

Chapter II

Experimental

2.1 Materials

All reagents and solvents were obtained from the following suppliers and used as received.

1. 2,4-Dihydroxybenzaldehyde : Fluka
2. 1,3-Diaminopropane : Fluka
3. Cobalt(II)acetate tetrahydrate : Fluka
4. Nickle(II)acetate tetrahydrate : Fluka
5. Copper(II)acetate monohydrate : Riedel-Deltaen
6. Diglycidyl ether of bisphenol-A (DGEBA), D.E.R. 330 : Fluka
7. Tetrabutylammonium hydroxide 0.8 M in methanol : Merck
8. Silicone rubber 3120 RTV: Dow Corning

2.2 Equipments

1. IR spectrometer : Nicolet Impact 410
2. Differential Scanning Calorimeter (DSC) : Perkin Elmer DSC 7
3. Dynamic Mechanical Analyzer (DMA) : Netzch DMA 242
4. Thermal Analyzer (STA) : Netzch TGA 7
5. Tensile Testing Equipment (ASTM D638) : Instron Model 4310
6. Shore Durometer Type D (ASTM D2240) : Zwick 750.120

2.3 Determination of Epoxy Equivalent Weight : Hydrochloric Acid in Dioxane²⁷

Reagents

HCl solution : 0.2622 N in dioxane.

NaOH solution : 0.0957 N in methanol

Cresol Red : freshly prepared dissolving 0.1g of cresol red into a mixture of acetone (8 ml) and water (2 ml)

Procedure

HCl solution (25.0 ml) was added into 2-4 meg of DGEBA. The mixture was stirred to effect solution and allowed to stand at room temperature for 15 mins. A few drops of indicator solution was added into the mixture. Then excess acid was titrated by NaOH solution.

Calculations

The weight per epoxy equivalent (WPE) was calculated as follows:

$$WPE = C/[N(B-A) + CD]$$

Where

A = Vol of NaOH used for sample (ml)

B = Vol of NaOH used for blank (ml)

C = weight of sample (milligram)

D = acidity of sample

N = normality of NaOH

Table 2.1 The results from WPE determination of DGEBA

Sample	Weight of DGEBA (g)	Vol. of 0.0957 N NaOH (ml)	Vol. of NaOH reacted (ml)	WPE
1	0.6099	34.10	34.40	185.2
2	0.6348	32.80	35.70	185.8
Blank		68.50		

As seen in Table 2.1 the WPE of DGEBA was 185.5

2.4 Synthesis of Metal Complexes²⁶

2.4.1 Preparation of the Copper Complex (CuL)

A methanolic solution (10 ml) of 1,3 diaminopropane 0.5 ml (10.64 mmol) was added dropwise into a methanolic solution (40 ml) of 2,4 dihydroxybenzaldehyde (2.94 g, 21.28 mmol) that was cooled (0-10 °C) with stirring in an ice bath. The mixture gradually turned yellow and was stirred for another 5 minutes. A solution (40 ml) of copper(II) acetate monohydrate (2.13 g, 10.64 mmol) was added dropwise by an addition funnel into the methanolic solution (50 ml) of the ligand that was cooled with stirring in an ice bath. This step took for 10 mins. The mixture was neutralized by a 2M sodium hydroxide (10.64 ml, 21.28 mmol). The green powder then precipitated and the mixture was stirred for an hour. The green precipitates were subsequently washed by filtration and dried. The yield of CuL was 87%.

IR spectrum (KBr) : 3494 cm⁻¹(s), 3000-3100 cm⁻¹(w), 2800-3000 cm⁻¹(w), 1611 cm⁻¹(s), 1400-1600 cm⁻¹(m), 1227 cm⁻¹(s), 990 cm⁻¹(m), 844 cm⁻¹(m)

2.4.2 Preparation of the Cobalt Complex (CoL)

CoL was synthesized using the same procedure as CuL using cobalt (II) acetate tetrahydrate (2.68 g, 10.78 mmol) instead of copper(II) acetate monohydrate. The brown precipitates were subsequently isolated by filtration and dried to give 85 % yield of CoL.

IR spectrum (KBr) : 3494 cm^{-1} (s), 3000-3200 cm^{-1} (w), 2800-3000 cm^{-1} (w), 1617 cm^{-1} (s), 1400-1600 cm^{-1} (m), 1233 cm^{-1} (s), 985 cm^{-1} (m), 845 cm^{-1} (m)

2.4.3 Preparation of the Nickel Complex (NiL)

NiL was synthesized using the same procedure as CuL using nickel (II) acetate tetrahydrate (2.68 g, 10.78 mmol) instead of copper(II) acetate monohydrate. The brown greenish precipitates were subsequently isolated by filtration and dried to give 90% yield of NiL.

IR spectrum (KBr) : 3467 cm^{-1} (s), 3000-3100 cm^{-1} (w), 2800-3000 cm^{-1} (w), 1615 cm^{-1} (s), 1400-1600 cm^{-1} (m), 1234 cm^{-1} (s), 990 cm^{-1} (m), 844 cm^{-1} (m)

2.5 Preparation of Metal-containing Epoxy Polymers by Using Tetrabutylammonium Hydroxide as a Catalyst

2.5.1 Copper-containing Epoxy Polymers

A mixture of CuL and hot degassed DGEBA was heated and degassed under vacuum with stirring, then cooled to room temperature and Bu_4NOH was added. The mixture was heated and degassed again until it was bubble free. The mixture was poured into the greased hot mold and then crosslinked in the oven at 150 $^{\circ}\text{C}$ for 4-5 hours. Then, the polymer was cooled at room temperature and removed from the mold. The heating temperature and time were shown in Scheme 2.1. Weights of CuL,

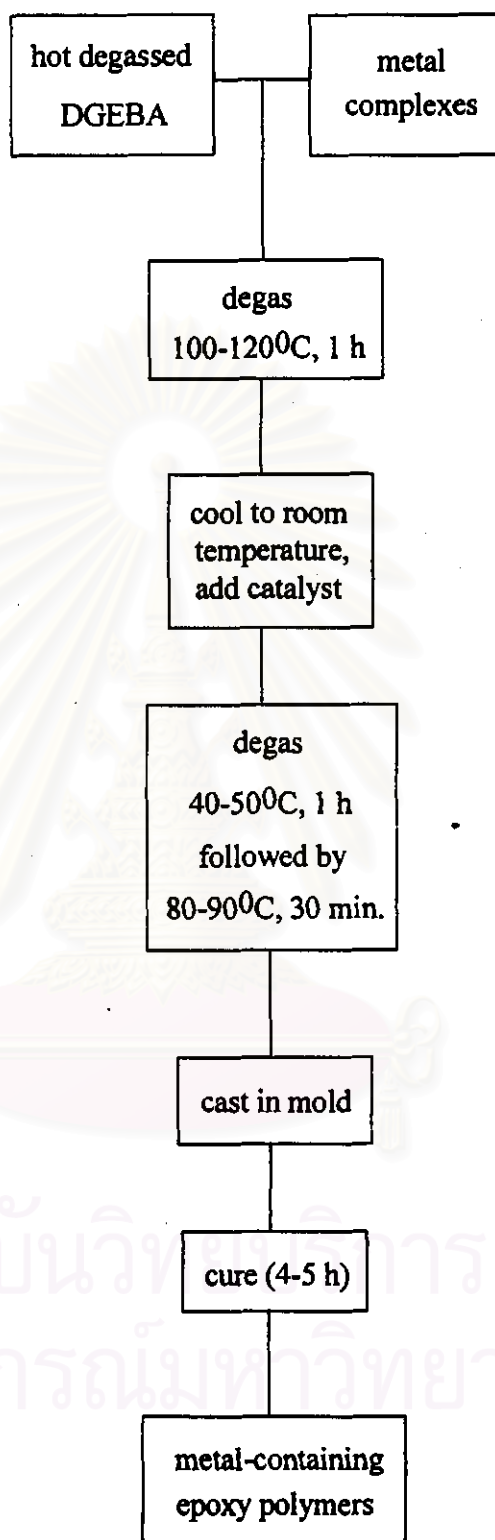
DGEBA, tetrabutylammonium hydroxide, curing temperature used at various equivalent weight ratios are shown in Table 2.2

Table 2.2 Weight of CuL, DGEBA and Bu₄NOH used in the preparation of copper-containing epoxy polymers

Equivalent weight ratio of CuL : DGEBA : Bu ₄ NOH	CuL(g)	DGEBA (g)	Bu ₄ NOH (ml)	Curing condition
1:4:0.2	0.7494	2.7000	0.45	150 ⁰ C, 4 h
1:6:0.2	0.4996	2.7000	0.30	150 ⁰ C, 4 h
1:8:0.2	0.3747	2.7000	0.23	150 ⁰ C, 4.5 h
1:10:0.2	0.2997	2.7000	0.18	150 ⁰ C, 5 h

2.5.2 Cobalt-containing Epoxy Polymers

The experiment was performed following the procedure described in Scheme 2.1 Weight of CoL, DGEBA, Bu₄NOH and curing temperatures used at various equivalent weight ratios are shown in Table 2.3.



Scheme 2.1 The procedure for preparation of metal-containing epoxy Polymers

Table 2.3 Weight of CoL, DGEBA and Bu₄NOH, used in the preparation of cobalt-containing epoxy polymers

Equivalent weight ratio of CoL : DGEBA : Bu ₄ NOH	CoL(g)	DGEBA (g)	Bu ₄ NOH (ml)	Curing condition
1:4:0.2	0.8062	2.7000	0.45	160 ^o C, 4h
1:6:0.2	0.5375	2.7000	0.30	160 ^o C, 4h
1:8:0.2	0.4031	2.7000	0.23	160 ^o C, 4.5h
1:10:0.2	0.3225	2.7000	0.18	160 ^o C, 5h

2.5.3 Nickle-containing Epoxy Polymers

The experiment was performed following the procedure described in Scheme 2.1 Weight of NiL, DGEBA, Bu₄NOH, and curing temperatures used at various equivalent weight ratios are shown in Table 2.4.

Table 2.4 Weight of NiL, DGEBA and Bu₄NOH used in the preparation of nickle-containing epoxy polymers

Equivalent weight ratio of NiL : DGEBA : Bu ₄ NOH	NiL(g)	DGEBA (g)	Bu ₄ NOH (ml)	Curing Condition
1:4:0.2	0.7403	2.7000	0.45	155 ^o C, 4 h
1:6:0.2	0.4936	2.7000	0.30	155 ^o C, 4 h
1:8:0.2	0.3702	2.7000	0.23	155 ^o C, 4.5 h
1:10:0.2	0.2961	2.7000	0.18	155 ^o C, 5 h

2.6 Study of the Crosslinking Reaction of DGEBA with Metal Complexes

2.6.1 DSC Study

The crosslinking temperature was obtained by using DSC. A mixture of DGEBA, metal complex and Bu_4NOH was heating in an aluminium pan at a heating rate of $20^\circ\text{C}/\text{min}$.

2.6.2 IR Spectroscopy

The crosslinking reaction of metal-containing epoxy polymers was followed by IR Spectroscopy using KBr technique. The preparation of metal-containing epoxy polymer was prepared by hand casting and crosslinked in a hot air oven. The polymer sample was taken every hour to follow the proceeding of reaction by observing the decrease of the epoxide peak of DGEBA at 920 cm^{-1} in the IR spectrum. The crosslinking reaction was completed when the peak at 920 cm^{-1} could not be observed. The time taken until the epoxide peak completely disappeared was the crosslinking time for preparation of metal-containing epoxy polymers.

2.7 Characterization of Metal-containing Epoxy Polymers

The obtained polymer was characterized by IR spectroscopy. Mechanical testing of the polymers were performed according to the procedure described in ASTM D638 (tensile testing) and ASTM D2240 (hardness testing). Glass transition temperature (T_g) was obtained with DMA by using three-point bending mode at a heating rate of $3^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) of the polymer samples were studied by using STA in air at a heating rate of $20^\circ\text{C}/\text{min}$. Isothermal TGA of the

polymer samples were carried out at 250⁰C. The metal-containing epoxy polymer samples with the size of 60 mm x 10 mm x 3 mm was weighted, then heated in a hot air oven at 250⁰C for 12 hours. The sample was taken from the oven, left cool and weighted again. The difference between the first and second weight was used to calculate the percentage of weight loss. The same experiment was repeated to calculate the percentage of weight loss at 24, 36 and 48 hours.



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