EUROPEAN POLYMER JOURNAL

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Published by Pergamon

An imprint of Elsevier Science Ltd

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April 28, 1999

Ref: 016/99

Professor N. Chantarasiri,
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Dear Professor Chantarasiri,

I write to follow up my email dated 14 April 1999 concerning your revised manuscript entitled:

"New Metal-Containing Epoxy Polymers from Diglycidyl Ether of Bisphenol A and Tetradentate Schiff Base Metal Complexes"

I am pleased to report that this paper is accepted for publication.

Manuscripts, diagrams etc. and proofs are kept in the Editorial Office for a period of 18 months after the above acceptance date. On request we are prepared to return these papers to the author(s) at the end of this period. Thereafter, this material will be destroyed.

Thank you for this contribution to European Polymer Journal.

Yours sincerely,

John Dawkins

Professor J.V. Dawkins

NEW METAL-CONTAINING EPOXY POLYMERS FROM DIGLYCIDYL ETHER OF BISPHENOL A AND TETRADENTATE SCHIFF BASE METAL COMPLEXES

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ABSTRACT

New epoxy polymers containing copper, cobalt and nickel ions have been prepared by curing diglycidyl ether of bisphenol A (DGEBA) with the Schiff base complexes of these metal ions. The Schiff base ligand was prepared from 2,4-dihydroxybenzaldehyde and 1,3-diaminopropane. Characterization of the metal complexes were carried out using infrared spectroscopy and elemental analysis. Tetrabutylammonium hydroxide was the most suitable catalyst for curing reaction. The introduction of metal ions, especially the copper ion, into the polymer matrices gave polymers with good thermal stability and mechanical properties such as tensile strength. The copper-containing epoxy polymer obtained at a mole ratio of copper complex : DGEBA = 1:12 showed a 2.1% weight loss after heating at 250°C for 48 hr and had a tensile strength of 69 N/mm^2, which is comparable to the epoxy-anhydride system.

INTRODUCTION

One of the major synthetic efforts is in the field of heat-resistant epoxy polymers. The need for such polymers is their potential use as materials for aircraft, spacecraft, automotive and electronic components. Incorporation of transition metals into polymer chains offers a possibility to access new useful heat-resistant polymers. To date, the methods to prepare metal-containing epoxy polymers are the use of metal chelates as the curing agents[1-9], use of organotransition-metal complexes as additives[10-12] and synthesis of epoxy resins containing transition metal ions[13-17]. It has been found that the metal-containing epoxy polymers possess high stength and thermal

stability and can be used for industrial production of one-plate glass-reinforced plastic springs for large-loaded motor vehicles[18].

The tetradentate Schiff base metal complexes are one of the most well known complexes since the ligands can be easily synthesized. These metal complexes are stable and have many applications such as catalysis and as O_2-storage devices[19]. The manganese-salen complex bearing a chiral tetradentate ligands is a catalyst for enantioselective oxidation of olefins. The so called cobalt salen or Salcomine is a very efficient catalyst for oxidation of phenols. Cobalt salen is known to form a stable O_2 complex in the solid state which can lose O_2 upon heating and were used in oxygen storage devices for submarines during World War II. Nevertheless, there has been no report regarding its application as an epoxy curing agent.

It is, thus, of interest to prepare a polymer through a curing reaction of DGEBA with new tetradentate Schiff base metal complexes. Since their structures are similar to bisphenol A in that they contain two phenol groups, they are expected to undergo similar reactions to yield metal-containing polymers with good properties and good thermal stability. The present work investigates the synthesis and properties of new metal-containing epoxy polymers by curing DGEBA with tetradentate Schiff base metal complexes. The hydroxyl groups in the metal complexes are expected to undergo a reaction with DGEBA to yield epoxy polymers.

EXPERIMENTAL

Materials

All chemicals were obtained from Baker, Fluka and Merck and were used as received. Diglycidyl ether of bisphenol A (DGEBA), D.E.R. 330 from Fluka, with epoxy equivalent of 185 was used as epoxy oligomer.

Analytical Methods

The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrophotometer. Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectra were obtained on a Bruker Bifex mass spectrometer by using α-cyanocinnamic acid as the matrix. Elemental analyses were carried out using a Perkin Elmer Analyzer 2400 CHN. Metal analyses were performed at Service Central d'Analyse, Vernaison, France.

The thermal properties of the metal complexes and epoxy polymers were investigated with Netzch and Perkin Elmer differential scanning calorimeters (DSC 200 and DSC 7), Netzch dynamic mechanical analyzer (DMA 240), and Netzch simultaneous thermal analyzer (STA 409 C). Tensile testing was performed on an Instron model 4301 following ASTM D638.

Synthesis

Preparation of the copper complex (CuL)

Tetradentate Schiff base ligand, L, was prepared by modification of the method reported in the literature[20]. A methanolic solution (10 ml) of 1,3-diaminopropane (0.5 ml, 10.64 mmol) was added dropwise to a methanolic

solution (100 ml) of 2,4-dihydroxybenzaldehyde (2.94 g, 21.28 mmol) at 0°C, and the mixture was stirred for 20 minutes. The color of the mixture gradually changed to yellow. An aqueous solution (40 ml) of copper (II) acetate monohydrate (2.13 g, 10.64 mmol) was then added dropwise at 0°C, and the mixture was stirred for 20 minutes. Upon adding a solution of 2N sodium hydroxide, the metal complex precipitated and was subsequently isolated by filtration and dried under vacuum. The copper complex was obtained as green solid (3.87 g, 87%) by recrystallization from hot methanol. IR (KBr, cm^{-1}) 3494, 3050, 2900, 1611, 1600, 1500, 1450, 1227, 990, 884; MALDI-TOF MS (m/z) 375 ($C_{17}H_{15}N_2O_4Cu.2H_2O$-$2H_2O$); Anal. calcd. for $C_{17}H_{16}N_2O_4Cu.2H_2O$: C 49.57; H 4.89, N 6.80; Cu 15.53; found C 48.74; H 4.63; N 6.34; Cu 15.84.

Preparation of the cobalt complex (CoL)

The cobalt complex was synthesized using the same procedure described previously employing cobalt (II) acetate tetrahydrate. The cobalt complex was obtained as brown solid (3.73 g, 85%). IR (KBr, cm^{-1}) 3494, 3100, 2900, 1617, 1600, 1500, 1450, 1233, 985, 845; MALDI-TOF MS (m/z) 371 ($C_{17}H_{16}N_2O_4Co.4H_2O$-$4H_2O$); Anal. calcd. for $C_{17}H_{16}N_2O_4Co.4H_2O$: C 46.06; H 5.25, N 6.55; Co 13.29; found C 46.75; H 5.46; N 6.32; Co 12.09.

Preparation of the nickel complex (NiL)

The nickel complex was synthesized in the same manner as CuL and CoL using nickel (II) acetate tetrahydrate. The nickel complex was obtained as green solid (3.95 g, 90%). IR (KBr, cm^{-1}) 3467, 3100, 2900, 1615, 1600, 1500, 1450, 1234, 990, 844; MALDI-TOF MS (m/z) 371 ($C_{17}H_{16}N_2O_4Ni.2H_2O$-

$2H_2O$); Anal. calcd. for $C_{17}H_{16}N_2O_4Ni.2H_2O$: C 50.16; H 4.95, N 6.88; Ni 14.42; found C 50.19; H 4.80; N 6.65; Ni 13.45.

Preparation of metal-containing epoxy polymers

Typically, a mixture of DGEBA, a metal complex and tetrabutylammonium hydroxide (Bu_4NOH) was degassed under vacuum then cast into a mold and cured by heating in a hot air oven. The completeness of curing was confirmed by the disappearance of the characteristic band of the epoxide groups of DGEBA at 917 cm^{-1} in the IR spectrum. Table 1 shows the time and temperature taken to complete the reaction with respect to ratio of curing agent : DGEBA at 1:6. A comparative polymer was prepared by curing DGEBA with maleic anhydride in the presence of benzyldimethylaniline[21, 22].

Table 1 Curing Time and temperature of DGEBA with metal complexes at a ratio of metal complex : DGEBA = 1:6

RESULTS AND DISCUSSION

Synthesis and Characterization of the metal complexes

It has been known that tetradentate Schiff base ligands can be synthesized by condensation reactions of primary amines and carbonyl compounds. The reaction proceeds with high yield to produce an imine or a Schiff base compound. In this study, the tetradentate Schiff base ligand was synthesized from the reaction between 2,4-dihydroxybenzaldehyde and 1,3-diaminopropane. The reaction involved an attack of amino group at the

carbonyl carbon of aldehyde followed by loss of water to give the tetradentate Schiff base ligand. The ligand, however, decomposed when isolation from the mixture was attempted. The metal complexes were thus prepared by adding metal acetates to the ligand solutions directly (Scheme 1).

Scheme 1 Synthesis of Schiff base metal complexes

IR and MALDI-TOF MS results agreed with the proposed structures of tetradentate Schiff base metal complexes. The IR spectrum of the CuL complex showed an absorption band of OH stretching at 3494 cm^{-1} and bands of C=N stretching at 1611 cm^{-1}. The bands at 990 and 844 cm^{-1} are correspond to the characteristic absorption peak of the aromatic bending of 1,2,4-trisubstituted benzene. CoL and NiL complexes gave similar IR absorption bands as the CuL complex. MALDI-TOF MS of all complexes showed peaks due to the molecular mass of the complexes. Elemental analyses of the complexes indicate that all complexes exist in monomer forms and contain water molecules in their structures.

Preparation of metal-containing epoxy polymers

DGEBA can be cured using a variety of phenolic compounds such as bisphenol A and 2,7-dihydroxynaphthalene to obtain epoxy polymers[21, 22]. Therefore, the tetradentate Schiff base metal complexes, which also contain phenolic groups in their molecules, were then applied as curing agents for DGEBA.

The curing of DGEBA with the metal complexes was studied using differential scanning calorimatry (DSC). The DSC experiment was performed by heating the mixture of metal complexes and DGEBA at the mole ratio of 1:6 in a DSC cell using an aluminum pan in air. The temperature range employed was 25 to 350°C at a heating rate of 20°C/min. All thermograms exhibit exothermic peaks which indicate curing. CuL and CoL gave the curing peaks in the range of 170-230°C and 160-250°C, respectively followed by the decomposition of material with the peak maxima at 200°C and 185°C, respectively. The curing peaks of NiL appears in the range of 200-280°C with the peak maximum at 255°C. Isothermal DSC curing of DGEBA with CuL and CoL at the mole ratio 1: 6 was done at 200°C and the reaction took 13 and 12 minutes to complete, respectively. Isothermal curing of DGEBA with NiL complexes was done at 250°C and the time taken for the reaction to be completed was 7 minutes.

The curing mechanism of DGEBA with the metal complexes is proposed to involve a ring opening of the epoxy group of DGEBA by the hydroxyl groups of the complex to give a secondary alcohol, which can then open another epoxy group. This is consistent with the disapearance of the IR band at 917 cm^{-1} due to epoxide groups in DGEBA. These reactions occurs repeatedly to produce the crosslinked metal-containing epoxy polymers as shown in Scheme 2.

Scheme 2 Proposed curing mechanism of DGEBA with the metal complexes

Effect of catalyst

It is of interest to compare the curing condition before and after using catalyst. The catalyzed reaction was expected to give the curing condition at a lower temperature. Curing reaction of DGEBA using phenolic compounds is normally accelerated using various catalysts such as sodium hydroxide, dimethylaniline and benzyltrimethylammonium hydroxide[21, 22].

When sodium hydroxide were used as a catalyst in curing of DGEBA with the metal complexes, little difference between the curing temperatures of the catalyzed and uncatalyzed reactions was observed. Dimethylaniline and benzyltrimethylammonium hydroxide gave complex exothermic curing peaks in DSC thermograms. Tetrabutylammonium hydroxide (Bu_4NOH) was the most suitable catalyst since it lowers the curing temperature and gives good DSC exothermic curing peaks. Curing parameters with different metal complexes with variable amounts of Bu_4NOH are collected in Table 2.

Table 2 Parameters of curing of DGEBA with curing agents at a mole ratio of curing agent : DGEBA = 1:6 and using Bu_4NOH as a catalyst

An example could be seen in the case of CuL : DGEBA : Bu_4NOH mixture at the ratios of 1 : 6 : 0 and 1 : 6 : 0.2. The use of Bu_4NOH decreased both T_b (temperature at the beginning of the reaction of DGEBA with curing agent) and T_{max} (temperature at the peak maximum) from 170 to 121°C and 200 to 148°C, respectively. Isothermal curing with CuL at 200°C showed T_c (curing time to achieve 100% conversion) of 13 minutes while curing condition using CuL in the presence of Bu_4NOH was finished in 12 minutes at 130°C.

Increase of Bu_4NOH amount also resulted in the decrease of T_b, T_{max} and T_c. Curing parameters of DGEBA using CoL and NiL showed the similar trend as in the case of CuL. Therefore, Bu_4NOH was chosen as a catalyst of choice for the preparation of metal-containing epoxy polymers.

Properties of metal-containing epoxy polymers

We have also prepared polymer samples for further investigation of their thermal properties. The mole ratios between metal complexes : DGEBA employed were 1:12, 1:10, 1:8, 1:6 and 1:4 to investigate the effect of the amount of metal complexes on the polymer properties. Without the use of Bu_4NOH, epoxy polymers at the mole ratios of 1:12, 1:10, 1:8 were not prepaerd since they required long curing times at high temperature. Thermal properties of the metal-containing epoxy polymers were studied by DMA and weight loss measurement.

Glass transition temperature

The glass transition temperature (T_g) was obtained from the DMA thermogram by observing the maximum value of the loss modulus. In the absence of Bu_4NOH, increasing the amount of the metal complexes resulted in higher T_g. When the catalyst was used, higher T_g were obtained with the same amount of curing agent. For example, T_g of the copper-containing polymer at the mole ratio of CuL : DGEBA = 1:6 increased from 78 to 153°C. T_g of the epoxy polymers obtained from various formulations of metal complex : DGEBA are shown in Table 3.

Thermal stability

Thermal stability of metal-containing polymers was determined by weight loss measurement upon heating polymers in a hot air oven at 250°C for 48 h. The weight loss data are shown in Table 4. In comparison to the known thermally stable epoxy polymer, copper-containing polymers obtained at mole ratios of CuL : DGEBA = 1:12, 1:10 and 1:8 possessed comparable thermal stability to the DGEBA-maleic anhydride system.

Table 3 T_g of the metal-containing epoxy polymers obtained from various mole ratios of curing agents : DGEBA

Table 4 Thermal stability of metal-containing polymers determined by weight loss measurement at 250°C for 48 h

Mechanical Property

Tensile testing was done on the metal-containing polymers obtained from metal complex : DGEBA at mole ratios 1:12, 1:10, 1:8 and 1:6 and Bu_4NOH was employed as a catalyst since these polymers showed good thermal stability. Their tensile strength values are shown in Table 5. The highest tensile strength was obtained at the mole ratio of CuL : DGEBA = 1:12, which was comparable to the epoxy-maleic anhydride system. Increasing the amount of CuL in the formulation resulted in a decrease of tensile strength since the mixture before curing became more viscous and the curing was catalyzed by Bu_4NOH. Therefore, the polymerization was difficult to controll.

When CoL and NiL were employed at the ratio of 1:12, low tensile strength values were obtained since both metal complexes were less reactive

towards the polymerization than CuL and therefore the curing was incomplete. The optimum ratio that yielded good tensile strength was 1:10. Further increase of the metal complex : DGEBA ratio caused a decrease in tensile strength due to the same explanation as in the case of CuL.

Table 5 Tensile strength of the epoxy polymers obtained from various mole ratios of curing agent : DGEBA and Bu_4NOH was used as a catalyst

CONCLUSIONS

New epoxy polymers containing transition metals were prepared by curing of DGEBA with tetradentate Schiff base metal complexes. The curing can be accelerated by tetrabutylammonium hydroxide. Introduction of Schiff base metal complexes into the polymer matrix results in good thermal stability and tensile strength, especially in the case of the copper-containing epoxy polymer, which is comparable to the known epoxy-anhydride system.

ACKNOWLEDGEMENTS

The authors thank Thailand Research Fund for financial support of this work. Metal analyses by Service Central d'Analyse, Vernaison, France and MALDI-TOF MS results from the Institute of Biotechnology and Genetic Engineering, Chulalongkorn University are acknowledged. The authors also thank Dr. Roderick W. Bates for general discussion.

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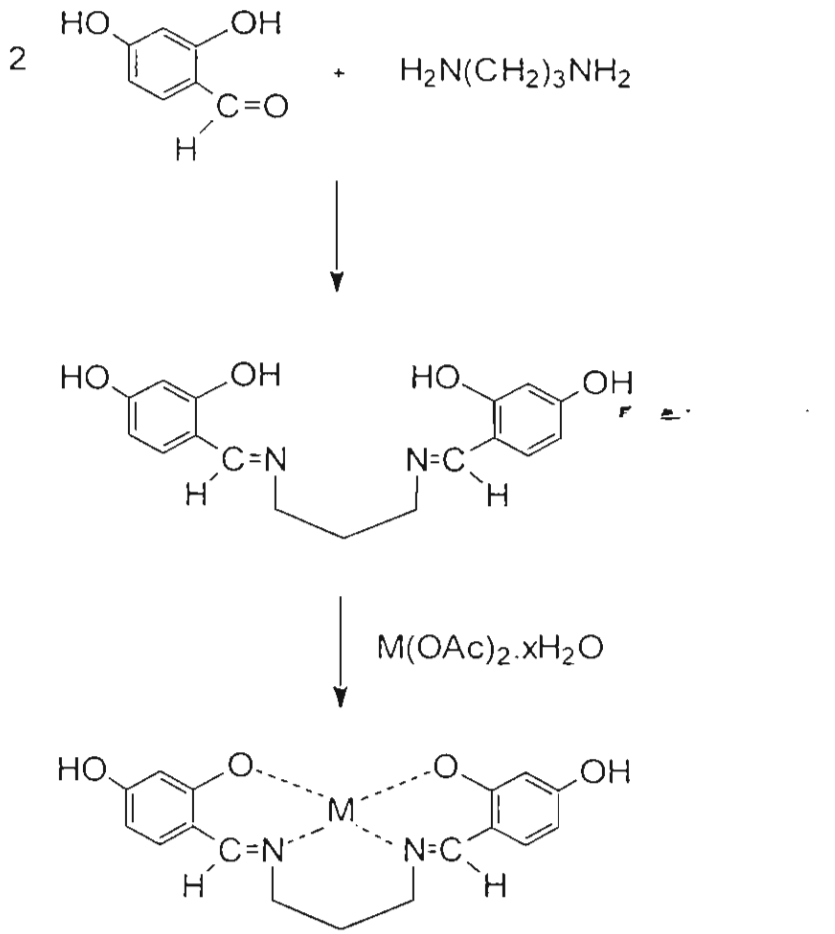
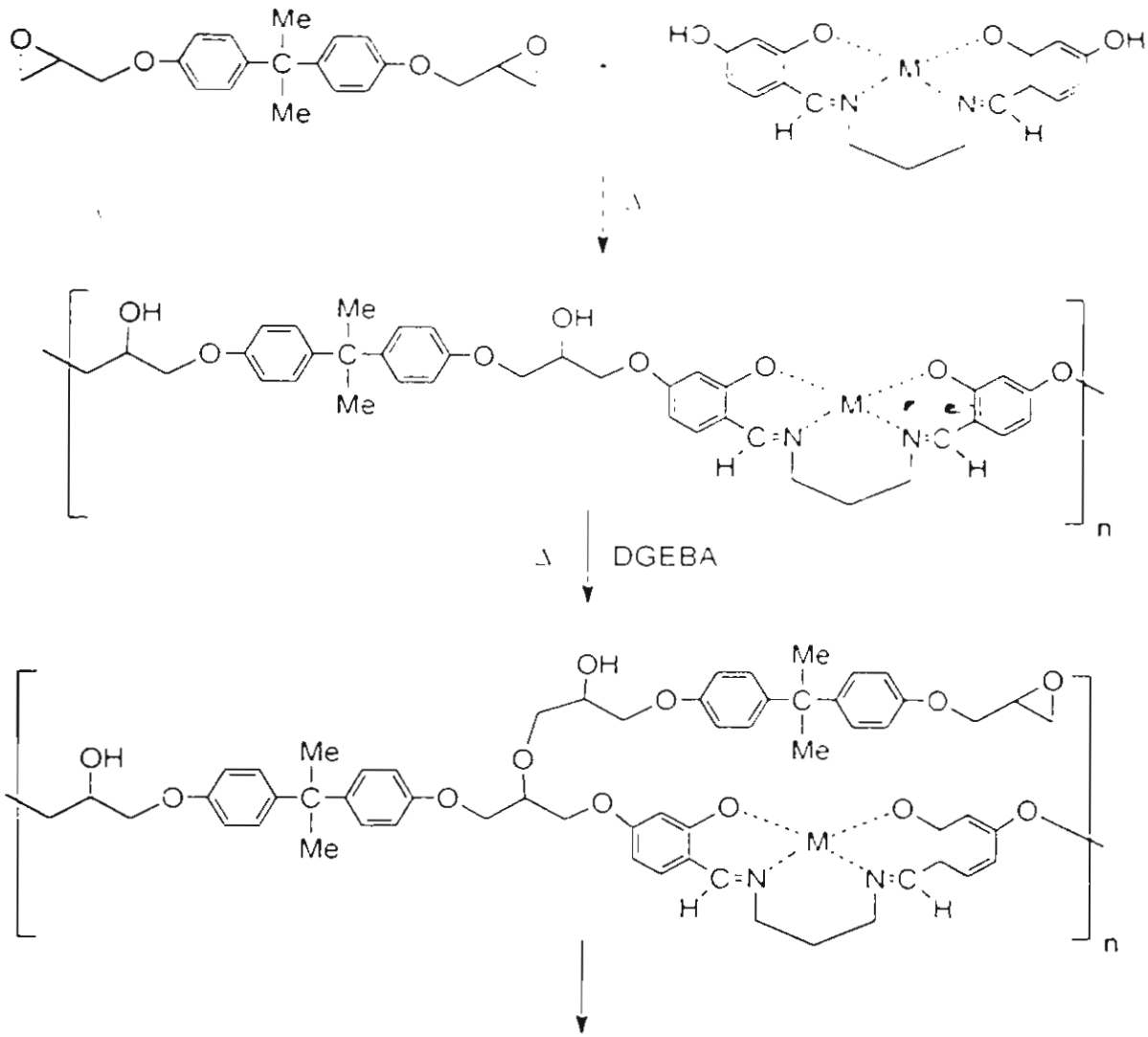
LIST OF SCHEMES AND TABLES



Scheme 1 Synthesis of Schiff base metal ccmplexes (M = Cu^{2+}, Co^{2+}, Ni^{2+})



Scheme 2 Proposed curing mechanism of DGEBA with the metal complexes

(M = Cu^{2+}, Co^{2+}, Ni^{2+})

Table 1 Curing Time and temperature of DGEBA with metal complexes at a ratio of metal complex DGEBA = 1 6

Metal complex	Curing conditions	
	Without catalyst	With Bu_4NOH[a]
CuL	200°C/3 hr	150°C/4 hr
CoL	200°C/5 hr	160°C/4 hr
NiL	240°C/3 hr	155°C/4 hr

[a] 20 mole% of the metal complex was employed

Table 2 Parameters of curing of DGEBA with curing agents at a mole ratio of curing agent : DGEBA = 1:6 and using Bu_4NOH as a catalyst

Curing agent \	Curing parameters of DGEBA				
	Amount of Bu_4NOH[a]	T_b (°C)[b]	T_{max}(°C)[c]	T_{end}(°C)[c]	T_c (min)[e]
CuL	0	170	200	-	13[f]
	10	136	157	207	15
	20	121	148	199	12
	40	112	138	200	3
CoL	0	160	185	-	12[f]
	10	107	179	248	28
	20	100	163	243	23
	40	91	149	223	12
NiL	0	200	255	-	7[g]
	10	140	167	245	16
	20	123	156	234	14
	40	107	139	220	6

[a] amount in mole% of curing agent

[b] temperature at the beginning of the reaction of DGEBA with curing agent

[c] temperature at the peak maximum

[d] temperature at the end of the reaction of DGEBA with curing agent

[e] curing time to achieve 100% conversion (obtained from isothermal DSC experiment at 130°C)

[f] T_c obtained at 200°C

[g] T_c obtained at 250°C

Table 3 T_g of the metal-containing epoxy polymers obtained from various mole ratios of curing agents : DGEBA

Curing agent	Mole ratio of curing agent : DGEBA	Tg (°C)[a]	
		Without Bu_4NOH	With Bu_4NOH[b]
CuL	1:12	-	130
	1:10	-	138
	1:8	-	133
	1:6	78	153
	1:4	133	146
CoL	1:12	-	82
	1:10	-	92
	1:8	-	113
	1:6	102	130
	1:4	108	112
NiL	1:12	-	103
	1:10	-	121
	1:8	-	117
	1:6	95	115
	1:4	120	140
Maleic anhydride		143	

[a] obtained from DMA thermogram by observing the maximum value of the loss modulus

[b] 20 mole% of the curing agent was employed

Table 4 Thermal stability of metal-containing polymers determined by weight loss measurement at 250°C for 48 h

Curing agent	Mole ratio of curing agent : DGEBA	% Weight loss after heating at 250°C for 48 hours[a]	
		Without Bu_4NOH	With Bu_4NOH[b]
CuL	1:12	-	2.1
	1:10	-	1.9
	1:8	-	2.1
	1:6	3.2	3.0
	1:4	2.7	4.9
CoL	1:12	-	5.3
	1:10	-	3.3
	1:8	-	4.0
	1:6	2.8	5.1
	1:4	3.4	5.9
NiL	1:12	-	4.6
	1:10	-	3.0
	1:8	-	2.0
	1:6	2.7	3.3
	1:4	2.1	5.5
Maleic anhydride		4.0	

[a] sample size was 1.0 x 5.0 x 0.3 cm

[b] 20 mole% of the curing agent was employed

Table 5 Tensile strength of the epoxy polymers obtained from various mole ratios of curing agent : DGEBA and Bu_4NOH was used as a catalyst[a]

Curing agent	Mole ratio of curing agent : DGEBA	Tensile strength (N/mm^2)
CuL	1:12	69
	1:10	60
	1:8	53
	1:6	41
CoL	1:12	44
	1:10	55
	1:8	43
	1:6	37
NiL	1:12	45
	1:10	59
	1:8	51
	1:6	40
Maleic anhydride	56	

[a] 20 mole% of the curing agent was employed

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Published by Pergamon

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May 13, 1999

Ref: 122/99

Professor N. Chantarasiri,
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Dear Professor Chantarasiri,

I write to follow up my email dated 21 April 1999 concerning your manuscript entitled:

"Application of Hexadentate Schiff Base Metal Complexes as Crosslinking Agents for Diglycidyl Ether of Bisphenol A"

I am pleased to report that this paper is accepted for publication.

Manuscripts, diagrams etc. and proofs are kept in the Editorial Office for a period of 18 months after the above acceptance date. On request we are prepared to return these papers to the author(s) at the end of this period. Thereafter, this material will be destroyed.

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Application of Hexadentate Schiff Base Metal Complexes as Crosslinking Agents for Diglycidyl Ether of Bisphenol A

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ABSTRACT

Nickel and zinc hexadentate Schiff base metal complexes have been synthesized and characterized by IR, NMR, FAB MS and elemental analysis. Crosslinking of the diglycidyl ether of bisphenol A (DGEBA) with these metal complexes gives Ni- and Zn-containing epoxy polymers. The crosslinking temperature could be lowered by using Bu_4NOH as a basic catalyst. The properties of the metal-containing epoxy polymers investigated were glass transition temperature, thermal stability and tensile strength. Ni- and Zn-containing epoxy polymers obtained from the mole ratio of metal complex: DGEBA:Bu_4NOH = 1:10:0.2 showed T_g at 110 and 151°C, respectively and tensile strength of 45 and 41 N/mm^2, respectively. Both metal-containing epoxy polymers have good thermal stability. Upon heating at 250°C for 48 h, the weight loss of Ni- and Zn-containing epoxy polymers were 2.3 and 3.7%, respectively, which is comparable to the DGEBA/maleic anhydride system.

INTRODUCTION

The synthesis of metal-containing epoxy polymers leads to thermally stable materials with good mechanical properties and thus offers various potential applications. The ways to obtain such polymers are the use of metal complexes as additives[1-3], synthesis of metal-containing epoxy resins[4-8], and the use of metal-containing crosslinking agents[9]. The last approach has received attention in attempts to enhance the thermal stability of the epoxy polymers. Various metal complexes such as those of titanium, tin and aluminium can be used as

crosslinking agents for the epoxy oligomers. The crosslinking agents can also be derived from metal complexes with O-, N- or S-containing ligands. For example, the intracoordination salts such as salicylates and anthranilates and the aliphatic amines or the aromatic amines can form strong five- or six-membered chelate rings and are able to produce the metal-containing crosslinking agents with the required properties[10-14]. It was found that thermal stability of epoxy polymers can be improved by using these metal-containing crosslinking agents. Other good properties of the resulting epoxy polymers are high mechanical strength and high deflection temperature.

Schiff base metal complexes are among the well known complexes since they are stable and have many applications[15]. Our previous work reported the synthesis of metal-containing polymers from the crosslinking reaction of DGEBA with tetradentate Schiff base metal complexes of Cu, Co and Ni, and Bu_4NOH was employed as a catalyst[16]. The resulting polymers showed good thermal stability and good tensile strength. However, these metal complexes have poor solubility in most organic solvents. In this work, we reported the synthesis and characterization of hexadentate Schiff base metal complexes and their use as crosslinking agents for DGEBA to obtain metal-containing polymers. These metal complexes were chosen because of their good stability, good solubility in organic solvents, cheapness and availability of their starting materials. Such metal complexes contain two amine groups and therefore are expected to undergo the crosslinking reaction with DGEBA to yield metal-containing polymers with good thermal stability.

EXPERIMENTAL

Materials

All chemicals were obtained from Baker, Fluka and Merck and were used as received. Diglycidyl ether of bisphenol A (DGEBA), D.E.R. 330 with epoxy equivalent of 185 from Fluka, was used as epoxy oligomer.

Analytical Methods

The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrophotometer. The NMR spectra were recorded in $CDCl_3$ solution on an ACF 200 Bruker instrument. Elemental analyses were carried out using a Perkin Elmer 2400 CHN Analyzer. FAB MS were obtained on a Finnigan MAT 90 mass spectrometer using glycerol as a matrix.

The crosslinking reaction of DGEBA with the metal complexes and thermal properties of the epoxy polymers were investigated with a Perkin Elmer DSC 7 differential scanning calorimeter and Netzch DMA 7 dynamic mechanical analyzer, respectively. Tensile testing was performed on an Instron model 4301 following ASTM D638.

Synthesis

Preparation of nickel complex (NiL)

A mixture of 2-hydroxybenzaldehyde (1.18 g, 9.66 mmol) and nickel (II) acetate tetrahydrate (1.03 g, 4.84 mmol) in methanol (15 ml) was prepared and then cooled to 0°C. A methanolic solution (10 ml) of triethylenetetramine (1.0 ml, 6.70 mmol) was added dropwise over a period of 20 minutes. This mixture was

then neutralized by adding a solution of 2N sodium hydroxide (5 ml) and stirring at room temperature for 1 hour. Upon standing at room temperature for 7 hours, NiL crystallized from the solution and was subsequently isolated by filtration and was dried under vacuum. The nickel complex was obtained as brown microcrystalline solid (1.77 g, 89% based on 2-hydroxybenzaldehyde). IR (KBr, cm^{-1}) 3640, 3300, 3000, 2960, 2800, 1638, 1601, 1448, 1250, 950, 850; FAB MS (m/z) 411.3 ($C_{20}H_{24}N_4O_2Ni$); Anal. calcd. for $C_{20}H_{24}N_4O_2Ni.3H_2O$: C 51.65; H 6.46; N 12.05; found C 52.05; H 6.21; N 12.19.

Preparation of zinc complex (ZnL)

The zinc complex was synthesized in the same manner as NiL using zinc (II) acetate dihydrate. The zinc complex was obtained as yellow solid (1.99 g, 99% based on 2-hydroxybenzaldehyde). IR (KBr, cm^{-1}) 3646, 3300, 3000, 2800, 1645, 1600, 1448, 1200, 930, 870; ^1H NMR δ ($CDCl_3$, ppm) 8.13 (2H, s, CH=N), 6.99-7.14 (4H, m, Ar-H), 6.67-6.71 (2H, m, Ar-H), 6.37-6.44 (2H, m, Ar-H), 4.05-4.29 (2H, m, CH_2), 3.21-3.48 (4H, m, CH_2), 2.73-2.92 (2H, m, CH_2), 2.35-2.61 (4H, m, CH_2); ^{13}C NMR δ ($CDCl_3$, ppm) 172, 168, 135, 133, 124, 119, 112, 56, 47, 43; FAB MS (m/z) 417.3 ($C_{20}H_{24}N_4O_2Zn$); Anal. calcd. for $C_{20}H_{24}N_4O_2Zn.H_2O$: C 55.12; H 6.01, N 12.79, found C 54.65; H 6.59; N 12.79.

Preparation of metal-containing epoxy polymers

A mixture of DGEBA and a metal complex was degassed under vacuum until it was free of bubbles. Tetrabutylammonium hydroxide (Bu_4NOH) was then added and the mixture was degassed again. The mixture was cast into a metal

mould or a silicone mould and cured in a heated air oven at 140 °C for 4 hours. The completeness of curing was confirmed by the disapearance of epoxide groups in DGEBA at 917 cm^{-1} in the IR spectrum.

Two polymers, DGEBA/Diethylenetriamine and DGEBA/maleic anhydride systems, were prepared in order to compare their properties with the Ni- and Zn-containing epoxy polymers. These polymers were prepared using the conditions described in the literature[17, 18].

RESULTS AND DISCUSSION

Synthesis and Characterization of the metal complexes

It is known that hexadentate Schiff base ligands can be synthesized by condensation reactions of primary amines and carbonyl compounds. The reaction proceeds with high yield to produce an imine group or Schiff base compound. In 1956, Marvel prepared many hexadentate Schiff base metal complexes to study their thermal stability[19]. In our study, the hexadentate Schiff base ligand (L) was synthesized from the condensation reaction between 2-hydroxybenzaldehyde and triethylenetetramine. However, low yields were obtained if the ligand L was first isolated and then its methanolic solution was mixed with the metal acetate to cause the complex formation. Therefore, the complexes were synthesized by a one-pot reaction by adding triethylenetetramine to a mixture of 2-hydroxybenzaldehyde and metal acetates as shown in Scheme 1.

Scheme 1 Synthesis of hexadentate Schiff base metal complexes

Both NiL and ZnL'are soluble in many organic solvents such as acetone, dichloromethane and methanol. The IR spectrum of NiL showed an important absorption band of CH=N stretching at 1638 cm^{-1}. The bands at 950 and 850 cm^{-1} correspond to the characteristic absorption peak of the aromatic bending of 1,2-disubstituted benzene. MS data gave m/z 411.3 which was M^+ for $C_{20}H_{24}N_4O_2Ni$.

The IR spectrum of ZnL showed absorption bands similar to those of NiL: imine stretching at 1645 cm^{-1} and aromatic C-H bending at 930 and 870 cm^{-1}. MS data showed m/e 417.3 corresponding to $C_{20}H_{24}N_4O_2Zn$. ^1H and ^{13}C NMR data also support the proposed structure. The peaks at δ 8.33 and 168 are assigned to the imine proton and carbon, respectively. In comparison between the ^1H NMR spectrum of ligand L[20] and ZnL, the imine protons shift from δ 8.33 to 8.13, aromatic protons also shift from δ 6.82-7.32 to 6.37-7.14. The CH_2 signals of L appeared as a multiplet at δ 2.41-2.65 (4H) and two triplets with J = 6.8 Hz at δ 3.72 (4H) and 2.70 (4H), while ZnL showed four multiplet CH_2 signals at δ 4.05-4.29 (2H), 3.21-3.48 (4H), 2.73-2.92 (2H) and 2.35-2.61 (4H). The ^{13}C NMR signals of ZnL are similar to those of L.

Crosslinking reaction of DGEBA with hexadentate Schiff base metal complexes

The crosslinking reaction of DGEBA with NiL and ZnL to yield metal-containing epoxy polymers was studied using differential scanning calorimetry (DSC). The DSC experiment was performed by heating the mixture of

NiL:DGEBA and ZnL:DGEBA at the mole ratio of 1:6 in a DSC cell using an aluminum pan in air. The temperature range employed was 25-300°C at a heating rate of 20°C/min. The thermograms obtained form NiL:DGEBA and ZnL:DGEBA exhibited crosslinking peaks in the temperature range of 112-253 and 108-277°C, respectively with the peak maxima at 159 and 187°C, respectively.

The crosslinking mechanism is proposed to involve a complex dissociation. Since the metal complexes are hexadentate, the chelation between NH and metal should be broken to give a free NH which is available for the crosslinking reaction. This NH group then opens the epoxide group of DGEBA to give a secondary alcohol. Another NH of the metal complexes or an oxygen of the newly formed secondary alcohol can then attack the epoxy group of another DGEBA molecule. This is consistent with the complete disappearance of the characteristic band of epoxide groups in DGEBA at 917 cm^{-1} in the IR spectrum after the crosslinking reaction is finished. The same reaction occurs repeatedly to produce the crosslinked metal-containing epoxy polymers (Scheme 2).

Scheme 2 Proposed crosslinking mechanism of DGEBA with the metal complexes

Effect of catalyst

Our previous work showed that Bu_4NOH is a good basic catalyst in the crosslinking of DGEBA with tetradentate Schiff base metal complexes and the optimum mole ratio of Bu_4NOH:metal complex was 0.2:1[16]. Therefore, Bu_4NOH was chosen as a catalyst in this work by using this ratio. The crosslinking

conditions could, again, be determined by the use of DSC. The thermograms obtained from NiL:DGEBA:Bu_4NOH and ZnL:DGEBA:Bu_4NOH at the ratio of 1:6:0.2 gave exothermic crosslinking peaks in the temperature range of 81-233 and 91-231°C, respectively with the peak maxima at 151 and 153°C, respectively. These are lower temperatures than in the crosslinking reaction without Bu_4NOH. Isothermal crosslinking behavior of NiL:DGEBA:Bu_4NOH and ZnL:DGEBA:Bu_4NOH at the ratio of 1:6:0.2 were investigated at 140°C. Crosslinking with NiL finished in 11 minutes and that of ZnL finished in 7 minutes. Therefore, a crosslinking temperature of 140°C was chosen and Bu_4NOH was used to prepare the metal-containing epoxy polymers for further investigation.

Properties of metal-containing epoxy polymers

In order to investigate the effect of the amount of metal complexes on the polymer properties, the metal-containing epoxy polymers were prepared at the mole ratios of metal complex:DGEBA = 1:14, 1:12, 1:10, 1:8 and 1:6. Bu_4NOH was used in the amount of 20 mole% of the metal complex. DMA and isothermal TGA were employed to study the thermal properties of Ni- and Zn-containing epoxy polymers. The glass transition temperature (T_g) was obtained from a DMA thermogram by observing the maximum value of the loss modulus. Table 1 shows T_g of the epoxy polymers obtained from variation of the mole ratios of the metal complex:DGEBA. In both cases of NiL and ZnL, it was found that the ratios 1:10, 1:8 and 1:6 yielded the polymers with high T_g. At the ratios of 1:14 and 1:12, low

T_g were obtained which might be due to the incomplete crosslinking reaction since less of the metal complexes were available.

The thermal stability of metal-containing polymers was determined using isothermal TGA by heating the polymer samples in a heated air oven at 250°C for 48 h and their weight losses were then measured (Table 2). In comparison between the use of metal complex crosslinking agents and the known curing agents, both Ni- and Zn-containing polymers possess comparable thermal stability to the polymers obtained from maleic anhydride crosslinking agent and much higher thermal stability than DGEBA cured with diethylenetriamine.

Mechanical Properties

The metal-containing polymers obtained from metal complex:DGEBA: Bu_4NOH at mole ratios 1:10:0.2 and 1:8:0.2 were chosen for tensile testing since these polymers showed high T_g and good thermal stability. Ni-and Zn-containing polymers at both mole ratios have almost the same tensile strength value in the range of 41-44 N/mm^2 (Table 3), which is comparable to DGEBA/ diethylenetriamine system.

CONCLUSIONS

Hexadentate Schiff base metal complexes were synthesized and characterized. These complexes can be used a crosslinking agents for DGEBA to afford Ni- and Zn-containing epoxy polymers. The crosslinking reaction can be accelerated by use of tetrabutylammonium hydroxide. The epoxy polymers have

good thermal properties compared to the known thermally stable DGEBA/maleic anhydride system.

ACKNOWLEDGEMENTS

The authors thank Thailand Research Fund for financial support of this work. An access to FAB MS at the Chulabhorn Research Institute is acknowledged. The authors also thank Dr. Roderick W. Bates for general discussion

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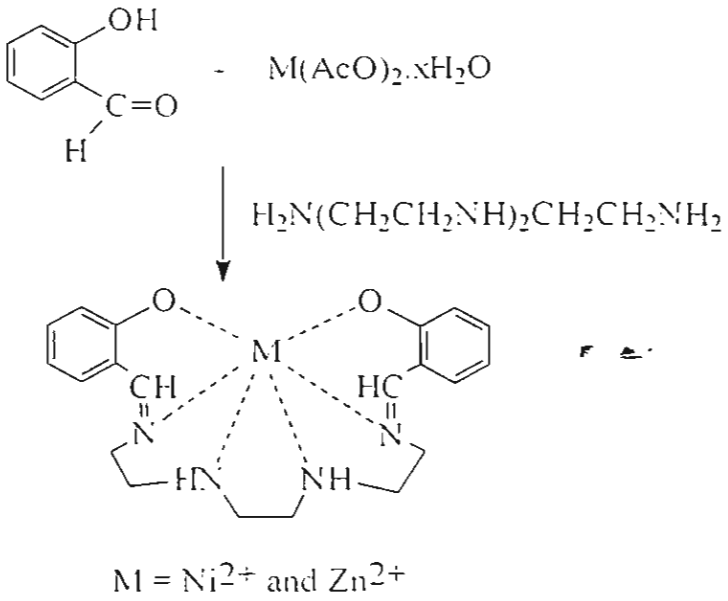
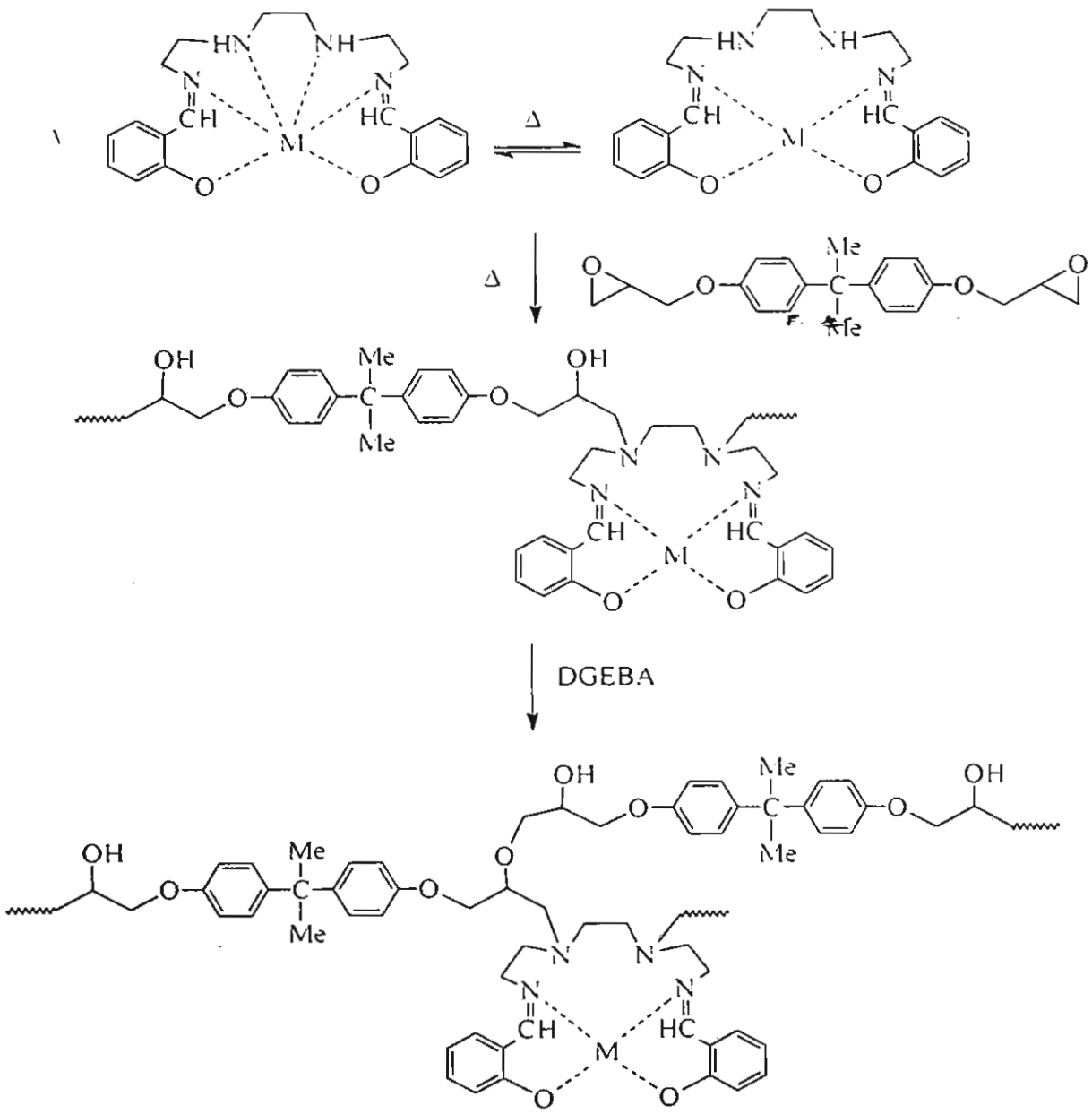
20. Ligand L was prepared by the following procedure: A cooled methanolic solution (10 ml) of triethylenetetramine (0.84 g, 5.65 mmol) was added dropwise to a solution of 2-hydroxybenzaldehyde (1.38 g, 11.28 mmol) in methanol (15 ml) at 0°C and stirred for 1 h. The yellow powder formed was then filtered and dried under vaccum. The ligand L was obtained as a yellow precipitate (1.71 g, 85% based on 2-hydroxybenzaldehyde). IR (KBr, cm^{-1}) 3462, 3200, 3000, 2800, 1639, 1608, 1400, 1285, 990, 860; ^{1}H NMR δ ($CDCl_3$, ppm) 8.33 (2H, s, CH=N), 7.20-7.32 (4H, m, Ar-H), 6.94 (2H, d, J = 7.4 Hz, Ar-H), 6.86 (2H, t, J = 7.4 Hz, Ar-H), 3.72 (4H, t, J = 6.8 Hz, CH_2), 2.70 (4H, t, J = 6.8 Hz, CH_2), 2.41-2.65 (4H, m, CH_2); ^{13}C NMR δ ($CDCl_3$, ppm) 168, 162, 132, 131, 118.5, 118, 117, 59, 58, 53.

LIST OF SCHEMES AND TABLES



Scheme 1 Synthesis of hexadentate Schiff base metal complexes



Scheme 2 Proposed crosslinking mechanism of DGEBA with the metal complexes

Table 1 T_g of the metal-containing epoxy polymers obtained from various mole ratios of crosslinking agent:DGEBA

Crosslinking agent	Mole ratio of crosslinking agent : DGEBA	Tg (°C)
NiL	1:14	69
	1:12	102
	1:10	110
	1:8	121
	1:6	127
ZnL	1:14	120
	1:12	135
	1:10	151
	1:8	145
	1:6	144
Maleic anhydride		143
Diethylenetriamine		96

Table 3 Tensile strength of the epoxy polymers obtained from various mole ratios of crosslinking agent:DGEBA

Crosslinking agent	Mole ratio of crosslinking agent : DGEBA	Tensile strength (N/mm^2)
NiL	1:10	45
	1:8	44
ZnL	1:10	41
	1:8	42
Maleic anhydride	56	
Diethylenetriamine	44	

Table 3 Tensile strength of the epoxy polymers obtained from various mole ratios of crosslinking agent:DGEBA

Crosslinking agent	Mole ratio of crosslinking agent : DGEBA	Tensile strength (N/mm^2)
NiL	1:10	45
	1:8	44
ZnL	1:10	41
	1:8	42
Maleic anhydride	56	
Diethylenetriamine	44	