Thermomechanical studies of thermally stable metal-containing epoxy polymers from diglycidyl ether of bisphenol A and amino-thiourea metal complexes

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ABSTRACT

New thermally stable epoxy polymers containing copper and nickel ions have been prepared by curing diglycidyl ether of bisphenol A (DGEBA) with amino-thiourea metal complexes. Characterization of the metal complexes was carried out using infrared spectroscopy, elemental analysis and mass spectrometry. Determination of the optimum value of the epoxy/thiourea metal complex ratio was studied by means of differential scanning calorimetry. This method is based on the search for the maximum enthalpy change. The properties of the resulting metal-containing epoxy polymers were investigated with respect to glass transition temperature, thermal stability, tensile strength, and viscoelastic properties. Introduction of metal ions, especially the copper ion, into the polymer matrices produced polymers with good thermal stability and mechanical properties. The polymer showed good thermal stability compared to the DGEBA-DDM (DDM: 4,4'-diaminodiphenylmethane) system. The copper-containing epoxy polymer obtained at a mole ratio of copper complex:DGEBA (24:100) showed a 2.6% weight loss after heating at 400 °C and had a storage modulus of 6080 MPa at 125 °C, which is comparable to the epoxy-DDM system.

1. Introduction

Thermally stable, high-performance resins are required for use in composite structures on aerospace vehicles such as supersonic aircraft and reusable launch vehicles. One of the major synthetic efforts is in the field of heat-resistant epoxy polymers. Incorporation of transition metals into polymer chains offers a possibility to access new useful heat-resistant polymers. The synthesis of metal-containing epoxy polymers leads to thermally stable materials with good mechanical properties and thus offers various potential applications. Routes to such polymers include the use of metal complexes as additives [1-3], synthesis of metal containing epoxy resins [4-8], and the use of metal-containing cross-linking agents [9,10]. The last approach has received attention in attempts to enhance the thermal stability of the epoxy polymers. Use of metal-containing epoxy polymers allows the possibility of producing epoxy polymers with good mechanical properties and high thermal stability as well as achieving low processing temperatures [11,12].

Various metal complexes such as those of titanium, copper, and nickel can be used as cross-linking agents for the epoxy oligomers. The cross-linking agents can also be derived from metal complexes with O-, N- or S-containing ligands. Thiourea derivatives are well known chelating agents for transition metals. Complexes of thiourea derivatives containing an amino functionality are also known as epoxy resin curing agents [13]. It has been found that the metal-containing epoxy polymers possess high strength and thermal

stability and can be used for industrial production of one-plate glass-reinforced plastic springs for large-loaded motor vehicles [14].

The thiourea-based metal complexes represent one of the best known classes of complex, since the ligands can be easily synthesized. These metal complexes are stable and have many applications, such as catalysis, as O_2-storage devices [15] and as epoxy resin cross-linking agents [13]. Thus, it is of interest to prepare polymers through a curing reaction of diglycidyl ether of bisphenol A (DGEBA) with new thiourea-based metal complexes. Surprisingly, to the best of our knowledge, transition metal complexes of ethyl 4-[3-(4-aminophenyl)thioureido)carbonyl]benzoate have not been described in the literature for epoxy cross-linking agents. The present work investigates the synthesis and properties of new metal-containing epoxy polymers by curing DGEBA with amino-thiourea metal complexes. The amino functional groups in the metal complexes are expected to undergo a reaction with DGEBA to yield thermally stable epoxy polymers.

2. Experimental

2.1. Materials and characterization

Diglycidyl ether of bisphenol-A (DGEBA), EPR 05322, epoxy equivalent weight 280 g/eq and solid content 100%, was obtained from Bakelite® AG through procurement. The other chemicals used, 4-nitrobenzoyl chloride, ammonium thiocyanate, ethyl p-aminobenzoate, 4,4'-diaminodiphenyl methane (DDM), hydrazine monohydrate, palladium-charcoal

(10 %) of analytical grade from Merck were used as received. All other reagents and solvents were of analytical grade and used without further purification.

The ^{1}H NMR and ^{13}C spectra were recorded in DMSO-d_6 solvent on Jeol ECS-400 and 300 MHz spectrophotometers using tetramethylsilane as an internal reference. The apparent resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet) and m (multiplet). Infrared measurements were recorded in the range 400-4000 cm^{-1} on a Spectrum 2000 spectrometer by Perkin Elmer. Elemental analysis was carried out using a Perkin Elmer CHNS/O 2400. Obtained results were within 0.4% of the theoretical values. FAB MS were obtained on a Finnigan MAG 90 mass spectrometer using glycerol as a matrix. Thin layer chromatography (TLC) analyses were carried out on 5×20 cm plates coated with silica gel GF$_{254}$ type 60 (25-250 mesh) using an ethyl acetate-petroleum ether mixture (1:2) as solvent. The cross-linking reaction of DGEBA with the metal complexes was investigated with FT-IR spectrophotometer using KBr pellets. Glass transition temperatures of metal-containing epoxy polymers were obtained on differential scanning calorimeter (DSC) and dynamic mechanical analyzer (DMA). The dynamic mechanical analysis was performed with a Diamond DMA provided with bending mode of deformation with a 50 mm span length. Samples used were in the shape of rectangular strips with dimensions of 50×10×2 mm. The tests were carried out at frequency of 1 Hz and a heating rate of 2 °C/min in a temperature range from 27 to 250 °C under inert atmosphere. Thermal stability of the polymers was determined using TGA by heating the polymer samples under nitrogen atmosphere and recording their weight losses. Moisture absorption was measured according to ASTM D570-63 standard. Rectangular shaped samples having dimensions 10×10×2 mm were dried under vacuum at 120 °C for 24 h until trace water had been expelled, then after cooling to room temperature the samples were weighed and placed in 100 °C boiling water for 6 h and weighed again. Tensile testing was performed on an Instron model 4301 according to ASTM D638 standard.

2.2. Synthesis

2.2.1. Synthesis of ligand

Ethyl 4-[3-(4-nitrophenyl)thioureido)carbonyl]benzoate (HL) was prepared as in our previous work [16-18]. A solution of 4-nitrobenzoyl chloride (1.85 g, 0.01 mol) in anhydrous acetone (80 mL) and 3% tetrabutylammonium bromide (TBAB) in dry acetone was added dropwise to a suspension of ammonium thiocyanate (0.76 g, 0.01 mol) in dry acetone (50 mL) and the reaction mixture was refluxed for 45 minutes. After cooling to room temperature, a solution of the corresponding ethyl *p*-aminobenzoate (1.65 g, 0.01 mol) in anhydrous acetone (25 mL) was added and the resulting mixture refluxed for 1.5 h. Hydrochloric acid (0.1 N, 400 mL) was added, and the solution was filtered. The solid product was washed with water and purified by recrystallization from an ethanol:dichloromethane mixture (1:2) (Scheme 1). M.p.: 179-180 °C. Yield 91%. IR (KBr pellet, cm^{-1}): 3350 (free NH), 3201 (assoc. NH), 1691 (C=O), 1735 (C=O ester), 1613 (C=N stretching), 1590 (aromatic C=C). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.56 (1H, br s, NH), 11.61 (1H, br s, NH), 8.23 (2H, d, *J*=9.1 Hz), 7.82 (2H, d, *J*=8.0 Hz), 7.66 (2H, d, *J*=7.9 Hz,), 7.62 (2H, d, *J*=7.2 Hz), 4.32 (2H,q, -CH$_2$), 1.31 (3H, t, -CH$_3$, *J*=7.1 Hz). ^{13}C NMR (300 MHz, DMSO-d_6, δ, ppm): 178.9 (C=S), 168.2 (C=O ester), 165.0 (C=O amide), 145.8, 130.0, 129.2, 126.5, 125.3, 124.1, 121.4, 60.7, 14.1. Anal. Calcd. for C$_{17}$H$_{15}$N$_3$O$_5$S (373.38): C, 54.68; H, 4.05; N, 11.25; S, 8.59. Found: C, 54.67; H, 4.06; N, 11.25; S, 8.58.
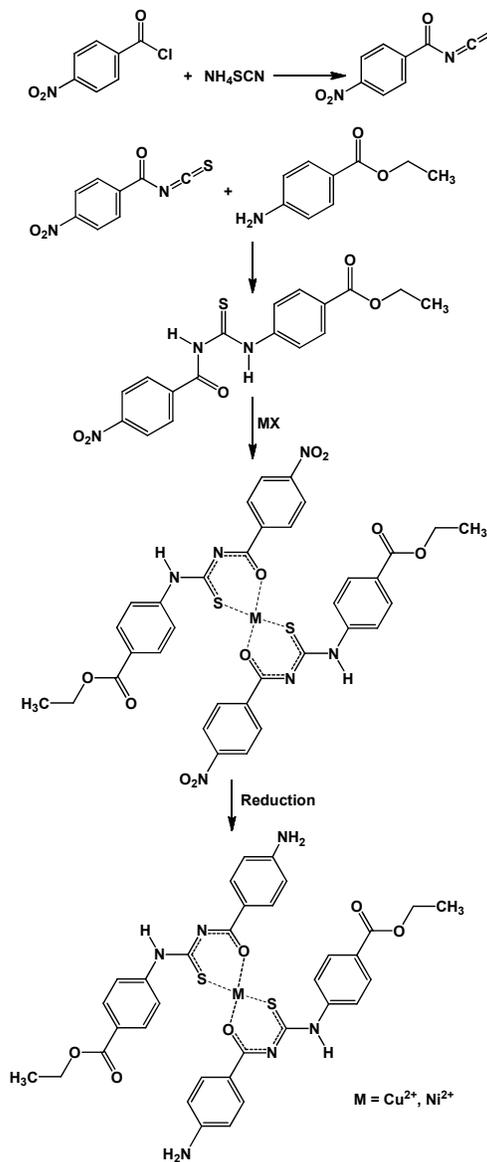
Scheme 1

2.2.2. X-ray structure determination of ethyl 4-[3-(4-nitrophenyl) thioureido) carbonyl] benzoate (HL)

Crystal data: C$_{17}$H$_{15}$N$_3$O$_5$S, monoclinic, space group *P*2$_1$/*n*, *a* = 4.3449(2), *b* = 18.7349(5), *c* = 10.4511(3) Å, β = 93.293(3)°, *V* = 849.33(5) Å^3, *T* = 100 K, *Z* = 2, *F*(000) = 388, *D*$_x$ = 1.460 g/cm^{-1}, μ = 0.226 mm^{-1}. A yellow plate 0.35×0.15×0.10 mm^3 was mounted on a glass fibre in inert oil. Measurements were performed on an Oxford Diffraction Xcalibur E diffractometer with monochromated Mo-Kα radiation to 2θ = 30.03°. The data were corrected for absorption using the multi-scan method. Of 53082 intensities, 4948 were independent (*R*$_{int}$ = 0.0348). The structure was refined anisotropically using SHELXL-97 [19]. The NH hydrogen was refined freely. The methyl group was refined as an idealised rigid groups allowed to rotate but not tip. Other hydrogen atoms were included using a riding model. The final *wR*2 was 0.0626, with a conventional *R*1 of 0.0260, for 244 parameters; *S* = 0.98; max. Δρ=0.238 e Å^{-3}.

2.2.3. Preparation of the copper and nickel complexes (CuL*₂ and NiL*₂)

#### 2.2.3.1. Preparation of the copper complex (CuL*₂)

The complexation of the thiourea derivative was carried out according to the reported procedures [20,21]. To 30 mL of ethanol containing HL (0.01 mol) was added an ethanol solution of CuCl₂.2H₂O (0.05 mol). The reaction mixture was filtered and left to crystallize by slow evaporation for two weeks. The catalytic reduction of this complex was carried out: CuL₂ (0.01 mol), 5 mL hydrazine monohydrate, 70 mL ethanol and 0.03 g of 10 % Pd-C were transferred into a 250 mL two-necked round-bottom flask and refluxed for 18 h. The reaction was monitored by thin layer chromatography (TLC). After completion, the reaction mixture was allowed to stand for one day and then filtered. The solvent was removed by rotary evaporation under reduced pressure. The copper complex (CuL*₂) was obtained as a green solid after two weeks by recrystallization from ethanol (Scheme 1). Yield: 1.50 g (85%). IR (KBr pellet, cm⁻¹): 3405, 3325 (NH₂), 1618 (N-H bending), 1529 (benzene ring), 1405 (C-N stretching), 1140 (C=S). MS (FAB, m/z): 803 (M⁺). Anal. Calcd. for $C_{34}H_{28}N_6O_{10}S_2Cu$ (802.73): C, 50.8; H, 3.4; N, 10.4; S, 7.9. Found: C, 50.9; H, 3.5; N, 10.1; S, 7.8.

2.2.3.2. Preparation of the nickel complex (NiL*₂)

To 30 mL of ethanol containing HL (0.01 mol) was added an ethanol solution of NiCl₂.6H₂O (0.05 mole), followed by NaOAc (0.01 mol) dissolved in ethanol was added, the reaction mixture was stirred at room temperature for 4 h, and filtered to give a light yellowish green solid, which was dried in air. The catalytic reduction of complex was carried out as follows. 0.01 mol of nickel complex, 5 mL hydrazine monohydrate, 70 mL ethanol and 0.03 g of 10 % Pd-C was transferred into a 250 mL two-necked round-bottom flask and refluxed for 18 h. The reaction was monitored by TLC. After completion, the reaction mixture was allowed to stand for one day and then filtered. The solvent was removed by rotary evaporation under reduced pressure. The nickel complex was obtained as a green solid after one week by recrystallization from an ethanol: dichloromethane (1:2) mixture (Scheme 1). Yield: 1.42 g (83%). IR (KBr pellet, cm⁻¹): 3405, 3323 (NH₂), 1619 (N-H bending), 1528 (benzene ring), 1403 (C-N stretching), 1142 (C=S). ¹H NMR (400 MHz, DMSO-d_6, δ, ppm): 12.32 (2H, br s, NH), 7.65-7.28 (16H, m, aromatic), 4.26 (4H, m, -CH₂), 1.27 (6H, m, -CH₃). MS (FAB, m/z): 801 (M⁺). Anal. Calcd. for $C_{34}H_{28}N_6O_{10}S_2Ni$ (800.75): C, 51.0; H, 3.5; N, 10.5; S, 8.0. Found: C, 51.1; H, 3.7; N, 10.5; S, 8.1.

2.3. Preparation of metal-containing epoxy polymers

A mixture of DGEBA and thiourea metal complex was dissolved in acetone at room temperature. Then the solvent was evaporated under vacuum and the blends were placed in the refrigerator before performing the DSC measurement. The mixture was cast into a metal or a silicone mould and crosslinked in a heated air oven (Scheme 2). The cured samples were then cooled slowly to room temperature to prevent cracking. The completeness of the crosslinking reaction was confirmed by the disappearance of the characteristic band of the epoxide groups in DGEBA at 912 cm⁻¹ in the IR spectrum.
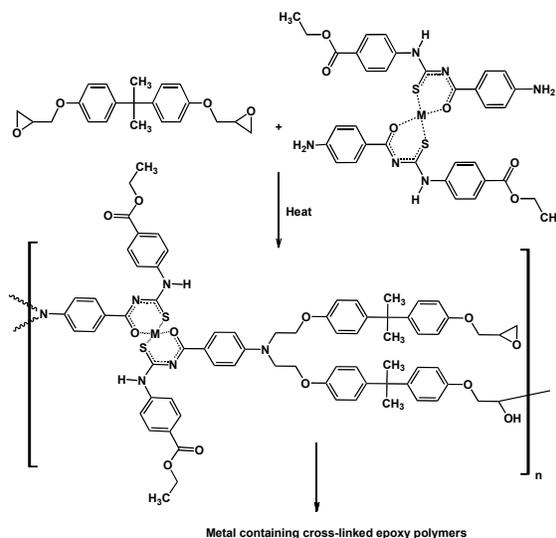
Scheme 2

The crosslinking temperature range for CuL*₂ and NiL*₂ was 180-210 °C. When CuL*₂ was employed, the crosslinking temperature was 210 °C. The crosslinking time was 2 h at the mole ratios of DGEBA:metal complex (100:24) for the copper complex and 100:31 for the nickel complex. A comparative polymer was prepared by crosslinking of DGEBA with DDM.

3. Results and discussion

3.1. Synthesis and characterization of the ligand and metal complexes

The synthetic pathway for the target compounds is outlined in Scheme 1. The use of a phase transfer catalyst (PTC) as a method of agitating a heterogeneous reaction system is gaining recognition [22,23]. In search of improving methods to prepare the target aroyl thiourea by reacting isothiocyanates with nucleophiles, we have found the use of tetrabutylammonium bromide (TBAB) as a PTC can afford aroyl isothiocyanates in good yield. In this communication, we have conducted our reaction using TBAB as a phase transfer catalyst to synthesize the intermediate aroylthiourea.

The structure of the free ligand HL is shown in Figure 1. There are three essentially planar regions of the molecule: (*i*) the ring C11-16 plus C17, C18, O2, O3, N1 (mean deviation 0.02 Å); (*ii*) the central thioamide moiety N1, S, C1, C2, C2, O1 (mean deviation 0.04 Å); (*iii*) the ring C21-26 plus N3, O4, O5, C2 (mean deviation 0.006 Å). Interplanar angles are 38° from (*i*) to (*ii*) and 26° in the opposite sense from (*ii*) to (*iii*). Consistent with this, the torsion angles along the chain C12-C11-N1-C1-N2-C2-C21-C26 are 36.5 (about C11-N1), –173.6, –4.3, –176.5 and –24.7°. There is an intramolecular hydrogen bond from N1-H1 to O1, with H…O 1.83(2) Å and N-H…O 146(2)°. The packing diagram (Figure 2) shows that the molecules are connected by three hydrogen bonds [N2-H02…O2 with H…O 2.55(2) Å, angle 163(1)°; C25-H25…O2, 2.48 Å, 133°; C15-H15…O5, 2.51 Å, 152°] to form layers parallel to (010). Curiously, the classical H bond is the longest of the three.
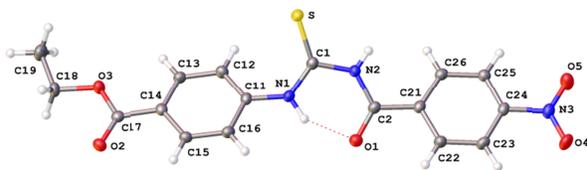
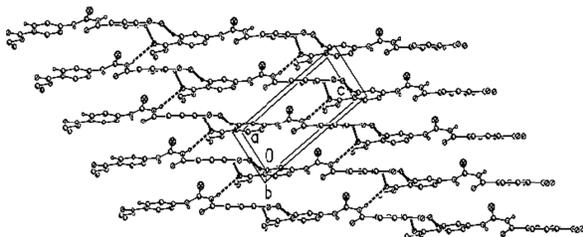**Figure 1.** Structure of the free ligand HL in the crystal. Ellipsoids represent 50% probability levels.

Figure 2. Packing diagram of HL viewed parallel to the ***b*** axis. Dashed lines indicate hydrogen bonds. The approximately horizontal chains of molecules lie in the direction [20$\bar{1}$] and the diagonal columns in [100]. H atoms not involved in H bonds are omitted for clarity.

Metal complexes of thiourea derivatives can be prepared by the reaction of metal salts with thiourea derivatives in the presence of sodium acetate. Arslan *et al.* reported a series of crystal structures of some metal complexes of various thiourea ligands [24-32]. The nickel and copper complexes were synthesized by a two-pot reaction. In the first stage, the nickel and copper complexes of ethyl 4-[3-(4-nitrophenyl)thioureido) carbonyl] benzoate were prepared and in the second step catalytic reduction was carried out. Both nitro functional groups were converted into amino functional groups by catalytic reduction. FT-IR spectrum of ethyl 4-[3-(4-nitro phenyl) thioureido)carbonyl]benzoate [HL] showed the stretching vibrations at 3350 and 3201 cm^{-1} for free and associated NH, 1691 cm^{-1} for the carbonyl and at 1534, 1327 and 1140 cm^{-1} for thioimides I, II and III, respectively. The FT-IR spectra of the complexes show significant changes when compared with the FT-IR spectra of the corresponding ligands. The most striking change is that the N-H stretching frequency at ~3200 cm^{-1} in the free ligands disappears completely, in agreement with both the ligand and complex structures and the complexation reaction. Another important change is observed for the carbonyl stretching vibrations. A strong vibration at 1691 cm^{-1} in the FT-IR spectra of the ligand is ascribed to the stretching of the carbonyl group, which shifts to higher frequency upon complexation of the thiourea ligand because the deprotonation induces delocalization of the carbonyl stretching vibration [27,28]. The same trend is usually observed for the thiocarbonyl stretching vibration frequencies, which are observed at approximately 1300 cm^{-1} in the free ligands, and shift to higher frequency after complexation; unfortunately, this vibration could not be assigned unambiguously.

The ^{1}H NMR data of the ligand obtained in DMSO-d_6 solution is given in the experimental section and is consistent with the structural results. The ^{1}H NMR spectrum shows the characteristic broad singlet for protons of N_1 and N_2 at δ (ppm) 11.61 and 12.56. ^{13}C NMR showed peaks at δ (ppm) 169.1, 179.5 for C=O (amide), C=S (thioamide), respectively. All proton signals of the ligand shift to lower fields upon binding to metal ions as expected. HL shows a peak at 11.61 ppm, corresponding to the proton of the N_1-H group attached with carbonyl group.

3.2. Preparation of metal-containing epoxy polymers

In a curable mixture of DGEBA and metal complex, the functional groups which undergo crosslinking reactions are the amino groups in the metal complexes and the epoxide groups in DGEBA. Curing of DGEBA, EPR 05322, with the nickel or copper complex at 215 °C produces a three-dimensional network. While curing, the epoxy monomer reacts with the curing agent whereby the -NH$_2$ functionality of the curing agent opens the epoxy ring of the epoxy monomer. Hence, a tertiary amine appears in the final network with the disappearance of primary -NH$_2$ and epoxide groups from DGEBA, EPR 05322. In the IR spectrum of the cured material, one notes the disappearance of asymmetric and symmetric stretching vibrations due to cycloxirane at 912 and 830 cm^{-1}, respectively and the appearance of a strong absorption at 3433 cm^{-1} due to O-H formation, confirming the opening of the epoxy ring. The appearance of an absorption band at 1359 cm^{-1} is due to tertiary C-N symmetric stretching; no absorption bands due to the primary N-H group were observed showing the -NH$_2$ functionality of the curing agent was used up in opening the epoxy ring and the reaction was complete.

The curing mechanism of DGEBA with the copper and nickel metal complexes is proposed to involve a ring opening of the epoxy group of DGEBA by the hydroxyl groups resulting from the epoxy ring openings to give secondary alcohols, which can then other epoxy groups. From FT-IR spectral analysis of the epoxy-hardeners, it can be concluded that network formation has occurred and reaction between DGEBA, EPR 05322, epoxy resin and the metal complex curing agent is complete. These reactions occur repeatedly to produce the cross-linked metal-containing epoxy polymers as shown in Scheme 2.

3.3. Thermal Studies by DSC and TGA Measurements

Thermal properties of the metal-containing epoxy polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. In order to evaluate the optimum ratio of resin and curing agent necessary for a posterior isothermal study, a dynamic study was carried out. DSC was run for different ratios. From these data it can be concluded that the optimum ratio values are 100/31 and 100/24, which corresponds to the maximum value of ΔH, respectively, for the nickel and copper complexes. The optimum values of epoxy/metal complex curing agents were also evaluated from T_g values. It is expected that ΔH maximum value corresponds to the maximum value of T_g. Table 1 shows the enthalpy and glass transition temperature T_g values for the different ratios used, from which it can be confirmed that 100/24 corresponds to the optimum ratio value for copper complex curing agent, whereas, the best optimum ratio value for nickel complex was 100/31. Two different ways were used in order to find the best mixing ratio value; the combined search for the maximum enthalpy and for the maximum glass temperature seems to be a very valuable approach.

The results of the TGA analysis showed no significant weight loss below 300 °C in a nitrogen atmosphere. The maximum degradation temperature (T_{max}) for metal-containing epoxy polymers lies between 400 and 450 °C. Thermal stability of the polymers was also evaluated in term of 10% weight loss (T_{10}), maximum degradation temperature (T_{max}) and residual weight at 500 °C as listed in Table 2. The enthalpy of formation of metal-containing epoxy polymers ranges from 500 to 525 J/g and was calculated by means of differential scanning calorimetry. Residual weight loss at 500 °C (R_{500}) was also measured and was found in the range of 31-41%. Comparison of thermogravimetric analysis of thiourea metal complex-epoxy and DDM-epoxy polymers is shown in Figure 3.

Table 1. ΔH and T*g* values for different epoxy/crosslinking combinations.

Complexes	Ratio epoxy resin: Crosslinking agent	ΔH (J/g)	Tg (°C)
CuL*₂	100:22	522.20	140.0
	100:23	556.14	142.0
	100:24	565.14	142.3
	100:25	539.45	141.0
	100:26	540.36	140.2
NiL*₂	100:29	522.20	138.0
	100:30	556.14	140.0
	100:31	565.14	141.0
	100:32	539.45	139.0
	100:33	529.25	139.0
DDM system	-	-	122.9

Table 2. Thermal stability of the cured metal containing epoxy polymers.

Complexes	Mole ratio of curing agent: DGEBA	T_{10} (°C)[a]	T_{max} (°C)[b]	R_{500} (%)[c]
CuL*₂	100:22	415	471	39.0
	100:23	412	473	40.5
	100:24	417	475	41.0
	100:25	414	473	39.9
	100:26	411	470	35.5
NiL*₂	100:29	410	452	28.0
	100:30	410	455	29.0
	100:31	415	459	31.2
	100:32	414	459	28.0
	100:33	414	455	27.0
DDM system	-	380	410	18.0

[a] Temperature at 10% weight loss.
[b] Maximum degradation temperature obtained from differential curves.
[c] Residual weight at 500 °C.
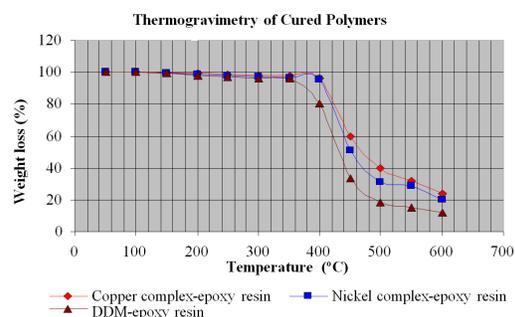
Figure 3. Thermogravimetry of cured polymers.

3.4. Mechanical properties of cured polymers

Tensile testing was done on the metal-containing polymers obtained from metal complex and DGEBA at different molar ratios since these polymers showed good thermal stability. Tensile testing was carried out using an Instron 4301 universal testing machine. Three specimens were cut from each polymer sheet for tensile testing. Results from samples that failed within the grips were excluded. The highest tensile strength was obtained at the mole ratio of ML*₂:DGEBA (31:100), which was comparable to the epoxy-DDM system (Table 3). Increasing the amount of ML*₂ in the formulation resulted in a decrease of tensile strength, since the mixture before curing became more viscous and therefore the polymerization was difficult to control.

It was found that copper-containing polymer obtained at the mole ratio of DGEBA:CuL*₂ (100:24) possessed high T_g, high tensile strength and good thermal stability which is comparable to the DGEBA-DDM system.

3.5. Moisture absorption behaviour

Moisture absorption will increase the dielectric constant of the cured polymer and have a disadvantageous effect on mechanical properties [33]. Furthermore; it will ionize the

ionic impurities and thus corrode the integrated circuits. Thus, to obtain a higher performance epoxy polymer, it is necessary to decrease the moisture absorption. The moisture absorption was calculated as percent weight gain:

$$\text{Moisture absorption \%} = (W/W_o-1) \times 100\% \qquad (1)$$

where W is the weight of the sample after dipping in 100 °C boiling water for 6 h and Wo is the weight of the sample after placing in vacuum oven for 24 h. Conventionally, the moisture absorption increases as the T_g increases in the cured polymers from novolac type epoxy resin and phenol novolac [34]. However, because of the hydrophobic nature of the thiourea metal complex, the cured polymer exhibited relatively low moisture absorption of 0.851-0.864 %, compared to that of DDM-epoxy of 1.250 %.

Table 3. Mechanical properties of epoxy polymers obtained from various mole ratios of curing agents and DGEBA.

Complexes	Mole ratio of curing agent: DGEBA	Tensile Strength(MPa)
CuL*₂	100:22	65
	100:23	68
	100:24	71
	100:25	68
	100:26	66
NiL*₂	100:29	63
	100:30	67
	100:31	69
	100:32	68
	100:33	68
DDM system	-	65

3.6. Dynamic Mechanical and Thermal Analysis (DMTA)

Dynamic mechanical observations were performed to analyze the dynamic elastic modulus and the occurrence of molecular mobility transitions such as glass transition [35]. The peak temperature of tan delta was taken as the glass transition temperature. Dynamic storage modulus (E´) is the most important property to assess the load bearing capability of a polymer and composite material, which is close to the flexural modulus. The ratio of the loss modulus (E") to the storage modulus is known as a mechanical loss factor (Tan D), damping factor, or dissipation factor. This quantity is the measure of balance between the elastic phase and the viscous phase in a polymeric structure. Tan δ shows very accurately the phase transition temperature, particularly the movement of certain parts of the polymer molecules when it is linearly heated. Loss behaviour of the copper complex, nickel complex and DDM/epoxy formulation is shown in Figure 4a. The DMTA measurement indicated that T_g of the cured polymers from copper and nickel metal complexes/epoxy system are 142.3 and 141 °C, respectively, which are comparatively higher than in the DDM/epoxy system (T_g = 122.9 °C). The tan delta value of the epoxy resin cured with the reference curing agent is higher. This shows that these polymeric materials cured with metal complex curing agents are relatively flexible, which is an essential requirement for the designing and manufacturing of high pressure and high temperature sustainable composite structures.

The DMTA curves of storage and loss modulus and tan δ versus temperature for the cured polymers with copper and nickel complex curing agents are shown in Figure 4a-c. The values of both the storage modulus and loss modulus for cured polymers containing NiL*₂ and CuL*₂ complexes/epoxy resin, over the range of temperature investigated are substantially higher than those of the DDM-epoxy sample. For instance, at 125 °C the storage modulus value for the copper complex-epoxy sample is 6080 MPa whereas its value for DDM-epoxy sample is 57.39 MPa at the same temperature. The maximum

loss modulus values of copper and nickel complex-epoxy resin were found to be 2230 and 2100 MPa respectively while that of DDM-epoxy resin was found to be 80.38 MPa as shown in Figure 4c.
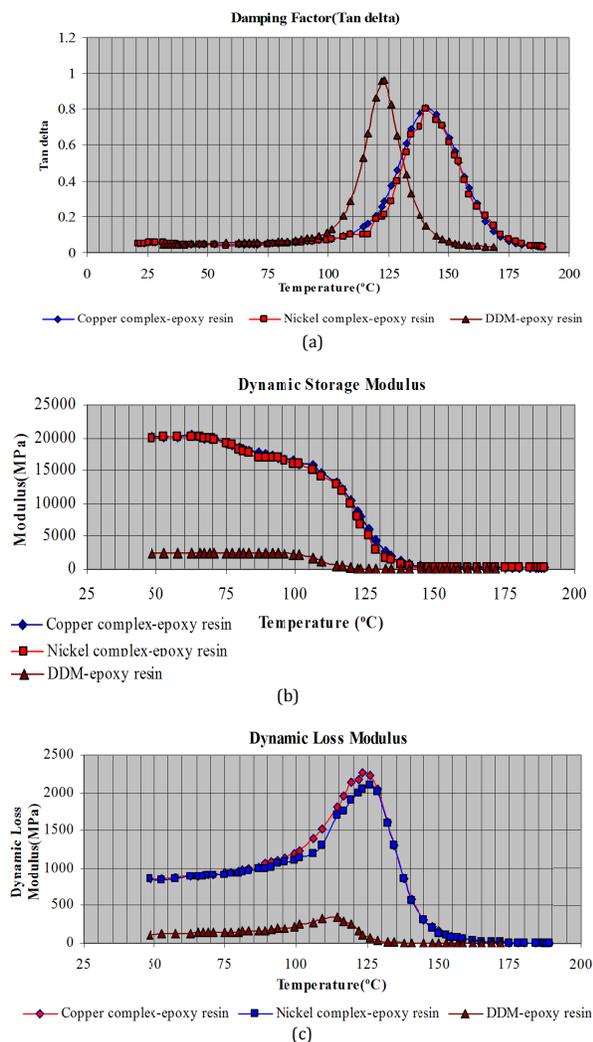
Damping Factor(Tan delta)

(a)

Dynamic Storage Modulus

(b)

Dynamic Loss Modulus

(c)

Figure 4. Dynamic mechanical property variation with temperature (a) Tan delta; (b) Dynamic Storage Modulus; (c) Dynamic Loss Modulus.

4. Conclusion

Two new transition metal containing amino-thiourea derivative complexes have been successfully prepared as cross-linking agents for an epoxy resin. Introduction of copper and nickel complexes into the polymer matrix results in good tensile strength, especially in the case of the copper-containing epoxy polymer, which is comparable to the known epoxy-DDM system. At 125 °C, the value of storage modulus for "copper complex-epoxy" sample is 6080 MPa and "nickel complex-epoxy" sample is 5060 MPa, whereas its value for the DDM-epoxy sample is 57.39 MPa at the same temperature. The maximum weight loss of the cured epoxy resins with copper and nickel complex at 400 °C was 4% and 4.5%, respectively, whereas the weight loss for DDM-epoxy system was 20% at the same temperature which indicates the high thermal stability of the cured polymeric materials. These polymeric materials may be considered as new processable high performance materials. These pronounced favourable properties make it an attractive candidate for electronic encapsulation applications and composite materials.

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