ELSEVIER

European Polymer Journal 36 (2000) 695–702

EUROPEAN POLYMER JOURNAL

New metal-containing epoxy polymers from diglycidyl ether of bisphenol A and tetradentate Schiff base metal complexes

Nuanphun Chantarasiri[a,*], Thawatchai Tuntulani[a], Pan Tongraung[a], Ratana Seangprasertkit-Magee[a], Walee Wannarong[b]

[a]*Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[b]*Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*

Received 18 January 1999; received in revised form 14 April 1999; accepted 28 April 1999

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 h and had a tensile strength of 69 N/mm^2, which is comparable to the epoxy-anhydride system. © 2000 Elsevier Science Ltd. All rights reserved.

1. 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 strength 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

---

* Corresponding author. Fax: +662-254-1309.
E-mail address: nuanphun.c@chula.ac.th (N. Chantarasiri).

PII: S0014-3057(99)00127-5

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 diglycidyl ether of bisphenol A (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.

2. Experimental

2.1. Materials

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

2.2. 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.

2.3. Synthesis

2.3.1. 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 min. 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 min. 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 ($C_{17}H_{16}N_2O_4Cu\cdot 2H_2O–2H_2O$); Anal. calcd. for $C_{17}H_{16}N_2O_4Cu\cdot 2H_2O$: 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.

2.3.2. 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 ($C_{17}H_{16}N_2O_4Co\cdot 4H_2O–4H_2O$); Anal. calcd. for $C_{17}H_{16}N_2O_4Co\cdot 4H_2O$: 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.

2.3.3. 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 ($C_{17}H_{16}N_2O_4Ni\cdot 2H_2O–2H_2O$); Anal. calcd. for $C_{17}H_{16}N_2O_4Ni\cdot 2H_2O$: 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.

2.3.4. 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

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 h	150°C/4 h
CoL	200°C/5 h	160°C/4 h
NiL	240°C/3 h	155°C/4 h

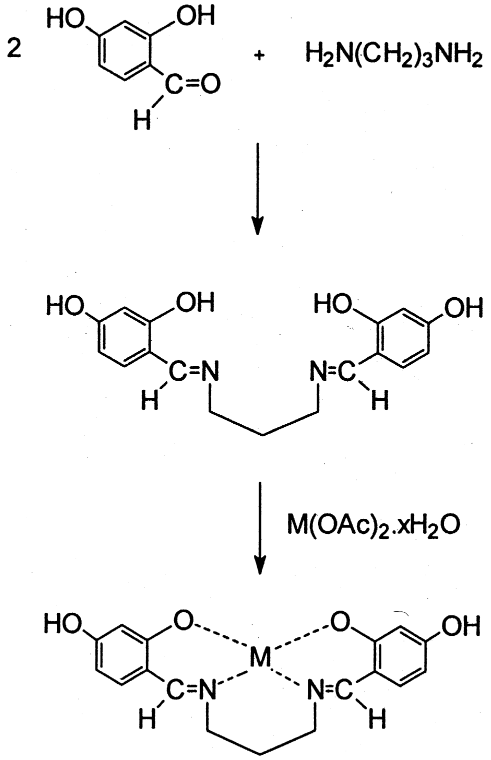
[a] 20 mol% of the metal complex was employed.

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].

3. Results and discussion

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

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} 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.

3.2. 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 calorimetry (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 25–350°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 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 min 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 min.

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 disappearance 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.

3.3. Effect of catalyst

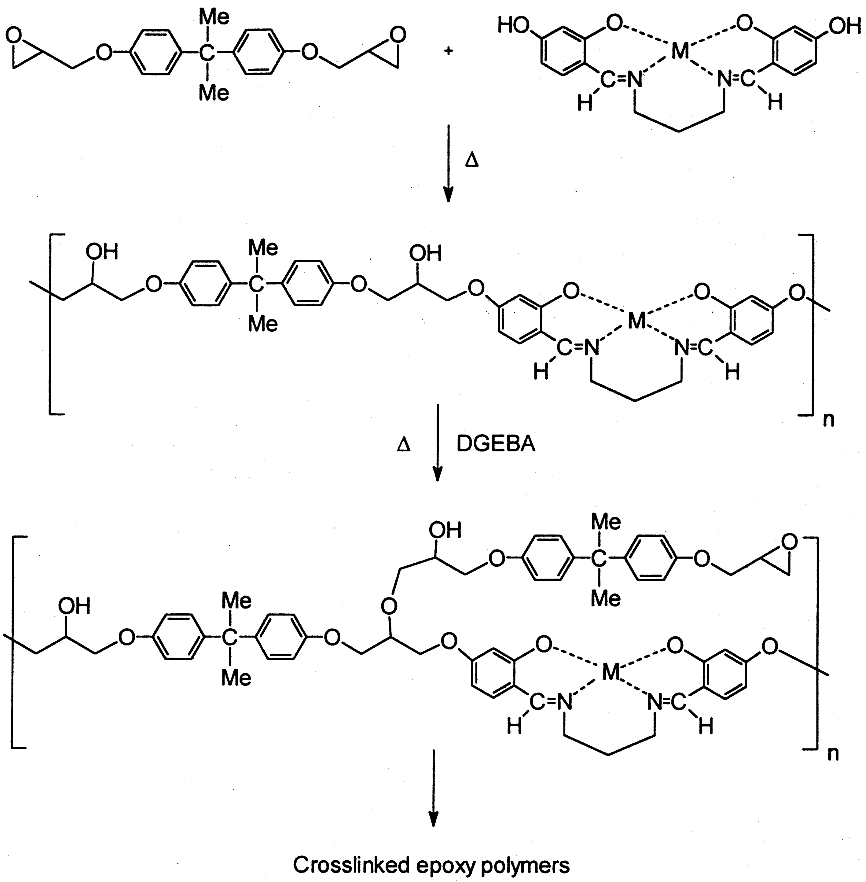
It is of interest to compare the curing condition before and after using catalyst. The catalyzed reaction was expected to give the curing condition at a lower temperature. Curing reaction of DGEBA using phenolic compounds is normally accelerated using various catalysts, such as sodium hydroxide, dimethylaniline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

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 min, while curing condition using CuL in the presence of Bu_4NOH was finished in 12 min 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.

3.4. Properties of metal-containing epoxy polymers

We have also prepared polymer samples for further



Scheme 2. Proposed curing mechanism of DGEBA with the metal complexes (M = Cu^{2+}, Co^{2+}, Ni^{2+}) at a ratio of 1 : 6 : 0.2.

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

Curing agent	Curing parameters of DGEBA				
	Amount of Bu_4NOH[a]	T_b (°C)[b]	T_{max} (°C)[c]	T_{end} (°C)[d]	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 mol% 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.

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 prepared; since they required long curing times at high temperature. Thermal properties of the

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	T_g (°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 mol% 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 h[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 × 5.0 × 0.3 cm.
[b] 20 mol% of the curing agent was employed.

metal-containing epoxy polymers were studied by DMA and weight loss measurement.

3.5. 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.

3.6. Thermal stability

Thermal stability of metal-containing polymers was

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 mol% of the curing agent was employed.

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.

3.7. 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 control.

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.

4. 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.

References

[1] Kurnoskin AV. Metal-containing epoxy polymers. In: Cheremisinoff NP, Cheremisinoff PN, editors. Handbook of applied polymer processing technology. New York: Marcel Dekker, 1996. p. 703–65.
[2] Kurnoskin AV. Metalliferous epoxy-chelate polymers: analytical review. JMS Rev Macromol Chem Phys 1996;C36(3):457–599.
[3] Kurnoskin AV. Thermal oxidative destruction of epoxy polymers. JMS Rev Macromol Chem Phys 1995;C35(3):419–94.
[4] Kurnoskin AV. Epoxy polymer modification with metals. Polym Comp 1993;14(6):481–90.
[5] Kurnoskin AV. Metalliferous epoxy chelate polymers: Part 1. Synthesis and properties. Polymer 1993;34(5):1060–7.
[6] Kurnoskin AV. Metalliferous epoxy chelate polymers: Part 2. Influence of structural fragments on properties. Polymer 1993;34(5):1068–76.
[7] Kurnoskin AV. Metalliferous epoxy chelate polymers: Part 3. Influence of structural fragments on the properties of similar matrices. Polymer 1993;34(5):1077–88.
[8] Kurnoskin AV. Structure of the epoxy chelate metal-containing matrices: theoretical aspects. J Appl Polym Sci 1993;48:639–56.
[9] Kurnoskin AV. Polymers based on epoxy oligomers and hardeners: chelates of metals with aromatic and heterocyclic amines. Ind Eng Chem Res 1992;31:524–9.
[10] Lin KF, Wang WH. Imidazole and chromium acetylacetonate as additives for the cure and fracture-toughness of epoxy resins and their composites. Polym Comp 1995;16(4):269–75.
[11] Lin KF, Shu WY, Wey TL. Organotransition-metal complexes as additives for epoxy resins: Part 1. Their effects on toughness and morphology of epoxy resins. Polymer 1993;34(2):277–88.
[12] Lin KF, Shu WY, Wey TL. Organotransition-metal complexes as additives for epoxy resins: Part 2. Interaction with epoxy resins. Polymer 1993;34(10):2162–8.
[13] Anand M, Srivastava AK. Synthesis and characterization of epoxy resins containing arsenic acrylate. Polym Eng Sci 1997;37(1):183–7.
[14] Anand M, Srivastava AK. Synthesis and characterization of epoxy resins containing chromium acrylate. Angew Makromol Chem 1994;219:1–10.
[15] Anand M, Srivastava AK. Synthesis of zinc-containing epoxy resin. J Appl Polym Sci 1994;51(2):203–11.
[16] Anand M, Srivastava AK. Synthesis and characterization of epoxy resins containing poly(copper acrylate). J Macromol Sci, Pure Appl Chem 1993;A30(5):435–46.
[17] Anand M, Srivastava AK. Synthesis and characterization of new epoxy resins containing transition metals. Polymer 1993;34(13):2860–4.
[18] Kurnoskin AV, Kanovitch MZ, Ilyin VM, Gusev LL,

Bekeshko VV. Application of epoxychelate composites in automobile industry. Inf Bull Khim Prom SEV 1990;6:25–9.

[19] Parshall GW, Ittel SD. In: Homogeneous catalysis. New York: Wiley, 1992. p. 155, 177, 239.

[20] Böttcher A, Elias H, Jager EG, Langfelderova H, Mazur M, Müller L, Paulas H, Pelikan P, Rudolph M, Valko M. Comparative study on the coordination chemistry of cobalt(II), nickel(II), and copper(II) with derivatives of salen and tetrahydrosalen: metal catalyzed oxidative dehydrogenation of the C–N bond in coordinated tetrahydrosalen. Inorg Chem 1993;32:4131–8.

[21] Lee H, Naville K. Handbook of epoxy resins. New York, McGraw-Hill, 1967. p. 5-16, 11-13, 12-8.

[22] May CA. In: Epoxy resins: chemistry and technology. New York: Marcel Dekker, 1988. p. 481, 526.