

Effect of fortifier on the cure kinetics and thermal stability of *N,N,N',N'*-tetraglycidyl ether of 4,4'-diaminodiphenyl methane using amines as curing agents

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Abstract

The curing reaction of the tetra-functional epoxy resin *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) with diaminodiphenyl methane (DDM) and diaminodiphenyl sulfone (DDS) in the presence or absence of fortifier has been studied by differential scanning calorimetry (DSC). The overall activation energy of the curing reaction is in the range of 85–180 kJ mol⁻¹. The thermal degradation studies of cured epoxy resin were carried out by thermogravimetric analysis (TGA). The overall activation energy for the degradation process is observed to be in the range of 53–82 kJ mol⁻¹.

INTRODUCTION

Epoxy resins based on tetra-*N*-glycidyl-4,4'-diaminodiphenyl methane (TGDDM) are widely used as matrix materials for high-performance fibre-reinforced structural composites in aerospace applications [1,2]. TGDDM is prepared by two routes: (i) condensation between diaminodiphenyl methane and epichlorohydrin followed by dehydrohalogenation by a base catalyst, and (ii) condensation between aniline dichlorohydrin and formaldehyde followed by dehydrohalogenation using a base catalyst. Although the product obtained by the second route is a mixture of isomers [3], this method is easier and less time-consuming than the first; therefore, we have adopted this method and have studied the cure kinetics of the final product.

Many workers have applied DSC to the study of the cure kinetics of TGDDM (Ciba-Geigy, "Araldite MY720", epoxy equivalent weight approx. 128 g equiv⁻¹) with different curing agents under varied conditions [4–10], but there is no reference in the literature giving information about the effect of the fortifier on the cure kinetics and thermal stability of TGDDM.

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In the present paper we report the results of our study on the effect of fortifiers on the cure kinetics of TGDDM using DDM and DDS as curing agents, using a heating rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. The thermal stabilities of the cured products were also investigated by thermogravimetric analysis at a heating rate of $10^{\circ}\text{C min}^{-1}$ in a static air atmosphere.

EXPERIMENTAL

Materials

Commercial grade aniline and epichlorohydrin were purified by distillation (b.p. $183\text{--}184^{\circ}\text{C}$ and $115\text{--}116^{\circ}\text{C}$, respectively). Sodium hydroxide, concentrated hydrochloric acid and formaldehyde (37%) were laboratory grade reagents. Benzyl triethylammonium chloride was used without further purification.

The resin *N,N,N',N'*-tetraglycidyl ether of 4,4'-diaminodiphenyl methane (TGDDM) was synthesised by the process reported in the patent [11].

The reagents required for the preparation of epoxy fortifier were phenyl glycidyl ether (PGE), prepared according to the reported method [12], 4-hydroxy acetanilide (HA), a pharmaceutical reagent, vinyl cyclohexane diepoxide (VCD), a laboratory grade reagent, and resorcinol, purified by vacuum distillation.

The epoxy fortifier (PGEHA) was prepared according to the published method [13,14]. The fortifier (VCDRC) was synthesised according to the process reported in the patent [15].

The curing agents *p,p'*-diaminodiphenyl methane (DDM) and *p,p'*-diaminodiphenyl sulfone (DDS) were used after recrystallisation from appropriate solvents.

The resin is characterized by epoxy equivalent weight (EEW), by number-average molecular weight and by its IR spectrum.

The EEW of the resin determined by the acetone-hydrochloride method [4] was found to be $124\text{--}126\text{ g equiv}^{-1}$. The number-average molecular weight \overline{M}_n determined by vapour pressure osmometry was found to be 552. The structure of the resin is shown in Fig. 1.

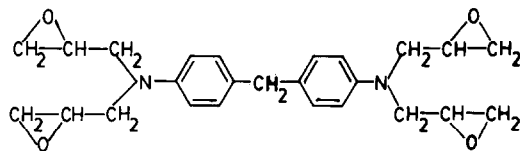


Fig. 1. Structure of resin (TGDDM).

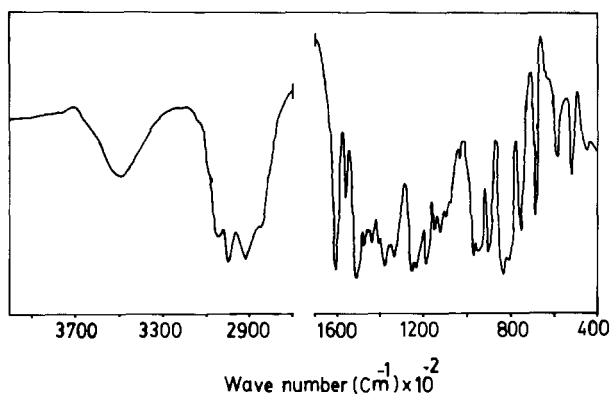


Fig. 2. IR spectrum of TGDDM.

The resin is also characterised by its IR spectrum, as shown in Fig. 2. The broad band observed at $3460\text{--}3520\text{ cm}^{-1}$ is due to the presence of hydroxyl group [4]. The bands at 2920 and 2998 cm^{-1} are due to the presence of methylene group and epoxide (--C--H) group [16], respectively. The absorption bands at 1615 and 1512 cm^{-1} are due to phenyl rings and the band at 1335 cm^{-1} to the presence of the tertiary amine group [17]. The absorption bands at 1165 and 1100 cm^{-1} are C–N stretching vibrations. The bands in the region of 1260 , 910 and 840 cm^{-1} are due to the presence of terminal epoxy groups. The single band at 760 cm^{-1} is due to the methylene group.

Curing procedure

Differential scanning calorimetry (DSC) of epoxy–amine systems

The samples for the DSC scans were prepared by mixing and heating TGDDM with and without fortifier (20 phr) to 100°C , cooling to about 80°C and mixing with stirring with DDM/DDS in stoichiometric amounts, i.e. one amine proton per epoxy group. The mixture was then de-gassed in a vacuum oven for 5 min and the void-free samples (5–8 mg) were then placed in hermetically sealed aluminium pans. The calorimetric measurements were made with a Du Pont 910 DSC module connected with a Du Pont 9900 thermal analyser under nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$ using an empty cell as reference. The DSC was calibrated with high purity indium (a Du Pont thermometric standard).

Thermogravimetric analysis (TGA) of cured epoxy resin

The samples remaining in the test tubes were then cured at 180°C for 4 h in the previously heated vacuum oven to achieve complete crosslinking. The cured samples were then crushed to a fine powder and used for thermogravimetric analysis (TGA) on a Du Pont 951 thermogravimetric

analyser connected with a Du Pont 990 thermal analyser in static air at a heating rate of $10^{\circ}\text{C min}^{-1}$.

Analysis of DSC and TGA data

DSC yields a continuous curve, showing the rate of heat flow for a given weight of the sample as a function of temperature. The base lines under the DSC traces were always drawn manually by joining the regions before the onset and after completion of the exothermic transition.

In order to derive directly the kinetic parameters associated with the curing reaction, such as activation energy (E), order of reaction (n), pre-exponential factor ($\log z$) and heat of reaction (ΔH) from a single DSC scan, the data were analysed using the method of Borchardt and Daniels [18] by assuming that the reaction follows n th order kinetics and that the temperature dependence of the reaction rate follows the Arrhenius expression. Essentially the same approach was used to estimate the above kinetic parameters of the curing reaction using the methods of Freemann and Carroll [19] and Barrett [20], following eqns. (1) and (2), respectively

$$\frac{\ln(dH/dt)}{\ln(A-a)} = n - \frac{(E/R)(\Delta 1/T)}{\Delta \ln(A-a)} \quad (1)$$

$$k = \frac{dH/dt}{A-a} \quad (2)$$

DSC data, when plotted according to eqn. (1) yield a straight line of slope $-E/R$ and intercept n . Data treatment according to eqn. (2) permits simultaneous evaluation of both activation energy (E) and pre-exponential factor ($\ln A$).

The thermal stabilities of TGDDM with DDM and DDS with and without fortifier were evaluated by thermogravimetric analysis. The thermograms obtained were analysed to obtain percentage weight loss as a function of temperature.

A Broido's relation [21] used to evaluate the activation energy (E) of the degradation process is shown in eqn. (3)

$$\ln(\ln 1/Y) = -(E/R)(1/T) + \text{const.} \quad (3)$$

The terms involved in the above equation have their usual meanings as reported in the literature [21]. To assess the overall nature of the TGA curves, IPDT values (integral procedure decomposition temperature) were determined using Doyle's method [22].

RESULTS AND DISCUSSION

The EEW of the TGDDM prepared was found to be 124–126 g equiv⁻¹ which is closely related to Ciba-Giegy "Araldite MY720" [4]. Typical

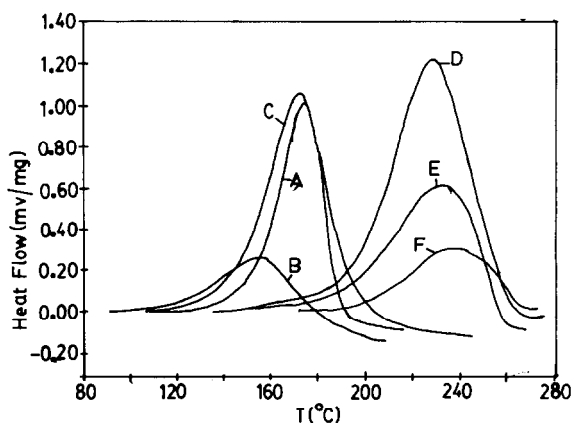


Fig. 3. Dynamic DSC scans at $10^{\circ}\text{C min}^{-1}$ for the systems: A, TGDDM:DDM; B, TGDDM:DDM:PGEHA (20 phr); C, TGDDM:DDM:VCDRC (20 phr); D, TGDDM:DDS; E, TGDDM:DDS:PGEHA (20 phr); F, TGDDM:DDS:VCDRC (20 phr).

results of the dynamic scans carried out at the single heating rate of $10^{\circ}\text{C min}^{-1}$ are shown in Fig. 3. Some cure characteristics such as onset of curing (T_i), peak exotherm temperature (T_p), complete cure temperature (T_f) and cure range, obtained from the DSC scans, are presented in Table 1.

In order to evaluate the kinetic parameters associated with the curing reaction, the DSC data were treated by three different methods [18–20]. Analyses of the selected data using eqns. (1) and (2) are illustrated by the plots in Figs. 4 and 5 respectively. The results obtained from the data analysis using the Borchardt and Daniels method [18] are presented in

TABLE 1
Curing characteristics of epoxy-amine systems

Epoxy resin-curing agent system with/without fortifier ^a	T_i ^b (°C)	T_p ^c (°C)	T_f ^d (°C)	Cure range (°C)
TGDDM + DDM	118	173.5	215	97
TGDDM + DDM + PGEHA	88	154	207	119
TGDDM + DDM + VCDRC	104	171	244	140
TGDDM + DDS	145	228	270	125
TGDDM + DDS + PGEHA	136	232	263	127
TGDDM + DDS + VCDRC	173	237	270	97

^a Resin, N,N,N',N' -tetraglycidyl ether of 4,4'-diaminodiphenyl methane (TGDDM); DDM, 4,4'-diaminodiphenyl methane; DDS, 4,4'-diaminodiphenyl sulfone; PGEHA and VCDRC (epoxy fortifiers) used at 20 phr levels.

^b T_i , temperature (°C) of the onset of curing.

^c T_p , temperature (°C) of peak of the exotherm.

^d T_f , temperature (°C) of the completion of curing.

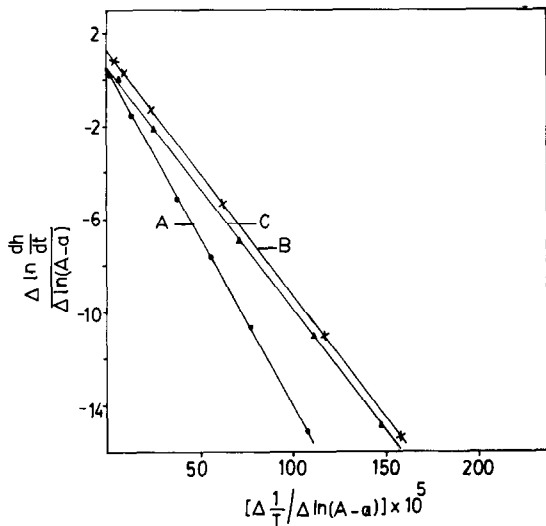


Fig. 4. A plot of $[\Delta \ln(dh/dt)]/[\Delta \ln(A-a)]$ vs. $\Delta 1/T \times 10^5/[\Delta \ln(A-a)]$ for the systems: A, TGDDM:DDM (\bullet); B, TGDDM:DDM:PGEHA (\times); C, TGDDM:DDM:VCDRC (\blacktriangle), using the Freeman-Carroll relation.

Table 2 and the results obtained using eqns. (1) and (2) are shown in Table 3.

The data presented in Table 1 reveal that the values of T_i , T_p and T_f depend on the curing agent used. These values are higher in the TGDDM-DDS system than in the TGDDM-DDM system which may be attributed to the fact that DDS contains an electron-withdrawing sulfonyl group in its backbone which lowers the reactivity of DDS. The effect of fortifiers

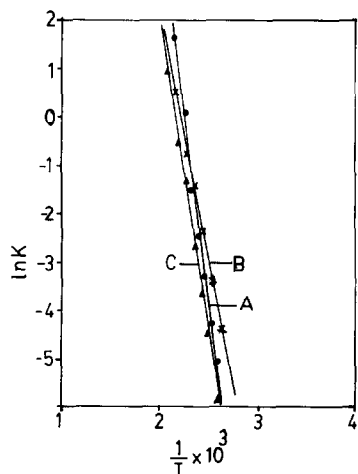


Fig. 5. A plot of $\ln K$ vs. $1/T \times 10^3$ for the systems: A, TGDDM:DDM (\bullet); B, TGDDM:DDM:PGEHA (\times); C, TGDDM:DDM:VCDRC (\blacktriangle), using the Barrett relation.

TABLE 2

Data evaluated using the Borchardt–Daniels relation

Epoxy resin–curing agent system with/without fortifier ^a	<i>n</i>	<i>E</i> ^b (kJ mol ⁻¹)	log <i>Z</i> ^b	Δ <i>H</i> (J g ⁻¹)
TGDDM+DDM	0.38	142	16.4	161.5
TGDDM+DDM+PGEHA	0.98	95	11.4	92
TGDDM+DDM+VCDRC	0.40	109	12.4	235.3
TGDDM+DDS	0.95	137.4	14.08	307.8
TGDDM+DDS+PGEHA	0.65	105	10.54	190
TGDDM+DDS+VCDRC	1.82	178.3	18.2	74.5

^a See Table 1 for key.^b Errors in *E* and log *Z*, ±2.

PGEHA/VCDRC in the epoxy–amine (DDS) system depends on both the structure of the fortifier and the structure of the amine. In the TGDDM–DDS–fortifier system the functionality of the fortifier plays the major role; the higher reactivity of VCDRC than PGEHA might be due to its higher functionality.

The effect of the fortifier VCDRC depends on the structure of the amines. In the system TGDDM–DDM, its incorporation decreases the temperature of the onset (*T*_i), while in the TGDDM–DDS system its incorporation increases the value of *T*_i as well as the reactivity. Such results may be due to the combined effect of the electron-withdrawing sulfonyl group of DDS and the higher functionality of the fortifier.

A similar trend is observed from the plot of 90% conversion time versus temperature shown in Fig. 6: the more reactive system shifts the curve towards lower temperatures. The lowering of the cure temperature with

TABLE 3

Kinetic parameters obtained using eqns. (1) and (2) ^a

Epoxy resin–curing agent system with/without fortifier	Eqn. (1)		Eqn. (2)	
	<i>E</i> ^b (kJ mol ⁻¹)	<i>n</i>	<i>E</i> ^b (kJ mol ⁻¹)	log <i>A</i> ^b
TGDDM+DDM	122	0.45	130.5	15.34
TGDDM+DDM+PGEHA	87	1.2	86	10.00
TGDDM+DDM+VCDRC	107	0.5	107	14.30
TGDDM+DDS	125.4	1.0	128	13.00
TGDDM+DDS+PGEHA	104.5	0.7	107	11.00
TGDDM+DDS+VCDRC	177	1.8	167	17.85

^a Eqn. (1), Freemann–Carroll relation; eqn. (2), Barrett relation.^b Errors in *E* and log *A*, ±2.

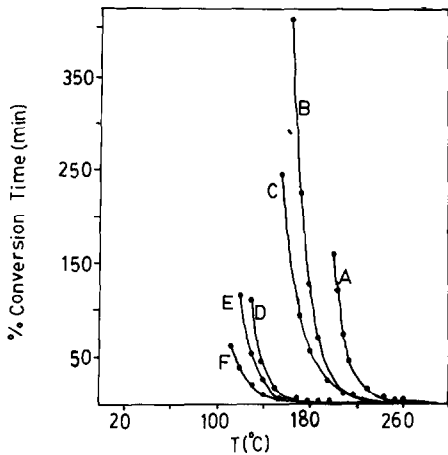


Fig. 6. Plots of 90% conversion time vs. temperature for the systems: A, TGDDM:DDS:VCDRC; B, TGDDM:DDS; C, TGDDM:DDS:PGEHA; D, TGDDM:DDM; E, TGDDM:DDM:VCDRC; F, TGDDM:DDM:PGEHA.

the incorporation of fortifier may be due to the hydroxyl group present in the fortifier which is responsible for catalysing the reaction [23].

The mechanism of the curing reaction is rather complex because of the chemical and physical changes that occur during the cure cycle [14] and also due to the fact that all fortifiers are more or less reactive because the possibility of side reactions cannot be ruled out. The fortifier may act as co-catalyst and may take part in opening the epoxy group in the epoxy resin.

In order to investigate the effect of the amine structure and the addition of the fortifier on the thermal stability of cured epoxy resins, selected thermograms obtained under dynamic conditions at a heating rate of $10^{\circ}\text{C min}^{-1}$ are reproduced in Fig. 7. An initial slight loss in weight takes place at about 245°C , then a sharp loss occurs in each of the thermograms,

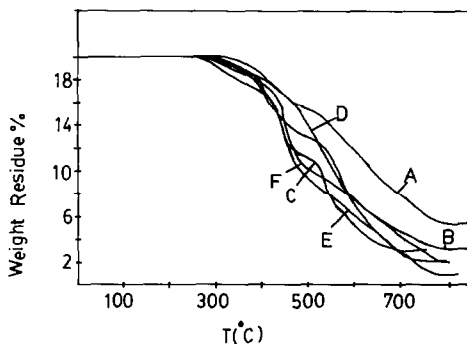


Fig. 7. TG curves for cured epoxy systems in static air at a heating rate of $10^{\circ}\text{C min}^{-1}$: A, TGDDM:DDS; B, TGDDM:DDS:PGEHA; C, TGDDM:DDS:VCDRC; D, TGDDM:DDM; E, TGDDM:DDM:VCDRC; F, TGDDM:DDM:PGEHA.

TABLE 4
Temperature characteristics of cured epoxy resins

Epoxy resin-curing agent system with/without fortifier ^a	T_0 (°C)	T_{10} (°C)	T_{20} (°C)	T_{30} (°C)	T_{\max} (°C)	T_{50} (°C)	IPDT ^b (°C)	E^c (kJ mol ⁻¹)
TGDDM + DDM	262.5	390	450	487.5	587.5	542	586	59.0
TGDDM + DDM + PGEHA	245	337.5	416	434	437.5	471	564	53.4
TGDDM + DDM + VCDRC	255	375	425	443	450	475	569	56.0
TGDDM + DDS	302.5	400	443	518	600	600	808	82.0
TGDDM + DDS + PGEHA	297.5	375	407	437.5	562.5	531	602	74.0
TGDDM + DDS + VCDRC	275	387.5	415	435	537.5	525	534.5	65.0

^a See Table 1 for key.

^b IPDT, integral procedure decomposition temperature.

^c Error, ± 2 .

indicating the initial decomposition process with rapid loss in weight. Finally, the decomposition rate decreases slowly, reaching a constant weight.

The temperature characteristics such as T_0 (temperature of the onset of decomposition), T_{10} (temperature for 10% weight loss), T_{20} (temperature for 20% weight loss), T_{30} (temperature for 30% weight loss), T_{\max} (temperature of maximum rate of degradation) and T_{50} (temperature of 50% weight loss) are shown in Table 4 along with the IPDT values and activation energy (E) of the degradation process.

It is observed that the higher the values of T_0 and T_{10} , the higher the heat stability [24]. However, for a quantitative assessment of the relative stability, IPDT values can be regarded of significant importance because they predict the overall nature of the TGA curves.

Figure 7 shows that the characteristic temperature varies with the curing agent used. Because the material having higher values of T_0 , T_{50} and T_{\max} can be regarded as thermally more stable, the trend observed from Table 4 for the thermal stability of the epoxy-amine systems with and without fortifier (20 phr) and for the activation energy of the degradation process is: TGDDM-DDS > TGDDM-DDS-PGEHA > TGDDM-DDS-VCDRC > TGDDM-DDM > TGDDM-DDM-VCDRC > TGDDM-DDM-PGEHA.

The epoxy resins cured with DDM/DDS gave relatively more stable cured resins; this may be due to the presence of the thermally stable linkage present within the aromatic nuclei [25,26]. The greater thermal stability of DDS-cured epoxy resin is because of the greater heat resistance of sulphur linkages compared with those of carbon [26].

The incorporation of fortifier PGEHA/VCDRC at 20 phr (parts per hundred of resin) lowers the thermal stability of the epoxy-amine system by fortifier; this may be due to the early loss of the chemically unbonded materials. However, although incorporation of the fortifier lowers the thermal stability of cured resin to some extent, it may also improve some mechanical properties [23].

CONCLUSIONS

DSC cure kinetics of epoxy-amine systems with and without fortifier follow Arrhenius-type kinetics with an activation energy in the range of 85–180 kJ mol⁻¹. The overall reactivity and thermal stability depend on the nature of the curing agent used as well as the fortifier. Incorporation of fortifier in epoxy-amine systems lowers the thermal stability to the some extent. The activation energy of the degradation process is in the range of 53–82 kJ mol⁻¹.

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