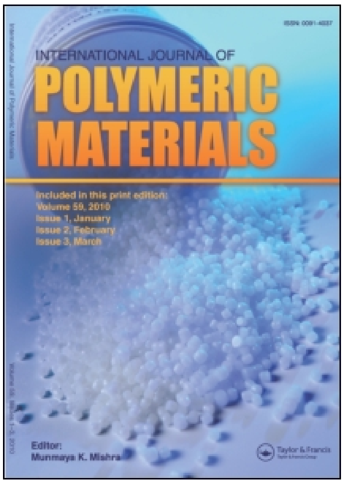

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Curing Kinetics, Thermal Stability and the Glass Fibre Reinforced Composites of Novel Tetrafunctional Epoxy Resin

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Curing Kinetics, Thermal Stability and the Glass Fibre Reinforced Composites of Novel Tetrafunctional Epoxy Resin

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The curing reactions of the epoxy resin 2,7-bis(4-*N*, *N*-diglycidyl amino phenoxy) naphthalene using diamino diphenyl sulfone (DDS), diamino diphenyl methane (DDM), triethylene tetra amine (TETA) and diethylene triamine (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 system is observed in the range 67.4–121.5 KJ 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°C min^{-1}. The thermal degradation reactions were found to proceed in a single step having an activation energy in the range 41.84–71.84 KJ mol^{-1}. The data were utilized in fabricating the glass-fibre reinforced epoxy composites. Glass fibre reinforced composites were fabricated using the matrix resin DGEBA and the above tetrafunctional epoxy resin in the ratio 80:20 using different curing agents and evaluated for their physical, mechanical, chemical and electrical properties.

Keywords: Epoxy resin; mechanical property; kinetics; thermal stability; chemical resistance

INTRODUCTION

Epoxy resins have gained increasing importance due to their wide range of applications. The earlier resin diglycidyl ether of bisphenol-A, which

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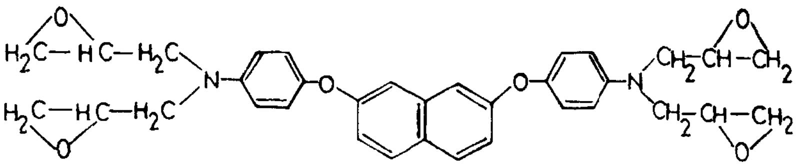
is suitable for many applications but for high performance applications, resins with higher functionality are essential. The kinetics of curing reactions of epoxy resins with amines have been studied by several workers [1 – 4]. However, no report has mentioned on the study of curing reactions and thermal stability of 2,7-bis(4-*N*,*N*-diglycidyl amino phenoxy)naphthalene resin cured with different amines as curing agents.

The present paper discusses the curing kinetics and thermal stability of the above mentioned epoxy resin using various amines as curing agents. The data were utilized in fabricating glass fibre reinforced epoxy composites and the composites were evaluated for their physical properties, *e.g.*, density of composite, %resin content, %void content, mechanical properties, *e.g.*, flexural strength, ILSS, shore-D hardness and electrical properties, *e.g.*, dielectrical constant loss tangent, dielectric loss, resistivity and resistance to chemical reagents.

EXPERIMENTAL

Materials

The resin 2,7-bis(4-*N*,*N*-diglycidyl amino phenoxy)naphthalene was prepared from a diamine 2,7-bis(4-amino phenoxy)naphthalene according to the method reported in literature [5, 6]. The structure of the above mentioned resin is as shown below.



The epoxy equivalent weight estimated by the hydrochlorination method [7] was found to be 131.5 g.equi^{-1}. The resin was also characterized by Nicolet 400-D FTIR spectrophotometer. IR spectrum shows absorption bands at 3050 and 1190 cm^{-1} which are the characteristic of the aromatic C—H stretching frequency [8]. The peak at 1175 cm^{-1} is due to C—N stretching frequency. The absorption bands in the regions of 1260, 920 and 855 cm^{-1} are due to terminal epoxy groups.

Curing Procedure

A Du Pont 900 differential scanning calorimeter was used for the kinetic study of the curing reaction. The instrument was calibrated with sample of known heat of fusion.

The epoxy resin and amines were mixed in the proportion 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 (5–6 mg) were used for the DSC studies at a heating rate of 10°C min^{-1} using and empty cell as reference.

The samples remaining in the test tubes were then cured 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 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 analyzed 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 [9], the rate constant K was estimated. By assuming that the value of K was 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 [10].

TG curves were analysed to give percentage weight loss as a function of temperature. Broido's method [11] was used to obtain the activation energy E of the degradation process. Using Doyle's method [12], IPDT values (integral procedure decomposition temperature) were obtained.

Composite Fabrication

Laminates were prepared using epoxy compatible, 0.254 mm (10 mil), plain weaved E-type glass cloth. Ten plies of 30.5 × 30.5 cm glass fabric were uniformly coated with the matrix resin diglycidyl ether of bisphenol-A (DGEBA) and 2,7-bis(4-*N*,*N*-diglycidyl amino phenoxy)-naphathalene in (80:20) proportion respectively using different amine as curing agent by hand lay up technique and dried in air for 20 min. The dried prepregs were stacked together between two mild steel plates having teflon sheets as mould release agent and then placed between the plates at a press. The temperature was held at 100°C for about 15 min. A pressure of 1.72 mpa (250 psi) was then applied and the temperature was maintained at 150°C for 1.5 h and at 180°C for 1 h. The mould was allowed to cool and the laminate was removed and cut into specimens for testing as per ASTM standards.

Characterization of Composites

All the physico-chemical measurements for characterizing the laminates were made at room temperature (~30°C). Resistance to chemical reagents was estimated according to ASTM D 543–67 (1978). Flexural and interlaminar shear strength (ILSS) were measured on a universal Instron Testing Machine Model 1193 according to the ASTM methods D 790–71 and D 2344–76, respectively. Shore-D hardness of the composite samples were measured on Shore-D Hardness tester TSE testing Machine. In order to study the dielectrical properties of laminated samples, the resistance was measured by a Hewlett packard 4329-A High Resistance Meter at an applied AC voltage of 250 V. The dielectric constant and the loss tangent (tan δ) were determined from the measured values of capacitance and dissipation factor on a digital LCR meter at a frequency of 1 KHz.

Density, resin content and void-content were determined and listed in Table III.

RESULTS AND DISCUSSION

The curing agents used in the present study were DDM, DDS, TETA and DETA. From the characteristic DSC scans, the temperatures at which curing reaction started (T_i), peaked (T_p), and completed (T_f) were noted. The data reveal that the value of T_i, T_p and T_f depends upon the curing agent. Considering the type of curing agents used, the

TABLE I Kinetic parameters of epoxy-amine system

System	*Borchardt Daniels relation*			*Freemann–Carroll relation*		*Barrett relation*		T_i [a]	T_p [b]	T_f [c]
	$E \pm 2$ *KJ/mol*	$\ln Z \pm 2$ min^{-1}	*n*	$E \pm 2$ *KJ/mol*	*n*	$E \pm 2$ *KJ/mol*	$\ln Z \pm 2$ min^{-1}	(°C)	(°C)	(°C)
Resin + DDS	91.6	13.07	4.06	89.0	4.01	89.2	11.05	145	193.30	215
Resin + DDM	88.5	12.48	3.37	82.5	3.11	82.3	12.04	132	180.87	203
Resin + TETA	84.0	8.96	2.64	79.8	2.42	79.3	7.98	42	102.00	178
Resin + DETA	81.0	8.72	2.37	76.4	2.27	76.1	7.92	42	96.26	172
Resin + DGEBA (20:80) + DDS	121.5	12.13	2.62	118.2	2.49	118.7	12.01	149	223.55	274
Resin + DGEBA (20:80) + DDM	67.4	7.98	1.62	61.3	1.57	61.1	7.88	64	147.68	219

Resin, 2,7-bis(4-*N*,*N*-diglycidyl aminophenoxy)naphthalene.
DGEBA, Diglycidyl ether of bisphenol-A.
DDS, *p*,*p*′-Diaminodiphenyl sulphone.
DDM, *p*,*p*′-Diaminodiphenyl methane.
TETA, Triethylene tetramine.
DETA, Diethylene triamine.

[a] T_i Temperature (°C) of the onset of curing.

[b] T_p Temperature (°C) of the peak of the exotherm.

[c] T_f Temperature (°C) of the completion of curing.

TABLE II Temperature characteristic and kinetic parameters of cured epoxy resins

System	T_0 (°C)	T_{10} (°C)	T_{30} (°C)	T_{max} (°C)	*IPDT* (°C)	$E \pm 2$ *KJ Mol*$^{-1}$
Resin + DDS	250.0	312.5	457.5	570.0	587.75	71.84
Resin + DDM	242.5	300	435	565.0	581.72	63.14
Resin + TETA	237.5	300	387.5	556.0	575.07	51.70
Resin + DETA	212.5	260	375.0	535.0	522.25	41.84
Resin + DGEBA (20:80) + DDS	275	360	387.5	598.6	595.48	71.38
Resin + DGEBA (20:80) + DDM	262.5	302.5	355	575.0	598.16	66.81

See Table I for the meaning of the abbreviations for the systems.
IPDT: Integral procedure decomposition temperature.

TABLE III Physical and Mechanical properties of glass cloth reinforced epoxy laminates

System	*Flexural strength (Kg/cm*^{2}*)*	*ILSS (Kg/cm*^{2}*)*	*Shore-D hardness*	*Density (g/cm*$^{-3}$*)*	*Resin content (%v/v)*	*Void content (%v/v)*
Resin + DGEBA + DDS	3.325	117.65	94	1.81	30.9	2.86
Resin + DGEBA + DDM	5.394	149.42	96	1.72	31.0	2.95
Resin + DGEBA + TETA	2.860	108.42	90	1.73	31.2	2.92
Resin + DGEBA + DETA	2.621	102.26	87	1.69	30.8	2.94

See Table I for the meaning of the abbreviations for the systems.

values are lowest for DETA and highest for DDS. This indicates that the rate of curing for resin-DETA system is highest among the systems used. The trend revealed for the ease of curing for the epoxy system is as follows.

resin-DETA > resin-TETA > resin-DDM > resin-DDS

Aliphatic amines DETA and TETA has highest reactivity, while DDS has the lowest reactivity, because of electron withdrawing sulfonyl group. DSC curves are reproduced in Figure 1. In the mixed system also the rate of curing for the resin + DGEBA + DDS system is lowest and highest for resin + DGEBA + DDM systems.

The kinetic parameters such as activation energy (*E*), order of reaction (*n*) and preexponential factor determined by analysing the

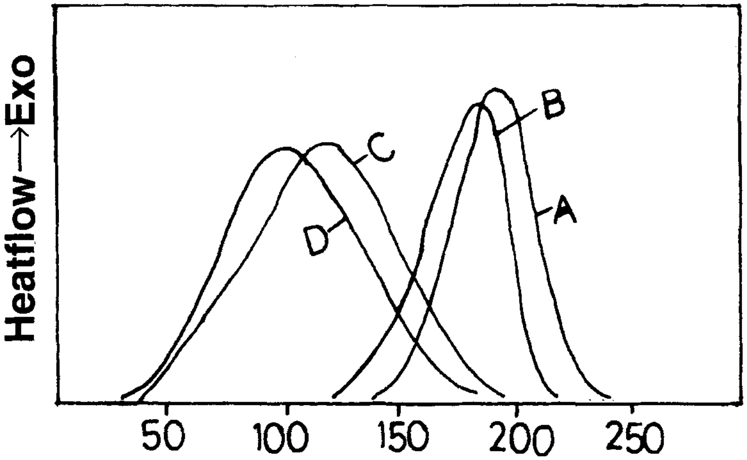


FIGURE 1 Dynamic DSC scans at 10°C.min^{-1} for the systems: A: Resin + DDS, B: Resin + DDM, C: Resin + TETA, D: Resin + DETA.

data of Borchardt–Daniel relation [13], Freeman–Carroll relation [10], and Barrett relation [9] are presented in Table I.

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_{30} (temperature for 30% weight loss), T_{max} (temperature of maximum rate of decomposition), IPDT (Integral procedural decomposition temperature), and the activation energy (E), of the degradation process were calculated and presented in Table II. 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 [14]. 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 agents.

The trend of the thermal stability for the amine cured epoxy resins as shown in Table II, is

resin-DDS > resin-DDM > resin-TETA > resin-DETA

It is deduced from the results that the epoxy resin cured by DDS is more thermally stable than that cured with DDM.

This may be ascribed to greater heat resistance character of the sulphur linkage refering to a carbon linkage [15]. The lowest stability observed in case of DETA and TETA cured resin systems is due to a purely aliphatic structure of DETA and TETA in the cured product. TG curves are reproduced in Figure 2.

Mechanical Properties

Examination of the data furnished in Table III shows that the mechanical properties like flexural strength, and interlaminar shear strength (ILSS), of the laminated samples are affected by the nature of the curing agent. The mechanical properties of the system resin + D-GEBA + DDM are superior compared to other systems. The increased flexural and interlaminar shear strength indicate that in the system resin + DGEBA + DDM there is increased interfacial bonding between the fibre and the matrix resin. This is a critical property in composites, Due to the aromatic structure in the

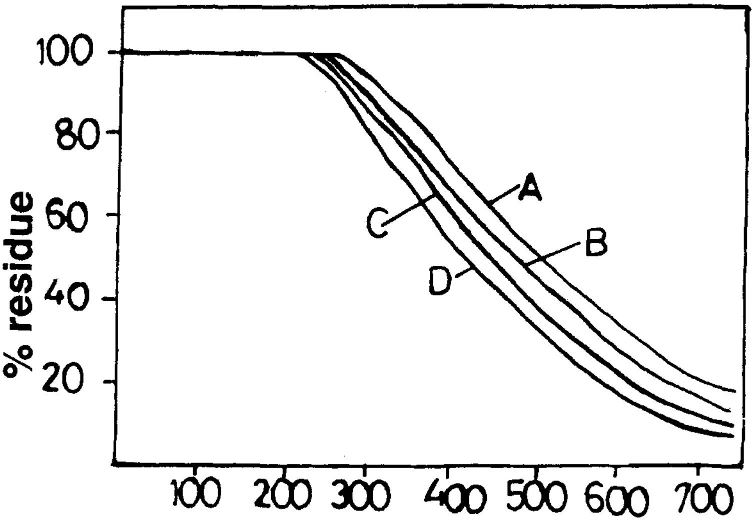


FIGURE 2 TG curves for cured epoxy systems in a nitrogen atmosphere at a heating rate at 10°C.min^{-1} for the systems: A: Resin + DDS, B: Resin + DDM, C: Resin + TETA, D: Resin + DETA.

backbone, the diamines like DDM and DDS impart better rigidity to the finally crosslinked network and hence they yield the composites with better mechanical properties. Under identical curing conditions, the more reactive a material, the greater will be its final degree of conversion [16], resulting in a tightly crosslinked network. The reactivity of DDM is higher compared to DDS and hence the mechanical properties of the system (resin + DGEBA + DDM) are superior to the system (resin + DGEBA + DDS). Even though DETA and TETA are highly reactive compared to DDM and DDS, the purely aliphatic nature of DETA and TETA are responsible for the least values of flexural and ILSS [17].

Chemical Resistance

Examination of the glass fibre reinforced composites showed that these composites had excellent chemical resistance properties. The composites specimens were dipped in water, 20% sodium hydroxide, 20% hydrochloric acid, and methyl ethyl ketone for 7 days. After 7 days their physical appearance was checked. Neither a loss in gloss nor a change in dimensions was observed. Data on percentage weight change showed that only about 2% weight change was observed in each case.

Dielectric Properties

The dielectric data for all the glass epoxy composites are given in Table IV. The data reveal that GFRC behave as a very good insulating materials.

TABLE IV Dielectric properties of glass cloth reinforced epoxy laminates

System	*Resistance* ($\Omega \times 10^{-15}$)	*Dissipation factor* (*tan* δ)	*Dielectric loss* (ε')	*Dielectric Constant* (ε'')
Resin + DGEBA + DDS	1.210	0.409	1.312	3.0186
Resin + DGEBA + DDM	0.960	0.402	1.210	2.917
Resin + DGEBA + TETA	0.710	0.406	1.232	2.823
Resin + DGEBA + DETA	0.621	0.401	1.1754	2.762

See Table I for the meaning of the abbreviations for the systems.

CONCLUSION

The curing reaction of the epoxy resin amine system follows Arrhenius type kinetics with an activation energy in the range of 67.4–121.5 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 41.89–71.84 KJ mol^{-1}. The mechanical properties depend on the structure of the curing agents.

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