CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

All reagents and solvents were of analytical grade quality. The solvents were obtained from Baker Chemical Company. DGEBA epoxy resin (D.E.R.330, epoxy eqivalent weight = 185), 2,4-dihydroxybenzaldehyde, 1,3-diaminopropane, cobalt(II) acetate tetrahydrate, nickel(II) acetate tetrahydrate, zinc(II) acetate dihydrate, maleic anhydride, benzyldimethylamine, tetrabutylammoniumhydroxide and sodium hydroxide were obtained from Fluka. Copper(II) acetate monohydrate was obtained from Riedel-de Haen. All chemicals were used with no further purification.

2.2 Analytical Procedures

The IR spectra were recorded on a Nicolet Impact 410. Elemental analyses and Mass Spectroscopy were carried out on a Perkin Elmer Elemental Analyzer 2400 CHN and Bruker (BIFLEX), respectively. The thermal properties of epoxy polymers were measured on a Netzch Differential Scanning Calorimeter (DSC 200). Netzch Dynamic Mechanical Analyzer (DMA 242) and Perkin Elmer Thermogravimetric Analyzer (TGA 7). Tensile strength was measured on an Instron Model 4310.

2.3 Preparation of Tetradentate Schiff's Base Metal Complexes (ML)

2.3.1 Preparation of Copper Complex (CuL), Cobalt Complex (CoL) and Nickel Complex (NiL)

These complexes were synthesized according to the method previously described by Tongraung.[22]

2.3.2 Preparation of Zinc Complex (ZnL)

A methanolic solution (10 ml) of 1,3-diaminopropane (1 ml, 10.59 mmol) was added dropwise into a stirred cool (0-10 °C) methanolic solution (40 ml) of 2,4-dihydroxybenzaldehyde (2.93 g, 21.18 mmol). The yellow solution of the Schiff's base ligand was stirred for another 15 minutes. A solution (40 ml) of zinc acetate dihydrate (2.32 g, 10.57 mmol) was added dropwise. Sodium hydroxide solution (2 N, 10 ml) was then added. The product started to precipitate out as yellow powder. The mixture was stirred for another 15 minutes. The metal complex was subsequently isolated by filtration and dried. The obtained ZnL (3.71 g, 93%) was then characterized by IR spectroscopy, mass spectroscopy and elemental analysis; m.p. 342, IR (cm^{-1}) : 3500-3300, 2921, 1600, 1600-1400, 1226, 995, 825; MS (m/z) : 315, 316, 317. Anal. Calc for $C_{17}H_{16}N_2O_4Zn.H_2O$: C 51.60; H 4.58; N 7.08; Found : C 51.96; H 5.03; N 7.53.

2.4 Reaction between Tetradentate Schiff's Base Metal Complexes and Maleic Anhydride

Typically, metal complexes (CuL, CoL, NiL and ZnL) and maleic anhydride (MA) at mole ratio of ML : MA = 1 : 1 were heated at 60 °C and stirred to become a homogeneous mixture. The mixture was then heated at 150 °C in an oven. The progress of the reaction was followed by IR spectroscopy.

2.5 Crosslinking of DGEBA with Metal Complexes and Maleic Anhydride

2.5.1 IR Study

The crosslinking temperatures of DGEBA with metal complexes and maleic anhydride were determined by heating a mixture of ML : MA : DGEBA at a mole ratio of 0.2 : 0.2 : 1 in an oven at different temperatures and followed the crosslinking reaction by using IR spectroscopy. The disappearance of the IR band of epoxide group at 917 cm^{-1} was observed when the reaction was completed. The crosslinking temperature for each metal complex was chosen so that the crosslinking reaction was completed in 3 hours. It was found that the suitable crosslinking temperature for CuL and CoL was 150 °C. For NiL and ZnL, the suitable crosslinking temperatures were 180 and 190 °C, respectively.

2.5.2 Isothermal DSC Study

The crosslinking temperatures obtained from IR study were then employed in isothermal DSC study. Metal complexes (CuL, CoL, NiL and ZnL), MA and DGEBA were mixed at the mole ratio of ML : MA : DGEBA = 0.2 : 0.2 :1 and 0.3 : 0.3 : 1. The mixture was heated in a DSC cell using an aluminum pan crucible in air at different aforementioned crosslinking temperatures.

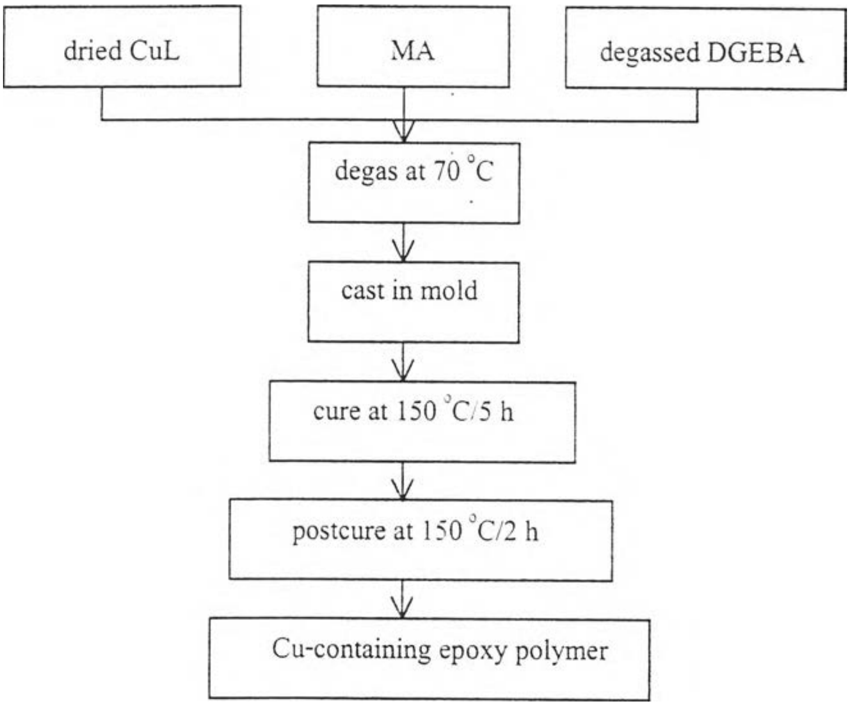
2.6 Preparation of Metal-Containing Epoxy Polymers Using Tetradentate Schiff's Base Metal Complexes and Maleic Anhydride as Crosslinking Agents

2.6.1. Copper-Containing Epoxy Polymer

Different mole ratios of CuL : MA : DGEBA were employed as shown in Table 2.1. A mixture of CuL, maleic anhydride and DGEBA in a 50 ml round bottom flask was heated at 70 °C, degassed and stirred until it became homogeneous. The degassed mixture was put into a metal or a silicone mold and crosslinked at 150 °C. The crosslinking time required for different ratios of CuL : MA : DGEBA were shown in Table 2.1. The Cu-containing epoxy polymers were then postcured for 2 h to ensure the complete reaction. The preparation scheme of Cu-containing epoxy polymers was shown in Scheme 2.1.

Table 2.1 Composition of starting materials in CuL : MA : DGEBA formulation

Mole ratio of CuL : MA : DGEBA	Weight of composition (g)			Crosslinking period (h)
	CuL	MA	DGEBA	
0.1 : 0.1 : 1	0.33	0.08	3	5
0.2 : 0.2 : 1	0.67	0.16	3	3
0.3 : 0.3 : 1	1.00	0.24	3	3
0.4 : 0.4 : 1	1.33	0.32	3	3



Scheme 2.1 Preparation scheme of Cu-containing epoxy polymers

2.6.2 Cobalt-Containing Epoxy Polymer

DGEBA was crosslinked with CoL and maleic anhydride at 150 °C by the same procedure described in 2.6.1. The mole ratios of CoL : MA : DGEBA were varied as shown in Table 2.2.

Table 2.2 Composition of starting materials in CoL : MA : DGEBA formulation

Mole ratio of CoL : MA : DGEBA	Weight of composition (g)		
	CoL	MA	DGEBA
0.1 : 0.1 : 1	0.36	0.08	3
0.2 : 0.2 : 1	0.72	0.16	3
0.3 : 0.3 : 1	1.07	0.24	3
0.4 : 0.4 : 1	1.43	0.32	3

2.6.3 Nickel-Containing Epoxy Polymer

DGEBA was crosslinked with NiL and maleic anhydride at 180 °C by the same procedure described in 2.6.1. The mole ratios of NiL : MA : DGEBA were varied as shown in Table 2.3.

Table 2.3 Composition of starting materials in NiL : MA : DGEBA formulation

Mole ratio of NiL : MA : DGEBA	Weight of composition (g)		
	NiL	MA	DGEBA
0.1 : 0.1 : 1	0.33	0.08	3
0.2 : 0.2 : 1	0.66	0.16	3
0.3 : 0.3 : 1	0.99	0.24	3
0.4 : 0.4 :1	1.32	0.32	3

2.6.4 Zinc-Containing Epoxy Polymer

DGEBA was crosslinked with ZnL and maleic anhydride at 190 °C by the same procedure described in 2.6.1. The mole ratios of ZnL : MA : DGEBA were varied as shown in Table 2.4.

Table 2.4 Composition of starting materials in ZnL : MA : DGEBA formulation

Mole ratio of ZnL : MA : DGEBA	Weight of composition (g)		
	ZnL	MA	DGEBA
0.1 : 0.1 : 1	0.32	0.08	3
0.2 : 0.2 : 1	0.64	0.16	3
0.3 : 0.3 : 1	0.96	0.24	3
0.4 : 0.4 : 1	1.28	0.32	3

Comparative polymers obtained by using maleic anhydride and diethylenetriamine as crosslinking agents were also prepared. Cure cycle for crosslinking of DGEBA with maleic anhydride was 100 °C/1 h followed by 160 °C/4 h. Curing condition of DETA was 100 °C/1 h.[1] Table 2.5 shows the composition of starting materials.

Table 2.5 Composition of starting materials in crosslinking reaction of DGEBA using maleic anhydride and diethylenetriamine as crosslinking agents

Crosslinking agent	Weight of composition (g)	
	Crosslinking agent	DGEBA
Maleic anhydride[a]	2.25 (23 mmol)	3 (8 mmol)
Diethylenetriamine	0.36 (4 mmol)	3 (8 mmol)

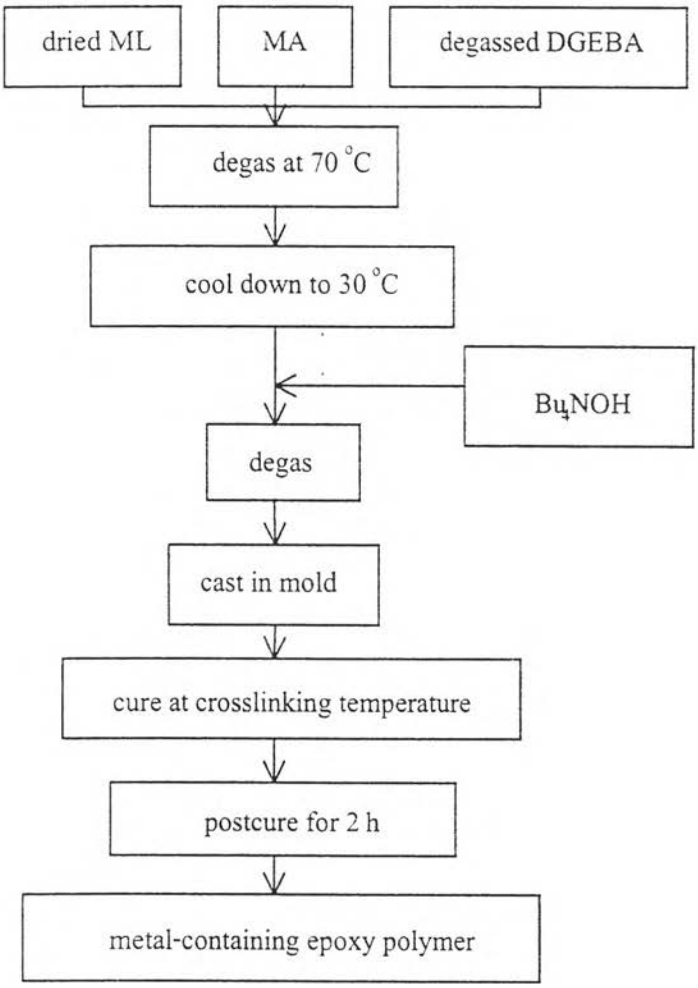
[a] benzyldimethylamine 0.0053 g (0.1 phr) was employed as a catalyst

2.7 Preparation of Metal-Containing Epoxy Polymers Using Tetradentate Schiff's Base Metal Complexes and Maleic Anhydride as Crosslinking Agents in the Presence of Bu_4NOH

From Chantarasiri N. and Wannarong, W. unpublished results, tetrabutylammoniumhydroxide (Bu_4NOH) was found to improve the thermal properties of the metal-containing epoxy polymers. Tetrabutylammoniumhydroxide was thus used as a catalyst at the amount of 20 mole % of the metal complexes. The crosslinking temperature used to prepare epoxy polymers in the presence of Bu_4NOH are the same as those without Bu_4NOH. The crosslinking time and the preparation scheme of metal-containing epoxy polymers were shown in Table 2.6 and Scheme 2.2, respectively.

Table 2.6 Time for crosslinking reaction of DGEBA at different ratios of ML : MA : DGEBA in the presence of Bu_4NOH

Mole ratio of ML : MA : DGEBA	Crosslinking time (h)
0.1 : 0.1 :1	3
0.2 : 0.2 : 1	1
0.3 : 0.3 :1	1
0.4 : 0.4 : 1	1



Scheme 2.2 Preparation scheme of metal-containing epoxy polymers in the presence of Bu_4NOH

2.8 Characterization of Metal-Containing Epoxy Polymers

2.8.1 IR Spectroscopy

The obtained polymers were characterized by IR spectroscopy. The samples were prepared as KBr pellets.

2.8.2 Thermal Properties

Glass transition temperatures (T_g) of the epoxy polymers were measured by dynamic mechanical analysis at the heating rate of 3 °C/min and thermogravimetric analysis at the heating rate of 10 °C/min, respectively.

2.8.3 Thermal Stability

Heat resistant of the epoxy polymers were studied by heating the polymer samples (1 cm x 5 cm x 3 mm) at 250 °C for 48 h in a hot air oven to obtain % weight loss of polymers at different times

2.8.4 Mechanical Properties

Tensile testing of epoxy polymers were performed according to the procedure described in ASTM D 638 (tensile testing).