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Thermally stable metal-containing epoxy polymers from an epoxy resin-Schiff base metal complex-maleic anhydride system

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Abstract

Crosslinking of diglycidyl ether of bisphenol A (DGEBA) with tetradentate and hexadentate Schiff base metal complexes of transition metals and maleic anhydride (MA) was investigated. The crosslinking reaction is proposed to proceed through a complex mechanism. Tetrabutylammonium hydroxide was found to be a suitable catalyst for such reaction. The properties of the resulting metal-containing epoxy polymers investigated were glass transition temperature, thermal stability and tensile strength. The copper-containing epoxy polymer obtained from tetradentate Schiff base metal complexes at the mole ratio of DGEBA:metal complex:MA = 1:0.2:0.2 showed T_g at 143°C and tensile strength of 62 N/mm^2. The polymer showed good thermal stability comparing to the DGEBA–MA system. Upon heating at 250° C for 48 h, the weight loss of the polymer was 2.8%.

Keywords: Epoxy polymers; Metal-containing polymers; Schiff base metal complexes

1. Introduction

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 [1]. A large number of such investigations have been reported [2–12]. Metal-containing epoxy polymers can be synthesized by various methods as follows: (1) use of metal-containing admixtures (2) crosslinking of metal-containing epoxy resins and (3) use of metal-containing crosslinking agents.

Previous work [13,14] from this laboratory involved the synthesis of metal-containing epoxy polymers by crosslinking of DGEBA with tetradentate and hexadentate Schiff base metal complexes of copper, cobalt, nickel and zinc (Scheme 1) so that the metal is incorporated in the polymer structure. The obtained polymers showed good thermal stability.

It is well known that epoxy resins can be crosslinked with various acid anhydrides in the presence of catalysts such as *N*,*N*-dimethylbenzylamine which produces crosslinked polymers with good physical and mechanical properties. Addition of metal salts is widely employed in the crosslinking of epoxy-anhydride systems with the purpose of reducing the crosslinking temperature and improving the polymer properties. One example is the use of calcium and magnesium salts of *p*-aminobenzoic acid in the crosslinking of DGEBA–hexahydrophthalic anhydride system [15,16]. The likely mechanism is that the amino groups of the metal salts first react with the anhydride group to generate carboxylate groups, which could then undergo further reaction with the epoxide groups in DGEBA to give the crosslinked polymers. Other examples of metal complexes employed for this purpose are acetylacetonate complexes [17,18].

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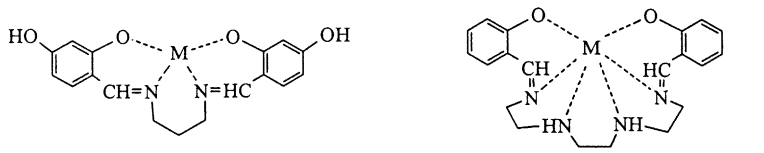


Tetradentate Schiff base metal complexes

$M = Cu^{2+}$, Co^{2+} and Ni^{2+}

Hexadentate Schiff base metal complexes

$M = Ni^{2+}$ and Zn^{2+}

Scheme 1. Structures of Schiff base metal complexes.

The metal-containing epoxy polymers in this present study were synthesized by the crosslinking reaction of DGEBA with mixtures of maleic anhydride (MA) and the previous mentioned tetradentate and hexadentate Schiff base metal complexes. The tetradentate Schiff base metal complexes contain two phenolic groups which should undergo the crosslinking reaction with MA and DGEBA to give the metal-containing epoxy polymers. The hexadentate Schiff base metal complexes contains two amine groups which should undergo similar crosslinking reaction to the tetradentate Schiff base metal complexes.

2. Experimental

2.1. Materials

The metal complexes used in this study were tetradentate Schiff base metal complexes (CuL_1, CoL_1 and NiL_1) and hexadentate Schiff base metal complexes (NiL_2 and ZnL_2) synthesized by employing the methods as reported previously [13,14]. MA and tetrabutylammonium hydroxide (Bu_4NOH) were obtained from Fluka and were used as received. The concentration of Bu_4NOH used was 0.8 M in methanol. As the DGEBA epoxy resin, D.E.R. 330 (Fluka) with the epoxy equivalent of 185 was used.

2.2. Analytical methods

The crosslinking reaction of DGEBA with the metal complexes and MA were investigated with a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets.

Glass transition temperature of metal-containing epoxy polymers were obtained on a Netzch DMA 240 dynamic mechanical analyzer. Thermal stability of the polymers were determined using isothermal TGA by heating the polymer samples (sample size 50 mm × 10 mm × 3 mm) in a heated air oven at 250°C for 48 h and their weight losses were then measured. Tensile testing was performed on an Instron model 4301 following ASTM D638.

2.3. Preparation of metal-containing epoxy polymers

A mixture of DGEBA, metal complex and MA was degassed at 70°C under vacuum until it was free of bubbles. The mixture was cooled down to room temperature. Bu_4NOH was then added and the mixture was degassed again. The mixture was cast into a metal mould or a silicone mould and crosslinked in a heated air oven. The completeness of the crosslinking reaction was confirmed by the disappearance of the characteristic band of the epoxide groups in DGEBA at 917 cm^{-1} in the IR spectrum.

The crosslinking temperature for CuL_1 and CoL_1 was 150°C. When NiL_1 was employed, the crosslinking temperature was 180°C. The crosslinking time was 1 h at the mole ratios of DGEBA:metal complex:MA = 1:0.2:0.2 and 1:0.3:0.3. At the mole ratio of 1:0.1:0.1, the crosslinking time was 3 h.

The crosslinking condition for both NiL_2 and ZnL_2 was 110° C/8 h for every mole ratio.

A comparative polymer was prepared by crosslinking of DGEBA with diethylenetriamine and MA in the presence of benzyldimethylamine [19,20].

3. Results and discussion

3.1. Reaction between metal complexes and maleic anhydride

3.1.1. Tetradentate Schiff base metal complexes

Considering a curable mixture of DGEBA:metal complex:MA, the functional groups which undergo crosslinking reactions are the phenol groups in the metal complexes, the anhydride group in MA and the epoxide groups in DGEBA. Thus, the three possible reactions are the phenolic group–anhydride group reaction, the phenolic group–epoxide group reaction and the epoxide group–anhydride group reaction. Since the reaction between phenolic group and anhydride group proceeds more rapidly than do the other two reactions, the phenol groups in the metal complexes should react preferentially with the acid anhydride group in MA in the initial

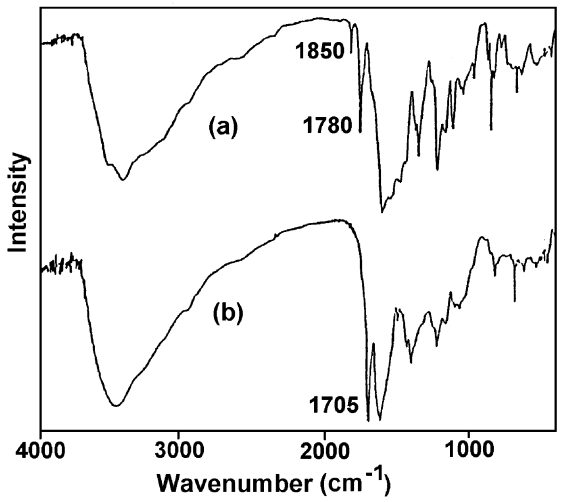


Fig. 1. Infrared spectra from the reaction between CuL_1 and MA at the mole ratio of 1:1: (a) initial at 150°C, (b) 1 h at 150°C.

stage of crosslinking reaction to form the product containing ester groups and carboxylic groups.

The reaction between metal complexes and MA was studied using IR spectroscopy. When a mixture of CuL_1:MA at the mole ratio of 1:1 was heated at 150°C for 1 h, the band of the anhydride group at 1850 and 1780 cm^{-1} disappeared and a band at 1705 cm^{-1} assignable to a carboxylic group could be observed (Fig. 1). When CoL_1 and NiL_1 were used instead of CuL_1, the IR bands of the anhydride group disappeared after heating at 150°C for 1 h and 3 h, respectively.

3.1.2. Hexadentate Schiff base metal complexes

In this case, the metal complexes contain two amine groups instead of two phenolic groups in tetradentate Schiff base metal complexes. These amine groups could undergo reactions with MA to yield the product containing amide groups and carboxylic groups. Similar results were obtained when the mixtures of NiL_2:MA and ZnL_2:MA at the mole ratio of 1:1 were heated at 130°C for 1 h. The anhydride band in the IR spectrum at 1850 and 1780 cm^{-1} also disappeared and the peak at 1708 cm^{-1} due to the formed carboxylic acid was observed.

3.2. Crosslinking reaction of DGEBA with the mixture of metal complexes and maleic anhydride

3.2.1. Tetradentate Schiff base metal complexes

Having obtained the results that the reaction between metal complexes and MA occurred at 150°C, the next step was to study the reaction between DGEBA, metal complexes and MA. IR spectroscopy was employed to determine the reactivity of the metal complexes towards the crosslinking reaction of DGEBA–MA system. A mixture of DGEBA:metal complex:MA at the mole ratio of 1:0.2:0.2 was heated and the completeness of the reaction was determined by the disappearance of the IR band at 917 cm^{-1} due to the epoxide groups in DGEBA. Crosslinking of DGEBA:CuL_1:MA and DGEBA:CoL_1:MA mixtures at 150°C took 3 h to complete. Reaction using NiL_1 required a higher crosslinking temperature at 180°C in order to finished in 3 h.

3.2.2. Hexadentate Schiff base metal complexes

The IR experiments performed in the same manner as in the case of tetradentate Schiff base metal complexes were carried out. The IR spectra suggested that the crosslinking reactions of both DGEBA:NiL_2:MA and DGEBA:ZnL_2:MA mixtures at the mole ratio of 1:0.2:0.2 were completed after heating at 130°C for 4 h.

3.3. Crosslinking mechanism

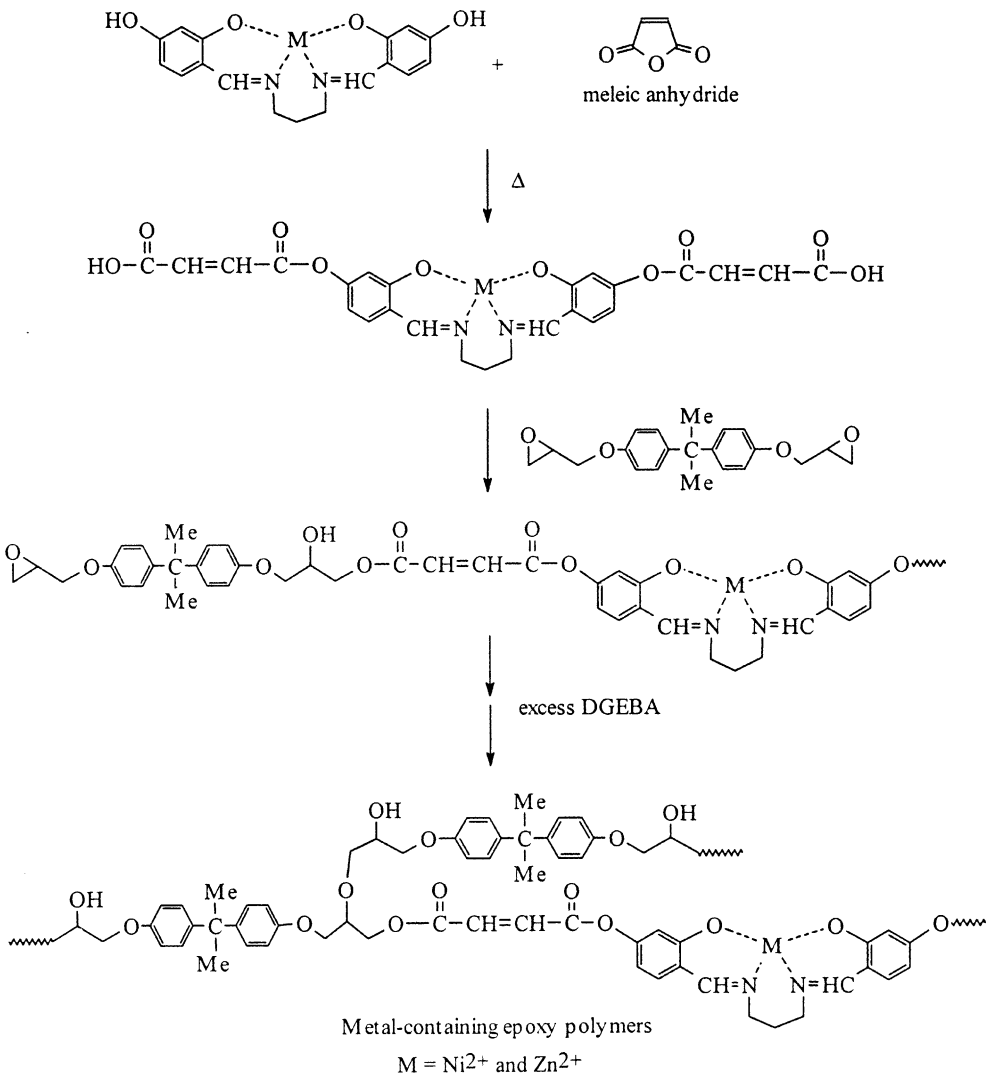
3.3.1. Tetradentate Schiff base metal complexes

As mentioned previously, the reaction occurred in the initial stage of the crosslinking reaction in the curable mixture of DGEBA:metal complex:MA was the reaction between the metal complex and MA to generate carboxylic groups. After all of the MA underwent reaction with the metal complexes, half of the metal complexes would not have reacted since equimolar amounts of MA and metal complexes were used.

In the second stage of the crosslinking process, there are two possible reactions, the carboxylic group–epoxide group and DGEBA hydroxyl group–epoxide group reactions. In this case, the carboxylic group–epoxide group reaction is faster than the hydroxyl group–epoxide group reaction. Therefore, all carboxylic groups should react with the epoxide groups to generate secondary alcohols which could then reacted with the other epoxide groups in DGEBA.

A likely crosslinking mechanism is proposed to involve a ring opening of MA by the phenolic groups in the metal complexes to give carboxylic groups. The carboxylic groups then react with DGEBA to give ester and secondary alcohol which can then react with another molecules of DGEBA. The reaction occurs repeatedly to produce the Cu-, Co- and Ni-containing epoxy polymers as shown in Scheme 2.

The unreacted metal complexes from the initial stage of the crosslinking reaction could also undergo the reaction with DGEBA to give the crosslinked polymers (Scheme 3). The mechanistic details were discussed previously [13]. Therefore, the total crosslinking reaction



Scheme 2. Proposed crosslinking mechanism of DGEBA with the mixtures of tetradentate Schiff base metal complexes and MA.

should involve the reactions shown in both Schemes 2 and 3. [1]

3.3.2. Hexadentate Schiff base metal complexes

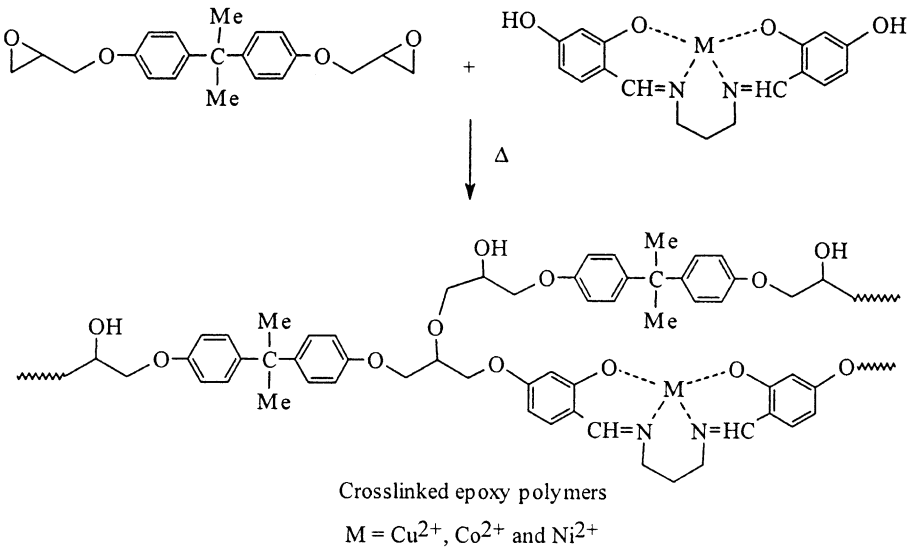
A possible crosslinking mechanism is proposed on the same basis as tetradentate Schiff base metal complexes. The metal complexes first dissociated from hexadentate into tetradentate coordination, then the amine groups open MA ring to generate carboxylic groups. The carboxylic groups then undergo reaction with DGEBA to give secondary alcohol which react further with DGEBA to give Ni- and Zn-containing epoxy polymers (Scheme 4).

The unreacted metal complexes from the initial stage of the crosslinking reaction would also be present. Scheme 5 shows the reaction between the metal complexes and DGEBA to give the crosslinked polymers as described in our previous report [14]. Hence, the final polymers should contain the structures resulting from the reaction shown in both Schemes 4 and 5. [1]

3.4. Effect of catalyst

Our previous work [13,14] showed that Bu_4NOH was a suitable catalyst in the crosslinking reaction of

[1] Another possible crosslinking mechanism is the reaction between the metal complexes and MA in the first step gives the adduct containing only one carboxylic group. This adduct then undergoes further reaction with DGEBA to yield the crosslinked polymers.



Scheme 3. Reaction between tetradentate Schiff base metal complexes and DGEBA.

DGEBA with tetradentate and hexadentate Schiff base metal complexes. It was found that the crosslinking reaction in the presence of Bu_4NOH proceeded more rapidly than the reaction without Bu_4NOH and the optimum amount of Bu_4NOH was 20 mol% of the metal complex. Therefore, Bu_4NOH was also chosen as a catalyst in this study.

3.4.1. Tetradentate Schiff base metal complexes

IR spectroscopy was again employed to study the crosslinking reaction of the DGEBA:metal complex:MA mixtures at the mole ratio of 1:0.2:0.2. In the case of tetradentate Schiff base metal complexes, the results from IR study showed that use of Bu_4NOH at the amount of 20 mol% of the metal complex reduced the crosslinking time when the reaction was done at the same temperature as those without Bu_4NOH. The crosslinking condition for both CuL_1 and CoL_1 was 150°C/1 h. Use of NiL_1 required 180°C/1 h.

Bu_4NOH might accelerate the crosslinking reaction by removing protons from the phenol groups of the metal complexes to generate phenolate groups which open MA ring to give carboxylate groups. Further reaction of the carboxylate groups with DGEBA gives crosslinked polymers.

3.4.2. Hexadentate Schiff base metal complexes

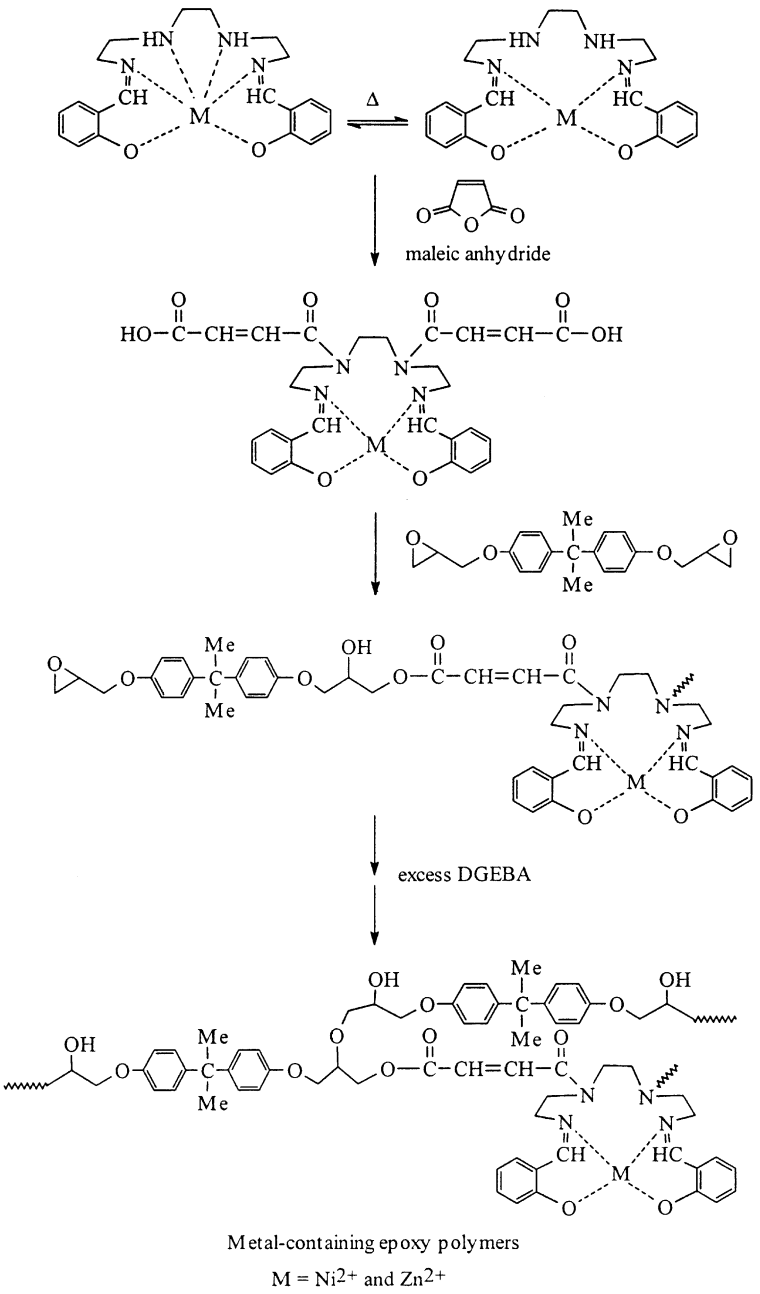
In the case of hexadentate Schiff base metal complexes, the presence of Bu_4NOH at the amount of 20 mol% of the metal complex also reduced the crosslinking time comparing to the reaction without Bu_4NOH. Crosslinking reaction for both NiL_2 and ZnL_2 at 130°C finished in 1 h. When the reaction was done at a lower temperature of 110°C, crosslinking was completed in 4 h.

A possible crosslinking mechanism is that the metal complexes first dissociates. The amine groups open the MA ring to generate carboxylate groups and theamines become ammonium salts. Bu_4NOH might accelerate the reaction by removing protons from the ammonium salts. The carboxylate groups then undergo reaction with DGEBA to give crosslinked polymers.

3.5. Properties of metal-containing epoxy polymers

Polymer samples were prepared from different mole ratios of DGEBA:metal complex:MA in the presence of 20 mol% Bu_4NOH for further investigation of their properties. The metal-containing epoxy polymers were characterized by IR spectroscopy. All epoxy polymers had similar IR spectra. The important absorption bands observed were alcoholic O–H at 3300–3500 cm^{-1} and ester C=O stretching at 1730–1735 cm^{-1}. The broad band at 1600–1660 was due to the C=N, aromatic and olefinic C=C stretching vibration.

Other properties of the polymers investigated were thermal and mechanical properties. Glass transition temperature of the polymers was determined from a DMA thermogram by observing the maximum value of the loss modulus. Thermal stability was determined and measuring the % weight loss from isothermal TGA technique. Table 1 shows T_g, % weight loss and tensile



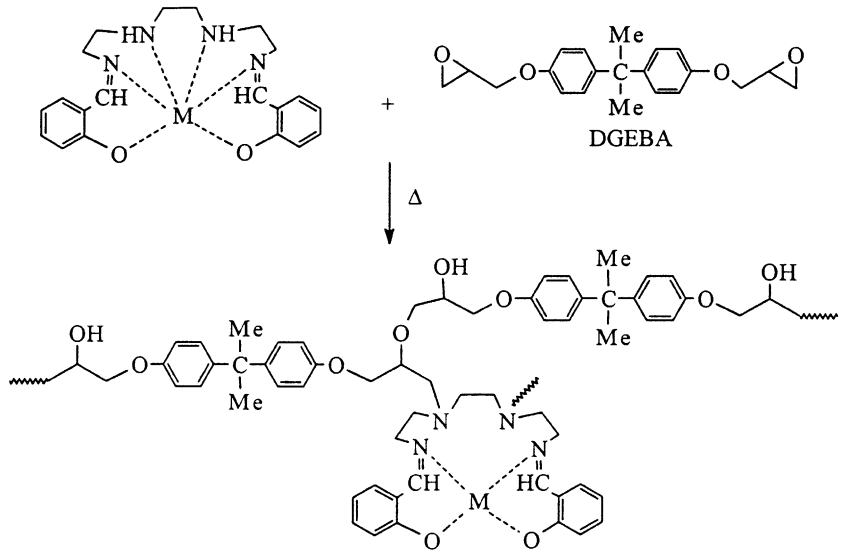
Scheme 4. Proposed crosslinking mechanism of DGEBA with the mixtures of hexadentate Schiff base metal complexes and MA.

strength of the epoxy polymers obtained from variation of the mole ratios of DGEBA:metal complex:MA.

It was found that copper-containing polymer obtained at the mole ratio of DGEBA:CuL_1:MA = 1:0.2:0.2 possessed high T_g, high tensile strength and good thermal stability which is comparable to the DGEBA–MA system.

4. Conclusions

Metal-containing epoxy polymers have been prepared from crosslinking reaction of DGEBA with a mixture of Schiff base metal complexes and MA. The crosslinking time and temperature can be decreased by use of Bu_4NOH. The metal-containing epoxy polymers



Metal-containing epoxy polymers

$M = Ni^{2+}$ and Zn^{2+}

Scheme 5. Reaction between hexadentate Schiff base metal complexes and DGEBA.

Table 1
T_g, tensile strength and thermal stability of the metal-containing epoxy polymers

Metal complex	Mole ratio of DGEBA:metal complex:MA	T_g (°C)	Tensile strength (N/mm^2)	% Weight loss
CuL_1	1:0.1:0.1	114	56	2.7
	1:0.2:0.2	143	62	2.8
	1:0.3:0.3	105	45	3.2
CoL	1:0.1:0.1	125	42	2.4
	1:0.2:0.2	128	51	2.7
	1:0.3:0.3	103	41	3.1
NiL_1	1:0.1:0.1	124	43	8.4
	1:0.2:0.2	125	53	9.0
	1:0.3:0.3	122	42	9.3
NiL_2	1:0.1:0.1	119	61	11.9
	1:0.15:0.15	139	48	7.7
	1:0.2:0.2	133	43	9.5
ZnL_2	1:0.1:0.1	132	59	19.6
	1:0.15:0.15	131	51	10.5
	1:0.2:0.2	129	48	14.6
Diethylene-triamine		125	57	26.6
MA		143	56	4.0

show good thermal and mechanical properties compared to the known DGEBA–MA system.

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