# Studies on the Curing Kinetics and Thermal Stability of Diglycidyl Ether of Bisphenol-A Using Mixture of Novel, Environment Friendly Sulphur Containing Amino Acids and 4,4′-Diaminodiphenylsulfone

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**ABSTRACT:** This article describes the curing behavior of diglycidyl ether of bisphenol-A using Cysteine (A)/ Methionine (B)/Cystine (C)/ mixture of 4,4′-diaminodiphenyl sulfone (DDS) and Cysteine/DDS and Methionine/DDS and Cystine in various molar ratios as curing agent. Differential scanning calorimetry was used to study the cure kinetics by recording the DSC scans at heating rates of 5, 10, 15, and 20°C/min. The peak exotherm temperature was found to be dependent on the heating rate, structure of the amino acids and on the DDS/amino acids molar ratio. A broad exotherm was observed in the temperature range of 150–245°C (EA), 155–240°C (EB), and 190–250°C (EC). Curing of DGEBA with mixture of amino acids and 4, 4′-diaminodiphenyl sulfone (DDS) resulted in a decrease in characteristic curing temperatures. Activation energy of curing reaction is determined in accordance to Ozawa's method and was found to be dependent on the structure of the amino acids and on the ratio of 4,4′-diaminodiphenyl sulfone (DDS) to amino acid. Thermal stability of the isothermally cured resins was evaluated using dynamic thermogravimetry in nitrogen atmosphere. No significant change has been observed in the char yield of all the samples, but it was highest in the system cured using either Cystine alone (EC-1) or a mixture of DDS/Cystine (EC-2, EC-3, and EC-4). © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 216–225, 2009

**Key words:** DGEBA; curing kinetics; amino acids; 4,4′-Diaminodiphenyl Sulfone (DDS); thermal stability

## INTRODUCTION

Epoxy resins are high performance thermosetting resins that display a unique combination of properties, including excellent adhesion, chemical and heat resistance, good mechanical properties, and good electrical insulating properties.[1,2] Beside this almost any properties of epoxy can be modified to meet a specific need. For example, despite the excellent dielectric properties of epoxy, silver filled epoxies with good electrical conductivity are widely available are considered promising alternatives for lead-containing solder alloy in the electronics industry.[3–8] Epoxy-based materials are also widely used in a variety of applications, such as paints and coatings, adhesives, industrial tooling and composites, flip-chip under fills,[9–12] low dielectric-constant components,[13,14] and semiconductor capsulation films in the electronics industry. Various types of curing agents, such as nitrogen containing agents (amines and polyamides), oxygen containing agents (anhydride), and sulfur containing agents (mercaptans), have been reacted with epoxy resins to provide cross-linked adhesives. Although these curing agents have been used for several decades, these systems do have some environmental problems that have been specially noted in recent years. One problem comes from halogen-containing epoxy resins, which are particularly useful for printed-circuit-board applications. They usually generate dense smoke and toxic decomposition products during combustion.[15,16] Halogen-free epoxy resins cured with phosphorous containing compounds exhibit good flame retardancy and are promising solutions to this problems.[17–26] Another environmental problem of epoxy resins is that all the curing agents are toxic before the cure.[1,2,27–30] Even for cured epoxy resins that seem to be safe, toxicity cannot be totally avoided because of the possibility of incomplete combustion of curing agents and subsequently the hazards introduced by residual curing agents. Therefore, the development of environmentally friendly epoxy systems is of great importance for designing green and biocompatible material in many

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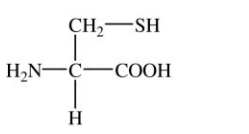
applications.[20,31–33] Recently, some advances have taken place to develop an ecofriendly-curing agent that could replace common hazardous agent (halogen containing compounds). Naturally occurring amino acids were successfully used as cross-linking agent for DGEBA. Although a very little work have been reported on amino acid tryptophan as novel and environmentally friendly curing agent for DGEBA. The curing reaction of tryptophan with imidazole has been studied and curing mechanism has been reported.[34] The present article describes the curing and thermal behavior of DGEBA using sulfur containing amino acids (Cysteine, Methionine and Cystine) as sulfur group will have an additional effect on the properties of a modified network along with its flexibilizing effect and it was observed that the structure of amino acid and amount of 4,4′-diaminodiphenyl sulfone (DDS) has a large effect on the curing characteristics. It was therefore considered of interest to investigate systematically the curing behavior of DGEBA using Cysteine/DDS or Methionine/DDS or Cystine/DDS in the molar ratio of 1 : 0, 0.75 : 0.25, 0.5 : 0.5 0.25 : 0.75, and 0 : 1. Thermal stability of DGEBA cured isothermally was evaluated using dynamic thermogravimetry in the nitrogen atmosphere.

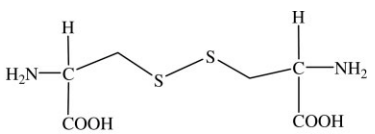
## EXPERIMENTAL

### Materials

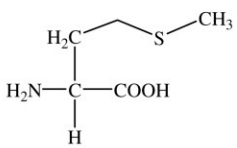
Diglycidyl ether of bisphenol-A (DGEBA, grade LY556, having epoxy equivalent 177) was procured from Hindustan Ciba Geigy; Ethyl Methyl ketone, Cysteine (A), Methionine (B), Cystine (C) and 4,4′-Diaminodiphenyl Sulfone (DDS) all purchased from Merck and were used as received and their structures are shown below:



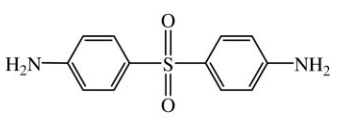

Cysteine




Cystine




Methionine




DDS

### Curing studies

Rheometric thermal analyzer having a 910 DSC module was used to record DSC scans at a heating rate of 5, 10, 15, and 20°C/min. For this purpose, samples were prepared by mixing required amount of DGEBA with Cysteine/Methionine/Cystine or DDS or mixture of DDS/Cysteine or DDS/Methionine or DDS/Cystine at different molar ratio using ethyl methyl ketone as solvent. After thorough mixing, the solvent was evaporated under vacuum and the freshly prepared samples were used for recording DSC traces in static air atmosphere at a programmed heating rate from room temperature up to 350°C. The sample weight was ranging from 3 to 7 mg.

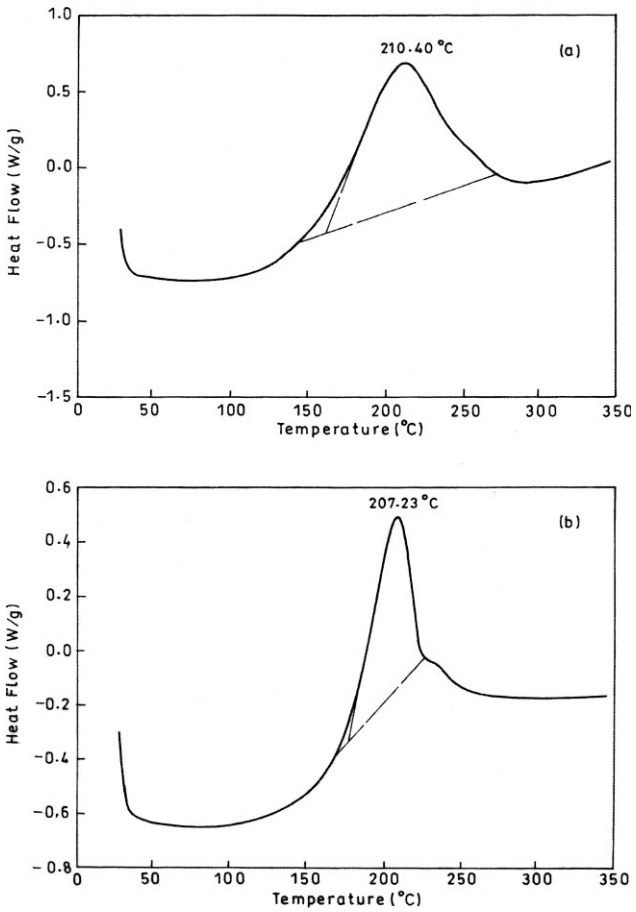



**Figure 1** DSC scan of DGEBA in the presence of mixture of DDS/Cysteine (EA-4 and EA-2) at heating rate = 10°C/min.

The epoxy samples cured using mixture of DDS/Cysteine or DDS/Methionine or DDS/Cystine have designated as EA, EB and EC respectively, followed by numerical suffix. For example epoxy resin cured with a Cysteine/DDS mixture in the molar ratio of 1.0 : 0.0, 0.75 : 0.25, 0.5 : 0.5 and 0.25 : 0.75 have been designated as EA-1, EA-2, EA-3, and EA-4 respectively. Similarly samples cured using mixture of Methionine/DDS or Cystine/DDS were designated as EB-1, EB-2, EB-3, and EB-4 or EC-1, EC-2,

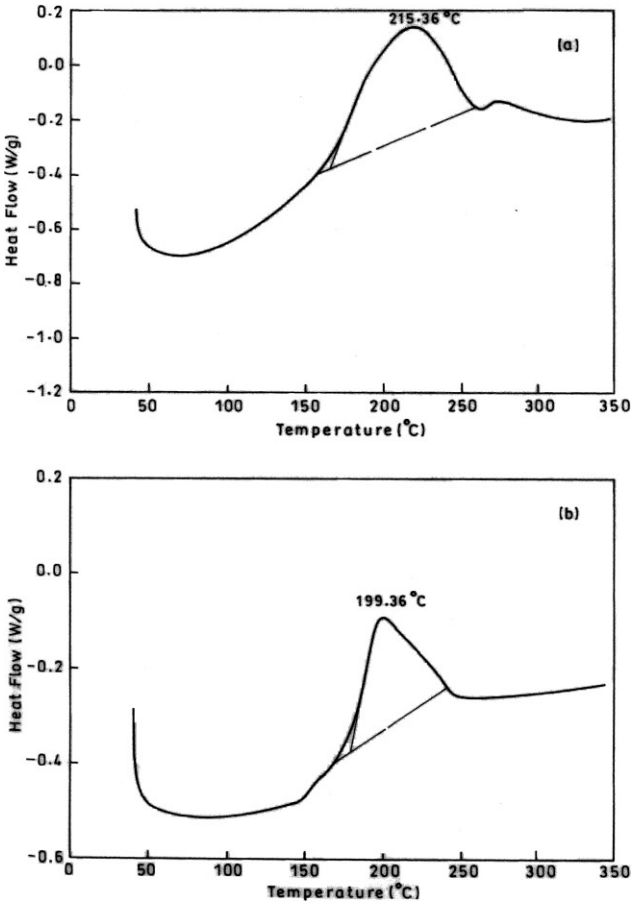



**Figure 2** DSC scans of DGEBA in the presence of mixture of DDS/Methionine (EB-4 and EB-2) at heating rate = 10°C/min.

EC-3, and EC-4, respectively. Epoxy resins cured using DDS alone has been designated as ED.

### Thermal studies

The thermal stability of epoxy resins cured isothermally (by heating in air oven at 185 and 256°C for 3 h) in presence of DDS/Cysteine or DDS/Methionine or DDS/Cystine mixture respectively, was evaluated using Rheometric thermal analyzer having TG 1500-module. Thermo gravimetric traces in nitrogen atmosphere (flow rate 60 $cm^3$/min.) were recorded at a heating rate of 20°C/min and powdered sample weighing 10 ± 5 mg was used in each experiment.

## RESULTS AND DISCUSSION

### Curing studies

DSC scans of samples (a) EA-4 and (b) EA-2 are shown in the Figure 1. The curing of epoxy resin depends upon on the structure of curing agents and its stoichiometry. In the present work, we did not change the stoichiometry; however the ratio of DDS/amino acid was varied to evaluate its effect on the curing behavior. The curing exotherm was characterized by noting the following parameters:

$T_i$ = kick-off temperature, where the curing starts; $T_{onset}$ = temperature where the first detectable heat is released. It was obtained by extrapolation of steepest portion of curve; $T_p$ = temperature of peak position of exotherm; $T_f$ = temperature of end of curing exotherm obtained by extrapolation of the end set of the exotherm transition; $\Delta H$ = heat of curing, calculated by measuring area under the exothermic transition.

Figures 1, 2, and 3 show the DSC scans of DGEBA in presence of mixture of Cysteine/DDS (EA-4 and EA-2); Methionine/DDS (EB-4 and EB-2); and Cystine/DDS (EC-2 and EC-4), respectively. A broad exothermic transition associated with curing was observed in the temperature range of 150–245°C (EA-1), 155–240°C (EB-1), and 190–250°C (EC-1) in the DSC scans of DGEBA cured using mixture of these amino acids with DDS in varying molar ratio. The high peak exothermic temperature ($T_P$) and kick-off temperature ($T_i$) of EC-1 sample is due to

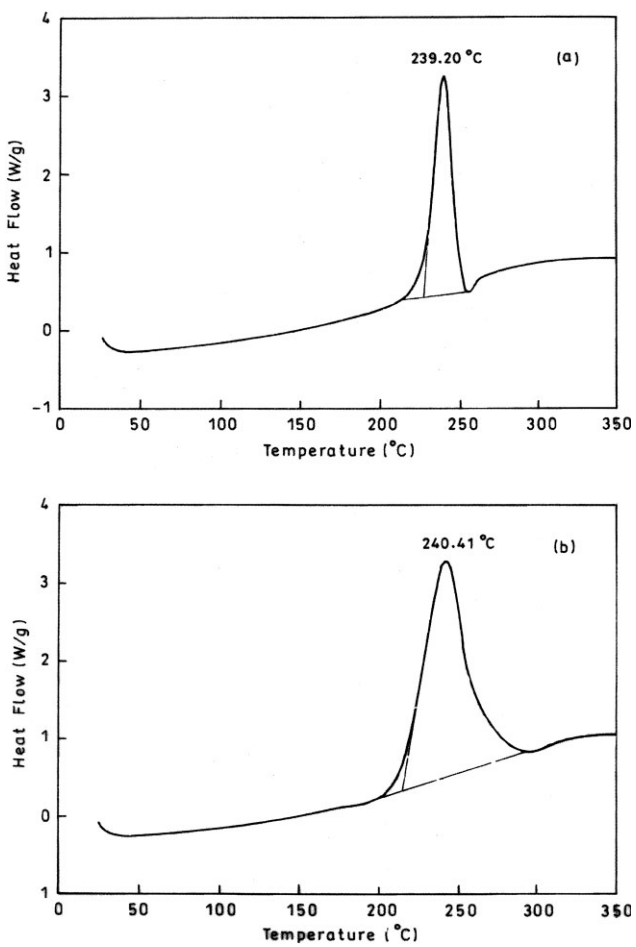



**Figure 3** DSC scan of DGEBA in the presence of mixture of DDS/Cystine (EC-2 and EC-4) at heating rate = 10°C/min.

**TABLE I**
**Results of DSC Scan of DGEBA in the Presence of Cysteine/DDS Mixture at Varying Rates**

| Sample designation | Cysteine/DDS molar ratio | Heating rate/°C min | $T_i$/°C | $T_o$/°C | $T_p$/°C | $T_f$/°C | $\Delta H$/ $Jg^{-1}$ | $E_a$/KJ mol |
|---|---|---|---|---|---|---|---|---|
| EA-1 | 1 : 0 | 5 | 154.22 | 175.97 | 198.24 | 229.36 | 152.1 | |
| | | 10 | 211.88 | 214.97 | 217.59 | 228.05 | 54.74 | 72.2 |
| | | 15 | 149.76 | 175.74 | 203.98 | 242.38 | 162.50 | |
| | | 20 | 185.01 | 196.12 | 220.95 | 245.02 | 159.0 | |
| EA-2 | 0.75 : 0.25 | 5 | 164.13 | 168.59 | 195.84 | 214.23 | 95.18 | |
| | | 10 | 161.52 | 171.88 | 207.23 | 226.20 | 107.7 | 103.4 |
| | | 15 | 179.27 | 182.86 | 215.76 | 239.80 | 162.30 | |
| | | 20 | 165.85 | 192.96 | 220.55 | 250.03 | 187.30 | |
| EA-3 | 0.5 : 0.5 | 5 | 166.74 | 175.33 | 200.0 | 211.37 | 20.63 | |
| | | 10 | 196.49 | 199.99 | 213.58 | 239.80 | 100.4 | 125.5 |
| | | 15 | 147.09 | 176.67 | 211.87 | 254.09 | 385.0 | |
| | | 20 | 182.40 | 197.21 | 221.45 | 258.58 | 166.6 | |
| EA-4 | 0.25 : 0.75 | 5 | 134.39 | 153.24 | 194.11 | 235.10 | 200 | |
| | | 10 | 142.74 | 161.91 | 210.40 | 274.24 | 348.6 | 90.7 |
| | | 15 | 154.74 | 168.67 | 215.06 | 279.46 | 215.6 | |
| | | 20 | 165.18 | 178.31 | 224.18 | 320.16 | 284.9 | |
| ED | 0 : 1 | 5 | 119.8 | 158.1 | 210.1 | 274.4 | 255.0 | |
| | | 10 | 131.4 | 174.6 | 224.0 | 295.7 | 264.4 | 74.0 |
| | | 15 | 143.9 | 181.7 | 232.4 | 294.4 | 225.5 | |
| | | 20 | 190.3 | 198.2 | 246.5 | 311.8 | 186.3 | |

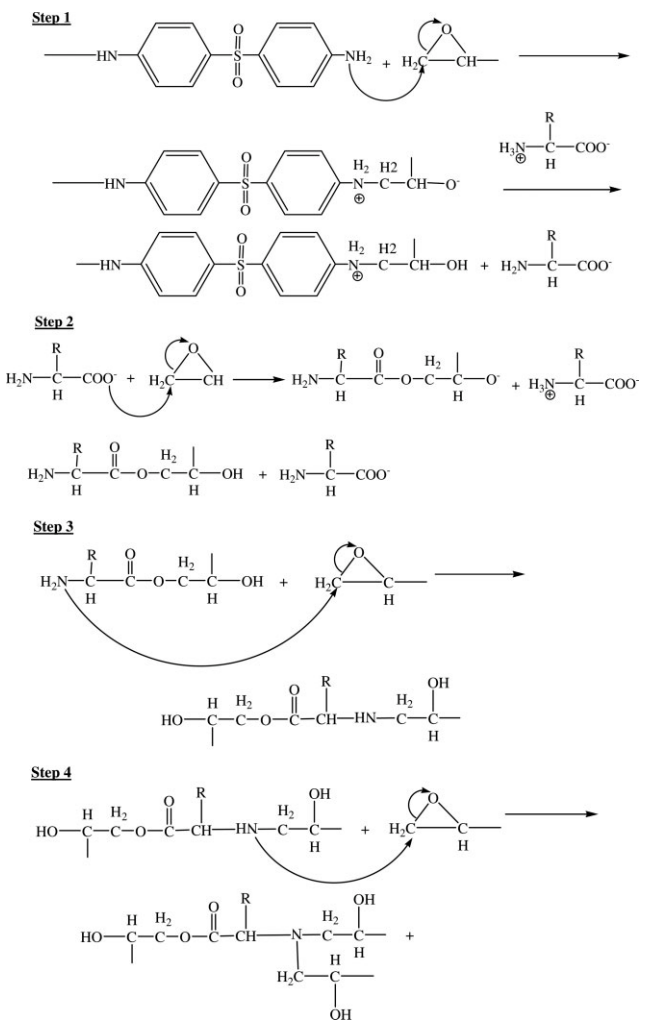
the presence of sulfur-sulfur (S—S) linkage in the case of Cystine. Nucleophilic addition of amines with oxirane group of DGEBA is responsible for the formation of a polymeric network structure. During the curing of epoxy resins by multifunctional amines, the oxirane ring is opened by amino group and a secondary amino group and a hydroxyl group is produced but sulfur because of its electronwithdrawing nature which decreases the nucleophillic character of amino group and more energy is needed to break that linkage (S—S) which result in the increase of peak exothermic temperature ($T_P$) and kick-off temperature ($T_i$) in the case of Cystine. The peak value ($T_P$) is low in the case of Methionine because of the +I effect of methyl group attached to the sulfur. The results of DSC scans are summarized in Tables I, II, and III. The curing mechanism of amino acids/DGEBA in presence of imidazole as catalyst has been reported by Wong and coworkers.[34] The decrease in the curing temperature of DGEBA upon addition of small amount of DDS to amino acids can be explained by recording the FTIR of mixture of DGEBA/amino acid with DDS as catalyst at different temperatures i.e., at room temperature, after heating at 150°C for 20, 30, and 90 min. Cure of epoxy-amino acids has been reported to be initiated by DDS. The activation of zwitterions by catalyst DDS initiates the reaction, and ionized

**TABLE II**
**Results of DSC scan of DGEBA in the presence of Methionine/DDS mixture at varying rates**

| Sample designation | Methionine/ DDS molar ratio | Heating rate/°C min | $T_i$/°C | $T_o$/°C | $T_p$/°C | $T_f$/°C | $\Delta H$/ $Jg^{-1}$ | $E_a$/KJ mol |
|---|---|---|---|---|---|---|---|---|
| EB-1 | 1 : 0 | 5 | 157.35 | 164.34 | 187.21 | 216.84 | 44.50 | |
| | | 10 | 174.57 | 184.15 | 205.54 | 217.88 | 22.80 | 169.5 |
| | | 15 | 171.44 | 186.75 | 209.62 | 227.27 | 38.27 | |
| | | 20 | 181.35 | 190.91 | 215.87 | 235.10 | 29.93 | |
| EB-2 | 0.75 : 0.25 | 5 | 159.96 | 165.17 | 185.57 | 215.27 | 39.39 | |
| | | 10 | 168.31 | 179.38 | 199.36 | 240.32 | 48.44 | 92.4 |
| | | 15 | 176.66 | 190.17 | 208.08 | 238.23 | 16.41 | |
| | | 20 | 191.79 | 196.09 | 212.30 | 231.45 | 18.31 | |
| EB-3 | 0.5 : 0.5 | 5 | 107.37 | 141.94 | 201.34 | 256.25 | 256.08 | |
| | | 10 | 161.10 | 172.98 | 223.23 | 261.23 | 82.52 | 82.30 |
| | | 15 | 165.18 | 180.94 | 230.15 | 264.71 | 113.60 | |
| | | 20 | 180.83 | 186.76 | 243.08 | 271.63 | 96.94 | |
| EB-4 | 0.25 : 0.75 | 5 | 173.39 | 170.85 | 204.43 | 242.41 | 54.80 | |
| | | 10 | 151.35 | 165.57 | 215.36 | 260.15 | 139.84 | 120.30 |
| | | 15 | 155.78 | 169.36 | 223.54 | 258.58 | 133.1 | |
| | | 20 | 167.26 | 178.41 | 226.15 | 272.15 | 123.10 | |

**TABLE III**
**Results of DSC Scan of DGEBA in the Presence of Cystine/DDS Mixture at Varying Rates**

| Sample designation | Cystine/DDS molar ratio | Heating rate/°C min | $T_i$/°C | $T_o$/°C | $T_p$/°C | $T_f$/°C | $\Delta H$/ $Jg^{-1}$ | $E_a$/KJ mol |
|---|---|---|---|---|---|---|---|---|
| EC-1 | 1 : 0 | 5 | 192.31 | 203.27 | 209.08 | 245.88 | 159.03 | |
| | | 10 | 201.70 | 217.32 | 222.38 | 231.97 | 195.21 | 99.60 |
| | | 15 | 209.53 | 225.06 | 234.31 | 247.62 | 150.87 | |
| | | 20 | 215.27 | 225.84 | 235.10 | 246.07 | 141.23 | |
| EC-2 | 0.75 : 0.25 | 5 | 204.00 | 215.50 | 233.08 | 254.18 | 188.2 | |
| | | 10 | 215.27 | 226.71 | 239.20 | 255.45 | 237.4 | 131.3 |
| | | 15 | 216.23 | 234.02 | 249.11 | 276.33 | 278.6 | |
| | | 20 | 214.37 | 238.49 | 255.38 | 301.04 | 290.5 | |
| EC-3 | 0.5: 0.5 | 5 | 171.32 | 188.95 | 223.33 | 254.84 | 172.12 | |
| | | 10 | 179.57 | 196.23 | 243.89 | 265.56 | 186.45 | 126.31 |
| | | 15 | 192.21 | 201.64 | 248.61 | 260.37 | 194.23 | |
| | | 20 | 198.33 | 237.59 | 254.04 | 286.33 | 240.34 | |
| EC-4 | 0.25 : 0.75 | 5 | 159.39 | 171.58 | 211.06 | 262.88 | 148.9 | |
| | | 10 | 202.08 | 223.61 | 240.41 | 292.30 | 143.2 | 58.51 |
| | | 15 | 199.44 | 231.93 | 244.87 | 294.68 | 153.6 | |
| | | 20 | 213.14 | 238.24 | 252.56 | 301.68 | 210.2 | |




**Scheme 1** Reaction mechanism of amino acid-cured epoxy. **Step 1:** The initiatio and activation of amino acid zwitterions. **Step 2:** The chain reactio between the carboxylatle anion and epoxy. **Step 3:** The nucleophillic substitution of the primary amine on the epoxy. **Step 4:** Further nucleophillic substitution of the secondary amine on the epoxy.

epoxide can extract a hydrogen from $NH_3^+$ in zwitterions and form a primary amine [Scheme 1(step 1)]. The formed primary amine (amino carboxylate anion), even in a small amount, can significantly increase the reactivity of $COO^-$ in the amino acid, and this triggers the esterification of carboxylate anion with epoxy and subsequently the extraction of hydrogen from another $NH_3^+$. These two reactions can be repeated in a chain mode and result in the formation of primary amine [Scheme 1(step 2)]. The resulting primary amine from the chain reaction can undergo a nucleophilic attack on an epoxy ring [Scheme 1(step 3)], and the formed secondary amine further reacts with another epoxy, giving a tertiary amine [Scheme 1(step 4)]. Meanwhile, formed hydroxyl group from the epoxy ring during the reaction can be auto catalyze those reaction. With the continuation of these reactions, a highly cross-linked structure can be formed in a relatively short period.

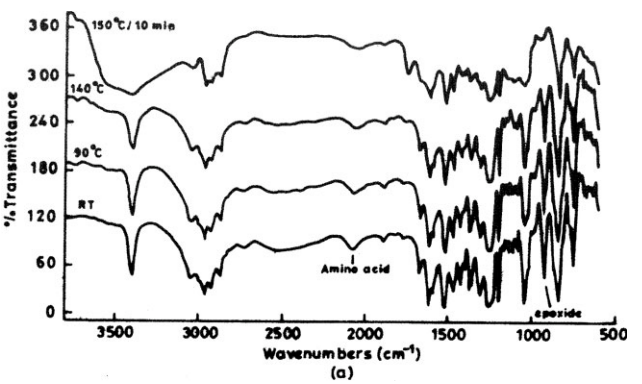



**Figure 4** FTIR spectra of a DGEBA/DDS mixture with the catalyst at various temperatures.

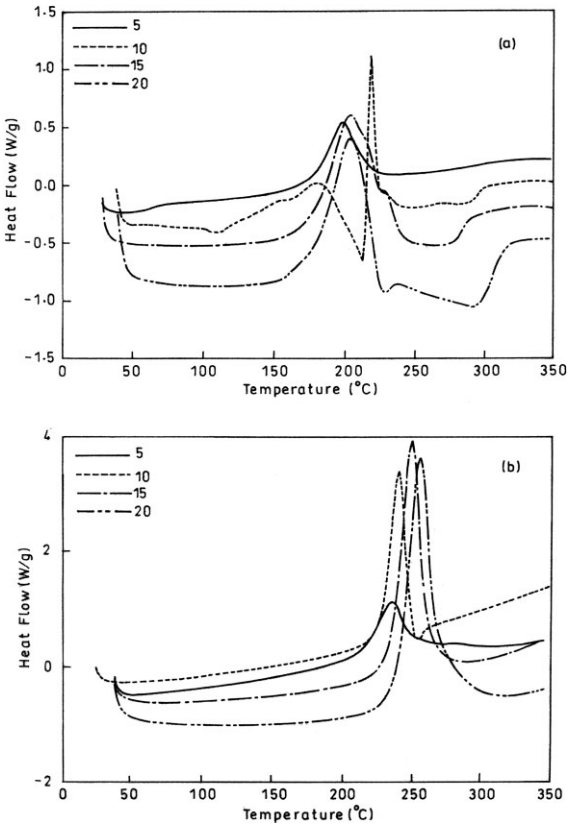



**Figure 5** DSC scans of DGEBA in the presence of mixture DDS/Cysteine and DDS/Cystine (EA-1 and EC-2) at heating rates = 5, 10, 15, and 20°C/min.

Nitrogen of amino group of DDS carries a lone pair of electron; the lone pair is most likely delocalized and is available for chain initiation reaction.

### FTIR of cured DGEBA/DDS with the catalyst

To understand the reaction mechanism of DGEBA/amino acid with DDS as a catalyst, FTIR spectra of DGEBA/DDS were collected during various steps of the curing process and are illustrated in Figure 4. It shows the spectra of DGEBA/DDS mixture at different temperatures. As can be seen from the spectra, no obvious peak change occurred from the room temperature to 140°C, whereas after 150°C was reached, an obviously varied spectrum was observed. The dramatically reduced peak strength for the epoxide group at 915 $cm^{-1}$ and amino acid characteristic peak at 2100 $cm^{-1}$ suggested a ring opening reaction between them.

### Curing kinetics

The kinetic parameters of the curing reaction can be obtained from dynamic DSC scan (i.e., multiple heating rate method) or using isothermal experiments. The dynamic method was used in the present study and the DSC scans were recorded at different heating rates for the samples. Figure 5 shows DSC scans for the resin samples EA-1 and EC-2 recorded at different

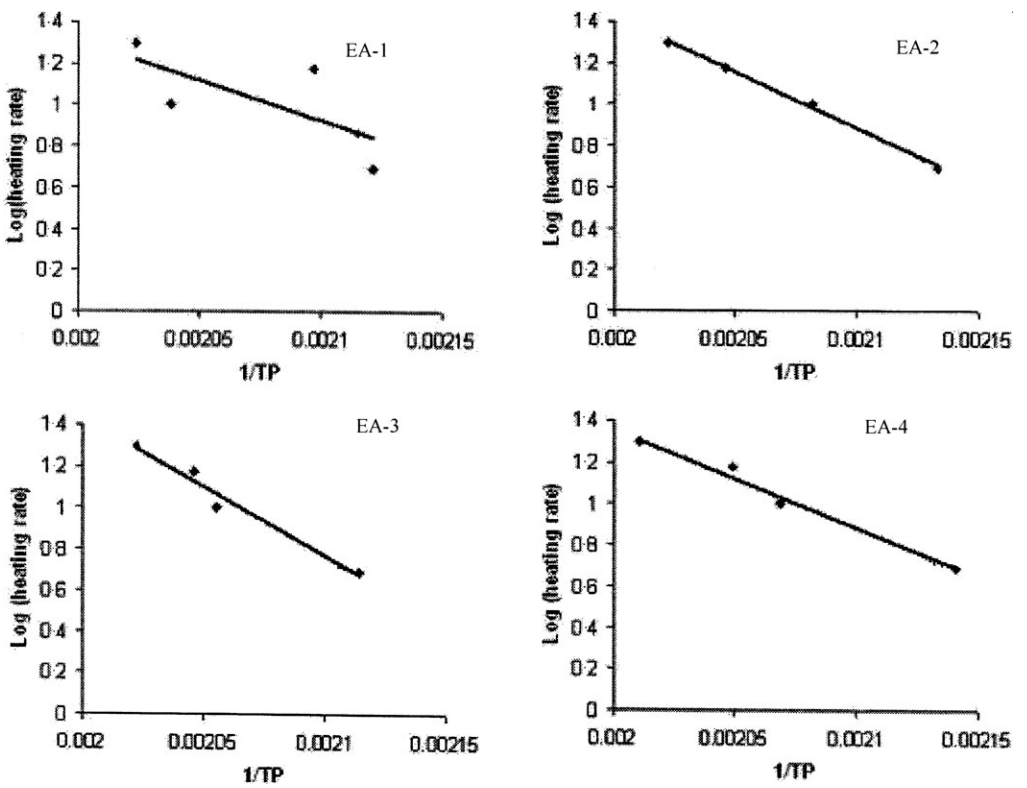



**Figure 6** Plots of log φ versus $1/T_p$ (EA, EA-1, EA-2, and EA-3).

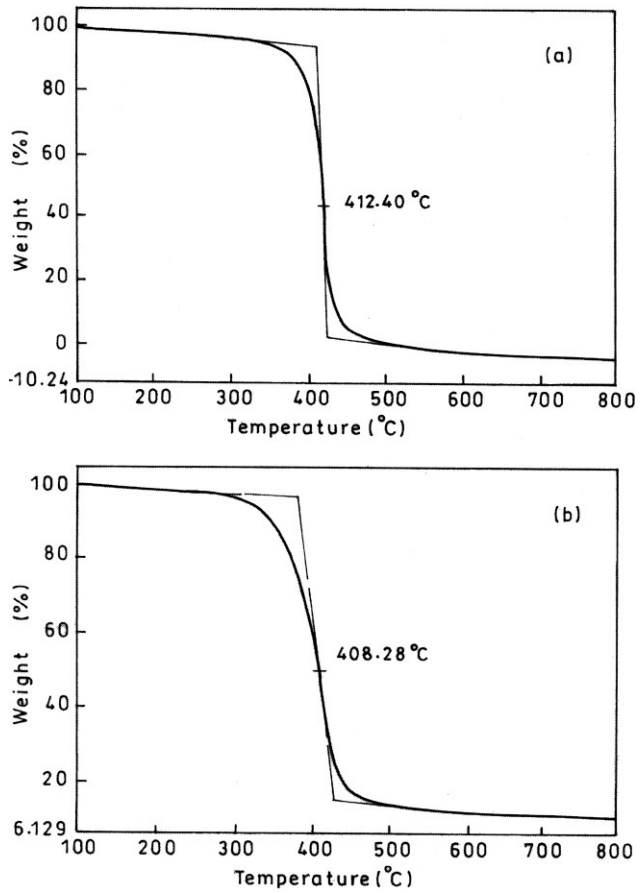



**Figure 7** TGA scan of DGEBA in the presence of mixture DDS/Cysteine (EA-4 and EA-2).

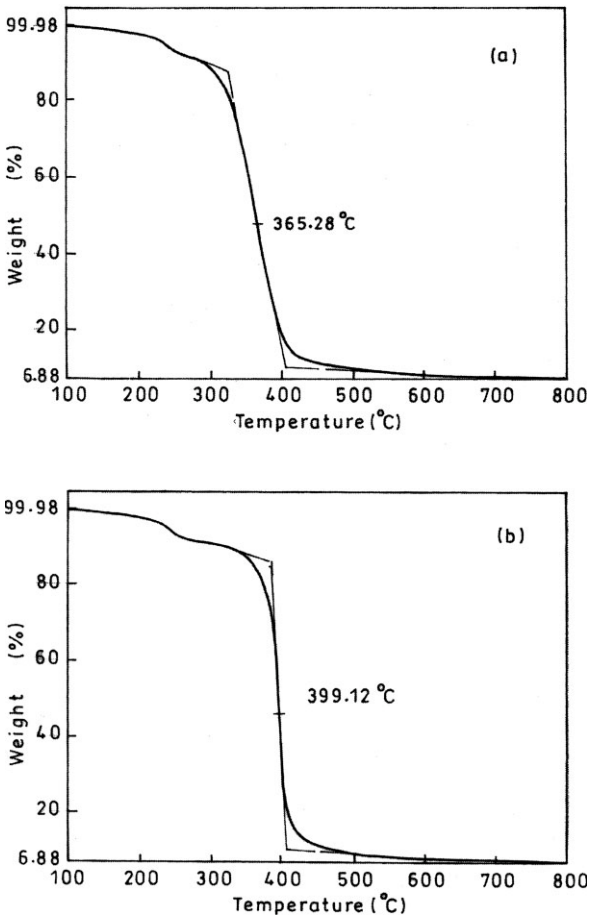



**Figure 8** TGA scan of DGEBA in the presence of mixture DDS/Methionine (EB-1 and EB-4)..

heating rates. The characteristics curing temperatures for DGEBA at different heating rates in presence of amino acids, DDS and mixture of Cysteine/DDS or Methionine/DDS or Cystine/DDS are summarized in Tables I, II, and III. As expected, curing temperatures increased with increasing heating rate. The activation energy of the curing reaction was calculated using Ozawa's method[35,36] by assuming the following conditions:

1. The peak exothermic temperature ($T_p$) represents a point of constant conversion.
2. The reaction follows the first order kinetics.
3. The temperature dependence of the reaction rate constant obeys Arrhenius equation.

The data from dynamic DSC measurements was analyzed in accordance to the following equation:

$$E_a = \frac{R\Delta \log \varphi}{0.4567\Delta(1/T_p)}$$

where $\varphi$ = heating rate (°C/min); $E_a$ = activation enegy (kJ/mol); $R$ = gas constant (8.314 J/mol K); $T_p$ = peak exothermic temperature ($K$).

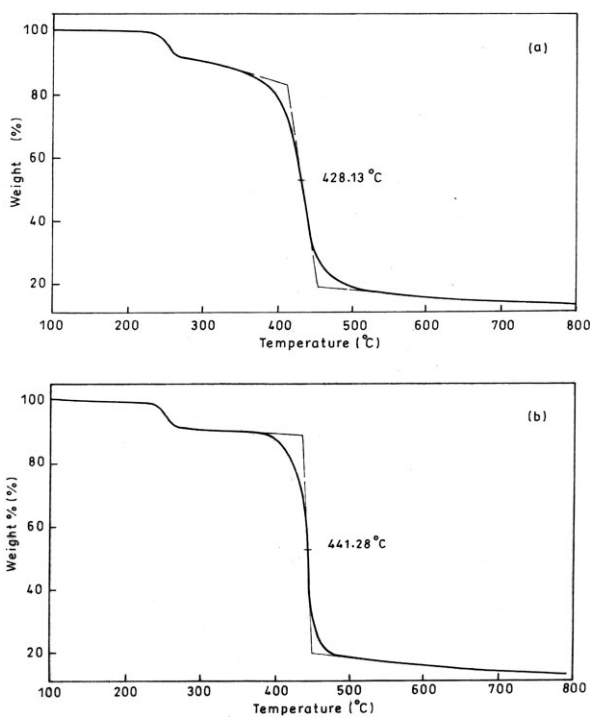



**Figure 9** TGA scan of DGEBA in the presence of mixture DDS/Cystine (EC-3 and EC-2).

**TABLE IV**
**Results of TG/DTG Traces of Cured Epoxy Resins in Nitrogen Atmosphere [DGEBA Cured Isothermally in Presence of Cysteine/DDS mixture by Heating in an Air Oven at 200 ± 20°C for 2 h]**

| Sample Designation | Cysteine/DDS molar ratio | IDT (°C) | $T_{max}$ (°C) | FDT (°C) | Char Yield at 800°C | LOI (%) |
|---|---|---|---|---|---|---|
| EA-1 | 1 : 0 | 323.14 | 379.30 | 427.19 | 26.5 | 28.1 |
| EA-2 | 0.75 : 0.25 | 340.5 | 408.28 | 455.53 | 24.6 | 27.3 |
| EA-3 | 0.5 : 0.5 | 353.13 | 417.60 | 473.7 | 30.8 | 29.8 |
| EA-4 | 0.25 : 0.75 | 376.3 | 412.40 | 489.16 | 30.8 | 28.1 |
| ED | 0 : 1 | 394.9 | 419.4 | 466.0 | 19.2 | 25.2 |

Assuming a constant conversion at the peak exotherm temperature, plots of log φ versus $1/T_p$ were obtained and the activation enegy was calculated using standard procedure. Plots of log φ versus $1/T_p$ are shown in Figure 6. Activation energy of curing was found to be dependent on the structure of amino acid and the molar ratio of Cysteine/DDS or Methionine/DDS or Cystine/DDS. Activation energy was higher for amino acid/DDS-cured system 125 kJ/mol (EA-3) and 131 kJ/mol (EC-2) except 169 kJ/mol (EB-1) as compared with DDS cured system 74 kJ/mol (ED) (Tables I, II, and III). Addition of 0.25 mol fraction of DDS to amino acid in a mixture results in a significant increase of activation energy except in the mixture of DDS/Methionine. Further increase in DDS content did not show any definite trend in the activation energy.

Activation energy for the system cured using mixture of amino acid and DDS is higher than the samples cured using either Cysteine or Cystine (EA-1 and EC-1) or DDS alone (ED) (Tables I, II, and III) and it is exceptionally high for the system cured using Methionine alone which may be due to the presence of electron releasing methyl group decreasing the reactivity of the system and slower the reaction. This could be due to the more complex mechanism of curing DGEBA in presence of mixture as reported earlier for catalyzed epoxy-amino acids. Considering the overall complex nature of curing reaction, the activation energy is an overall value including various steps of curing reaction.

In the DSC scans of isothermally cured samples (curing done by heating at 194 ± 30°C for Cysteine/DDS (EA samples), at 185 ± 30°C for Methionine/DDS (EB samples) and 209 ± 30°C for Cystine/DDS (EC samples) in an air oven for 3 h), no shift in the base line was observed in the temperature range upto 350°C. Absence of exothermic transition indicated the completion of curing. It was not possible to determine the glass transition temperature of cured resins from DSC scans as no shift in base line was observed under the experimental conditions.

### Thermal stability

Figures 7 [(a) EA-4 and (b) EA-2], 8 [(a) EB-1 and (b) EB-4], and 9 [(a) EC-3 and (b) EC-2] show the TG/DTG traces of isothermally cured epoxy resins. Isothermal curing of epoxy resin i.e., EA (Cysteine/DDS mixture) and EB (Methionine/DDS mixture) and EC (Cystine/DDS mixture) samples was performed by heating in an air oven for 3 h at 185 ± 40°C. All the samples were stable up to 265 ± 20°C and started losing weight above this temperature.

The relative thermal stability of the cured resins was evaluated by noting initial decomposition temperature (IDT), final decomposition temperature (IDT), temperature of maximum rate of weight loss ($T_{max}$) and percent char yield at 800°C. The results of TG/DTG scans are summarized in Tables IV, V, and VI. DGEBA cured with Cysteine and Methionine alone (EA-1 and EB-1) had lower value of IDT, $T_{max}$, and FDT as compared with ED, whereas DGEBA cured using either Cystine alone (EC-1) or a mixture of Cystine/DDS (EC-2, EC-3, and EC-4) had higher value of IDT, $T_{max}$ and FDT than ED which

**TABLE V**
**Results of TG/DTG Traces of Cured Epoxy Resins in Nitrogen Atmosphere [DGEBA Cured Isothermally in Presence of Methionine/DDS mixture by Heating in an Air Oven at 200 ± 20°C for 2 h]**

| Sample Designation | Methionine/DDS molar ratio | IDT (°C) | $T_{max}$ (°C) | FDT (°C) | Char Yield at 800°C | LOI (%) |
|---|---|---|---|---|---|---|
| EB-1 | 1 : 0 | 264.17 | 365.28 | 415.30 | 24.7 | 27.4 |
| EB-2 | 0.75 : 0.25 | 323.34 | 388.93 | 431.04 | 30.2 | 29.6 |
| EB-3 | 0.5 : 0.5 | 299.15 | 423.93 | 465.11 | 29.3 | 29.2 |
| EB-4 | 0.25 : 0.75 | 360.01 | 399.12 | 420.41 | 29.5 | 29.3 |

**TABLE VI**
**Results of TG/DTG Traces of Cured Epoxy Resins in Nitrogen Atmosphere [DGEBA Cured Isothermally in Presence of Cystine/DDS Mixture by Heating in an Air Oven at 200 ± 20°C for 2 h]**

| Sample Designation | Cystine/DDS molar ratio | IDT (°C) | $T_{max}$ (°C) | FDT (°C) | Char Yield at 800°C | LOI (%) |
|---|---|---|---|---|---|---|
| EC-1 | 1 : 0 | 397.12 | 422.5 | 491.07 | 34.3 | 31.22 |
| EC-2 | 0.75 : 0.25 | 423.18 | 441.28 | 523.15 | 34.1 | 30.14 |
| EC-3 | 0.5 : 0.5 | 409.17 | 428.13 | 503.26 | 32.62 | 29.54 |
| EC-4 | 0.25 : 0.75 | 400.81 | 452.52 | 512.25 | 20.3 | 30.9 |

again may be due to the presence of S—S linkage in Cystine. Several reactions are possible when a mixture of amine, amino acid, and DGEBA are reacted together, such as formation of more stable imides structures or cross-linking through the reaction of Cysteine/Methionine/Cystine with hydroxyl group. Thermal stability of the resin is dependent on the structure of network, degree of cross-linking etc., which in turn is dependent on the nature and amount of curing agent. The char yield was found to be highest in the system cured using either Cystine alone (EC-1) or a mixture of Cystine/DDS (EC-2, EC-3, and EC-4) whereas rest of the samples had in the range of 27–30 higher than ED.

Char yield can be used as criteria for evaluated limiting oxygen index (LOI) of the resins in accordance to Van Krevelen and Hoftyzer equation.[37]

$$\mathrm{LOI} = 17.5 + 0.4\mathrm{CR}$$

where CR = char yield.

All the samples had LOI values, calculated based on their char yield, greater than 28. These results clearly show that flame resistant DGEBA resin can be obtained by using sulfur containing amino acids as curing agents.

## CONCLUSIONS

From these results, it can be concluded that changing the molar ratio of curing agents and nature of the curing agents can alter curing behavior of epoxy resins. The peak exothermic temperature was highest in the case of DGEBA cured with Cystine, which is more elecron withdrawing due to presence of S—S linkage. The thermal stability of the cured material was found to be dependent on the structure of network. Epoxy resins obtained with DDS/Cystine have much higher thermal stability. Composition of the mixture had a large effect on the curing and thermal behavior. Optimum curing characteristics with excellent thermal stability was obtained in case of system cured using either Cystine alone (EC-1) or a mixture of DDS/Cystine (EC-2, EC-3, and EC-4).

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