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KINETICS OF CURING AND THERMAL STABILITY OF A NOVEL TETRAFUNCTIONAL EPOXY RESIN, *N,N,N′,N′*-TETRAGLYCIDYL-1,1′-BIS[4-(*p*-AMINOPHENOXY)PHENYL]CYCLOHEXANE, USING VARIOUS AMINE CURING AGENTS WITH OR WITHOUT FORTIFIER

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ABSTRACT

A novel tetrafunctional epoxy resin, *N,N,N′,N′*-tetraglycidyl-1,1′-bis[4-(*p*-aminophenoxy)phenyl]cyclohexane, was synthesized. The curing kinetics of different epoxy resin–curing agent formulations and thermal stabilities of the cured products were investigated. The overall activation energy for curing is 58.5–136.1 kJ mol^{-1}. The cured products have good thermal stability.

INTRODUCTION

In recent years, epoxy resins containing *N,N,N′,N′*-tetraglycidylmethylene dianiline (TGDDM) have been used extensively in the manufacture of fiber-reinforced structures for aerospace applications. The presence of a greater number of aromatic rings, along with the ether bridge, in a tetrafunctional *N*-glycidyl epoxy resin is thought to enhance both thermal stability and mechanical properties. With this in mind, a tetrafunctional epoxy resin, *N,N,N′,N′*-tetraglycidyl-1,1′-bis[4-(*p*-aminophenoxy)phenyl]cyclohexane (TGBAPC) was prepared. The curing reactions of this resin using different amine curing agents, in presence or absence of a fortifier, and the thermal stabilities of the cured products have been studied.

EXPERIMENTAL

Materials

TGBAPC was prepared from the diamine 1,1′-bis-[4-(*p*-aminophenoxy) phenyl]cyclohexane [1], according to the method of ref. 2. The structure of this resin is shown in Scheme 1.

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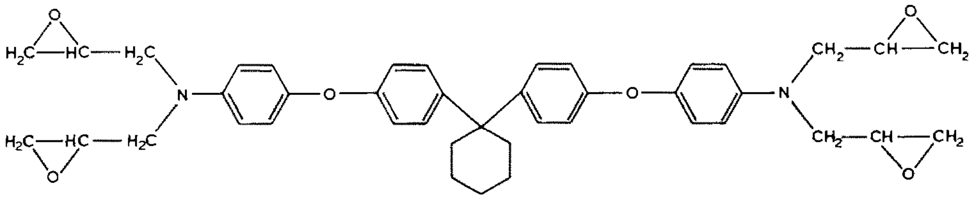

Scheme 1.

The functionality of the resin, having less than 4 epoxide groups per molecule, was 3.54 per formula weight and its epoxy equivalent weight 190 g equiv^{-1}. The number average molecular weight as determined by vapour pressure osmometry was 674.

The epoxy fortifier PGEHA [3,4], is the condensation product of phenyl glycidyl ether (PGE) and 4-hydroxyacetanilide (HA).

All the amine curing agents were laboratory-grade reagents.

Curing procedure

A Du Pont 900 differential scanning calorimeter was used for the dynamic scans, at a heating rate of $10\,^\circ\text{C min}^{-1}$. Prior to scanning, the DSC cell was calibrated with samples of known heat of fusion and melting points. The samples for DSC scans were prepared by mixing the stoichiometric amounts of resin, curing agent and, in some experiments, 20 parts per hundred epoxy fortifier. About 10 mg samples was taken in an aluminium pan, placed in the DSC cell and each scan was run with an empty pan as reference.

The samples left after taking the DSC scans were cured and kept in a previously heated oven (about 200 °C) for about 2h to ensure complete curing. Cured products were powdered and subjected to thermal analysis in a Du Pont 951 thermogravimetric analyser at a heating rate of $10\,^\circ\text{C min}^{-1}$ under a nitrogen atmosphere.

Analysis of DSC and TG scans

The exotherms obtained in the DSC scans were analysed to obtain two basic parameters, the peak height, dH/dt, and the area, a, under the exotherm, and also some characteristic parameter such as the temperature of initiation of curing (T_i) or the peak temperature (T_p). The rate constant k was estimated from the Barrett relation [5] and from this k value kinetic parameters such as activation energy, E_a, and frequency factor, $\ln A$, were derived. The values of E_a and the order of the curing reactions, n, were also calculated from the Freeman–Carroll relation [6]. The two values obtained

TABLE 1

Curing characteristics and kinetic parameters of epoxy–amine systems

Epoxy resin [a]–curing agent system	T_i [b] (°C)	T_p [c] (°C)	E_a^d (kJ mol^{-1})	ln A [d]	n
Epoxy–DDS	170	225	136.1	24.8	0.95
Epoxy–DDS–PGEHA	145	205	111.2	19.4	1.00
Epoxy–DDE	125	160	103.5	23.4	0.85
Epoxy–DDE–PGEHA	95	135	86.7	21.5	0.90
Epoxy–DDM	105	155	85.8	20.8	0.95
Epoxy–DDM–PGEHA	75	130	78.1	18.4	1.10
Epoxy–DETA	65	114	79.3	17.9	1.00
Epoxy–DETA–PGEHA	50	90	58.5	16.5	1.10

[a] Resin, N,N,N',N'-tetraglycidyl-1,1'-bis[4-(p-aminophenoxy)phenyl]cyclohexane; PGEHA, epoxy fortifier; DDS, p,p'-diaminodiphenyl sulfone; DDE, p,p'-diaminodiphenyl ether; DDM, p,p'-diaminodiphenyl methane; DETA, diethylenetriamine.

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

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

[d] Errors in E_a and ln A, ± 2.

for E_a were in good agreement and the average values are reported in Table 1.

TG curves were analysed to give percentage weight loss as a function of temperature. Using Broido's method [7] the activation energy, E_a, of the degradation process was estimated. Integral procedure decomposition temperature (IPDT) values were obtained using the method of Doyle [8].

RESULTS AND DISCUSSION

Some selected DSC curves of epoxy–amine systems are reproduced in Fig. 1. For each of the systems studied, the exothermic transition was observed in a specific temperature range, depending on the curing agent used. The amine curing agents used in this study were p,p'-diaminodiphenyl ether (DDE), p,p'-diaminodiphenyl methane (DDM), p,p'-diamino-di-

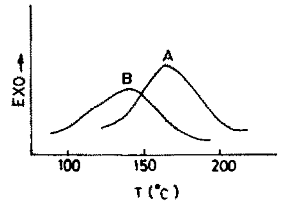

Fig. 1. Dynamic DSC scans at 10 °C min^{-1} for the systems: A, epoxy–DDE; B, epoxy–DDE–PGEHA.

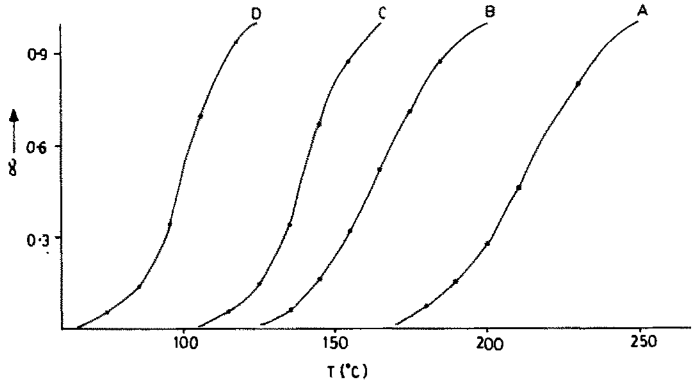

Fig. 2. Plots of fraction converted, α, against temperature (°C) for the systems: A, epoxy–DETA; B, epoxy–DDM; C, epoxy–DDE; D, epoxy–DDS.

phenyl sulfone (DDS) and diethylenetriamine (DETA). Table 1 lists some of the temperature data, viz. the temperatures at which curing reactions started (T_i) and peaked (T_p), along with the activation energy of curing reaction (E_a), frequency factor (ln A) and order of the reaction (n).

The data listed in Table 1 show that the values of T_i and T_p are lowest for the epoxy–DETA system while the highest values are observed for the epoxy–DDS system. The rate of curing is highest for the epoxy–DETA system, the trend for the ease of curing being epoxy–DETA > epoxy–DDM > epoxy–DDE > epoxy–DDS. In Fig. 2 the plots of fraction converted, α, against temperature show that in the more reactive systems the curve shifts towards lower temperature. The ease of curing depends upon the reactivity of the amines, with DETA being the most reactive. Among the aromatic diamines, DDS is the least reactive because of its electron-withdrawing sulfonyl group. A similar trend in T_i and T_p has been observed when *N*,*N*,*N*′,*N*′-tetraglycidyl-2,2-bis-[4-(*p*-aminophenoxy)phenyl]propane (TGBAPP) was cured with the same amines [9].

Incorporation of PGEHA fortifier in the resin–amine systems lowers the cure temperature, an effect attributed to the catalytic action of the hydroxyl group present in the fortifier [10]. Similar behaviour was observed by Schechter et al. [11] in the reaction of epoxide and amine in presence of certain hydrogen donors.

Thermal stability of the cured epoxy systems was assessed from the thermograms. Figure 3 shows the TG thermograms of the systems (A) epoxy–DDS, (B) epoxy–DDS–PGEHA, (C) epoxy–DETA, and (D) epoxy–DETA–PGEHA and indicates that the degradation of amine-cured epoxy systems proceeds in a single step. To investigate the trend in the thermal stability of amine-cured epoxy systems, the TG parameters T_0 (temperature of the onset of decomposition), T_{10} (temperature for 10% weight loss), T_{max} (temperature of maximum rate of degradation), IPDT and

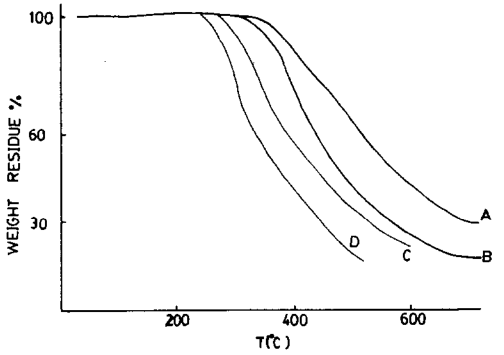

Fig. 3. TG curves of cured epoxy systems in nitrogen atmosphere at a heating rate of 10 °C min^{-1}: A, epoxy–DDS; B, epoxy–DDS–PGEHA; C, epoxy–DETA; D, epoxy–DETA–PGEHA.

activation energy, E_a, of the degradation process were calculated. The data are reported in Table 2 and show that the epoxy resin cured with DDS has the highest thermal stability and that cured with DETA has the lowest. The thermal stability of the cured resin depends on the structure of the curing agent used, with the relative order of thermal stability being epoxy–DDS > epoxy–DDE > epoxy–DDM > epoxy–DETA. In our previous communication [9], a similar trend was observed when a tetrafunctional epoxy resin TGBAPP was cured with the same diamines. Thermal stability of amine-cured TGBAPC resin is higher than that of amine-cured TGBAPP resin, perhaps because the cyclohexane ring in TGBAPC increases the rigidity to the final cured crosslinked structure.

TABLE 2

Temperature characteristics and kinetic parameters for thermal degradation of various epoxy systems

Epoxy resin–curing agent system [a]	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	IPDT [b] (°C)	E_a [c] (kJ mol^{-1})
Epoxy–DDS	345	397	525	655	94.1
Epoxy–DDS–PGEHA	320	372	450	637	75.4
Epoxy–DDE	330	349	399	608	63.2
Epoxy–DDE–PGEHA	305	325	356	576	52.9
Epoxy–DDM	312	332	387	553	58.1
Epoxy–DDM–PGEHA	287	298	354	542	48.7
Epoxy–DETA	278	297	341	527	47.3
Epoxy–DETA–PGEHA	248	275	293	503	31.9

[a] See Table 1 for abbreviations.

[b] IPDT, integral procedure decomposition temperature.

[c] Error, ±2

Table 2 shows that addition of fortifier lowers the thermal stability, and effect associated with early loss of chemically unbonded materials [4].

Even though the epoxy fortifier reduces the thermal stability, it may improve certain mechanical properties [12].

CONCLUSION

The curing of N,N,N',N'-tetraglycidyl-1,1′-bis-[4-(*p*-aminophenoxy) phenyl]cyclohexane (TGBAPC) with amine curing agents obeys first-order kinetics, having an activation energy in the range 58.5–136.1 kJ mol^{-1}. Thermal stability of the cured resin systems depends on the structure of the curing agent used. Activation energies of degradation are 31.9–94.1 kJ mol^{-1}.

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