Journal of Thermal Analysis, Vol. 39 (1993) 229-238

COMPARATIVE STUDIES ON THE CURING KINETICS AND THERMAL STABILITY OF TETRAFUNCTIONAL EPOXY RESINS USING VARIOUS AMINES AS CURING AGENTS

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(Received August 19, 1991; in revised form April 29, 1992)

The curing reactions of the epoxy resins tetraglycidyl diaminodiphenyl methane (TGDDM) and tetraglycidyl methylenebis (*o*-toluidine) (TGMBT) using diaminodiphenyl sulfone (DDS), diaminodiphenyl methane (DDM) and diethylenetriamine (DETA) as curing agents were studied kinetically by differential scanning calorimetry. The dynamic scans in the temperature range 20°–300°C were analyzed to estimate the activation energy and the order of reaction for the curing process using some empirical relations. The activation energy for the various epoxy systems is observed in the range 71.9–110.2 $kJ \cdot mol^{-1}$. The cured epoxy resins were studied for kinetics of thermal degradation by thermogravimetry in a static air atmosphere at a heating rate of 10 $deg \cdot min^{-1}$. The thermal degradation reactions were found to proceed in a single step having an activation energy in the range 27.6–51.4 $kJ \cdot mol^{-1}$.

Keywords: epoxy resins, kinetics, thermal stability

Introduction

Epoxy resins have gained increasing importance due to their wide range of applications. The earlier resin is diglycidyl ether of bisphenol-A, which is suitable for many applications. But for high performance applications, resins with higher functionality are essential. The kinetics of curing reactions of epoxy resins with amines have been studied by several workers [1–4]. However, no report has mentioned on the study of curing reactions and thermal stability of tetraglycidyl methylene-bis (*o*-toluidine) (TGMBT) resin cured with three different amines.

The present paper discusses the curing kinetics and thermal stability of TGMBT resin using different amine curing agents and its comparison with the

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curing reactions and thermal stability of TGDDM resin. The effect of epoxy curing reactions were investigated.

Experimental

The resin tetraglycidyl diaminodiphenyl methane (TGDDM) was prepared according to the method reported [5]. Tetraglycidyl methylene bis (*o*-toluidine) was prepared from a diamine, 4, 4'-diaminodiphenyl, 3, 3'-dimethyl methane [6], following the method reported [5] in the literature.

The epoxy equivalents estimated by the hydrochlorination method [7] for TGDDM and TGMBT were 118 and 127 respectively. The number average molecular weights determined by vapour pressure osmometry were 452 and 490 respectively for TGDDM and TGMBT.

The resins TGDDM and TGMBT were also characterized by their IR-spectra (*a*) and (*b*) respectively as shown in Fig. 1. The broad band observed at 3400–3600 cm^{-1} in (*a*) and (*b*) is due to the presence of hydroxyl group. The hydroxyl absorption suggest that some of the epoxide rings may have reacted as in the commercial grade diglycidyl ether of bisphenol A. This may account for the decrease in average functionality [5]. The bands at 2920 and 3000 cm^{-1} in both (*a*) and (*b*)

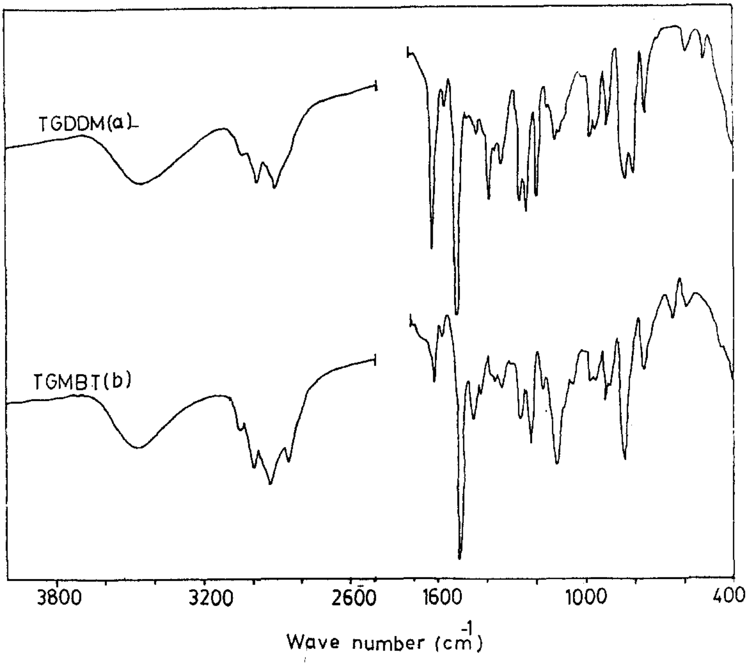

Fig. 1 IR-spectra of TGDDM (*a*) and TGMBT (*b*)

are due to the presence of methylene group and epoxide (C–H) group [8] respectively. The absorption bands at 1615, 1512 cm^{-1} are of phenyl rings and the bands at 1335 cm^{-1} are due to the presence of tertiary amine group [9]. The band in the region 2870 cm^{-1} in (*b*) is attributed to methyl C–H symmetric stretching vibration which is absent in (*a*). The absorption bands in the region 1260, 910 and 840 cm^{-1} in both (*a*) and (*b*) are due to terminal epoxy groups. The single band at 760 cm^{-1} is because of methylene group.

Differential scanning calorimetry

Te cure temperatures were determined by differential scanning calorimetry (DSC) using a Du Pont 9900 Thermal Analyzer with a DSC module (Du Pont Model 910). The instrument was calibrated with high purity indium (Du Pont thermometric standard) under nitrogen at a heating rate of 10 deg·min^{-1}. The epoxy resin and amines were mixed in the composition corresponding to one amine proton per epoxy group. The samples were scanned at a scanning rate of 10 deg·min^{-1} using an empty cell as reference.

Thermogravimetric analysis (TG) of the cured epoxy samples

The samples remaining in the test tubes were then cured and kept in a previously heated oven (about 200°C) for about 2h for complete curing. The thermograms of the cured products were obtained at a heating rate of 10 deg·min^{-1} of the powdered sample in nitrogen atmosphere. A Du Pont 951 thermogravimetric analyzer was used for the study.

Analysis of DSC and TG scans

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 method of Borchardt and Daniels [10] allows the calculation of activation energy (E), pre-exponential factor ($\log Z$) and order of reaction (n) from a single DSC scan. The method [10] assumes that the reaction follows n^{th} order kinetics and that the temperature dependence of the reaction rate follows the Arrhenius expression. Also the activation energy (E) and order of reaction (n) were determined from the Freeman-Carroll relation [11]. Using Barrett relation [12] the kinetic parameters such as activation energy (E) and pre-exponential factor ($\ln A$) were obtained.

The thermal stabilities of TGDDM and TGMBT with different amine curing agents were evaluated by thermogravimetric analysis. The activation energy E of the degradation process was obtained by Broido's method [13]. Integral procedure decomposition temperature (IPDT) values were obtained by using Doyle's method [14].

Results and discussion

The present study deals with the effect of amine structure as well as the effect of methyl group on the curing reactions and thermal behaviour of various epoxy resin compositions using different amines as curing agents. The curing agents used were DETA, DDM and DDS. From the characteristic DSC scans, the temperatures at which curing reaction started (T_i), peaked (T_p) and completed (T_f), the cure range and the cure time for the various epoxy resin systems are presented in Table 1 and the selected DSC curves are furnished in Fig. 2.

Table 1 Curing characteristics of epoxy-amine systems

System	T_i /	T_p /	T_f /	Curing range T_f–T_i /	Cure time at T_p/
			°C		min
TGDDM–DETA	37	93	147	110	6.2
TGDDM–DDM	65	146	205	140	11.9
TGDDM–DDS	120	206	220	100	17.6
TGMBT–DETA	52	106	212	160	7.1
TGMBT–DDM	87	166	220	133	13.6
TGMBT–DDS	144	213	234	90	18.3

A comparison of the curing behaviours of different epoxy systems as shown in Table 1, reveals that the values of T_i, T_p and T_f depends upon the curing agent as well as the structure of resin. Considering the type of curing agents used, the values are lowest for DETA and highest for DDS. This indicates that the rate of curing of resin-DETA system is highest among the systems used. The trend revealed for the ease of curing for the epoxy systems is as follows:

resin-DETA > resin-DDM > resin-DDS

An identical trend of the reactivity of different resin-amine systems can be observed from Fig. 3, in which conversion time (min) is plotted against temperature for 99% conversion. A more reactive system shifts the curve towards a lower temperature than that of a less reactive system. The ease of curing depends upon the reactivity of amines. In case of DETA which is purely aliphatic has the highest reactivity, while DDS has the lowest reactivity, because of electron whithdrawing sulfonyl group.

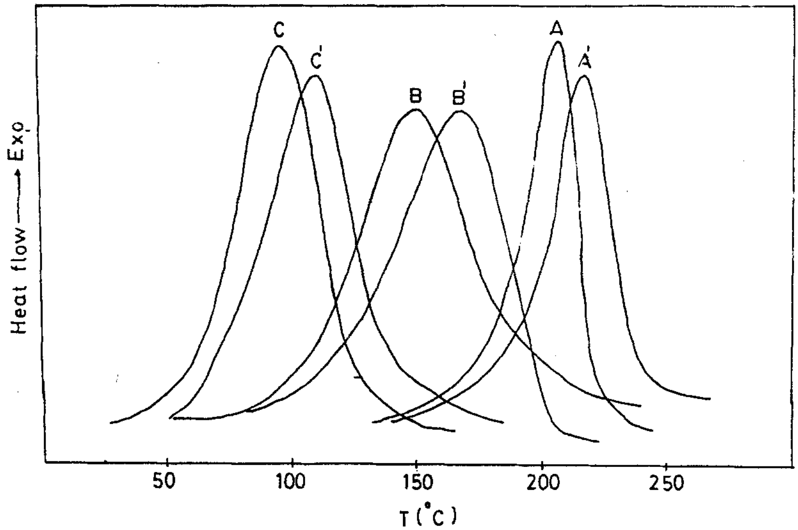

Fig. 2 Dynamic DSC scans at 10 deg·min^{-1} for the systems. A:TGDDM-DDS, A':TGMBT-DDS, B:TGDDM-DDM, B':TGMBT-DDM, C:TGDDM-DETA, C':TGMBT-DETA

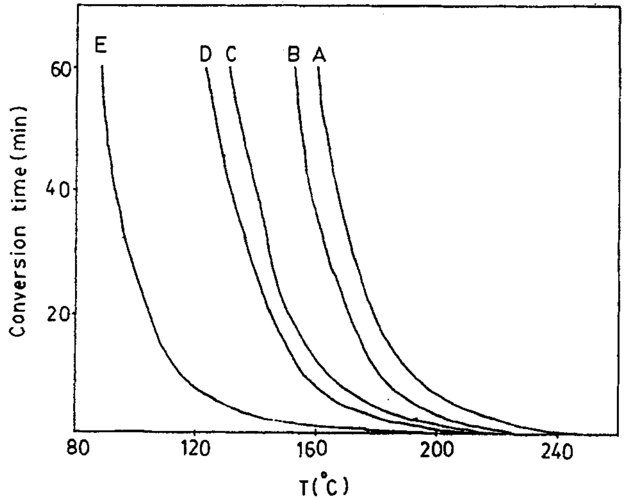

Fig. 3 Plots of conversion time as a function of temperature for 99% conversion for the systems. A:TGMBT-DDS, B:TGDDM-DDS, C:TGMBT-DDM, D:TGDDM-DDM, E:TGMBT-DETA

Considering the structure of the resin utilized, the ease of curing for the epoxy-curing agent system is as follows:

TGDDM-DETA > TGMBT-DETA > TGDDM-DDM >

TGMBT-DDM > TGDDM-DDS > TGMBT-DDS.

From the above trend it can be observed that the reactivity of TGMBT-curing agent system is lower compared to TGDDM-curing agent system which may be due to the steric hindrance exerted by methyl groups present in TGMBT resin.

The kinetic parameters such as activation energy (E), order of reaction (n) and pre-exponential factor determined by analysing the data of Borchardt-Daniels relation [10], Freeman-Carroll relation [11] and Barrett relation [12], are presented in Table 2. Selected plots using Freeman-Carroll and Barrett relation are shown in Fig. 4 and Fig. 5 respectively.

Selected thermograms obtained under dynamic conditions at a heating rate of 10 deg·min^{-1} are reproduced in Fig. 6. In order to determine thermal stability trend, the temperature characteristics such as T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), T_{20} (temperature for 20% weight loss), T_{max} (temperature of maximum rate of degradation), IPDT (Integral procedural decomposition temperature) and the activation energy (E) of the degradation process were calculated and presented in Table 3. T_0 and T_{10} are two of the main criteria of the heat stability of polymers. The higher the values of T_0 and T_{10}, the higher will be the heat stability of the system [15]. However T_0, T_{10} and T_{max} are single features of the TG curves. To obtain the quantitative picture of the relative stability, IPDT values can be regarded of significant importance, since they represent the overall nature of the TG curves.

The thermal stability of amine-cured epoxy system is affected by the structure of the amine used as curing agent as well as the structure of the resin. The trend of the thermal stability for the amine cured epoxy resins as shown in Table 3, is

TGDDM-DDS > TGMBT-DDS > TGDDM-DDM >

TGMBT-DD> TGDDM-DETA > TGMBT-DETA.

The curing agents DDM and DDS gave relatively more stable cured resins because of the thermally stable linkages present within the aromatic nuclei [16, 17]. The greater stability of the DDS cured resin may be ascribed to a greater heat resistance character of the sulphur linkage compared with those of carbon [17]. The lowest stability observed in case of DETA cured resin systems is due to a purely aliphatic structure of DETA in the cured product.

The resin structure also affects the thermal stability of the amine-cured epoxy system. As stated earlier in Table 1, the low reactivity of the TGMBT resin system may be attributed to the steric hindrance generated by alkyl group at ortho position. The steric factors are related to the configuration and conformation of chains in the resin network during curing. Due to these steric factors, chemical reaction between the functional groups becomes difficult at certain locations throughout the resin network resulting into lowering in the thermal stability of

Table 2 Kinetic parameters of epoxy-amine systems

System	Borchardt-Daniels relation			Freemann-Caroll relation		Barrett relation	
	E±2 / kJ·mol^{-1}	ln$Z$ ±2 / min^{-1}	n	E±2 / kJ·mol^{-1}	n	E±2 / kJ·mol^{-1}	ln$A$±1 / min^{-1}
TGDDM–DETA	79.0	25.6	1.4	81.0	1.3	85.1	26.7
TGDDM–DDM	81.1	22.4	1.2	82.4	1.2	71.9	20.4
TGDDM–DDS	102.7	24.8	1.1	95.3	1.0	93.4	23.0
TGMBT–DETA	72.0	22.2	1.3	86.9	1.1	83.0	23.5
TGMBT–DDM	85.7	22.9	1.0	87.2	1.0	76.2	18.9
TGMBT–DDS	99.1	23.3	1.2	110.2	0.9	97.5	23.3

Table 3 Temperature characteristics and kinetic parameters of cured epoxy resins

System	T_0 / °C	T_{10}/ °C	T_{20} / °C	$T_{\max}$ / °C	IPDT / °C	E±2 / kJ·mole^{-1}
TGDDM–DETA	150	300	338	400	485	31.8
TGDDM–DDM	225	313	375	420	532	41.7
TGDDM–DDS	250	325	395	430	571	51.4
TGMBT–DETA	125	280	310	325	443	27.6
TGMBT–DDM	213	310	350	410	512	34.8
TGMBT–DDS	238	320	388	425	550	42.5

TGMBT curing agent system. The trend in the thermal stabilities of the cured resins can also be deduced from the values of activation energy E.

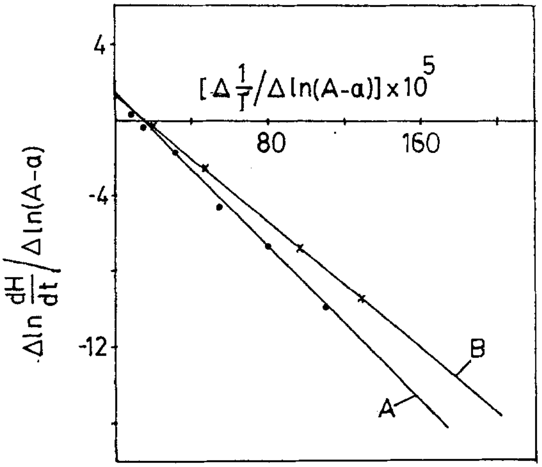

Fig. 4 Freeman-Carroll plots for the scans of selected epoxy systems at 10 deg·min^{-1}, A:TGDDM-DETA, B:TGMBT-DETA

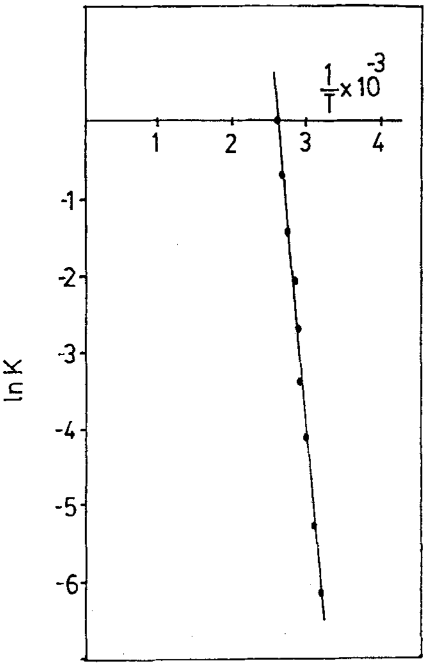

Fig. 5 A plot of ln$k$ vs. $1/T \times 10^3$ for TGDDM-DETA by using Barrett relation

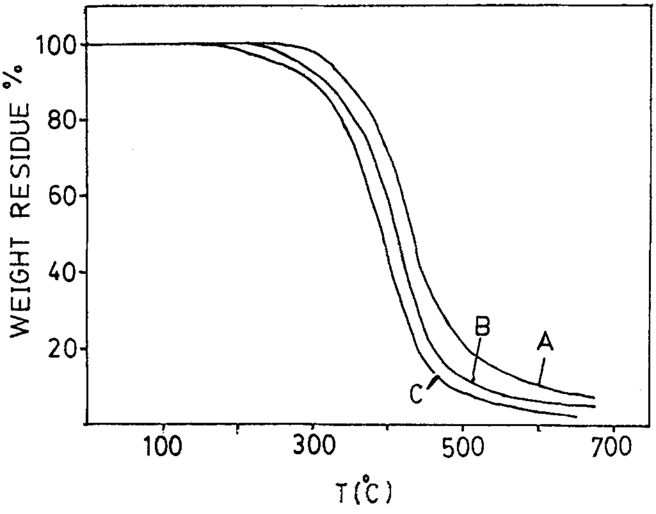

Fig. 6 TG curves for cured epoxy systems in a nitrogen atmosphere at a heating rate 10 deg·min^{-1}.
A:TGDDM-DDS, B:TGDDM-DDM, C:TGDDM-DETA

Conclusion

The curing reaction and the thermal stability of the epoxy-amine systems depends upon the curing agent used as well as on the resin structure. The dynamic DSC cure kinetic study of resin-amine curing agent systems reveals that the systems are found to follow simple n^{th} order Arrhenius-type kinetics having an activation energy in the range of 71.9–110.2 kJ·mol^{-1}. The activation energy of the thermal degradation is in the range of 27.6–51.4 kJ·mol^{-1}.

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Zusammenfassung — Die Vernetzungsreaktionen der Epoxidharze Tetraglycidyl-diaminodiphenyl-methan (TGDDM) und Tetraglycidyl-methylen-bis(*o*-toluidin) (TGMBT) unter Verwendung von Diaminodiphenylsulfon (DDS), Diaminodiphenylmethan (DDM) und Diethylentriamin (DETA) als Vernetzungsmittel wurden kinetisch mittels DSC untersucht. Die dynamischen Scans im Temperaturbereich 20°–300°C wurden analysiert, um unter Anwendung einiger empirischer Gleichungen die Aktivierungsenergie und die Reaktionsordnung des Vernetzungsprozesses zu ermitteln. Die Aktivierungsenergie der einzelnen Epoxy-Systeme liegt im Bereich 71.9–110.2 kJ·mol^{-1}. An der ausgehärteten Harze wurde mittels TG in einer statischen Luftatmosphäre un deiner Aufheizgeschwindigkeit von 10 Grad/min die Kinetik des termischen Abbaues untersucht. Man fand, daß die thermiscehn Abbaureaktionen in einem Schritt ablaufen und ihre Aktivierungsenergie im Intervall 27.6–51.4 kJ·mol^{-1} liegt.