## Synthesis and curing kinetics of colored epoxy resin containing azo moiety

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Online publication date: 27 October 2010

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# SYNTHESIS AND CURING KINETICS OF COLORED EPOXY RESIN CONTAINING AZO MOIETY

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*Colored epoxy resin containing azo moiety was synthesized by reaction between epichlorohydrin and bis-azodiol, which was synthesized by coupling bisphenol-A with aromatic amine. Colored epoxy resin was characterized by epoxy equivalent weight, IR spectra, Viscosity and UV visible spectroscopy. The curing of colored epoxy resin and DGEBA were characterized by differential scanning calorimetry (DSC). The thermal stability of cured products was characterized by thermogravimetric analysis (TGA). The cured products have good thermal stability. Several glass fiber epoxy composites were fabricated and their mechanical properties, electrical properties and chemical resistance were studied.*

## INTRODUCTION

In the recent history of polymers, epoxy resins have gained increasing importance due to their wide range of applications in many fields like coating, casting, molding, electric components and hardware applications [1−4]. For this purpose commercial epoxy resin, diglycidyl ether of bisphenol-A (DGEBA), is widely used and has been studied by

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several researchers [5, 6]. Many applications of pigmented colored epoxy resins and composites became known. For example, colored epoxy resins are used for colored coating wires, in transmission cables, for colored bathtubs, for powder paints, for printing inks, in electrical application (printed circuit boards) [7−10]. However, very few references are reported where the color is imparted to the resin by introducing an azo group in the resin molecule.

In the present investigation to impart color, diazotized p-chloroaniline is first coupled with bisphenol-A to prepare bis-azodiol which is then treated with epichlorohydrin for the preparation of colored epoxy resin.

Glass fiber reinforced composites of colored epoxy resins and DGEBA in the ratio of 15 : 85 were prepared using diethyl tetramine (DETA), triethyl tetramine (TETA), p-p'-diamino diphenyl sulphone (DDS), and p-p'-diamino diphenyl methane (DDM) as curing agents. The fabricated composites were evaluated for mechanical strength, electrical properties and their resistance to various chemicals.

## EXPERIMENTAL

### Materials

Commercial grades of p-chloroaniline, hydrochloric acid, sodium nitrate, sodium hydroxide and epichlohydrin (b.p.: 115−116°C) were used. A conventional epoxy resin DGEBA (EEW: 190 g·eq$^{-1}$) was obtained from Synpol Pvt. Ltd., Ahmedabad. The curing agents DETA, TETA, DDM, DDS used were of laboratory grade.

### Synthesis of Resin

P-chloroaniline was diazotized using hydrochloric acid and sodium nitrate while maintaining temperature 0−5°C, and coupled with bisphenol-A for the formation of bis-azodiol. The bis-azodiol (0.04 mol) was then reacted with epichlorohydrin (0.48 mol) in presence of sodium hydroxide (0.08 mol) at 100°C for 5 hrs. Excess epichlorohydrin was distilled out under 50 mm Hg pressure and the salt was then removed. The resin shows dark orange color.

### Characterization of Epoxy Resin

The epoxy equivalent weight of colored epoxy resin (CER) was found to be 308 g·eq$^{-1}$. Its proposed structure is shown in Figure 1. The intrinsic viscosity in DMF measured by Ubbelohde viscometer at 30°C was observed to be about 0.025 dl·gm$^{-1}$.
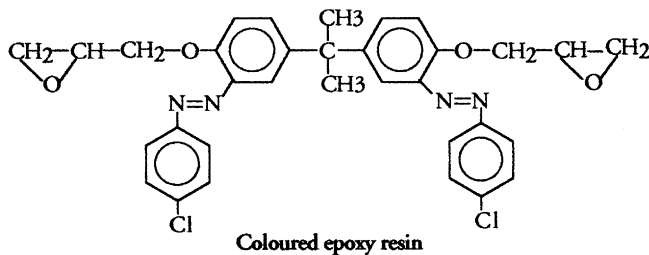
**FIGURE 1** Colored epoxy resin (CER).

The colored epoxy resin (CER) was characterized by Nicolet-400 D FT-IR spectrometer. IR-spectra (Figure 2) shows broad band at 3395 cm$^{-1}$ due to hydroxyl group, band at 3000 cm$^{-1}$ and 1150 cm$^{-1}$ due to aromatic C–H vibrations, bands at 2930 cm$^{-1}$ and 2878 cm$^{-1}$ due to ether methylene C–H vibration, bands at 1609 cm$^{-1}$ and 1515 cm$^{-1}$ due to presence of phenyl rings, the bands at 1266 cm$^{-1}$, 920 cm$^{-1}$ and 850 cm$^{-1}$ due to terminal epoxy group. Bands at 688 cm$^{-1}$ and 700 cm$^{-1}$ indicate presence of C–Cl bond and at 1510–1540 cm$^{-1}$ indicates the presence of azo group (N=N). The resin



**FIGURE 2** IR spectra of colored epoxy resin (CER).

was also characterized by UV visible spectroscopy, the value of $\lambda_{\max}$ was found to be 369 nm.

## Fabrication of Composites

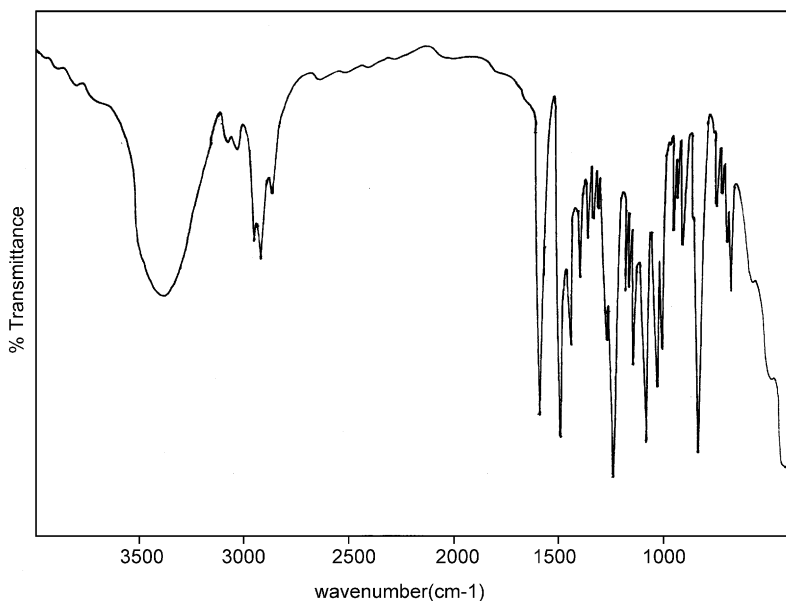Formulation described in Table 3 were dissolved in acetone and were applied on $10 \times 10$ cm$^2$ pieces of woven glass-fiber cloth (an epoxy compatible, 10 mil, plain woven E types, 10 plies) by hand lay-up technique. The impregnated plies were kept in an oven heated up to 60°C for about 20 min. for evaporation of solvent. The plies were then stacked together, put between Teflon-coated glass cloths, and placed between flat plates for compression molding. Temperature was maintained at 100°C for about 30 min. Then, pressure of about $1.74 \times 10^4$ kPa was applied and the temperature of the mold was maintained at 150°C for 1.5 hrs. and at 180°C for 1 hr. After cooling down to room temperature the composites were taken out of the mold and cut to get the specimens required for evaluation as per ASTM standard for testing.

## Measurement

Differential scanning calorimetry (DSC) scans were obtained using Dupont 910 DSC module connected with a Dupont 9900 thermal analyzer under nitrogen atmosphere at heating rate of 10°C min$^{-1}$ using an empty cell reference.

Thermal gravimetric analysis (TGA) of cured products was performed on Dupont 951 thermogravimetric analyzer connected with Dupont 990 thermal analyzer in static air at heating rate of 10°C min$^{-1}$.

Flexural strength of composites was determined according to ASTM D-790-71 on dutron machine. Shore D hardness of composites was measured using a Shore D hardness tester TSE testing machine according to ASTM D-785.

The dielectric properties of the composites (dielectric constant and loss factor) were determined from the measured value of capacitance and dissipation factor on digital LCR meter. Resistance to various chemicals was determined according to ASTM D-543-67.

## RESULTS AND DISCUSSION

DSC curves at heating rate of 10°C min$^{-1}$ are shown in Figure 3. Characteristic behavior of curing such as the temperature at which curing reaction started ($T_i$), peak temp. ($T_p$), complete cure temp ($T_f$),
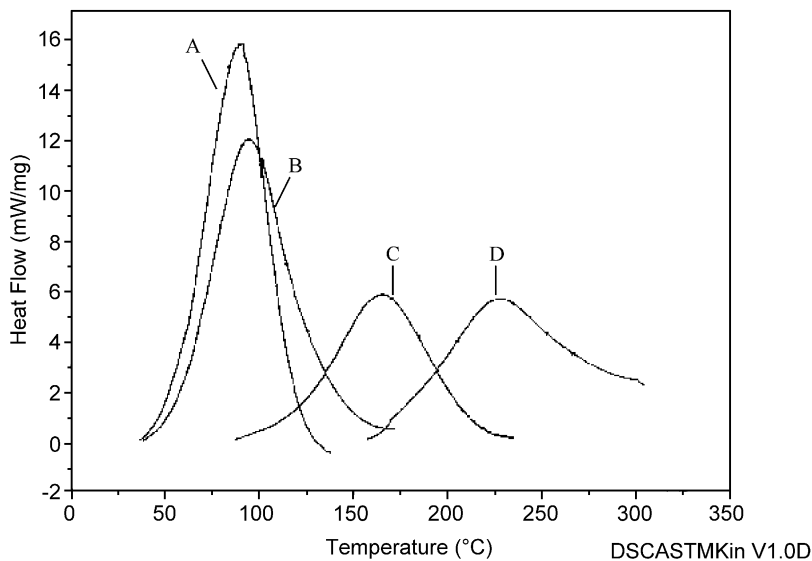
**FIGURE 3** Dynamic DSC scans at $10^{\circ}$C min$^{-1}$ for the following systems: (a) CER + DGEBA + DETA, (b) CER + DGEBA + TETA, (c) CER + DGEBA + DDM, and (d) CER + DGEBA + DDS.

activation energy of curing reaction(Ea), order of reaction(n) and pre-exponential factor (log Z) are listed in Table 1. The activation energy values from Borchardt-Danials method fall in the range of $80-100$ kJ $\cdot$ mol$^{-1}$.

In order to investigate the effect of amine structure on the thermal stability of cured epoxy resin, the parameter such as $T_i$ (temperature onset of decomposition), $T_{50}$ (temperature for 50% weight loss), $T_{max}$ (temperature of maximum rate of degradation), the integral procedure decomposition temperature (IPDT), and activation energy (Ea) of the degradation process were calculated and presented in Table 2. Two thermograms are shown in Figure 4.

**TABLE 1** Kinetic Parameters of Epoxy Amine System

| Resin system | Ratio | Curing agent | $T_i$ | $T_P$ | $T_f$ | Ea kJ $\cdot$ mol$^{-1}$ | n | Log Z (min$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | | DETA | 36 | 89.55 | 141 | 86.5 | 1.57 | 12.41 |
| CER + | 15 : 85 | TETA | 38 | 94.12 | 170 | 88.4 | 2.23 | 12.47 |
| DGEBA | | DDM | 69 | 165.23 | 240 | 62.6 | 0.87 | 6.69 |
| | | DDS | 154 | 225.26 | 304 | 96.8 | 2.33 | 9.60 |

**TABLE 2** Temperature Characteristic and Kinetic Parameter of Cured Epoxy Resin

| Epoxy system | Ratio | Curing agent | $T_i$ | $T_{50}$ | $T_{max}$ | IPDT$^\circ$C | $E_a$ kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| CER + DGEBA | 15 : 85 | DETA | 294 | 342 | 317 | 410 | 49.6 |
| | | TETA | 308 | 367 | 339 | 466 | 59.17 |
| | | DDM | 325 | 389 | 395 | 490 | 60 |
| | | DDS | 344 | 411 | 387 | 510 | 69.38 |

The data revealed that the trend of thermal stability for amine-cured epoxy resins is DDS > DDM > TETA > DETA.

The lowest stability observed in the case of DETA is due to the purely aliphatic structure of DETA. The highest stability observed in the case of DDS is due to the aromatic nature of curing agent. The epoxy resin, cured by DDS, is thermally more stable than that cured with DDM. This may be ascribed to the greater heat resistance character of sulfur linkage relative to carbon linkage.

The results of mechanical properties such as flexural strength, interlaminar shear strength (ILSS) and shore-D hardness of epoxy
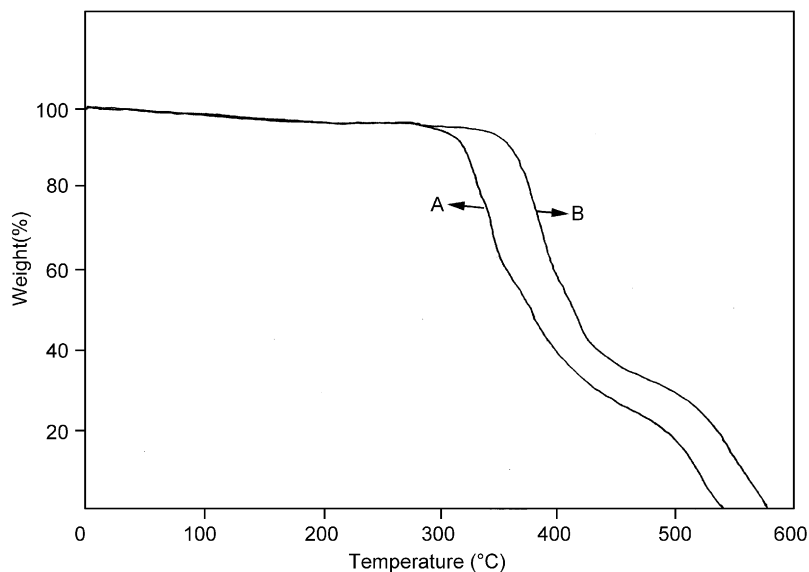


**FIGURE 4** TG thermograms at $10^\circ$C min$^{-1}$ for the following systems: (a) CER + DGEBA + TETA and (b) CER + DGEBA + DDS.

**TABLE 3.** Mechanical and Dielectric Properties of Glass-Fiber Reinforced Composites

| Resin system | Ratio | Curing agent | Flexural strength (Kg cm$^{-2}$) | ILSS (Kg cm$^{-2}$) | Shore-D | Dielectric constant ($\varepsilon'$) | Dielectric loss ($\varepsilon''$) | Tan $\delta$ |
|---|---|---|---|---|---|---|---|---|
| | | DETA | 3755 | 127 | 94 | 35.17 | 16.28 | 0.463 |
| CER + | 15 : 85 | TETA | 4237 | 132 | 95 | 31.40 | 14.85 | 0.473 |
| DGEBA | | DDM | 5065 | 225 | 96 | 30.68 | 13.95 | 0.455 |
| | | DDS | 5750 | 251 | 98 | 28.13 | 13.75 | 0.489 |

cured laminates are shown in Table 3. The data show that the mechanical properties are affected by the curing agent used. Aromatic amines DDS and DDM give better mechanical properties than the aliphatic amines DETA and TETA due to the aromatic character of curing agents. Furthermore the DDS cured epoxy system shows better mechanical properties compared to DDM, which may be due to the presence of rigid $SO_2$ linkage in DDS imparting better rigidity to the cross-linked structure.

Dielectric properties like dielectric constant, dielectric loss and tan $\delta$ of composites are shown in Table 3.

The chemical resistance of composites specimen to various chemical reagents such as acetone, water, 20% NaOH, 20% HCl were tested by dipping the specimen in the reagents for seven days. No particular change was observed in discolouration and loss in gloss, but an increase in weight of sample was observed in every case, in the range of 1−3%.

## CONCLUSION

DSC cure kinetics of epoxy resin−amine system shows activation energy in the range of 80−100 kJ·mol$^{-1}$. The cured products show good thermal stability according to structure of the curing agent. The mechanical properties such as flexural strength, ILSS, shore-D of glass fiber reinforced composites depend on the structure of the curing agents. The epoxy DDS system gives the best mechanical properties.

## REFERENCES

[1] Mark, H. F. and Bikales, N. M. (1970). *"Encyclopedia of Polymer Science and Technology"*, **12**, Wiley-Interscience, New York, 1.
[2] Dusek, K. (1985). *Adv. Polym. Sci.*, Springer, Berlin, **78**, 115.

 [3] Lee, H. and Neville, K. (1967). *"Handbook of Epoxy Resins"*, McGraw-Hill, New York.
 [4] May, C. and Tanaka, Y. (1973). *"Epoxy Resins Chemistry and Technology"*, Dekker, New York.
 [5] Patel, M. B., Patel, R. D., Patel, R. G. and Patel, V. S. (1991). *High Performance Poly.*, **3**, 107.
 [6] Dusek, K. (1985). *Adv. Polym. Sci.*, Springer, Berlin, **72**(1).
 [7] Wiederhold, hermann. FR. 1,597,488 (1971). *Chem. Abstr.*, **74**, 88761k.
 [8] Dai Nippon Toryo Co. Ltd. Japan Kokai, 74,125,472 (1975). *Chem. Abstr.*, **82**, 141268y.
 [9] Additive Technology Corp. Ger. Offen 2,922,304 (1981). *Chem. Abstr.*, **94**, 201806g.
[10] Nippon Gakki Co. Ltd. Japan Kokai, 76,22767 (1976). *Chem Abstr.*, **85**, 6746z.