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STUDIES ON THE KINETICS OF CURING AND THERMAL STABILITY OF A NOVEL TETRAFUNCTIONAL EPOXY RESIN, *N,N,N′,N′*-TETRAGLYCIDYL-2,2-BIS-[4-(*p*-AMINOPHENOXY)-PHENYL]PROPANE, USING VARIOUS AMINE CURING-AGENTS WITH OR WITHOUT FORTIFIER

RASMIKA H. PATEL and RANJAN G. PATEL *
Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120 (India)
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ABSTRACT

A novel tetrafunctional epoxy resin, *N,N,N′,N′*-tetraglycidyl-2,2-bis[4-(*p*-aminophenoxy)phenyl]propane, has been synthesised. The curing kinetics and thermal stability of the cured product have been investigated using various amine curing-agents. The overall activation energy for the curing reaction is observed to be in the range 30.3–126.2 kJ mol^{-1}. The cured products have good thermal stability.

INTRODUCTION

The growing use of composite materials in commercial and military equipment has led to the synthesis of a novel type of epoxy resin, *N,N,N′,N′*-tetraglycidyl-2,2-bis[4-(*p*-aminophenoxy)phenyl]propane. The presence of an aromatic ring along with the ether bridge in the backbone chain of this tetrafunctional resin is reflected in the improved thermal stability and some of the mechanical properties of the cured resin. This investigation was undertaken to provide some information on the stability of this tetrafunctional epoxy resin.

The present paper discusses the curing reaction of the above-mentioned tetraglycidyl resin using various amine curing-agents with or without fortifier. The thermal stabilities of the final cured products are also investigated.

* Author to whom correspondence should be addressed.

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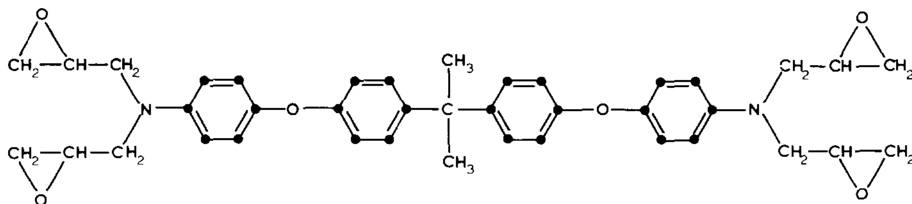
EXPERIMENTAL

Materials

The novel tetrafunctional epoxy resin, *N*,*N*,*N*′,*N*′-tetraglycidyl-2,2-bis[4-(*p*-aminophenoxy)phenyl]propane, was prepared from a diamine, 2,2-bis[4-(*p*-aminophenoxy)phenyl]propane [1], according to the method reported [2] in the literature. The structure of the above-mentioned resin is as shown below.



The functionality of this resin, having less than 4 epoxide groups per molecule, was 3.46 per formula weight. The epoxy equivalent weight was 183 g $equiv^{-1}$. The number-average molecular weight as determined by vapour pressure osmometry was found to be 634.

An epoxy fortifier, PGEHA [3,4], was prepared by condensing phenylglycidyl ether (PGE) and 4-hydroxyacetanilide (HA).

The curing agents, various amines, were laboratory grade reagents.

Curing procedure

A DuPont 900 differential scanning calorimeter was used for the kinetic study of the curing reaction. The instrument was calibrated with samples of known heats of fusion.

The epoxy resin and amines were mixed in the proportions corresponding to one amine proton per epoxy group. The resin and solid diamines were heated with vigorous stirring for 5 min at the required temperature. The mixture was then placed into a vacuum oven for 10 min to remove gaseous bubbles. The void-free mixtures were used for the DSC studies using 5–6 mg samples at a heating rate of $10\,^{\circ}C\ min^{-1}$ and using an empty cell as reference.

The samples remaining in the test tubes were then cured and kept in a previously heated oven (about 200 °C) for about 2 h for complete curing. Cured products were powdered and taken for thermal analysis at a heating rate of $10\,^{\circ}C\ min^{-1}$ in nitrogen atmosphere. A DuPont 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 [5], the rate constant k was estimated. By assuming that the value of k has Arrhenius-type temperature dependence, the kinetic parameters, such as activation energy E and frequency factor $\ln A$, were obtained. The activation energy E and order of the reaction n were determined from the Freeman–Carroll relation [6].

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

RESULTS AND DISCUSSION

In order to investigate the effect of amine structure on the curing reaction and thermal behaviour of cured tetrafunctional epoxy resin, various diamines such as p,p'-diaminodiphenyl ether (DDE), p,p'-diaminodiphenylmethane (DDM), p,p'-diaminodiphenylsulfone (DDS) and one polyamine, diethylenetriamine (DETA), were used as curing agents. The role of the fortifier in the curing reaction and on the thermal stability of the amine-cured epoxy system was also studied. Selected DSC scans are reproduced in Fig. 1. From the characteristic DSC scans, the temperature at which the curing reaction started T_i, and peaked T_p, some kinetic parameters such as activation energy E, frequency factor $\ln A$ and order of curing reaction n were obtained for various epoxy systems and are presented in Table 1.

The data listed in Table 1 show that curing of the resin–DDS system starts at high temperatures (155°C) and peaks at 217°C. The activation energy of this system is highest compared to other resin–amine systems. The peak temperature decreases in the order DDS > DDE > DDM > DETA.

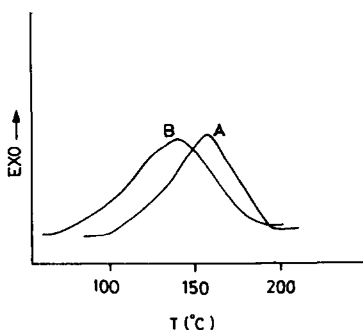


Fig. 1. Dynamic DSC scans at 10°C min^{-1} for the systems: A, epoxy–DDM; and B, epoxy–DDM–PGEHA.

TABLE 1

Curing characteristics and kinetic parameters of epoxy–amine systems

Epoxy [a] resin–curing agent system	T_i [b] (°C)	T_p [c] (°C)	Barrett relation		Freeman–Carroll relation	
			E (kJ mol^{-1}) [d]	ln A [d]	E (kJ mol^{-1}) [d]	n
Epoxy–DDS	155	217	126.2	23.4	125.1	0.95
Epoxy–DDS–PGEHA	140	195	98.5	19.2	99.2	1.00
Epoxy–DDE	120	155	96.1	20.1	92.5	1.21
Epoxy–DDE–PGEHA	85	125	84.4	18.5	82.3	1.00
Epoxy–DDM	100	150	79.6	17.2	72.6	0.90
Epoxy–DDM–PGEHA	60	135	63.2	14.3	68.1	1.10
Epoxy–DETA	55	95	80.5	16.9	85.1	0.85
Epoxy–DETA–PGEHA	45	85	30.3	12.1	36.3	0.90

[a] Resin, N,N,N',N'-tetraglycidyl-2,2-bis[4-(p-aminophenoxy)phenyl]propane; PGEHA, epoxy fortifier; DDS, p,p'-diaminodiphenylsulfone; DDE, p,p'-diaminodiphenyl ether; DDM, p,p'-diaminodiphyenylmethane; 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 and ln A, ± 2.

The activation energy values also follow the same order. Incorporation of fortifier in the resin–amine system lowers the peak temperature; the activation energy values of these systems also decrease. The presence of the hydroxyl group in the structure of PGEHA fortifier is responsible for the lowering in peak temperature and activation energy value and the increase in the reactivity of the curing reaction. The plot of fraction conversion (α) against temperature, see Fig. 2, reveals that the more reactive systems tend to shift the curve towards lower temperatures.

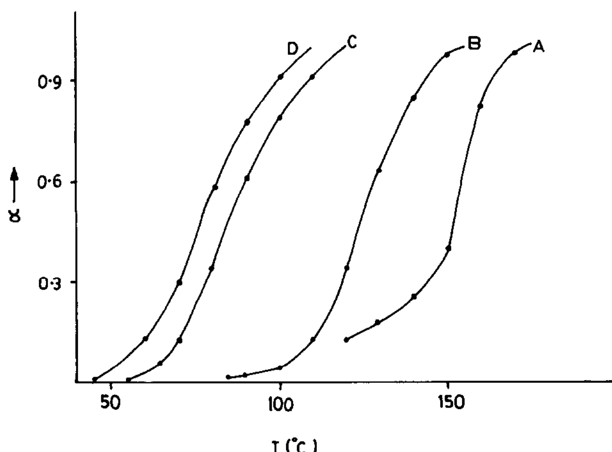


Fig. 2. Plots of fraction conversion (α) against temperature (°C) for the systems: A, epoxy–DDE; B, epoxy–DDE–PGEHA; C, epoxy–DETA; D, epoxy–DETA–PGEHA.

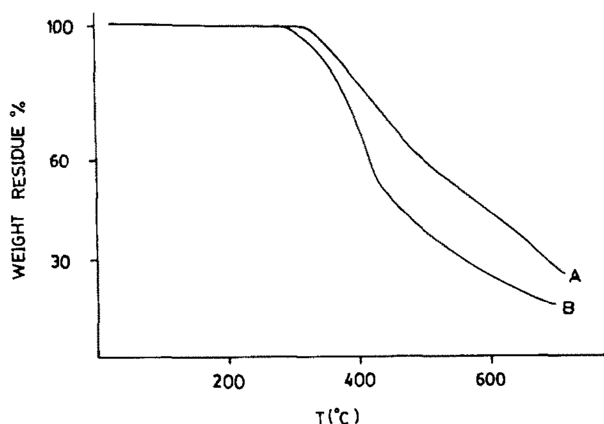


Fig. 3. TG curves for cured epoxy systems in a nitrogen atmosphere at a heating rate 10 °C min^{-1}: A, epoxy–DDS; B, epoxy–DDS–PGEHA.

In order to determine the thermal stability trend, TG parameters such as T_0 (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 were calculated. IPDT represents the overall nature of the TG thermogram over the entire range of the TGA curve.

Figure 3 shows the nature of some selected thermograms. Accepting T_0, T_{10}, T_{max} and IPDT as the criteria of relative thermal stability, resin cured with DDS can be ranked as thermally more stable than resin cured with other amines.

TABLE 2

Temperature characateristics 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 [c] (kJ mol^{-1})
Epoxy–DDS	325	375	425	602	84.5
Epoxy–DDS–PGEHA	275	348	409	598	71.2
Epoxy–DDE	300	365	400	573	46.8
Epoxy–DDE–PGEHA	250	331	391	568	38.1
Epoxy–DDM	275	355	387	539	59.3
Epoxy–DDM–PGEHA	225	323	349	512	42.7
Epoxy–DETA	267	312	350	526	30.9
Epoxy–DETA–PGEHA	250	298	339	493	23.5

[a] See Table 1 for the meanings of the abbreviations for the epoxy resin–curing agent systems.
[b] IPDT, integral procedure decomposition temperature.
[c] Error, ±2.

It has been observed that the thermal stability of amine-cured epoxy systems is most affected by the structure of the amine used as curing agent. In our case, the resin structure is the same in all the products. The variation in thermal stability will, therefore, be mainly due to differences in the amine structure. The order of thermal stability is epoxy–DDS > epoxy–DDE > epoxy–DDM > epoxy–DETA.

Addition of fortifier to the epoxy–amine system decreases the thermal stability. Table 2 shows that fortifier-incorporated systems are thermally less stable when compared with the same system without fortifier. This may be due to the early loss of chemically unbonded material [4]. Incorporation of fortifier in the eopxy–amine systems was found to improve mechanical properties [9] and lower the curing temperature. Thus, even though the epoxy fortifier decreases the thermal stability, certain mechanical properties can be improved.

CONCLUSION

The curing reaction of the epoxy–amine systems follows first-order kinetics, having an activation energy in the range 30.3–126.2 kJ mol^{-1}. The thermal stability of the cured epoxy system depends on the structure of the curing agent used. The activation energy of the thermal degradation is in the range 25.2–84.5 kJ mol^{-1}.

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