SYNTHESIS, CHARACTERIZATION AND THERMAL CONDUCTIVITY OF DIGLYCIDYL MONOMER BEARING THIOUREA ANDSALICYLADEHYDE GROUP EPOXY RESIN

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ABSTRACT
Noveldiglycidyl monomers bearing phenylthiourea and azomethine groups were prepared using 4,4^0-diaminodiphenyl ether and 4,4^0-diaminodiphenylsulphone as reactants. The monomers were characterized byFTIR and ^{1}H-NMR spectroscopic methods. The monomers were blended with epoxy based trickle impregnation resinandcured.Thecuredresinswereсubjected toThermaogravimetricanalysis and Differential scanning colorimetry analysisinpresence of 3% by weight of the diglycidyl monomers bearing thiourea and azomethine groups in the cured blends did not alter the thermal stability but increased the thermal conductivity. The thermal conductivity of the cured blends was approximately 2.1 times higher than that of epoxy-based trickle impregnation resin.
Keywords: Diglycidyl monomers; Phenylthiourea; Thermal conductivity, Spectral analysis, TEM.

INTRODUCTION

Epoxy resins are low molecular weight pre-polymers or higher molecular weight polymers which normally contain at least two epoxide groups. The epoxide group is also sometimes referred to as a glycidyl or oxirane group. Epoxy resins are polymeric or semi-polymeric materials, and as such rarely exist as pure substances, since variable chain length results from the polymerisation reaction used to produce them. High purity grades can be produced for certain applications, e.g. using a distillation purification process. One downside of high purity liquid grades is their tendency to form crystalline solids due to their highly regular structure, which require melting to enable processing. Epoxy resins are fundamentallyprepolymers that have on an average two or more epoxide groups per molecule[1].Formulations of epoxy resin play significant role in the electronics industry and are employed in transformers, transistors, generators, integrated circuits,andmotors. These resins are very good electrical insulators and protect electrical com- ponents from moisture,dust and short circuiting. Both elec- trical and electronic equipment have newly been improved in size and performance with designs to diffuse the heat from internal components efficiently.

Electronic and electrical equipment should be insulated with materials that have higher thermal conductivities usually thermoset composites containinginorganic ceramic powders having elevated thermal conductivity are used. Silicon Carbide, Aluminum oxide and magnesium oxide particles are some of the inorganic fillers used for the development of thermal conductivity of polymers[2]. The fillerspresently in use for epoxy molding compositions consist of fused silica, alumina, fiber glass, calciumsilicate and clays.

The use of inorganic ceramics improves thethermal conductivity of the resin to a little extent, they posetroubles in

working, processing, modeling, and curing reactions[3]. A higher percentage of fillerscritically alters the polymer component and can formagglomerates, which induces the stress concentration and decreases the tensile strength, modulusand ductility of thematerial.A possible solution would be to improve the thermal conductivities of the insulating resins themselves ortoblend the commercial resin with a modified epoxy resin which enhances the thermal conductivity. Heat is transported rapidly through the molecular chain direction if theresin is highly ordered. In this direction the liquid crystalline epoxy resins have gained considerable interestduetotheiradvantages like controlled curing rate and goodmechanicalproperties[4].

Modified epoxide novolacs and polyether- grafted-epoxide polysiloxanes with commercial epoxide and their effect on the thermal properties of the cured resin have been reported[5]. Study on majority of the liquid crystalline epoxy resins mainly focuses on the mechanical properties and thermal stability of the cured products[6-7]. Diepoxy monomers, with phenyl benzoate units, when cured with diaminodiphenyl methaneascuringagent yield epoxyresins of high thermal conductivity[8]. Schiff-base-bearing epoxy resins may fit into this category.

Epoxy resin containing azomethine groupwhen cured with diglycidyletherofbisphenol(DGEBA)showed improved mechanical properties[9]. Phenylthiouraand its derivatives were reported for their use as thermal stabilizer for PVC[10]. In this study the objective is to provide an improved epoxy molding composition containingdiepoxy monomer bearing phenylthiourea and azomethinegroups, for better thermalconductivity.

EXPERIMENTAL

Material and Methods

The4,4^{0}-diamino- diphenylsulphone (Aldrich) were recrystallized before use. N,N-dimethylformamide (DMF) was dried and distilled under reduced pressure. Salicylaldehyde(Aldrich) was used as received. Two-component epoxy based trickle impregnation resin (Dobeckot 605 and Hardener 758 triethylenetetraamine) was AR grade from ELANTAS Beck India Ltd. ULTIMEG 2050 epoxy based resin with 20% fillers is used as received.

Synthesis of bisthiourea Monomer

Thiourea monomer was prepared by modifying the procedure reported earlier[11]. In a 250 ml porcelain evaporatingdish, 0.01Mof4,4^{0}-diaminodiphenyl sulphone,10.5 ml concentrated HCl, 0.04 M of ammonium thiocyanate and 75 ml of water were taken and heated with a steam bath for 1 h and allowed to cool. The contents were evaporated slowly to dryness over a period of 4h. The light yellow color solid was boiled with ethanol along with activated charcoal. The product4,4^{0}-bis(thiourea) biphe-nylsulphonewas recrystallized with ethanol and dried. The4,4^{0}-bis (thiourea)biphenyl sulphone were synthesized according to theprocedureusing4,4^{0}-diaminodiphenyl sulphone respectively.

Preparation of Dihydroxy Monomers Bearing Thiourea and Azomethine

4,4^{0}-Bis(thiourea) biphenyl ether (0.05 molsalicylaldehyde(0.1 mol) were heated in round-bottomed flask with catalytic quantity of p-toluene sulfonic acid in DMF at 110°C. After heating initially for 15 min., the azeotrope was removed under reduced pressure and the contents were heated for further period of 4h.The contents were poured into water with stirring to precipitate the dihydroxymonomer

Preparation of Diglycidyl Monomers Bearing Thiourea and Azomethine

Monomer was synthesized by dissolving 0.5 g of monomer in 40 ml. of epichlorohydrin and heated to 110°C for 1h with stirring. After obtaining a clear solution, catalytic quantity of benzyltrimethylammonium was added and the contents were allowed to reflux for another 3 h. Excess epichlorohydrin was removed by distillation,the remaining solid was washed by water and dried at 50°C under vacuum. Synthesis of the diglycidyl monomer bearing thiourea and azomethine groups is shown in Fig.1.

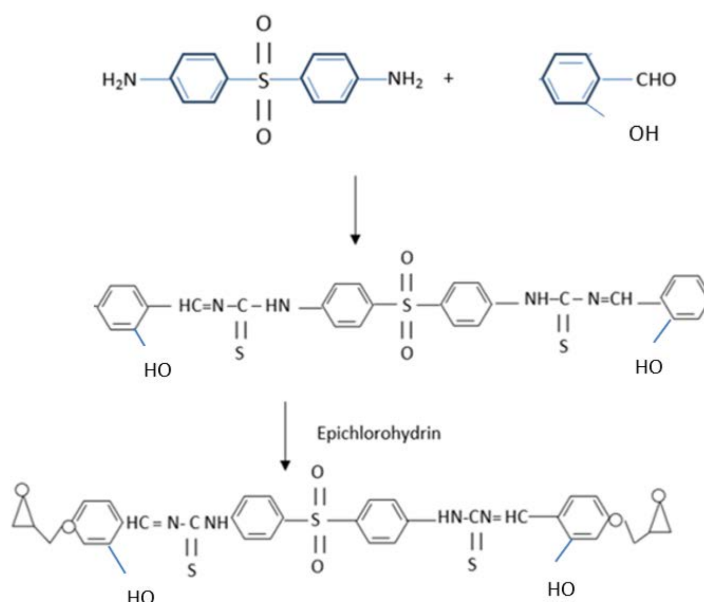

Fig. 1.Synthesisofdiglycidyl monomer bearing thiourea and azomethine

Table 1
Thermal conductivity of new resin and other reported resins

Run	Blend code	Blendcomposition	Thermal conductivity ($Wm^{-1} K^{-1}$)
1	NEAT	Dobeckot 605 epoxy resin (100: 0)	0.24
2	PATE	Dobeckot 605 epoxy resin: 3a (97:3)	0.38
3	ULTG	ULTIMEG 2050 epoxy based resin with 20% inorganic materials	0.40
4	BPE[a]	4,4′-Biphenoldiglycidylsulphone	0.32
5	CEP[b]	Conventional epoxy resin	0.19–0.26

[a]Value of 4,4-Biphenol diglycidylsulphone
[b]Value of conventional resin

Curing of the resin and their blends with dobeckot 605

Cured epoxy resin plate was obtained as follows: pre-weighed resin, Dobeckot 605 were poured in to a beaker and stoichiometric amounts of the hardener triethylenetetraamine were added at room temperature, stirredand curedat100°C,150°C,180°Cand200°Cfor1hea chwithout any treatment. For the comparison purpose commercial epoxy resin containing 22% inorganic filler materials (ULTIMEG 2050) was cured in the comparable manner. The composition of the resin is given in Table1.

Measurements

FTIR measurements were carried out on a IR affinity Spectrophotometer, withKBr(Shimadzu Make),^{1}H-NMR spectra was recorded in the solvent DMSO-d_6 using a Bruker instrument. Thermo gravimetric analysis was recorded ataheatingrateof10°C=mininair atmosphere. DSC measurement was recorded withToledoDSC822.Thermalconductivitiesoft hecuredepoxyresins were measured using C-ThermTCi.USA instrument.

RESULTS AND DISCUSSION

The synthesized thiourea base aromatic expoxy resins were yellowish colour powder in nature. The melting point ($188^{o}C$) 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. 2. The NH_2 stretching frequency of the diamine$4,4^{0}$-diphenylsulphoneappears asdoubletat 3265 cm^{-1} and 3163 cm^{-1} has undergone significant changesinthemonomer$4,4^{0}$-(bisthiourea)diphenylsulphone. The $–NH_2$ stretching frequency of the thioureadiamine appeared at 2968cm^{-1}.

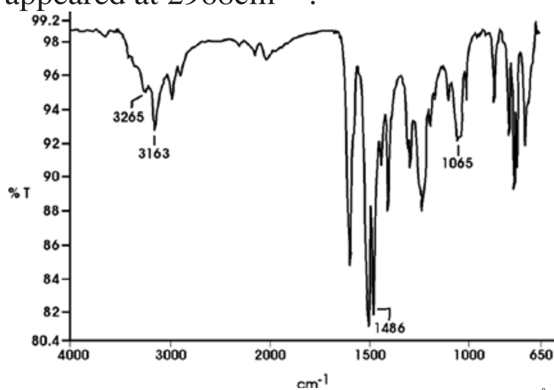

Fig. 2. FTIRspectrumofmonomer$4,4^{0}$-bis(thiourea) biphenylsulphone

The -NH stretching and that of -NH bending frequencies of the thioamide appeared at 2863 cm^{-1} and 1486 cm^{-1} respectively. The C=S stretching frequency in the monomer appeared at 1065 cm^{-1}. The structure of the dihydroxy monomers, bearing thiourea and azomethine groups, were confirmed through IR and ^{1}H-NMR spectroscopic analysis. The $–NH_2$ stretching frequency appeared at 3265 cm^{-1}thediamine$4,4^{0}$- (bisthiourea) diphenyl sulphone has completely disappeared in the formation of and the hydrogen bonded –OH stretching frequency appeared asabroadbandintheregion3265–3163cm^{-1}therebyconfirming the condensation of resin with salicylaldehyde[11] The other important observations that are made from Fig. 2 are: -N=CH- stretching frequency at 1571 cm^{-1} and –NH stretching frequency at1612cm^{-1}.

The ^{1}H NMR spectra of the monomers are shown in Fig., respectively. The signals are assigned in the figures. The –NH and –OH signalsappeared around10.0 ppm, while that of the –N CH– protons appeared at8.4 ppm. The aromatic protons appeared in the range *d ¼* 7.7–6.4ppm.

IR-spectra of the diglycidyl monomers bearing thiourea and azomethinegroupsare shown if Fig.5. Theepoxy–CH stretching frequency was observed at 3308 cm^{-1}, the imine –CH was shoround 2933 cm^{-1}, the –N=CH– band was observed at 1678 cm^{-1} and that of the –NH band was seenat 1598 cm^{-1}. ^{1}H-NMR spectra of theepoxy monomers shownin Fig 3. The epoxy protons were observed at 4.49–2.94 ppm. The other aromatic, azomethine and amide protons are assigneditself.

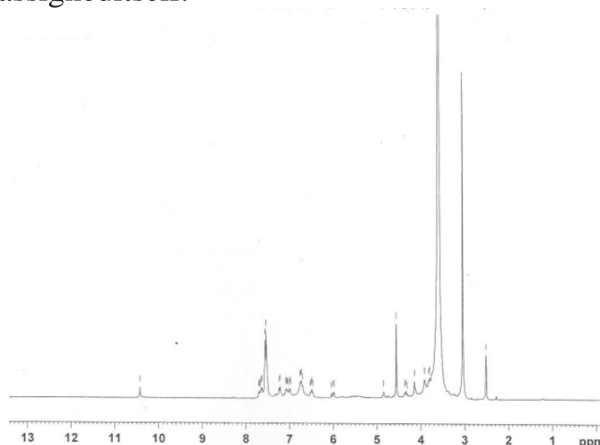

Fig. 3.^{1}H-NMR spectrum of monomer

Thermal Properties

The aim of this investigation is to determination of the thermal conductivity of the blends without altering thethermal stability and other favorable properties of theDobeckot 605(NEAT) epoxyresins. Hence the diglycidylethermonomer 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) andone blend combinations, viz., PATE 1 in static air. These studies indicate that the decomposition behavioristhe same for all the samples with 5% weight loss occurring around 188°C. This observation indicates thatinclusionof3%weightofdiglycidylmonomersbearing thiourea and azomethine groups, with the Dobeckot 605 (NEAT) resin have not altered the thermalstability.

The DSC traces of the NEAT resin and the blends (PATE 1) are shown in Fig. 4.

The DSC curve of the NEAT and blended resins showed no exothermic peak, which indicated the completion of the curingreaction. Tg of the cured NEAT resin (trickle impregnation resin Dobeckot605)wasfoundtobe69.7°C.TheTgoft hecured blends PATE 1 was 61°C and 62°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 theresinsisacomplementaryone.Thedecreasein Tgofthe blended resins makes it easier in application to delicate parts of the apparatus to becoated.

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 knownforthebiphenylcontainingepoxies.Biph enylepoxies with ester linkages and stillbene units have shown liquid crystalline properties. The present work deals with epoxieswiththioamidelinks.Generallypolymer swithamide 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 thestrength of the intermolecular hydrogen bond is reduced by proper substitution inthering in the positions neighboringtothe–NHOC– groups, they showed thermotropic liquid crystal-lineproperties[12].Whencomparedtotheamidelin ks,thioa- midelinkshaveconsiderably reduced thehydrogenbonding effects due to the presence of thiocarbonylgroups[13]. The polarizingmicrographofthediglycidylmonome r, bearingthiourea and azomethine groups, is shown in Fig. 4. These monomers have rigid rodlike structures and whenplacedbetweentwocrossedpolarizersund eranoptical microscope showed birefringence with no clear established structure. This suggests the formation of liquid crystalline state, probably during curing around150°C.The thermal conductivities of the epoxy based trickle impregnationresin(Dobeckot605),20%inorga nicmaterials 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). Thermal conductivity of the present blends are slightly higher than the commercial epoxy based resin (ULTIMEG 2050) filled with20%. alumina and silicate (run 5, Table 1). Thermal conductivity values of the investigated blends are twice the value ofcon- ventionalepoxy resins(run6,7,Table1)0.17$Wm^{-1}K^{-1}$.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 con- ductivity 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 basedtrickle impregnation resin forms crystal-like structure which sup- press the phonon scattering to some extent. Suppression in the phonon scattering to some extent might have resulted intheimprovementinthermalconductivityofthe blends.

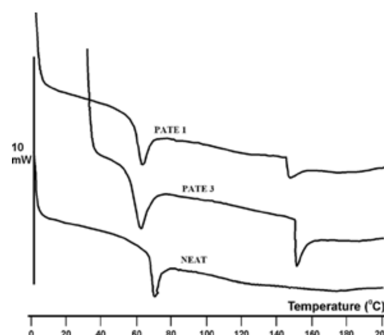

Fig.4. DSC trace the NEAT and blended resin

CONCLUSIONS

Epoxy based trickle impregnation cured resin (Dobeckot605) when blended with new rigidrodlikediglycidyl monomer bearing thiourea and azomethine groups by 3%weightshowedsuperiorthermalconductivity .Thermal conductivity of the cured epoxy based trickle impregnation resin and the

blended resins (PATE) were0.20and0.34–0.36$Wm^{-1}K^{-1}$,respectively.Incorporation of the new diglycidyl monomers in the blend did not alter the thermal stability of the cured resins when com- paredtothe NEAT resin.Workon increasingthe % of monomer in the blends and its effect on thermal conductivity and mechanical properties is in progress.

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