Thermochimica Acta, 202 (1992) 97–104
Elsevier Science Publishers B.V., Amsterdam

Effect of the anhydride structure on the curing kinetics and thermal stability of tetrafunctional epoxy resin

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(Received 13 September 1991)

Abstract

The kinetics of curing of epoxy resin, *N,N,N',N'*-tetraglycidyl-1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane (TGBATC) with six different anhydrides in stoichiometric amounts were investigated by means of differential scanning calorimetry. The overall kinetics of curing follows a simple Arrhenius-type temperature dependence with an activation energy range of 53.2–124.6 kJ mol^{-1}. The kinetics of thermal degradation of the cured epoxy resins were studied by thermogravimetry in a static air atmosphere at a heating rate of 10°C min^{-1}. The thermal degradation reactions were found to proceed in a single step with an activation energy in the range 28.0–65.0 kJ mol^{-1}.

INTRODUCTION

Currently, *N,N,N',N'*-tetrafunctional epoxy resin is used extensively in high-performance applications. Because of its multifunctionality, its degree of crosslinking is higher than for standard difunctional resins and consequently, its heat distortion temperature is also higher. The presence of an aromatic ring together with the cyclohexane moiety in the backbone chain of this (TGBATC) resin, is reflected in its improved thermal stability and in some of the mechanical properties of the cured resin.

The base-catalysed curing of the epoxy resins with acid anhydrides as curing agents has been reviewed by several workers using various analytical methods [1–6]. The present paper discusses the curing reactions of the TGBATC resin using various anhydride curing agents. The thermal stabilities of the final cured products are also investigated.

EXPERIMENTAL

Materials

The tetrafunctional epoxy resin TGBATC was prepared from a diamine, 1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane [7], following the method re-

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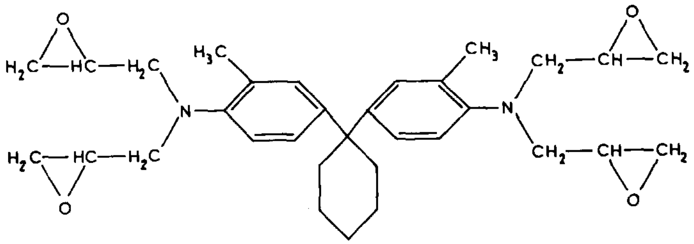

Scheme 1.

ported in the literature [8]. The structure of the above-mentioned resin is as shown in Scheme 1.

The epoxy equivalent weight as calculated by the hydrochlorination method [9] was found to be 142 g equiv^{-1}. The number average molecular weight determined by vapour pressure osmometry was 550. The curing agents (various anhydrides) were laboratory grade reagents.

Curing procedure

The cure temperatures were determined by differential scanning calorimetry (DSC) using a Du Pont 9900 thermal analyser 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°C min^{-1}. The samples of the resin system (approx. 2 g) for the DSC scans were prepared by mixing the resin and the curing agent in stoichiometric amounts, using 1% w/w triethylamine as curing catalyst, just before the start of the scan. The samples were scanned at a scanning rate of 10°C min^{-1} using an empty cell as reference.

Thermogravimetric analysis (TGA) of the cured epoxy samples

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

Analysis of DSC and TG scans

The exothermic peaks obtained in the DSC scans were analysed to give heat flow data as a function of temperature and time. These data were processed further to obtain the fractional conversion and the rate of reaction. Using the Barrett relation [10], the rate constant K was estimated. By assuming that the values of K have Arrhenius-type temperature dependence, the kinetic parameters, such as activation energy E and frequency factor $\ln A$, were obtained. The activation energy E and the order of reaction n were determined from the Freeman–Carroll relation [11].

The TG curves were analysed to give percentage weight-loss as a function of temperature. The activation energy E of the degradation process was obtained by Broido's method [12]. Integral procedure decomposition temperature (IPDT) values were obtained using Doyle's method [13].

RESULTS AND DISCUSSION

Curing reactions were established with the help of DSC for various epoxy resin compositions using different acid anhydrides as curing agents in stoichiometric amounts and triethylamine (1% w/w) as catalyst. In order to study the effect of the structure of the anhydride on the curing characteristics, the more general anhydrides such as phthalic anhydride (PA), hexahydrophthalic anhydride (HHPA), trimellitic anhydride (TMA), pyromellitic dianhydride (PMDA), nonyl succinic anhydride (NSA) and benzophenone tetracarboxylic dianhydride (BTDA) were used.

Typical results of selected dynamic scans carried out at a heating rate of 10°C min^{-1} are shown in Fig. 1. Some cure characteristics such as the temperature at which curing started T_i, peaked T_p and completed T_f, as well as the cure range and cure time obtained from DSC scans are

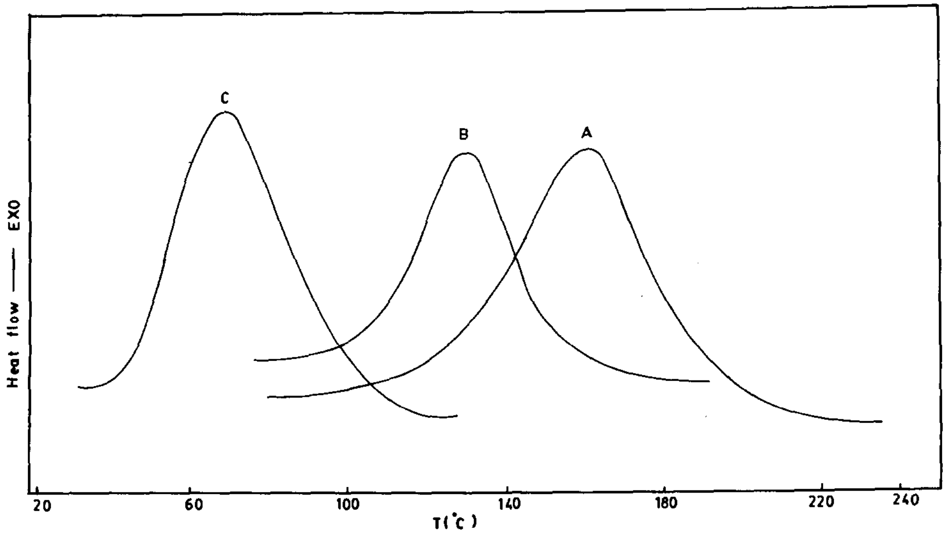

Fig. 1. Dynamic DSC scans at 10°C min^{-1} for the systems: curve A, TGBATC–NSA; curve B, TGBATC–HHPA; curve C, TGBATC–PMDA.

TABLE 1

Curing characteristics of epoxy–anhydride systems

Epoxy resin–curing agent system [a]	T_i^b (°C)	T_p^c (°C)	T_f^d (°C)	Curing range (°C)	Cure time (min)
TGBATC–NSA	88	163	233	145	12.7
TGBATC–PA	82	132	217	135	9.6
TGBATC–HHPA	80	128	181	101	9.2
TGBATC–TMA	52	91	150	98	5.5
TGBATC–BTDA	43	83	138	95	4.8
TGBATC–PMDA	42	69	120	78	3.4

[a] Resin, *N,N,N′,N′*-tetraglycidyl-1,1-bis[(4-amino-3-methyl)phenyl]cyclohexane; NSA, nonyl succinic anhydride; PA, phthalic anhydride; HHPA, hexahydrophthalic anhydride; TMA, trimellitic anhydride; BTDA, benzophenone tetracarboxylic dianhydride; PMDA, pyromellitic dianhydride.

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

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

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

presented in Table 1. Kinetic parameters associated with the curing reaction, such as activation energy E, order of reaction n, and pre-exponential factor ln A, obtained using the methods of Freeman and Carroll [11] and Barrett [10] are presented in Table 2. Selected plots obtained from the analysis of the data using these two methods are shown in Figs. 2 and 3 respectively.

The curing characteristics listed in Table 1 show that the values of T_i, T_p and T_f depend on the curing agent. The peak temperature decreases in the order NSA > PA > HHPA > TMA > BTDA > PMDA.

An acid anhydride showing lower values of T_p under the same set of curing conditions is more reactive towards the epoxy resin employed. In this way, PMDA can be regarded as having the highest reactivity, while NSA has the lowest reactivity, towards the epoxide–anhydride reaction.

TABLE 2

Kinetic parameters of epoxy–anhydride systems

Epoxy resin–curing agent system [a]	Barrett relation		Freeman–Carroll relation	
	E (kJ mol^{-1}) [b]	ln A [b]	E (kJ mol^{-1}) [b]	n
TGBATC–NSA	124.6	38.5	120.8	1.2
TGBATC–PA	96.5	23.8	95.3	1.0
TGBATC–HHPA	83.4	27.4	81.2	1.1
TGBATC–TMA	74.8	26.5	69.0	1.2
TGBATC–BTDA	66.7	24.8	64.3	1.4
TGBATC–PMDA	53.2	22.1	55.7	1.3

[a] See Table 1 for key.

[b] Errors in E and ln A, ±2.

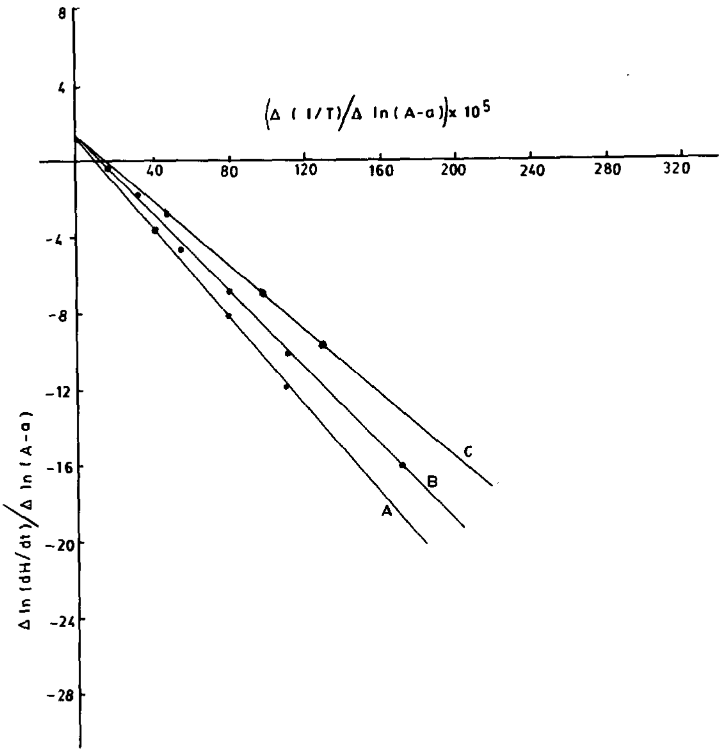

Fig. 2. Freeman–Carroll plots for the scans of selected epoxy systems at 10°C min^{-1}: curve A, TGBATC–PA; curve B, TGBATC–TMA; curve C, TGBATC–BTDA.

The lowest reactivity of NSA may be attributed to its lowest acidity which in turn is due to the long alkyl chain in its structure. The highest reactivity of PMDA may be attributed to the multifunctionality involved in its structure. The higher reactivity of HHPA over PA may be due to the comparatively lower stability of HHPA over PA. TMA shows a reactivity higher than that of HHPA. This may be explained on the basis of the electron-withdrawing effect of a –COOH group which makes the anhydride group more acidic.

Selected thermograms obtained under dynamic conditions at a heating rate of 10°C min^{-1} are reproduced in Fig. 4. The temperature characteristics such as T_o (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), T_{max} (temperature of maximum rate of degradation), IPDT (integral procedure decomposition temperature) and the activation energy E of the degradation process are shown in Table 3.

T_o and T_{10} are two of the main criteria indicating the heat stability of polymers. The higher the values of T_o and T_{10}, the higher the thermal stability of the system [14]. However, T_o, T_{10} and T_{max} are the sole features of TGA curves. To obtain a quantitative assessment of the relative stability,

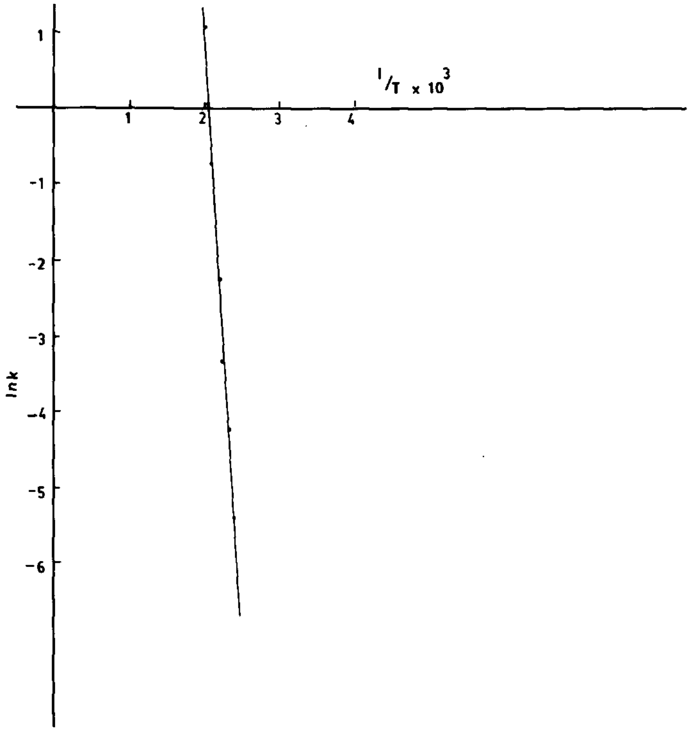

Fig. 3. A plot of ln K vs. $1/T$ for the system TGBATC–PA using the Barrett relation.

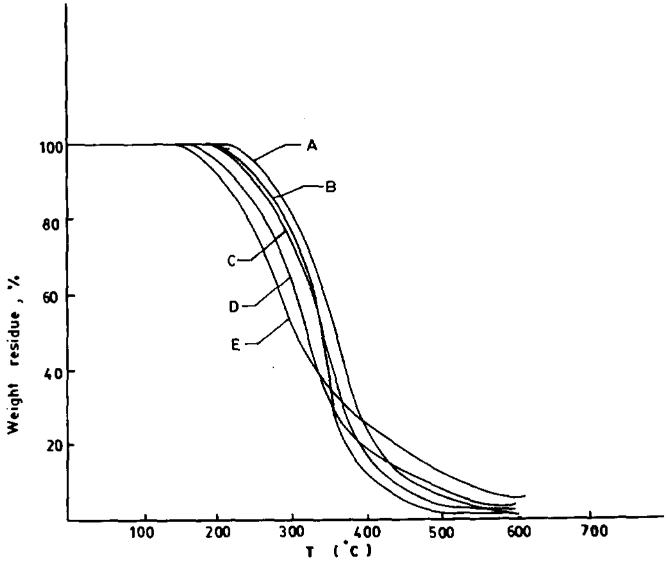

Fig. 4. Typical thermograms of the cured epoxy systems in nitrogen at a heating rate of 10°C min^{-1}: curve A, TGBATC–PMDA; curve B, TGBATC–BTDA; curve C, TGBATC–HHPA; curve D, TGBATC–PA; curve E, TGBATC–NSA.

TABLE 3

Temperature characteristics and kinetic parameters of cured epoxy resins

Epoxy resin–curing agent system [a]	T_o (°C)	T_{10} (°C)	T_{20} (°C)	T_{max} (°C)	IPDT [b] (°C)	E (kJ mol^{-1}) [c]
TGBATC–NSA	150	210	250	315	380	28
TGBATC–PA	175	225	270	325	419	32
TGBATC–HHPA	200	250	285	338	444	38
TGBATC–TMA	200	245	290	350	472	43
TGBATC–BTDA	210	260	295	363	490	50
TGBATC–PMDA	225	275	310	375	512	65

[a] See Table 1 for key.

[b] IPDT, integral procedure decomposition temperature.

[c] Error, ±2.

IPDT values can be regarded as having significant importance because they represent the overall nature of the TGA curves.

The trend of the thermal stability for the acid-anhydride-cured epoxy resins as shown in Table 3, is TGBATC–PMDA > TGBATC–BTDA > TGBATC–TMA > TGBATC–HHPA > TGBATC–PA > TGBATC–NSA.

The curing agents PMDA and BTDA gave relatively more stable cured resins because of the multifunctionality of both PMDA and BTDA. The lower stability of TGBATC–BTDA compared with that of TGBATC–PMDA may be due to the presence of a carbonyl group between the phenyl rings in the chain. The greater stability of TMA-cured resins over PA-cured resins may be ascribed to the higher functionality of TMA, resulting in a tightly crosslinked network. The lowest stability observed in the case of TGBATC–NSA is due to the presence of the long alkyl chain of NSA in the cured product.

CONCLUSIONS

The curing kinetics of the amine-catalysed epoxy–anhydride systems reveal that the variation in the structure affects the reactivity of an anhydride towards the curing process, which is found to follow Arrhenius-type kinetics, having activation energies in the range 53.2–124.6 kJ mol^{-1}. The thermal stability of the cured epoxy system also depends on the structure of the curing agent used. The activation energy of the thermal degradation is in the range 28.0–65.0 kJ mol^{-1}.

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