGEPG, triglycidyl ether of propoxylated glycerin; T_i, temperature (°C) of the onset of curing; T_p, temperature (°C) of the peak of the exotherm; E, activation energy; A, pre-exponential factor; n, order of the reaction.

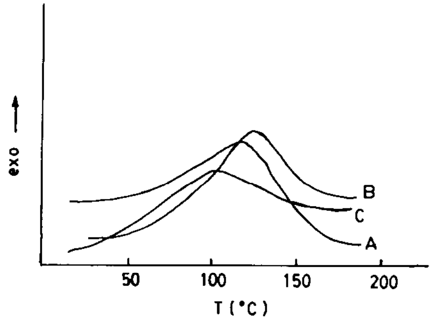


Fig. 1. Dynamic DSC curves at 10 °C min^{-1} for the systems (A) DGEBA, (B) DGEBA–DGEPG and (C) DGEBA–DGEPG–PGEHA.

peak temperature T_p, and some kinetic parameters such as activation energy E, frequency factor ln A and order of the reaction n are shown in Table 1. These values of kinetic parameters were obtained from eqn. (1) and eqn. (2). The values of E obtained from both of these equations are nearly the same and are shown in Table 1.

The data listed in Table 1 show that the system DGEBA–DGEEG, cured with diamine, has the lowest peak temperature T_p. As the chain length of diluent increases, the peak temperature increases, i.e. the epoxies are cured at higher temperatures. Figure 1 shows some selected DSC curves which were obtained at a single heating rate of 10 °C min^{-1}. Table 1 shows that the peak temperature is highest for the system DGEBA–TGEPG, cured with diamine. The presence of a greater number of glycidyl groups in the TGEPG structure makes the curing temperature of this resin higher. Incorporating a fortifier (PGEHA) in the epoxy blends lowers the peak temperature. This is because of the hydroxyl group in the fortifier which plays an important role in the curing reaction. Addition of a fortifier to the DGEBA–diluent system in the presence of an amine also increases the reactivity of the system. This is clear from Fig. 2, in which the fraction conversion (α) is plotted as a function of temperature for the epoxy systems DGEBA, DGEBA–DGEPG and DGEBA–DGEPG–PGEHA. A more reactive system tends to shift the curve towards lower temperatures. The Arrhenius plot of ln k against $1/T$ is shown in Fig. 3. Good linearity of these plots indicate an approximately 80% completion of the reaction.

The thermal stability of aromatic amines cured with different DGEBA–diluent systems were studied; these have very promising technical applications. The thermal stability of epoxies cured with amines depends upon the amine structure. Reports [10] show that the aromatic amines have better thermal stability than aliphatic amines. The aromatic diamine was prepared, see above, and the temperature characteristics for the various resin systems, such as T_o (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss) and T_{max} (temperature of maximum rate of

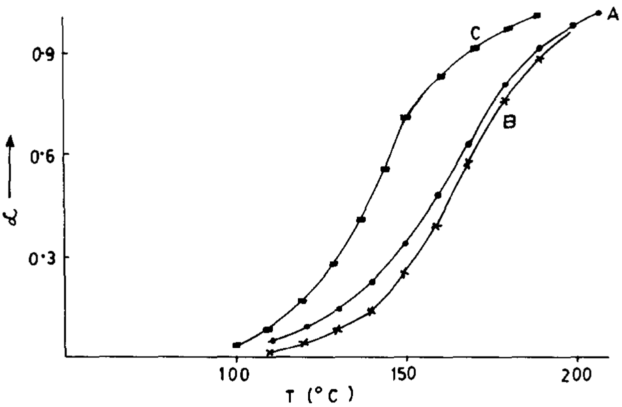


Fig. 2. Plots of fraction conversion (α) against temperature (°C) for the systems (A) DGEBA, (B) DGEBA-DGEPG and (C) DGEBA-DGEPG-PGEHA.

degradation) were determined and are shown in Table 2. The data in the table show that epoxies cured with the diamine 2,2-bis[4-(*p*-aminophenoxy)phenyl]propane have good thermal stabilities compared with the epoxies cured with other diamines [11].

Some selected curves obtained under dynamic conditions with a heating rate 10 °C $\min^{-1}$ are shown in Fig. 4. The degradation of cured epoxy resins proceeds in a single step. An initial slight loss in weight takes place at about 250 °C, then a sharp break occurs in each curve, indicating the onset of a

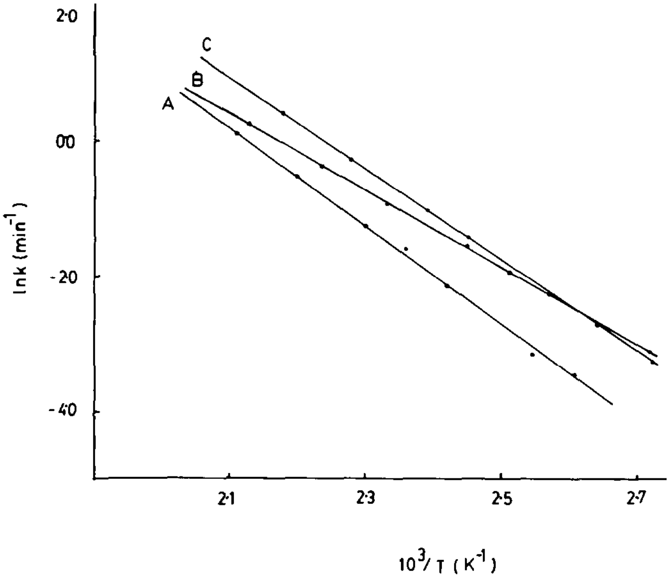


Fig. 3. Arrhenius plot of ln *k* against $1/T$ for the systems (A) DGEBA, (B) DGEBA-DGEEG and (C) DGEBA-DGEEG-PGEHA.

TABLE 2

Temperature characteristics of cured epoxy resins and kinetic parameters for thermal decomposition of various epoxy systems using Doyle's * method and Broido's ** method

Epoxy systems	T_o (°C)	T_{10} (°C)	T_{max} (°C)	IPDT * (°C)	$E+2$ ** (kJ mol^{-1})
DGEBA	200	300	425	505.5	52.6
DGEBA-PGEHA	200	325	450	489.3	38.0
DGEBA-DGEEG	250	350	425	498.0	57.3
DGEBA-DGEEG-PGEHA	275	362	450	473.5	52.2
DGEBA-DGETEG	225	337	412	495.2	84.5
DGEBA-DGETEG-PGEHA	250	362	450	468.0	51.9
DGEBA-DGEPG	275	325	450	503.2	78.6
DGEBA-DGEPG-PGEHA	250	325	425	443.5	60.8
DGEBA-TGEPG	250	337	437	479.4	70.1
DGEBA-TGEPG-PGEHA	250	312	425	453.2	48.3

Key (see Table 1 for the meaning of the abbreviations for the epoxy systems): T_o, temperature (°C) of onset of decomposition; T_{10}, temperature (°C) for 10% weight loss; T_{max}, temperature (°C) of maximum rate of degradation; IPDT, integral procedure decomposition temperature (°C); E, activation energy for thermal decomposition.

decomposition process involving a rapid loss in weight. Finally, the decomposition rate decreases.

The values of activation energy E and the IPDT of various epoxy resin–curing agent systems are shown in Table 2. During the analysis of the curves for estimating activation energy for thermal degradation, it was assumed that the reaction is first-order, and the appropriate plots of

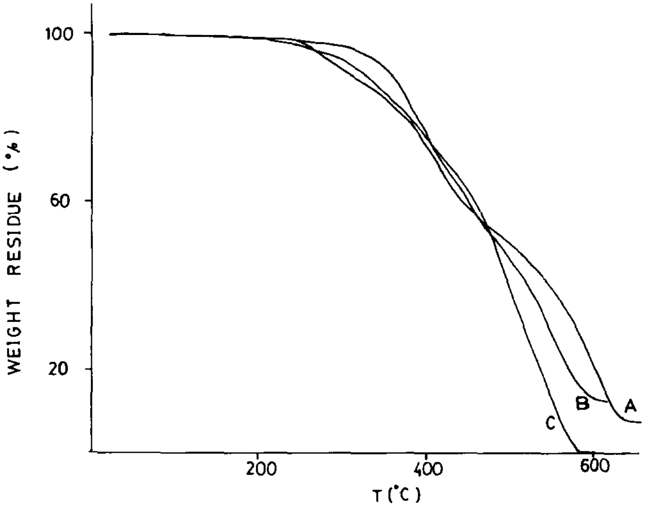


Fig. 4. Typical curves of the cured epoxy systems in air with a heating rate of 10 °C min^{-1}: (A) DGEBA; (B) DGEBA–TGEPG; (C) DGEBA–TGEPG–PGEHA.

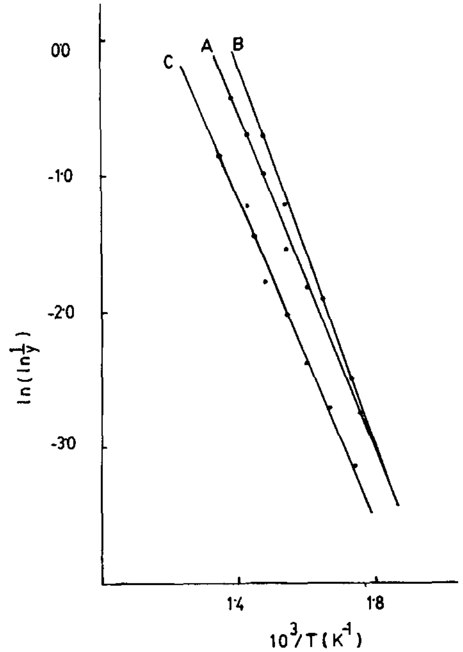


Fig. 5. Plots of ln(ln $1/y$) against $1/T$ using Broido's equation for the systems (A) DGEBA, (B) DGEBA–DGETEG and (C) DGEBA–DGETEG–PGEHA.

ln(ln $1/y$) against $1/T$ (using Broido's method) were drawn. Some of these plots are shown in Fig. 5. If the assumption that the reaction is first-order is incorrect, a deviation from linearity would be observed.

From Table 2, the conclusion can be drawn that the system having a higher activation energy for decomposition has greater thermal stability. The IPDT values can be regarded as significant because they indicate the overall nature of the TG curve. These values are obtained using Doyle's relation. Incorporation of fortifier PGEHA 20 PHR in the DGEBA–diluent blend lowers the thermal stability. This may be due to the early loss of some chemically unbonded material. McLean et al. [12] have observed a lowering of the glass transition temperature when using fortifier. However, the fortifier improves certain mechanical properties [12], lowers the curing temperature and speeds up the curing reaction.

CONCLUSIONS

The curing reactions of epoxy–amine systems in the presence of different diluents were studied. The study has shown that changes in diluent structure in the DGEBA–diluent blend changes the curing temperature and that their thermal stability is also affected. The curing reaction follows first-order kinetics, having an activation energy in the range 48.1–71.4 kJ mol^{-1}. The activation energy of thermal degradation is in the range 48.3–84.5 kJ mol^{-1}.

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