

Thermal Behaviour Of Diglycidyl Ether Of Bisphenol-A (DGEBA)/ Dithiols Bearing An Azomethine Group

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Abstract: The curing behaviour of diglycidyl ether of bisphenol-A (DGEBA) with aromatic dithiols having azomethine group and ether/ sulfone/ methylene linkages was studied using differential scanning calorimetry (DSC). Three dithiols of varying linkage groups were synthesized by reacting 2 moles of 4-mercaptobenzaldehyde (H) with 1 mole of 4,4'-diaminodiphenylether[E] or 4,4'-diaminodiphenyl methane [M] or 4,4'-diaminodiphenyl sulfone [S]. The dithiols prepared by reacting H with S, M, and E have been designated as HS, HM and HE respectively. The mixture of the dithiols and 4,4'-diaminodiphenyl sulfone (DDS) at ratio of 0:1, 0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0 were used to investigate the curing behaviour of DGEBA. A broad exothermic transition was observed and the peak exotherm temperature was found to be dependent on the structure of dithiols. The peak exotherm temperature (T_p) was lowest in case of dithiols HE and highest in case of dithiols HS. Thermal stability of isothermally cured DGEBA in the presence of dithiols was evaluated by dynamic thermogravimetry. The char yield was highest for resin cured with dithiols HE.

Keywords: Diglycidyl ether of bisphenol-A; dithiols; curing; thermal stability, 4,4'-diaminodiphenyl sulfone (DDS).

1 Introduction

Epoxy resins are very important class of thermosetting polymers that often exhibit high tensile strength and modulus, excellent chemical, corrosion resistance and good dimensional stability. Hence they are widely used in structural adhesives, surface coatings, engineering composites, electrical laminates etc. (1, 2) On curing these resins become highly cross-linked and amorphous thermosets. They are brittle and have poor resistance to crack growth. The epoxy resin network is formed during the cross-linking reaction using a wide variety of cross-linking agents or hardeners such as acids, anhydrides and amines. However, the conventional epoxy resins are inefficient to satisfy the required properties in the field of advanced materials, which require high

thermal and flame resistance (3-5). Several approaches were used in the past to control the crosslink density of an epoxy network. These include varying the epoxy resin/curing agent functional group ratio, using a difunctional epoxy prepolymer with a different average chain length, and varying the molecular size of the difunctional curing agent.

The diglycidyl ether of bisphenol-A (DGEBA) is the most commonly used epoxy resin as it has many attractive properties such as fluidity, low shrinkage during cure and ease of processing. The cured products have good physical strength, excellent moisture, solvent and chemical resistance. Their main problem is relatively poor thermal stability and flame resistance which limits their applications in

more demanding areas such as aerospace and electronic industry.

The variation in the functional group ratio of the epoxy resin/ curing agent (6-9) has the problems of residual chain ends and the existence of uncrosslinked soluble fractions. Use of different average chain length of the difunctional epoxy prepolymers poses processing problems because of the higher melting temperature and viscosity of the prepolymers. (9, 10) Variation in the molecular size of the curing agent is expected to provide networks with similar structures, except in the molecular weight between the crosslinks. Use of speciality curatives such as polythiols has reportedly improved the performance of the epoxy resin. DGEBA type epoxy resin has been modified with liquid polysulfide rubber, because polysulfide is compatible with epoxy resin (11-13). The polysulfide of low molecular weight of general -SH terminal, (R-SH) reacts with the epoxy groups to cause chain extension but not crosslinking and it becomes an integral part of three-dimensional networks (14) and therefore, do not migrate during subsequent ageing/ storage and also impart flexibility of high order (15, 16).

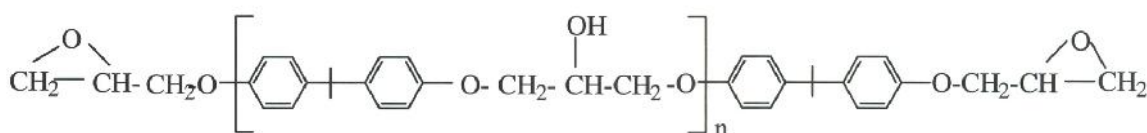
Therefore, the present paper deals with the effect of the structure of thiols HS, HM and HE {obtained by reacting 2 moles of 4-mercaptobenzaldehyde (H)

with 1 mole of 4,4'-diaminodiphenylether[E] or 4,4'-diaminodiphenyl methane [M] or 4,4'-diaminodiphenyl sulfone [S]} on the curing and thermal behaviour of diglycidyl ether of bisphenol-A (DGEBA). Curing of DGEBA in the presence of stoichiometric amounts of thiol was investigated using differential scanning calorimetry (DSC). Thermal behaviour of isothermally cured resins was evaluated using dynamic thermogravimetry in nitrogen atmosphere. Extensive work has also been carried out into the use of thiols in the formulation of epoxy resin systems and when co-cured with amines. This behaviour has also been investigated using mixture of thiols and 4, 4'-diamino diphenylsulfone (DDS).

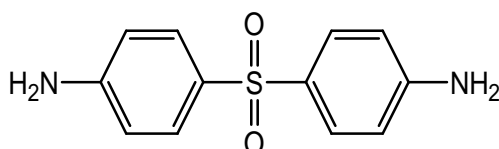
2 Experimental

2.1 Materials

Diglycidyl ether of bisphenol-A (DGEBA, grade LY556, having an epoxide equivalent of 177) was procured from Hindustan Ciba Geigy Ltd. 4-mercaptobenzaldehyde (H) ,4,4'-Diaminodiphenyl sulfone (S), 4,4'-diaminodiphenyl ether (E), 4,4'-diaminodiphenyl methane (M) were purchased from Aldrich and used as received. Methanol and dioxin (CDH) were used as such.



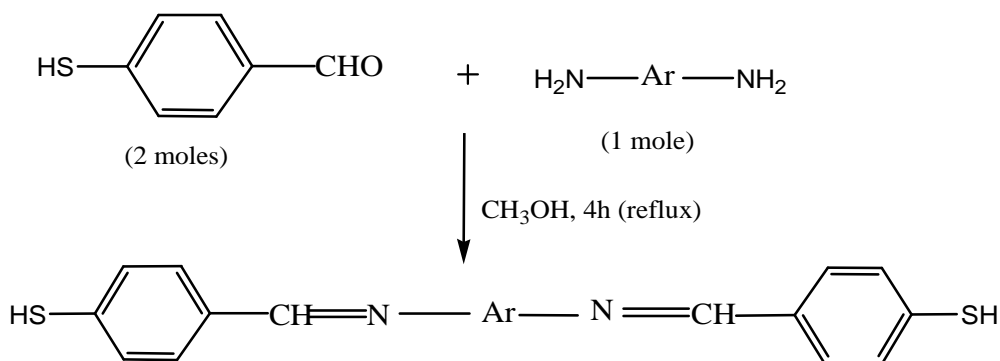
DGEBA



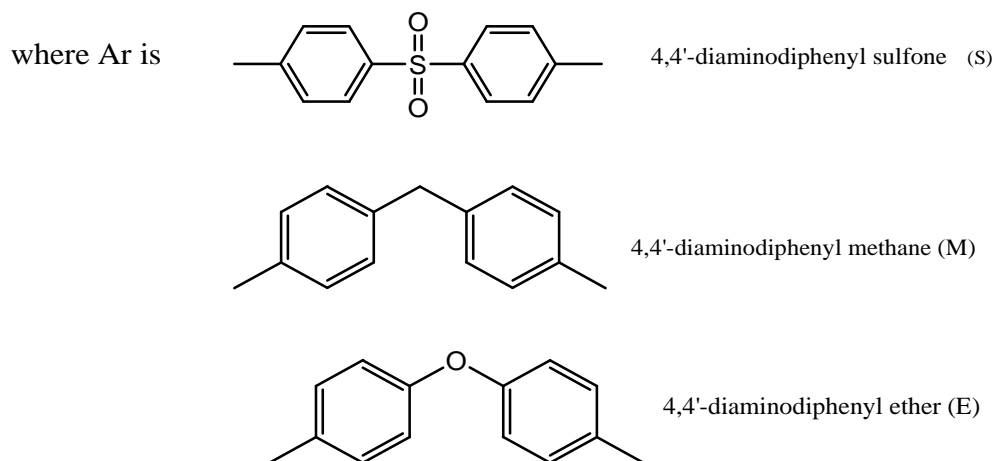
4,4'-diaminodiphenyl sulfone (DDS)

2.2 Synthesis of dithiols with azomethine group

Dithiols with azomethine groups were synthesized by the following reaction scheme:

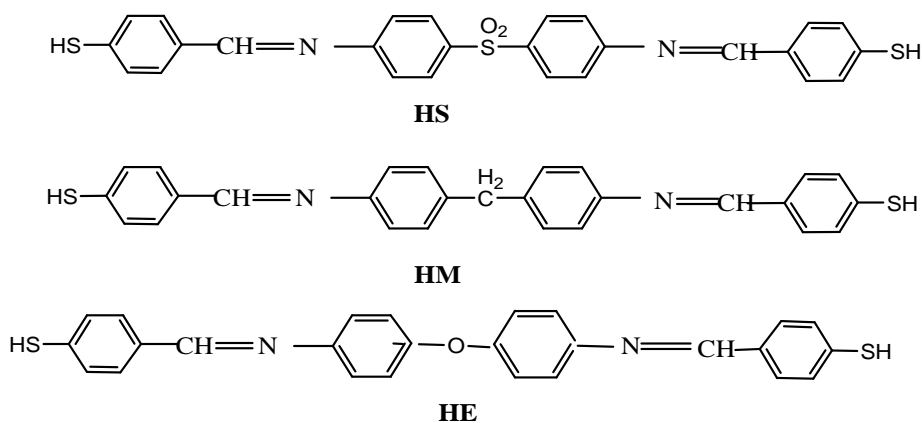


Scheme: Synthesis of dithiols



A mixture of 4-mercaptobenzaldehyde (H) (0.1mole) and 4, 4'-diaminodiphenyl sulfone (DDS) (S) (0.05mole) was refluxed in methanol for 4hours. Then the reaction mixture was then cooled and the resulting solid was recrystallized from dioxin to give dithiol having azomethine groups.

Similarly, the other azomethine dithiol monomers were prepared from 4-mercaptobenzaldehyde (H) and diamines 4,4'-diaminodiphenyl ether (DDE) (E)/ 4,4'-diaminodiphenyl methane (DDM) (M) . The structure of azomethine as follows:



2.3. Characterization

The synthesized dithiols were characterized by elemental analysis. Infra-red spectra in KBr pellets were recorded using a Biorad Digilab FTS-40 FTIR spectrometer. ¹H-NMR spectra were recorded on a Bruker AC 300 spectrometer at a frequency of 300 MHz using DMSO-d₆ as solvent and tetramethyl silane as an internal standard.

2.4. Curing studies

TA 2100 thermal analyzer having 910 DSC module was used for recording DSC traces at heating rate of 10°C min⁻¹ and 5±2 mg of sample was used in each experiment. For curing studies, the samples were obtained by mixing stoichiometric amounts of dithiols(HS/HE/HM) and DDS with DGEBA in the varying molar ratio of 0:1, 0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0 using minimum amount of low boiling solvent. After thorough mixing, the solvent was evaporated under vacuum and the freshly prepared samples were used for recording DSC traces in the static air atmosphere at a programmed heating rate from room temperature upto 350°C. The epoxy samples have been designated by adding prefix E to HS/HE/HM followed by a numerical suffix. For example, epoxy cured using mixture of HS: DDS in the ratio of 0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0 has been designated as EHS-1, EHS-2, EHS-3 and EHS-0. The sample with DGEBA and DDS has been designated as ED. Similarly samples cured using mixture of other dithiols and DDS were designated.

2.5. Thermal stability

Thermal stability of the cured resin in nitrogen atmosphere (flow rate 60 cm³/min) was evaluated using a Du Pont 2100 thermal analyser having a 951 TG module. A sample weight of 10 ±2 mg and a heating rate of 20°C/min was used. Thermogravimetric analysis is also used as a fast and exact method for determination of the kinetics

of thermal degradation of polymers. The activation energy and order of reaction (n) were evaluated by using integral equation of Coats and Redfern (17).

$$\log_{10} \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \log_{10} \frac{ZR}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] - \frac{E_a}{2.3RT}$$

T is the absolute temperature in Kelvin, E_a is the activation energy is gas constant, n is the order of reaction, Z is pre-exponential factor, β is heating rate.

3 Results and Discussion

3.1 Structural Characterization of dithiols

The aromatic dithiols were of white to orange in colour and insoluble in acetone and chloroform but were soluble in DMF and DMSO. The formula molecular weight, percentage yield and results of elemental analysis of aromatic dithiols are reported in the Table 1. The calculated values of CHN agreed well with the experimentally determined values. The experimented values are marginally lower (~ 1-2 %) than the theoretical calculated values.

3.2 FTIR

In the FTIR spectra of all aromatic dithiols, the absorption band due to azomethine (C=N) group stretching was observed at 1610-1630cm⁻¹. In dithiol HS, strong absorption bands were observed at 1320cm⁻¹ and 1149 cm⁻¹, which have been attributed to asymmetric and symmetric stretching vibration of the sulfone group (-SO₂-). In dithiol HE, strong absorption band due to Ar-O-Ar linkage was observed at 1013 cm⁻¹. The thiol(-SH) group absorption peak was found at 2572 cm⁻¹. The broad peak around 1580-1660 cm⁻¹ implies the C=C stretch in benzene ring. All other characteristic absorption bands due to aromatic stretching were observed at their usual position.

Table 1: Results of C, H, and N elemental analysis

| Sample designation | Molecular formula | Yield (%) | Elemental Analysis (%) | | |
|--------------------|--|-----------|------------------------|----------|----------|
| | | | C | H | N |
| HS | C ₂₆ H ₂₀ N ₂ S ₃ O ₂ | 78 | 63.1(63.9) | 3.9(4.1) | 5.2(5.7) |
| HE | C ₂₆ H ₂₀ N ₂ S ₂ O | 80 | 69.8(70.9) | 4.2(4.5) | 5.9(6.4) |
| HM | C ₂₇ H ₂₂ N ₂ S ₂ | 69 | 73.7(74.0) | 4.6(5.0) | 5.9(6.4) |

Numerical values within parenthesis represent the calculated values.

Table 2: Results of $^1\text{H-NMR}$ spectra along with their assignment

| Sample Designation | (ppm) | | |
|--------------------|---------|--------------|---------|
| | -SH | Aromatic H's | -CH=N- |
| HS | 3.8(2H) | 6.8-7.9(20H) | 8.1(2H) |
| HE | 3.7(2H) | 6.8-8.3(20H) | 8.3(2H) |
| HM | 3.8(2H) | 6.8-7.6(20H) | 8.2(2H) |

3.3 $^1\text{H-NMR}$

In the $^1\text{H-NMR}$ spectrum of dithiols (HS/HM/HE), a signal due to -SH proton was observed at $\delta=3.8\text{ppm}$ (singlet) and a multiplet due to aromatic protons was observed in the range of $\delta=6.8-8.3\text{ppm}$. In HM sample, a singlet due to methylene protons (-CH₂-) was also observed at 1.6 ppm. A signal due to CH=N proton of azomethine group was observed at $8.3 \pm 0.3\text{ ppm}$. The integration was used to calculate the number of protons. The position of signals observed in the $^1\text{H-NMR}$ spectra of all the thiol along with their assignment are given in Table 2.

The structure of aromatic thiol thus synthesized was confirmed by using FTIR and NMR spectroscopy.

3.4 Curing studies

The curing behaviour of epoxy resin depends on the structure and molecular size of the dithiols investigated by recording DSC traces. In the DSC scan of DGEBA alone, no exothermic transition was seen in the temperature range of 50-350°C thereby

indicating the absence of curing or crosslinking. In the DSC scans of DGEBA in the presence of dithiols, a broad exothermic transition in the temperature range of $165 \pm 20^\circ\text{C}$ - $290 \pm 30^\circ\text{C}$ was obtained. The exothermic transition associated with crosslinking or curing was characterized by noting the following temperatures (Fig 1):

T_i = kick-off temperature, where the curing starts.

T_{onset} = temperature of onset of exotherm obtained by extrapolating the steepest portion of the exotherm to the base line.

T_p = temperature of peak position of exotherm.

T_f = temperature of end of curing exotherm. This was taken as the temperature where the exotherm levels with the base line in the final stage of curve.

ΔH = heat of curing reaction, obtained from the area under the exothermic transition.

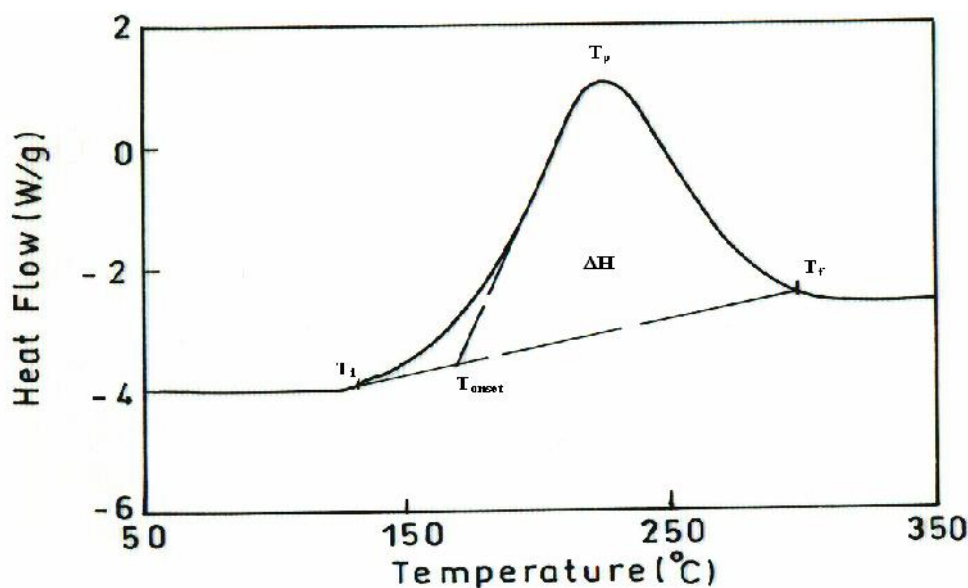
**Fig.1**

Table 3: Results of DSC scan of DGEBA in the presence of dithiols HS/ HE/ HM, DDS and its mixture in varying molar ratios at 10°C min⁻¹

| Sample designation | Molar ratios of HS/ HE/ HM: DDS | T _i /°C | T _{onset} /°C | T _p /°C | T _f /°C | H /J g ⁻¹ |
|--------------------|---------------------------------|--------------------|------------------------|--------------------|--------------------|----------------------|
| ED | 0:1 | 131.1 | 174.6 | 224.0 | 295.7 | 264.4 |
| EHS-1 | 0.25: 0.75 | 145.2 | 175.5 | 214.3 | 297.3 | 277.3 |
| EHS-2 | 0.5: 0.5 | 147.1 | 148.9 | 214.5 | 297.3 | 248.2 |
| EHS-3 | 0.75: 0.25 | 140.6 | 180.8 | 207.1 | 299.4 | 293.7 |
| EHS-0 | 1:0 | 170.8 | 194.0 | 231.7 | 317.2 | 179.8 |
| EHE-1 | 0.25: 0.75 | 158.8 | 175.4 | 218.8 | 269.9 | 195.7 |
| EHE-2 | 0.5: 0.5 | 165.9 | 175.4 | 214.4 | 257.1 | 286.6 |
| EHE-3 | 0.75: 0.25 | 169.2 | 181.5 | 216.7 | 268.3 | 150.2 |
| EHE-0 | 1:0 | 156.7 | 182.2 | 198.9 | 260.0 | 137.8 |
| EHM-1 | 0.25: 0.75 | 142.2 | 176.6 | 217.8 | 297.3 | 104.4 |
| EHM-2 | 0.5: 0.5 | 141.8 | 191.8 | 216.3 | 284.0 | 283.6 |
| EHM-3 | 0.75: 0.25 | 167.1 | 201.9 | 224.4 | 265.8 | 211.2 |
| EHM-0 | 1:0 | 140.1 | 155.2 | 203.0 | 320.5 | 112.4 |

Table 4: Results of thermal stability of DGEBA cured isothermally using HS /HE/ HM/ DDS / or Mixture in nitrogen atmosphere (heating rate = 20°C min⁻¹)

| Sample designation | IDT /°C | T _{max} /°C | FDT /°C | Char yield /% at 800°C | LOI /% | Activation energy, E _a (kJ/mole) |
|--------------------|---------|----------------------|---------|------------------------|--------|---|
| EHS-1 | 432.0 | 456.2 | 484.7 | 30.2 | 29.6 | 323.6 |
| EHS-2 | 416.1 | 438.4 | 458.1 | 28.3 | 28.8 | 310.1 |
| EHS-3 | 402.1 | 432.3 | 451.4 | 28.2 | 28.8 | 283.9 |
| EHS-0 | 353.0 | 386.7 | 414.4 | 28.3 | 28.8 | 162.3 |
| EHE-1 | 447.1 | 462.7 | 487.9 | 28.2 | 28.8 | 398.3 |
| EHE-2 | 402.3 | 431.5 | 466.2 | 30.6 | 29.7 | 389.8 |
| EHE-3 | 395.2 | 428.9 | 460.6 | 31.8 | 30.2 | 235.0 |
| EHE-0 | 353.2 | 393.4 | 424.8 | 35.2 | 31.6 | 203.7 |
| EHM-1 | 402.4 | 436.7 | 462.3 | 25.3 | 27.6 | 256.3 |
| EHM-2 | 394.8 | 440.5 | 468.6 | 26.2 | 28.0 | 277.4 |
| EHM-3 | 406.2 | 441.1 | 469.2 | 27.4 | 28.5 | 289.7 |
| EHM-0 | 362.4 | 390.7 | 417.5 | 34.5 | 31.3 | 236.8 |

The results of DSC scans are summarized in Table 3. The curing temperatures were dependent upon the structure of diamines used in the preparation of thiol. Comparing the curing behaviour, the following trend in T_i was observed as:

$$\text{EHE} < \text{EHM} < \text{EHS}$$

Reaction of an thiol group with an oxirane ring is a nucleophilic addition and the presence of an electron withdrawing group is expected to reduce the nucleophilicity of thiol. This is obvious from T_p value, which was highest in the case of DGEBA/HS (EHS) due to the decreased nucleophilicity of dithiol (HS) which is caused by the presence of electron withdrawing (SO₂) group.

DDS is generally used as hardener for curing of epoxies. The incorporation of thiols along with DDS

was expected to affect the curing behavior and the thermal stability of the cured network. In the DSC scans of DGEBA cured using mixture of thiols (HS, HM, HE), the presence of small amount of DDS in a mixture resulted in a significant increase in the peak exothermic temperature. H values showed no definite trend.

The isothermally curing of DGEBA in the presence of stoichiometric amounts of dithiols was done by heating in an air oven (165±20°C for 3h), which was then used for the determination of the glass transition temperature using DSC. In the DSC scans of isothermally cured samples, absence of exothermic transition indicates the completion of curing.

3.5 Thermal behaviour

The thermal stability of epoxy resin samples cured isothermally with a stoichiometric amount of dithiols was determined by recording TG/ DTG derivative traces in nitrogen atmosphere. The relative thermal stability of the cured resins was compared by noting initial decomposition temperature (IDT), final decomposition temperature (FDT), temperature of maximum rate of weight loss (T_{max}) and percent char yield at 800°C. The results are summarized in Table 4. All the samples were stable upto 350°C and a significant weight loss occurred only beyond this temperature. The char yield was tend to be dependent on the structure of dithiols and it was highest for EHE and lowest for EHS. Lower char yield observed in case of EHS could be due to the loss of SO₂, which is present in the dithiols. IDT, T_{max} , FDT and char yield increased significantly when 0.25 mole of DDS was added to the mixture of HS/ HM/ HE.

Char yield can be used as a criteria for evaluating limiting oxygen index (LOI) of the resin in

accordance with Van Krevelen and Hoftyzer equation²⁵.

$$LOI = 17.5 + 0.4 CR$$

Where CR= char yield

All the samples had LOI values calculated based on their char yield was higher than 28 except for DGEBA/ HS-DDS (EHS). On the basis of LOI values, such materials can be classified as self-extinguishing resin and flame resistant DGEBA resin can be obtained by using dithiols as curing agents.

Conclusions

From these results, it can be concluded that the curing behaviour of epoxy resins can be altered by changing the molar ratio of curing agents and nature of the curing agents.. Curing behavior was found to be maximum in case of sulfone containing moiety. Composition of the mixture had a large effect on the thermal behaviour of epoxy resin. Thermal stability showed reduction with higher concentration of thiols.

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