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Synthesis and Thermal Degradation Studies of Aromatic Based Epoxy Resins Bearing Salicylaldehyde and Epichlorohydrin group.

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ABSTRACT

The thermal degradation of epoxy resin 4, 4' – bis (thiourea) biphenyl sulphone, salicylaldehyde and epichlorohydrin blend was investigated by using thermogravimetric analysis (TGA). Spectroscopic analysis Fourier transform infrared spectroscopy and proton Nuclear Magnetic Resonance were performed for product identification. Thermal, chemical stability and hardness testing were conducted on the cured and uncured product. The results of TGA revealed that the activation energy calculated by Sharp Wentworth and Freeman Carroll methods are in good agreement with each other. The monomers were blended with epoxy based trickle impregnation resin and cured. The cured resins were subjected to TGA and DSC analysis. Presence of 3% by weight of the diglycidyl monomers bearing salicylaldehyde and epichlorohydrin groups in the cured blends did not alter the thermal stability but increased the thermal conductivity. The thermal conductivity of the cured blends were approximately 1.6 times higher than that of epoxy-based trickle impregnation resin and comparable with the epoxy-based resin filled with 20% inorganic fillers.

Keywords: Epoxy resin, FTIR, Thermal degradation, SEM, DGEBA, Epichlorohydrin.

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INTRODUCTION

Epoxy resins belong to the most important thermosetting polymers with good heat, moisture and chemical resistance, toughness, electrical and mechanical strength and good adhesion to many substrates. The linear epoxy is cured into three dimensional cross-linked networks by curing agents to give a hard and infusible thermoset resin. The secured polymers are applicable to surface coatings, painting materials, composites, laminates, encapsulates for semiconductors and insulating materials for electrical devices. Recently much attention has been made to modify the structural make-up of epoxy resins in the attempts to enhance the flexibility and toughness as well as thermal properties[1,2] of the final product. An example is the incorporation of long hydrocarbon chain with intermittent ether bond into the polymer backbone[3]. This modification did affect flexibility to the resin but at the expense of a lowered glass transition. Introducing a saturated cycloaliphatic ring into the backbone structure was previously attempted [4-8] which displayed lower viscosity before curing; their cured polymers show the advantages of good dielectric properties and durable performance for outdoor use. However, some inherent features of the resulting polymers such as the relatively low glass transition temperature (T_g), inferior cracking-resistance when subjected to severe temperature and moisture environment, and low reactivity towards amine curing agents, may cause limitation to their application. On the other hand, introducing rigid ring structures such as phenyl [9] or naphthalene rings into chain backbone would induce a higher T_g . Not much work has been attempted to study a system of epoxy resin with rigid phenyl ring both at the backbone and as pendant group. In this work, an aromatic based epoxy resin with pendant phenyl group was synthesized and their thermal and curing properties were studied.

MATERIALS AND METHOD

Materials

All the chemicals used were of AR grade. 4, 4' – bis (thiourea) biphenyl sulphone, salicylaldehyde and 38 % HCl were obtained from Aldrich. These materials were used without further purification. Epichlorohydrin were also obtained from Aldrich and freshly distilled prior to use.

Methods

Synthesis of 4,4' diamino bis (thiourea) biphenyls: The procedure adopted for the synthesis of 4,4' diamino bis(thiourea) biphenyls is given below. 0.01M of 4,4' diamino diphenyl ether is taken in a evaporating dish, 10.5ml of concentrated HCl, 0.04M of ammonium thiocyanate and 75 ml of water were taken and heated with a steam bath for 1 hour and allowed to cool. The contents were evaporated slowly to dryness over a period of 6 hours. The light yellow coloured precipitate obtained was washed several times with ether and recrystallized in absolute alcohol. The product 4,4'Diamino bis(thiourea) bisphenyl methane was dried at 60°C using vacuum drying oven for the period of 6 hours. Similarly, the 4,4' Diamino bis(thiourea) bisphenyl ether and 4,4' Diamino bis(thiourea) bisphenylsulphone were prepared according to the above procedure using 4,4'diaminodiphenyl ether and 4,4'diamino diphenylsulphone respectively. The synthesis of 4,4' diamino bis(thiourea) biphenyls is shown in Fig. 1.

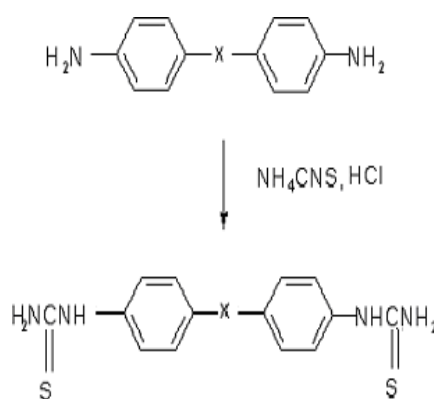


Figure 1: Synthesis of 4,4' diamino bis(thiourea)biphenyls

Synthesis of diglycidyl monomers bearing thiourea and azomethine groups

Diglycidyl monomers bearing thiourea and azomethine groups have been carried out in two steps. First step involves the preparation of the dihydroxy monomer bearing thiourea and azomethine and in the second step, the diglycidyl monomers were prepared. The scheme for both the steps are given in Fig. 2 and discussed below.

Dihydroxy monomer bearing thiourea and azomethine groups prepared by dissolving 4,4'-bis(thiourea)biphenyl ether (0.05 mol), *p*-hydroxybenzaldehyde (0.1 mol) were taken in a round bottomed flask, a catalytic quantity of *p*-toluene sulfonic acid in DMF was added and heated at 110 °C. After the initial heating for 15 min., the azeotrope was removed under reduced pressure and the contents were heated for a period of 4 hour. The contents were poured into a beaker containing cold water with constant stirring to precipitate the dihydroxy monomer. It was then recrystallized from 1: 1 DMF/water mixture. Other two monomers were prepared by employing the above procedure using 4,4 bis(thiourea) biphenylmethane and 4,4'-bis(thiourea)biphenyl sulfone respectively.

Diglycidyl monomers bearing thiourea and azomethine groups were prepared by dissolving 0.5 g of dihydroxy monomer of step I in 35 ml of epichlorohydrin and heated to 110°C for 1 hour with constant stirring. After obtaining a clear solution, catalytic quantity of benzyl trimethyl ammonium was added and the contents were refluxed for another 3 hour. Excess epichlorohydrin was removed by distillation and the remaining solid was washed with water and dried at 60°C under vacuum.

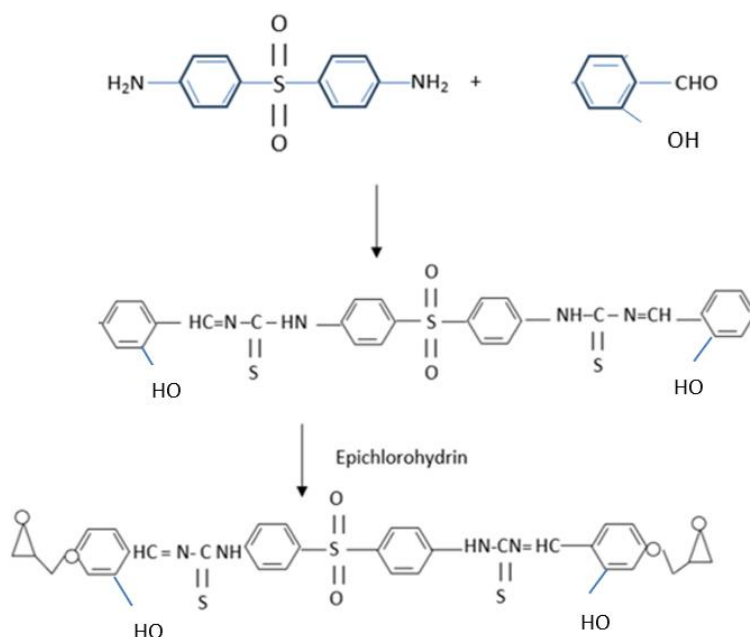


Figure 2: Synthesis of Epoxy Resin bearing thiourea and azomethine groups

RESULTS AND DISCUSSION

The synthesized thiourea base aromatic epoxy resins were dark yellowish in colour powder in nature. The melting point (188°C) of the resin determined by using differential scanning calorimeter (DSC).The bis(thiourea) monomers were prepared using the earlier reported protocol and well established. Representative FTIR spectrum of monomer indicated in Fig. 3. The NH₂ stretching frequency of the diamine 4,4'-diphenylsulphone appears as doublet at 3275 cm⁻¹ and 3183 cm⁻¹ has undergone significant changes in the monomer 4,4'-bis(thiourea)diphenyl sulphone[11]. The -NH₂ stretching frequency of the thiourea diamine appeared at 2970cm⁻¹.

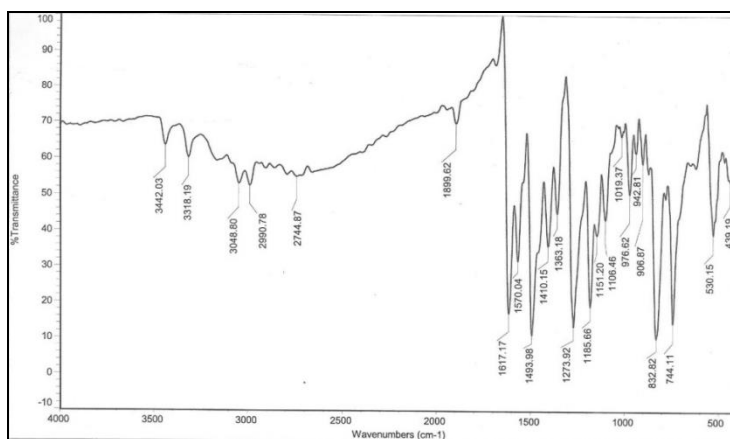


Fig 3: FTIR spectrum of monomer 4, 4'-bis (thiourea) biphenylsulphone

The -NH stretching and that of -NH bending frequencies of the thioamide appeared at 2873 cm^{-1} and 1466 cm^{-1} respectively. The C=S stretching frequency in the monomer appeared at 1085 cm^{-1} . The structure of the dihydroxy monomers, bearing thiourea and azomethine groups, were confirmed through IR and $^1\text{H-NMR}$ spectroscopic analysis. The $-\text{NH}_2$ stretching frequency appeared at 3275 cm^{-1} the diamine 4,4'-(bisthiourea) diphenyl sulphone has completely disappeared in the formation of and the hydrogen bonded $-\text{OH}$ stretching frequency appeared as a broad band in the region $3275\text{--}3183\text{ cm}^{-1}$ there by confirming the condensation of resin with salicylaldehyde¹¹ The other important observations that are made from Fig. 3 are: $-\text{N}=\text{CH}-$ stretching frequency at 1671 cm^{-1} and $-\text{NH}$ stretching frequency at 1512 cm^{-1} .

The $^1\text{H NMR}$ spectra of the monomers are shown in Fig.4, respectively. The signals are assigned in the Fig. 4 The $-\text{NH}$ and $-\text{OH}$ signals appeared around 10.0 ppm, while that of the $-\text{N CH}-$ protons appeared at 8.4 ppm. The aromatic protons appeared in the range 7.7–6.4 ppm.

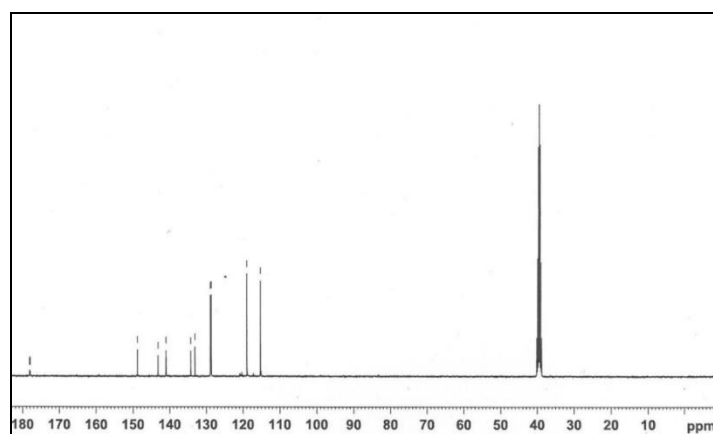


Fig 4: $^1\text{H-NMR}$ spectrum of monomer

The major aim of this investigation is to investigate the thermal conductivity of the blends without altering the thermal stability and other favorable properties of the epoxy resins. Hence the diglycidyl ether mono-mer bearing thiourea and azomethine groups were taken in only 3% weight in the blends (Table 1). TGA studies were made for the Dobeckot 605 (NEAT) and three blend combinations, viz., PATE 1 in static air. These studies indicate that the decomposition behavior is the same for all the samples with 5% weight loss occurring around 195°C . This observation indicates that inclusion of 3% weight of diglycidyl monomers bearing thiourea and azomethine groups, with the Dobeckot 605 (NEAT) resin has not altered the thermal stability.

The DSC traces of the resin and the blends (PATE 1) are shown in Fig. 5. The DSC curve of the NEAT and blended resins showed no exothermic peak, which indicated the completion of the curing reaction. Tg of the cured NEAT resin (trickle impregnation resin Dobeckot605) was found to be 68.7°C. The Tg of the cured blends PATE 1 was 62°C and 63°C, respectively. When compared to the neat resin the Tg of the blended resins decreased by about 8°C. Such a decrease in Tg values without compromising the thermal stability of the resins is a complementary one. The decrease in Tg of the blended resins makes it easier in application to delicate parts of the apparatus to be coated.

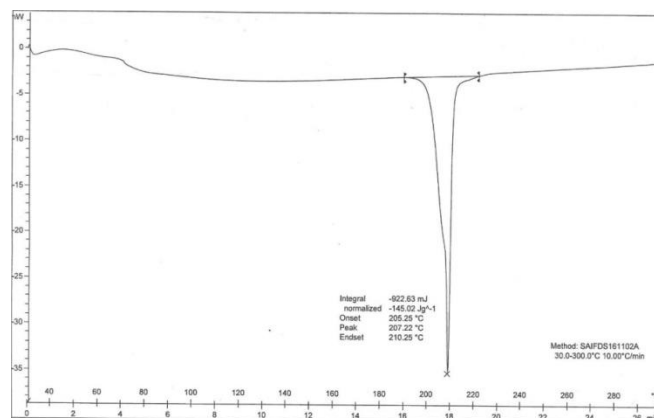


Fig 5: DSC trace the NEAT and blended resin

It is clear that that the blends PATE showed one more transition around 150°C which is absent in the neat resin. Such types of transitions are known for the biphenyl containing epoxies. Biphenyl epoxies with ester linkages and stillbene units have shown liquid crystalline properties. The present work deals with epoxies with thioamide links. Generally polymers with amide links which show liquid crystalline properties in solution have been classified as lyotropic polymers. Due to the strong intermolecular hydrogen bonding they do not show liquid crystalline properties on melt. However, if the strength of the intermolecular hydrogen bond is reduced by proper substitution in the ring in the positions neighboring to the–NHOC– groups, they showed thermotropic liquid crystal- lineproperties[12]. When compared to the amide links, thioamide links have considerably reduced the hydrogen bonding effects due to the presence of thiocarbonyl groups[13]. These monomers have rigid rodlike structures and when placed between two crossed polarizers under an optical microscope showed birefringence with no clear established structure.[14]. This suggests the formation of liquid crystalline state, probably during curing around150°C.The thermal conductivities of the epoxy based trickle impregnation resin (Dobeckot605), 20% inorganic materials filled epoxy based resin (ULTIMEG 2050), other reported epoxy based resins and the present epoxy blends are given in Table 1. It is clear from Table 1 that the investigated resin blends comprising new diepoxy monomer bearing phenylthiourea and azomethine groups (runs 2,3,4, Table 1) shows about 1.9 times higher thermal conductivity than the commercial epoxy based trickle impregnationresin (run 1, Table 1) (Dobeckot 605).

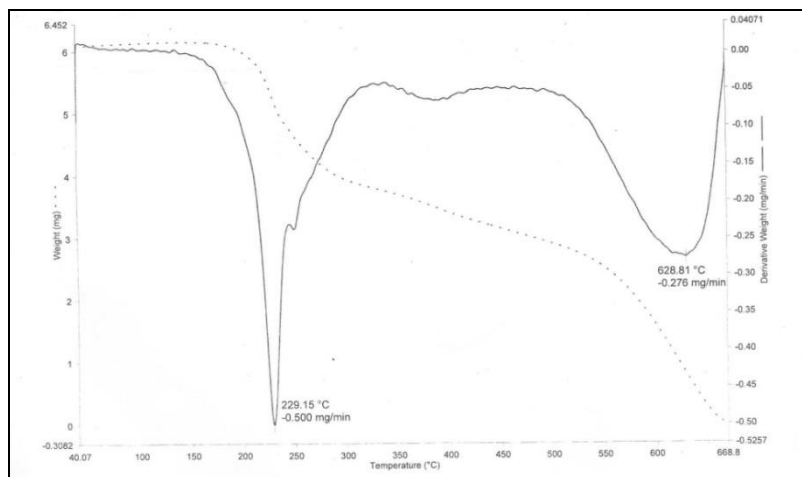


Figure 6: TG Graph of Epoxy resin

Thermal conductivity of the present blends are slightly higher than the commercial epoxy based resin (ULTIMEG 2050) filled with 20% alumina and silicate (run 5, Table 1). Thermal conductivity values of the investigated blends are twice the value of conventional epoxy resins (run 6,7, Table 1) $0.17 \text{ Wm}^{-1} \text{ K}^{-1}$. The cured neat and blended resins (NEAT, PATE) were transparent and light brown in color, while the cured resin containing inorganic fillers (ULTIMEG 2050) was opaque. The improved thermal conductivity of the epoxy blends containing phenylthiourea and azomethine groups when compared to the neat resin is possibly due to the presence of rigid rod like structure. The diglycidyl monomers bearing thiourea and azomethine groups when cured with the epoxy based trickle impregnation resin forms crystal-like structure which suppress the phonon scattering to some extent. Suppression in the phonon scattering to some extent might have resulted in the improvement in thermal conductivity of the blends [15].

Table 1: Thermal conductivity of new resin and other reported resins

Run	Blend code	Blend composition	Thermal conductivity ($\text{Wm}^{-1} \text{ K}^{-1}$)
1	NEAT	Dobeckot 605 epoxy resin (100: 0)	0.26
2	PATE	Dobeckot 605 epoxy resin: 3a (97:3)	0.40
3	ULTG	ULTIMEG 2050 epoxy based resin with 20% inorganic materials	0.44
4	BPE	4,4'-Biphenoldiglycidylsulphone	0.35
5	CEP	Conventional epoxy resin	0.14–0.27

CONCLUSIONS

Epoxy resin containing thiourea and azimethine group and by using salicylaldehyde and epichlorohydrin have synthesized. Resin based trickle impregnation cured resin when blended with new rigid rod like diglycidyl monomer bearing thiourea and azomethine groups by 3% weight showed superior thermal conductivity. Thermal conductivity of the cured epoxy based trickle impregnation resin and the blended resins (PATE) were 0.20 and 0.34–0.36 $\text{Wm}^{-1} \text{ K}^{-1}$, respectively. Incorporation of the new diglycidyl monomers in the blend did not alter the thermal stability of the cured resins when compared to the resin.

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