

Glass Fiber-Reinforced Composites of Diglycidyl Ether of 2,7-Dihydroxy Naphthalene

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ABSTRACT: The curing reactions of epoxy resin diglycidyl ether of 2,7-dihydroxy naphthalene (DGEDHN) with different aliphatic and aromatic amines have 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 fiber-reinforced composites were fabricated, and their mechanical, electrical properties and resistance to chemicals were studied. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1345–1349, 2000

Key words: diglycidyl ether of 2,7-dihydroxy naphthalene; curing; composite

INTRODUCTION

In the recent history of polymers, epoxy resins have gained increasing importance due to their wide range of applications in casting, coating, moulding, electric components, and hardware applications, for aircraft missiles and space structures due to the formation of a three-dimensional infusible, hard, thermoset network via the curing process.^{1–4}

In the present article, we have synthesized diglycidyl ether of 2,7-dihydroxy naphthalene (DGEDHN). The curing kinetics of resin DGEDHN using various amines as the curing agent have been studied. The curing of said resin in the presence of conventional epoxy resin DGEBA in the ratio of 20 : 80 has been also discussed using *p,p'*-diaminodiphenyl methane (DDM) and *p,p'*-diamino diphenyl sulfone (DDS) curing agents. The thermal stabilities of all the final cured products are investigated. Glass-fiber-reinforced composites of resin DGEDHN in presence of DGEBA in the ratio of 20 : 80 were pre-

pared using diethyl triamine (DETA), triethyl tetramine (TETA), DDM, and DDS as curing agents. The fabricated composites were evaluated for their mechanical strengths, electrical insulation properties, and their resistance to various chemicals.

EXPERIMENTAL

Materials

Commercial-grade 2,7-dihydroxy naphthalene and epichlorohydrine (bp 115–116°C) were used. The sodium hydroxide used was of laboratory grade.

A conventional epoxy resin DGEBA was obtained (EEW, 190 g eq⁻¹) from Synpol Pvt. Ltd., Ahmedabad.

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

Synthesis of Resin

The resin diglycidylether of 2,7-dihydroxy naphthalene (DGEDHN) was synthesized by treating

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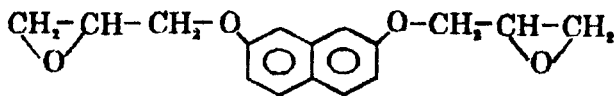


Figure 1 Diglycidyl ether of dihydroxy naphthalene (DGEDHN).

2,7-dihydroxy naphthalene (20 g, 0.125 mol) with epichlorohydrine (115 g, 1.25 mol) at 110°C for 2 h. The structure of resin is shown in Figure 1.

Characterization of the Resin

The epoxy equivalent weight (EEW) of the resin was found to be 145 g eq⁻¹. The intrinsic viscosity in dimethylformamide (DMF) measured by Ubbelohde viscometer at 30°C was observed to be about 0.131 dL g⁻¹.

The resin was characterized by Nicolet-400D FTIR spectrophotometer. The infrared (IR) spectra showed a band at 3460 cm⁻¹ due to the hydroxy group, bands at 3040 and 3100 cm⁻¹ due to aromatic C—H stretching, at 2900 and 2930 cm⁻¹ due to ether methylene linkage, at 1510 and 1600 cm⁻¹ due to aromatic moiety, and at 1260, 900, and 840 cm⁻¹ due to terminal epoxy groups.

Fabrication of Composite

Formulations (described in Table III) were dissolved in acetone and were applied on 10 × 10 cm² pieces of woven glass-fiber cloth (an epoxy-compatible, 10 mil; plain-woven E type, 10 plies) by a

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 then stacked together, put between Teflon-coated glass cloth, and placed between flat plates for compression molding. Temperature was maintained at 100°C for about 30 min. A pressure of about 1.72 × 10⁴ kPa was applied, and the temperature of mold was maintained 150°C for 1.5 h and 180°C for 1 h. After cooling down the mold to room temperature, the composite was taken out and cut to get required specimens for evaluation as per ASTM standards for testing.

Instruments and Test Methods

Differential scanning calorimetry (DSC) scans were obtained using Du Pont 910 DSC module connected with a Du Pont 9900 thermal analyzer under a 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 Du Pont 951 thermogravimetric analyzer connected with a Du Pont 990 thermal analyzer in static air at a heating rate of 10°C min⁻¹.

Flexural and interlaminar shear strength of composite were determined according to ASTM D-790-71 and D-2344-76, respectively. Shore-D hardness of the composites were measured on Shore-D Hardness tester TSE testing Machine according to ASTM D-785.

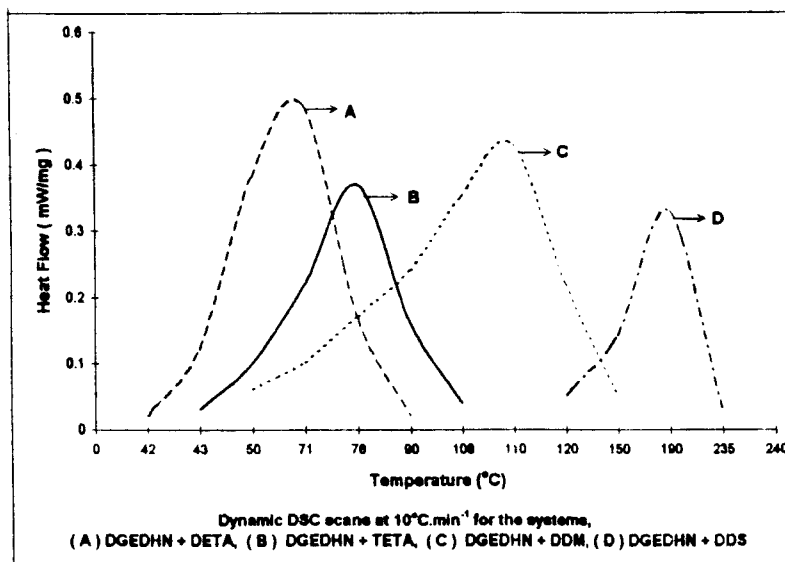


Figure 2 Dynamic DSC scans at 10°C min⁻¹ for the following systems: (A) DGEDHN + DETA; (B) DGEDHN + TETA; (C) DGEDHN + DDM; (D) DGEDHN + DDS.

Table I Kinetic Parameter of Epoxy–Amine System

Epoxy Systems	Mass Ratio	Curing Agent	T_I (°C)	T_p (°C)	T_f (°C)	Freeman–Carroll Relation		Barrett Relation	
						E (kJ mol)	n	E (kJ mol)	ln A
DGEDHN	—	DETA	42	71.2	90	151.15	1.9	145.5	20
DGEDHN	—	TETA	43	75.5	108	125.54	1.5	142.17	26.02
DGEDHN	—	DDM	50	110.6	150	69.52	1.75	74.8	12.0
DGEDHN	—	DDS	120	190	235	70.67	2.0	64.01	10.6
DGEDHN + DGEBA	20 : 80	DDM	75	156.7	225	60.84	1.3	58.2	8.6
DGEDHN + DGEBA	20 : 80	DDS	160	231	270	126.37	1.5	113.9	14.6

The dielectric properties of composite (dielectric constant and the loss factor) were determined from the measured value of capacitance and dissipation factor on Digital LCR meter. Resistance to electrical current was measured using a Hewlett Packard 4329-A high-resistance meter at applied voltage of 250 V (ac). Resistance to various chemicals was determined according to ASTM D-543-67.

RESULTS AND DISCUSSION

Some selected DSC curves at a heating rate $10^\circ\text{C min}^{-1}$ are shown in Figure 2. The characteristic behavior of curing, such as the temperature at which the 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 Barrett⁵ and the Freeman–Carroll⁶ relation are nearly the same and range within 58.2 to 151.15 kJ mol⁻¹.

In order to investigate the effect of the amine structure on the thermal stability of the cured epoxy resins, the parameters, such as T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), T_{20} (temperature for 20% weight loss), T_{max} (temperature of maximum rate of degradation), the Integral procedure decomposition temperature (IPDT),⁷ and the activation energy (E_a),⁸ 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 the heat stability of the system⁹ will be.

The thermal stability of amine-cured epoxy systems is affected most by the structure of the amine used as curing agent. The following trend for thermal stability for amine-cured epoxy resin is revealed from Table II.

**DGEDHN—DDS > DGEDHN—DDM
> DGEDHN—TETA > DGEDHN—DETA**

The lowest stability observed in the case of DGEDHN–DETA is due to purely aliphatic struc-

Table II Temperature Characteristic and Kinetic Parameter of Cured Epoxy Resins

Epoxy Systems	Mass Ratio	Curing Agent	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	IPDT (°C)	Activation Energy E_a (kJ mol ⁻¹)
DGEDHN	—	DETA	175	260	570	425	37.67
DGEDHN	—	TETA	212.5	287.5	585	392	44.79
DGEDHN	—	DDM	240	290	590.5	473	39.0
DGEDHN	—	DDS	287.5	340	612.5	472.8	49.15
DGEDHN + DGEBA	20 : 80	DDM	262.5	312.5	600	440.75	53.8
DGEDHN + DGEBA	20 : 80	DDS	300	362.5	575	492	55.32

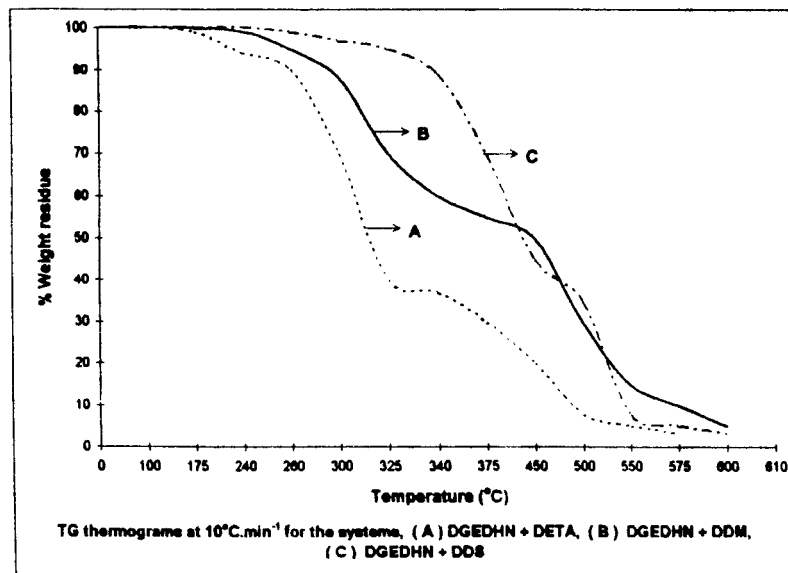


Figure 3 TG thermograms at 10°C min⁻¹ for the following systems: (A) DGEDHN + DETA; (B) DGEDHN + DDM; (C) DGEDHN + DDS.

ture of DETA in the cured product. The highest stability observed in the system DGEDHN–DDS is due to aromatic nature of curing agent. The epoxy resin, cured by DDS, is more thermally stable than that cured with DDM. This may be ascribed to the greater heat resistance character of the sulphur linkage, referring to a carbon linkage.¹⁰ The nature of some selected thermograms are shown in Figure 3. They were found to proceed in two steps.

The results of mechanical properties like flexural strength, interlaminar shear strength, and Shore-D hardness of the composite are shown in Table III. The data show that the mechanical properties are greatly affected by the curing agent used. Aromatic amine DDM and DDS give better mechanical properties than the aliphatic amine DETA and TETA due to the aromatic character of the curing agents. Furthermore, the DDS cured

epoxy system shows better properties compared to DDM, which may be due to presence of the rigid —SO₂ linkage present in DDS, which impart 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, and change in dimensions were examined. No particular change was observed in discoloration, change in dimensions, and loss in gloss, but an increase in the weight of samples was observed. The weight gain, for every case, is in the range of 1–3%.

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

Table III Mechanical and Dielectrical Properties of Glass Fiber-Reinforced Composite

Epoxy System	Mass Ratio	Curing Agent	Flexural Strength (kg cm ⁻²)	ILSS (kg cm ⁻²)	Shore-D	Resistance (ohm)	$\tan \delta$
DGEDHN + DGEBA	20 : 80	DETA	1239.6	120	85	0.39×10^{14}	0.522
DGEDHN + DGEBA	20 : 80	TETA	1562.3	137.5	89	0.32×10^{14}	0.433
DGEDHN + DGEBA	20 : 80	DDM	2578.3	144.7	92	0.45×10^{14}	0.455
DGEDHN + DGEBA	20 : 80	DDS	2834.4	190.5	95	0.30×10^{14}	0.546

CONCLUSIONS

DSC cure kinetic of an epoxy resin–amine system follows Arrhenius-type kinetics with an activation energy in the range of 58.2–151.15 kJ mol⁻¹.

The mechanical properties of glass fiber-reinforced composite depends on the structure of curing agents.

All composites behaved as very good insulating materials.

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