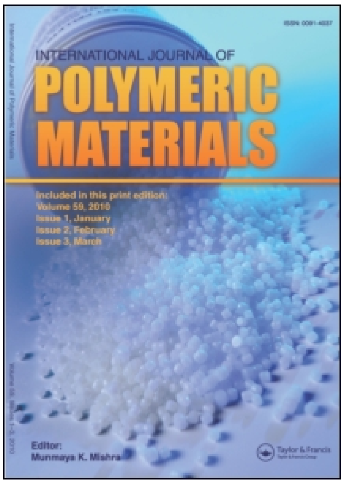

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Properties of Glass-fibre Reinforced Epoxy Composites of Tetrafunctional Epoxy Resin

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The curing reaction of epoxy resin 1,1,2,2-tetrakis(4-glycidyloxyphenyl) ethane(TKGOPE) with different aliphatic and aromatic amines has been studied by differential scanning calorimetry (DSC). The thermal stability of the cured products was also studied by thermogravimetric analysis (TGA). Using these data, different glass fibre reinforced epoxy composites were fabricated and their mechanical and electrical properties and their resistance to chemicals were studied. Activation energies of curing reactions is in the range of 80–187.27 KJ·mol^{-1}. The cured products have good thermal stability, the composites have good mechanical strength, electrical insulation properties and chemical resistance.

Keywords: TKGOPE resin; DGEBA; composites; properties

INTRODUCTION

Epoxy resins are found very useful in casting, coating, moulding, electric component, high strength composites and hardware applications for aircraft missiles and space structures due to the formation of three dimentional infusible, hard thermoset network via curing process [1–4]. Our previous communications describes the kinetic studies and glass reinforced composites of various epoxy resins [5–8].

The present paper discusses the curing kinetics of TKGOPE resin using various amines as curing agent. The curing of said resin in

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*Corresponding author.

presence of conventional epoxy resin DGEBA in ratio 20:80 has been also discussed using DDM and DDS curing agents. The thermal stabilities of all the final cured products are investigated. Glass fibre reinforced composite of resin TKGOPE in presence of DGEBA, (ratio 20:80) were prepared using DETA, TETA, DDM and DDS as curing agent. The fabricated composites were evaluated for their mechanical strengths, electrical insulation properties and resistance to chemicals.

EXPERIMENTAL

Materials

Commercial grade phenol and epichlorohidrine were purified by distillation (b.p. 180 and 115–116°C respectively), sodium hydroxide, concentrated HCl and glyoxal used were of laboratory grade.

A conventional epoxy resin DGEBA was obtained (epoxy equivalent weight = 190 gm·eq^{-1}) from Synpol Pvt. Ltd., Ahmedabad.

The curing agents used were diethyl triamine (DETA), triethyltetramine (TETA), *p,p'*-diamino diphenyl methane (DDM) and *p,p'*-diamino diphenyl sulfone (DDS) of laboratory grade.

Synthesis of Resin

The resin 1,1,2,2-tetrakis(4-glycidyloxy phenyl)ethane (TKGOPE) was synthesized by the process reported in literature [9]. The structure of resin is shown in Figure 1.

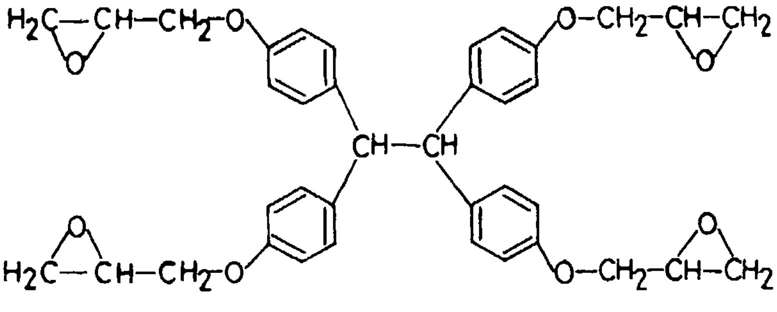

FIGURE 1 1,1,2,2-Tetrakis(4-glycidyloxy phenyl)ethane (TKGOPE).

Characterization of the Resin

The Epoxy Equivalent Weight (EEW) of resin was found to be 166 gm·eq^{-1}. The intrinsic viscosity in DMF measured by Ubbelohde viscometer at 30°C was observed to be about 0.042 dl g^{-1}.

The resin was characterized by Nicolet-400 D FT-IR spectrophotometer. Figure 2 shows a broad band at 3460 cm^{-1} due to the —OH group. The band at 3040 cm^{-1} and 1190 cm^{-1} due to aromatic C—H vibration, bands at 2930 cm^{-1} and 2880 cm^{-1} due to ether methylene C—H vibration, bands at 1600 cm^{-1} and 1510 cm^{-1} due to the presence of phenyl rings. The bands 1260, 920 and 840 cm^{-1} are due to the presence of terminal epoxy groups and band 760 cm^{-1} is due to methylene group.

Fabrication of Composites

Formulation described in Table III were dissolved in acetone and were applied on (10 × 10) cm^2 pieces of woven glass-fibre cloth (an epoxy compatible, 10 mil, plain woven E type, 10 plies) by hand lay up technique. The impregnated plies were kept in an oven heated to 60°C for about 20 min. for evaporation of solvent. The plies were than

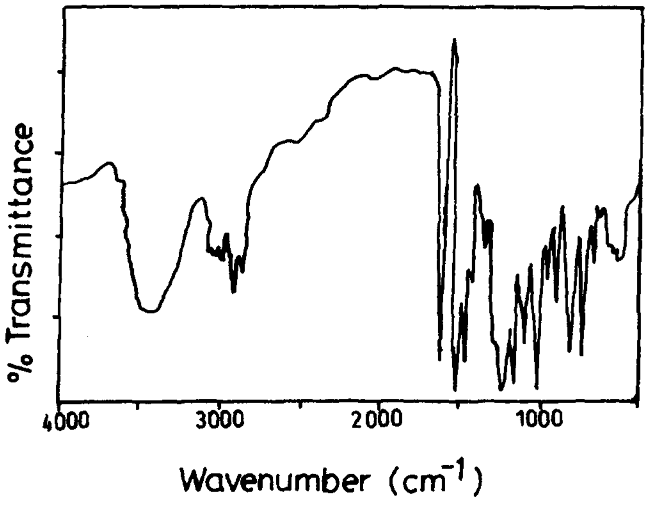

FIGURE 2 IR spectra of TKGOPE resin.

stacked together, put between teflon coated glass cloth, placed between flat plates for compression moulding. Temperature was maintained at 100°C for about 30 min. Pressure of about 1.72×10^4 kPa was applied temperature of mould was maintained 150°C for 1 1/2 h and 180°C for 1 h. After cooling down the mould to room temperature the composites were taken out and cut to get required specimens for evaluation as per ASTM standards for testing.

Measurements

Differential Scanning Calorimetry (DSC) scans were obtained using DuPont 910 DSC module connected with a DuPont 9900 thermal analyzer under nitrogen atmosphere at a heating rate of 10°C min^{-1} using an empty cell as reference. Thermal gravimetric analysis (TGA) of the cured epoxy resins were performed on DuPont 951 thermogravimetric analyzer connected with a DuPont 990 thermal analyzer in static air at a heating rate of 10°C min^{-1}.

Flexural and interlaminar shear strength of composites were determined according to ASTM D-790-71 and D-2344-76, respectively. Shore D hardness of composites were measured using a Shore D hardness tester TSE testing machine according to ASTM D-785.

The dielectric properties of composites (dielectric constant and the loss factor) were determined from the measured value of capacitance and dissipation factor on Digital LCR meter. Resistance to electric current was measured using Hewlett Packard 4329-A high resistance meter at applied voltage of 250 V.

Resistance to various chemicals was determined according to ASTM D-543-67.

RESULTS AND DISCUSSION

Some selected DSC curves at heating rate 10°C min^{-1} are shown in Figure 3. Characteristic behaviour of curing such as the temperature at which curing reaction started (T_i), peak temperature (T_p), complete cure temperature (T_f), activation energy of curing reaction (E_a), order of reaction (n) and frequency factor (ln A) are listed in Table I. The values of activation energy obtained from Barrett [10] and Freeman-

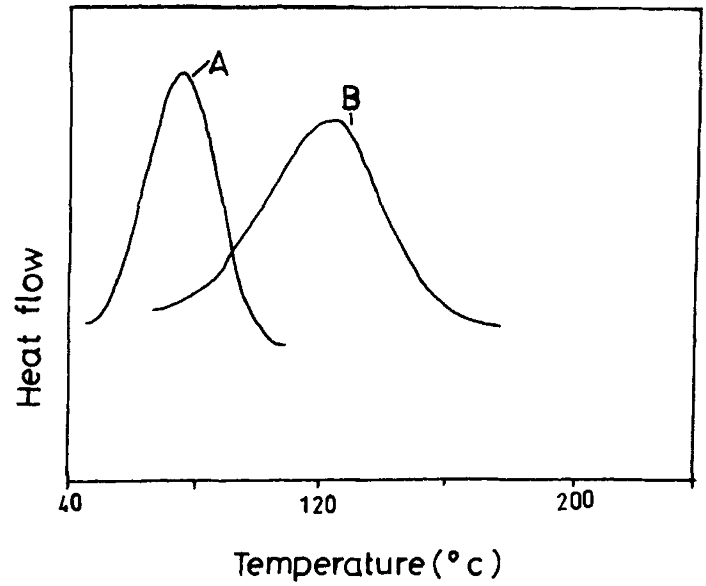

FIGURE 3 Differential scanning calorimetry curves (A) TKGOPE-DETA (B) TKGOPE-DDM.

TABLE I Curing characteristics and kinetic parameters of epoxy curing agents system

Epoxy systems	*Ratio*	*Curing agent*	T_i	T_p	T_f	*Berret relation*		*Freeman-Carrol relation*	
						E_a $KJmol^{-1}$	*ln A*	E_a $KJmol^{-1}$	*n*
TKGOPE	–	DETA	46	76	109	160	25.3	166.7	2.5
TKGOPE	–	TETA	49	77	108	124.2	14.96	121.69	2.8
TKGOPE	–	DDM	53	122	172	106.4	14.0	108.6	2.4
TKGOPE	–	DDS	135	183	135	169	18.42	168.2	3.0
TKGOPE + DGEBA	20:80	DDM	75	148	210	77.5	11.5	71.52	1.0
TKGOPE + DGEBA	20:80	DDS	177	216	250	183	18.4	187.28	2.0

TKGOPE = 1,1,2,2-Tetrakis (4-glycidyloxy phenyl)ethane, DETA = Diethyltriamine, TETA = Triethylene tetraamine, DDM = 4,4′-Diamino diphenyl methane, DDS = 4,4′-Diamino diphenyl sulfone.

Carrol [11] relation are nearly same and range within 80 to 187.28 KJ·mol^{-1} .

The thermal stabilities of cured epoxy systems are shown in Table II. In order to obtain clear picture of degradation process, temperature

TABLE II Temperature characteristics of cured epoxy resins and kinetic parameters for thermal decomposition using Doyle's and Broido's method

Epoxy systems	*Ratio*	*Curing Agent*	T_0	T_{10}	T_{max}	*IPDT* °*C*	*Ea* *KJmol*$^{-1}$	
TKGOPE		DETA	225	307.5	500	497.6	50.57	65.5
TKGOPE	–	TETA	225	307.5	500	504.1	52.3	53.38
TKGOPE	–	DDM	175	300	475	526	34.32	68.6
TKGOPE	–	DDS	200	300	525	522.6	36.6	61.0
TKGOPE + DGEBA	20:80	DDM	250	352.5	475	521.8	45.7	76.26
TKGOPE + DGEBA	20:80	DDS	237.5	307.5	475	529.3	52.29	61.01

TKGOPE = 1,1,2,2-Tetrakis(4-glycidyloxy phenyl)ethane,
DETA = Diethyl triamine, TETA = Triethylene tetraamine.
DDM = 4, 4'-Diamino diphenyl methane, DDS = 4, 4'-Diamino diphenyl sulfone.

T_0 (Temperature on set of curing reaction), T_{10} (temperature for 10% weight loss) and T_{max} (Temperature of maximum rate of degradation), IPDT [13] (Integral Procedure Decomposition Temperature) and activation energy (E_a) [12] of decomposition process are reported in Table II. Nature of some selected thermograms are shown in Figure 4. They were found to proceed in two steps.

The results of mechanical properties like flexural strength, inter laminar shear strength and shore D hardness of epoxy cured systems are shown in Table III. The data show that the mechanical properties are greatly affected by the curing agent used. Aromatic amines DDM and DDS gives better mechanical properties than the aliphatic amines DETA and TETA due to the aromatic character of the curing agents. Further more the DDS cured epoxy system shows better properties compared to DDM that may be due to presence of the rigid SO_2-linkage present in DDS which imparts better rigidity to the finally crosslinked structure.

The chemical resistance tests of composite specimens to various chemical reagents like acetone, water, 20% NaOH, and 20% HCl were performed by dipping the specimens into the reagents for 7 days. Physical properties like discoloration, loss in gloss, change in dimensions were examined. No particular change was observed in discolouration, change in dimensions and loss in gloss but increase in weight of the samples was observed. The weight gain for every case is in the range of 1–4%.

Dielectric properties like resistance to current and dielectric loss factor (tan δ) of the composites are shown in Table III. The data shows good insulation properties of composites.

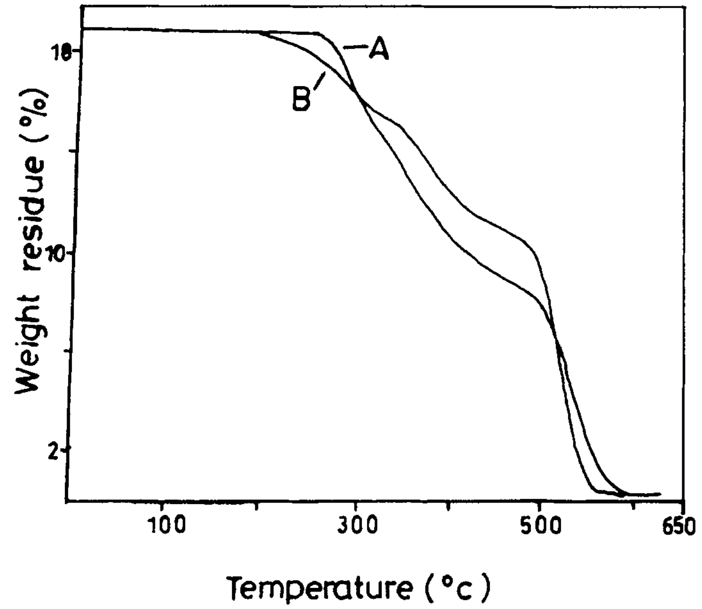

FIGURE 4 TG thermograms at 10°C $\min^{-1}$ (A) TKGOPE-DETA (B) TKGOPE-DDM.

TABLE III Mechanical and dielectric properties of glass fibre reinforced composites

Epoxy systems	*Mass ratio*	*Curing agent*	*Flexural strength ($Kg.cm^{-2}$)*	*ILSS ($Kg.cm^{-2}$)*	*Shore D*	*Resistance Ohm*	*tan δ*
TKGOPE+DGEBA	20:80	DETA	2328	114.8	92	0.15×10^{11}	0.655
TKGOPE+DGEBA	20:80	TETA	2586	115.3	90	0.52×10^{11}	0.404
TKGOPE+DGEBA	20:80	DDM	4106	135.0	95	0.6×10^{13}	0.433
TKGOPE+DGEBA	20:80	DDS	5520	180.0	98	2.8×10^{14}	0.655

TKGOPE = 1,1,2,2-Tetrakis(4-glycidyloxy phenyl) ethane,
DETA = Diethyl triamine, TETA = Triethylene tetraamine,
DDM = 4,4′-Diamino diphenyl methane, DDS = 4, 4′-Diamino diphenyl sulfone.

CONCLUSIONS

DSC cure kinetics of an epoxy-amine system follows Arrhenius type kinetic with activation energy in the range of 80 – 187.28 KJ·mol^{-1}.

The mechanical properties such as flexural strength, inter laminar shear strength and shore D of glass fibre reinforced composites depends on the structure of the curing agents. All composites behaved as very good insulating materials. The epoxy-DDS system gives better mechanical properties than the epoxy-DDM system.

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