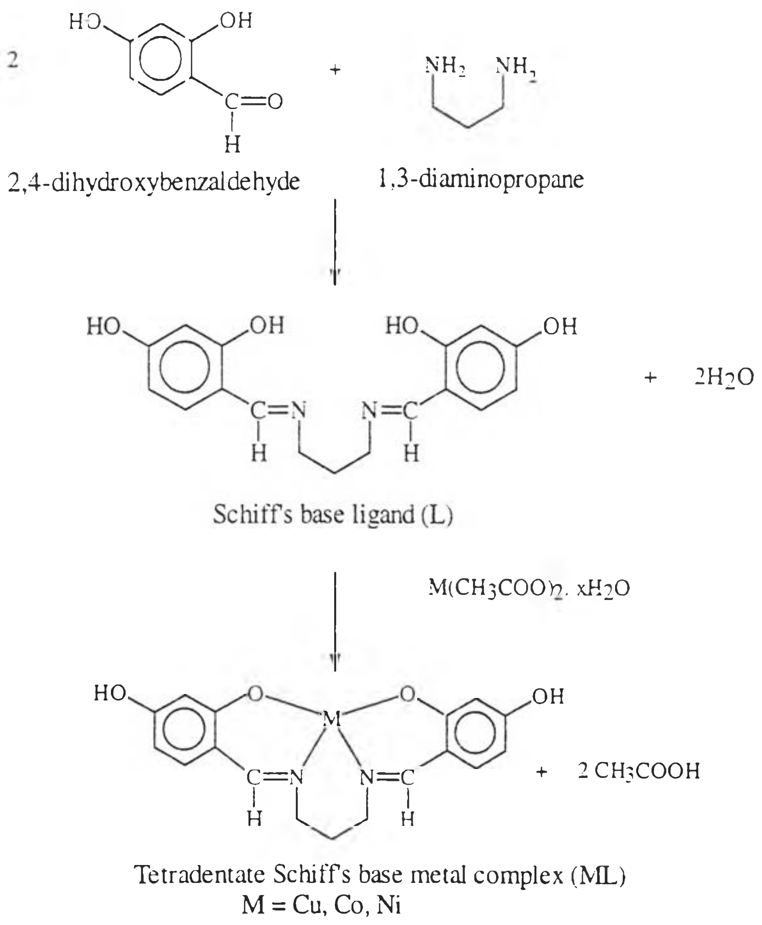
CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of Tetradentate Schiff's Base Metal Complexes (ML)

Tetradentate Schiff's base metal complexes were synthesized according to the procedure described by Tongraung.[22] Starting from 2,4-dihydroxybenzaldehyde and 1,3-diaminopropane, an amine nitrogen attacked on the carbonyl group of aldehyde followed by a loss of water to give the Schiff's base ligand. Complexation with metal acetates gave metal complexes as shown in Scheme 3.1.



Scheme 3.1 Synthesis of metal complexes

Following the above synthetic procedure, ZnL was synthesized by the similar reactions. ZnL was characterized by IR spectroscopy, elemental analysis and mass spectroscopy.

IR absorption characteristic of ZnL was similar to those of CuL, CoL and NiL. The IR spectrum (Figure 3.1) showed an absorption band of O-H stretching at 3300-3500 cm^{-1} and a band of aliphatic C-H stretching vibration at 2921 cm^{-1}. The absorption bands at 1600 and 1226 cm^{-1} coincided with the characteristic absorption peaks of C=N stretching and aromatic C-O stretching, respectively. The absorption band at 845 and 799 cm^{-1} were due to 1,2,4-substituted benzene bending.

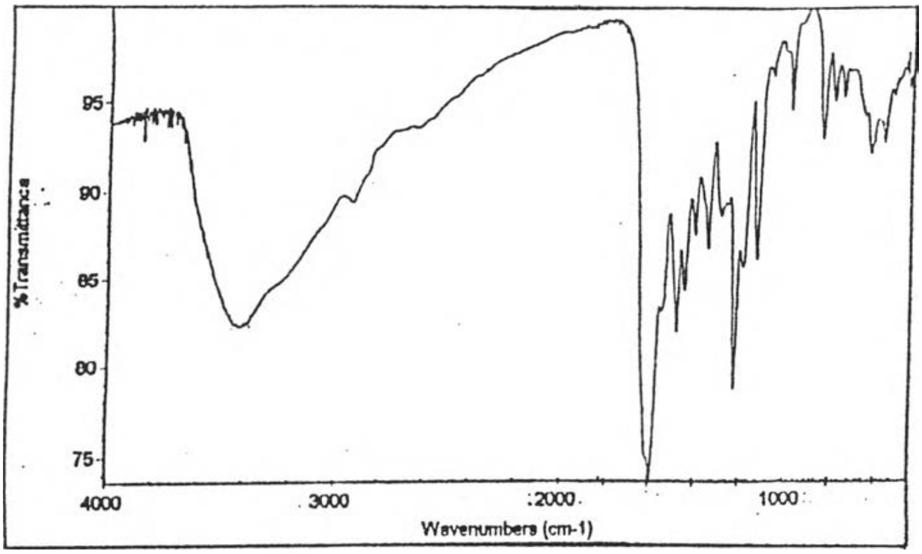


Figure 3.1 IR spectrum of ZnL

Elemental analysis of ZnL indicated that the complex had water in its composition and existed in a monomer form. The empirical formula of ZnL is $C_{17}H_{16}N_2O_4Zn.H_2O$. Matrix assisted laser desorption ionization-time of flight mass spectroscopy (MALDI-TOF MS) was studied to confirm the structure of the complex. The parent peak at m/z 315 (Figure 3.2) corresponded to the protonated ligand (LH^+).

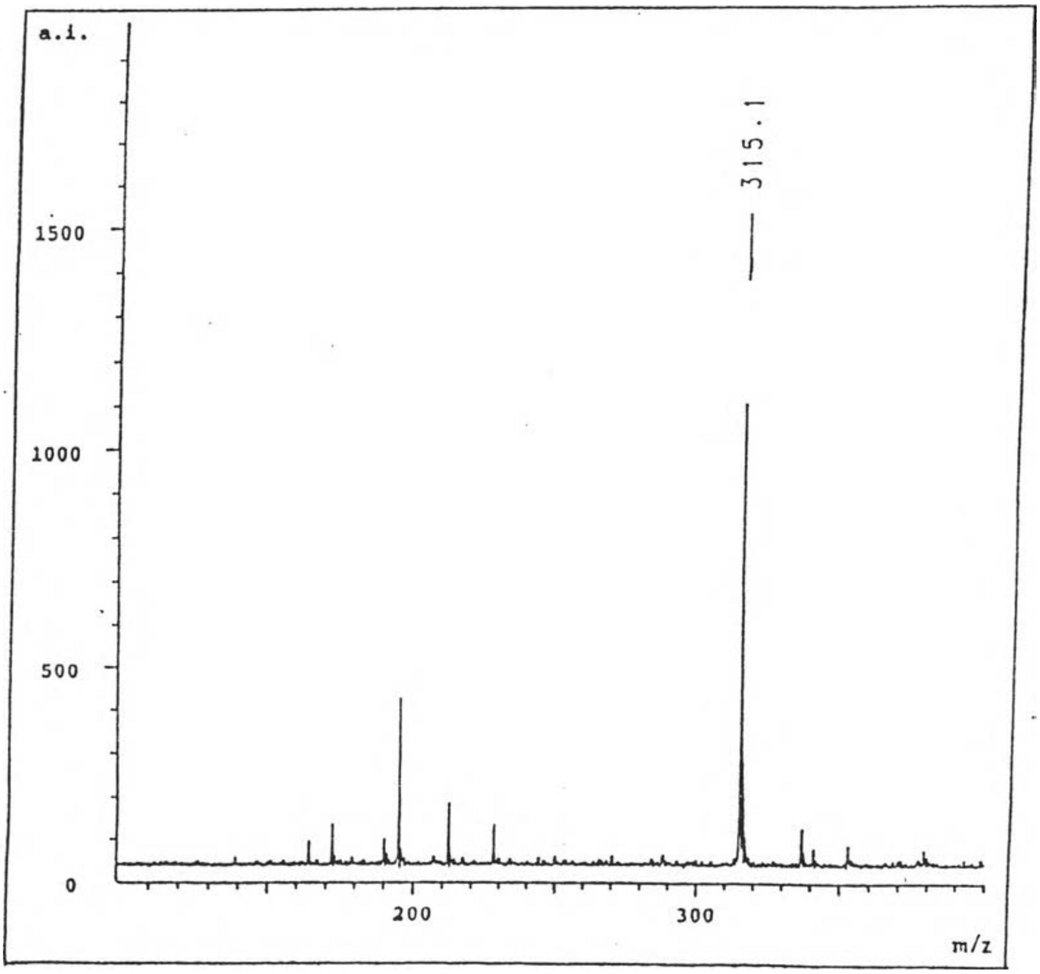


Figure 3.2 MALDI-TOF MS of ZnL

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

Curing the epoxy resins with anhydrides were studied.[23,24] For example, in 1990, Boshel and Fedtke studied the crosslinking of DGEBA with hexahydrophthalic anhydride and 2,6-dimethylol-*p*-cresol as crosslinking agents.[25,26] The phenolic groups in 2,6-dimethylol-*p*-cresol opened the anhydride ring to give carboxylic group initiating the polymerization of DGEBA to yield the crosslinked epoxy polymers.

Therefore, the metal complexes which also contain the phenolic groups should be able to undergo the same crosslinking reaction. The thermal reaction between metal complexes and maleic anhydride was studied by using IR spectroscopy. The metal complexes used in this study were CuL, CoL, NiL and ZnL.

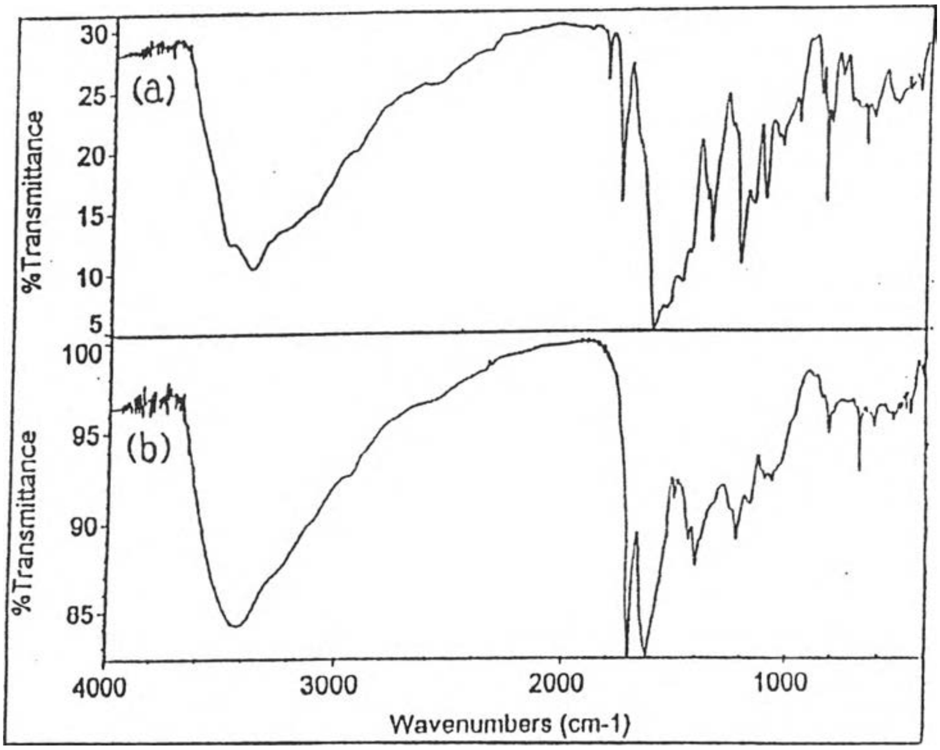
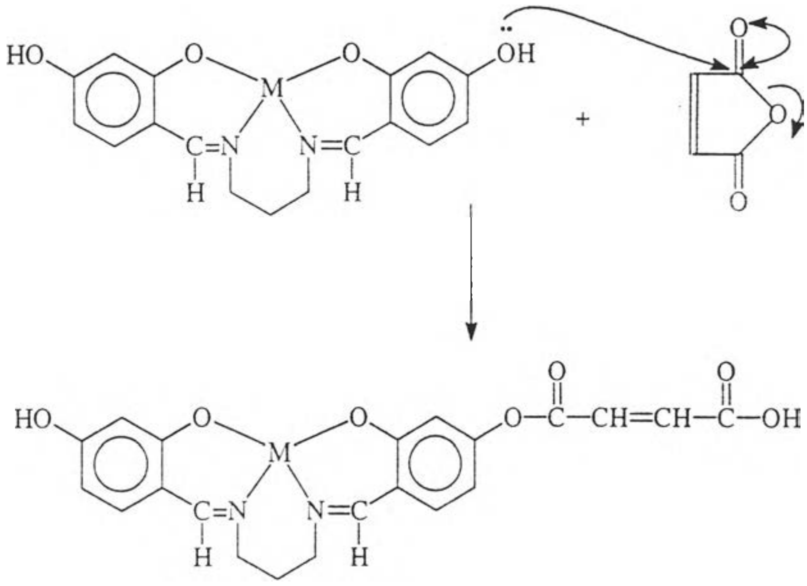


Figure 3.3 IR spectra of a mixture of CuL and maleic anhydride at the mole ratio of 1 : 1 (a) before heating and (b) after heating at 150 °C for 1 hour

Figure 3.3 showed IR spectra of a mixture of CuL and maleic anhydride at a mole ratio of 1 : 1 before and after heating. The C=O bands of anhydride group at 1850 and 1780 cm^{-1} disappeared after heating at 150 °C for 1 hour. This indicated that. the anhydride ring could be opened by the phenolic group of CuL to generate carboxylic group (Scheme 3.2) which showed its band at 1705 cm^{-1}. When CoL, NiL and ZnL were used, the IR bands of the anhydride group disappeared after heating at 150 °C for 1 hour, 3 hours and 3.5 hours, respectively.



M = Cu, Co, Ni, and Zn

Scheme 3.2 Reaction between metal complexes and maleic anhydride

3.3 Crosslinking Reactions of DGEBA Epoxy Resin with Tetradentate Schiff's Base Metal Complexes and Maleic Anhydride

3.3.1 IR Study

IR spectroscopy was employed to determine the suitable crosslinking parameters for crosslinking DGEBA with ML and MA by observing the disappearance of the IR band of the epoxide group in DGEBA at 917 cm^{-1}. In the case of CuL, the IR spectra obtained when a mixture of CuL : MA : DGEBA at the mole ratio of 0.2 : 0.2 : 1 were heated at 150 °C at different times were shown in Figure 3.4. It was found that the reaction was completed in 3 h.

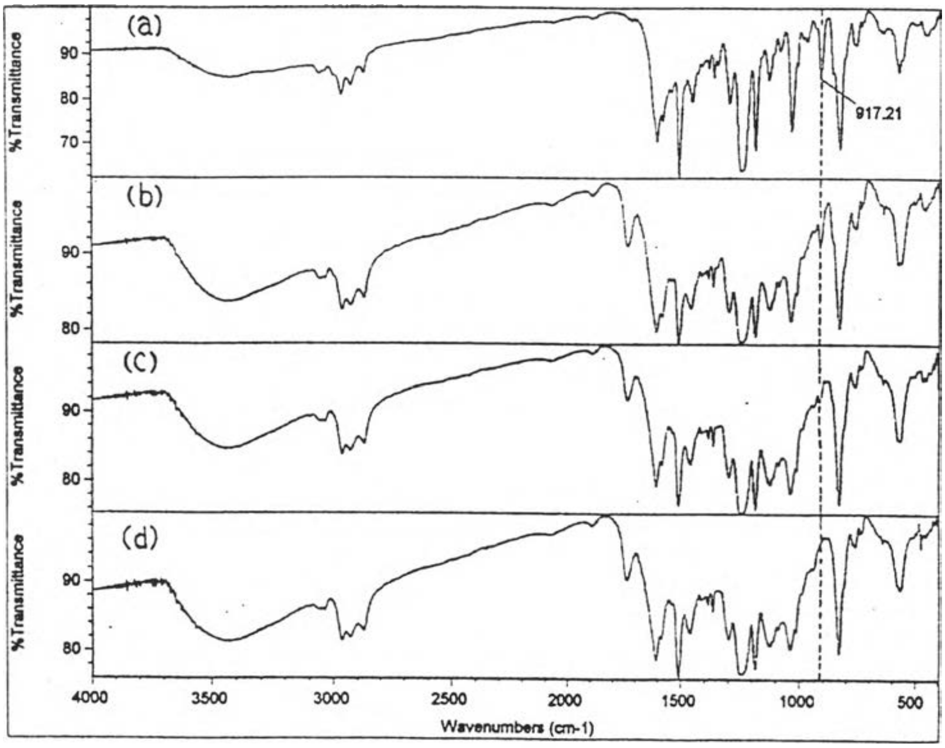


Figure 3.4 IR spectra of the mixture of CuL, MA and DGEBA at the mole ratio of 0.2 : 0.2 : 1 (a) before heating (b) after heating at 150 °C for 1 h (c) after 2 h and (d) after 3 h

By using the same method, the crosslinking parameters of DGEBA with other metal complexes and MA were obtained as shown in Table 3.1.

Table 3.1 Crosslinking parameters for crosslinking reaction of DGEBA using different metal complexes and maleic anhydride

Metal complex	Crosslinking temp (°C)	Crosslinking time (h)
CuL	150	3
CoL	150	3
NiL	180	3
ZnL	190	3

3.3.2 Isothermal DSC Study

To determine the order of reactivity of the metal complexes towards crosslinking reaction, isothermal DSC experiments were employed by heating a mixture of metal complex, maleic anhydride and DGEBA in a DSC cell at the mole ratio of ML : MA : DGEBA = 0.2 : 0.2 : 1 and 0.3 : 0.3 : 1. When the mole ratio of CuL : MA : DGEBA was 0.2 : 0.2 : 1, crosslinking reaction finished in about 27 minutes at 150 °C (Figure A. 3.1). At the higher mole ratio of 0.3 : 0.3 : 1, the reaction was faster (Figure A. 3.2) since there was more CuL to react with DGEBA and maleic anhydride. The result of isothermal crosslinking behavior of DGEBA with CoL, NiL and ZnL (Figure A. 3.3-3.8) showed the same trend as in the case of CuL as summarized in Table 3.2.

Table 3.2 Crosslinking temperature and time taken to complete the crosslinking reaction of DGEBA with metal complexes and maleic anhydride

Metal complex (ML)	Mole ratio of ML: MA : DGEBA	Crosslinking temperature (°C)	Time (min)
CuL	0.17 : 0 : 1[a]	200	13
	0.2 : 0.2 : 1	150	27
	0.3 : 0.3 : 1	150	16
CoL	0.17 : 0 : 1[a]	200	12
	0.2 : 0.2 :1	150	28
	0.3 : 0.3 : 1	150	14
NiL	0.17 : 0 : 1[a]	250	7
	0.2 : 0.2 : 1	180	26
	0.3 : 0.3 : 1	180	21
ZnL	0.2 : 0.2 : 1	190	23
	0.3 : 0.3 : 1	190	21

[a] results from Tongraung's thesis[22]

The isothermal DSC results indicated that the order of reactivity of metal complexes were CuL≈CoL>NiL>ZnL.

In comparison to the previous results from Tongraung's work, when only metal complexes were employed as crosslinking agents, crosslinking reactions of DGEBA with CuL, CoL and NiL required high temperatures. ZnL required very high temperature up to 349°C according to the DSC thermogram (Figure 3.5) and therefore the polymerization could not be possible to process using the available apparatus.

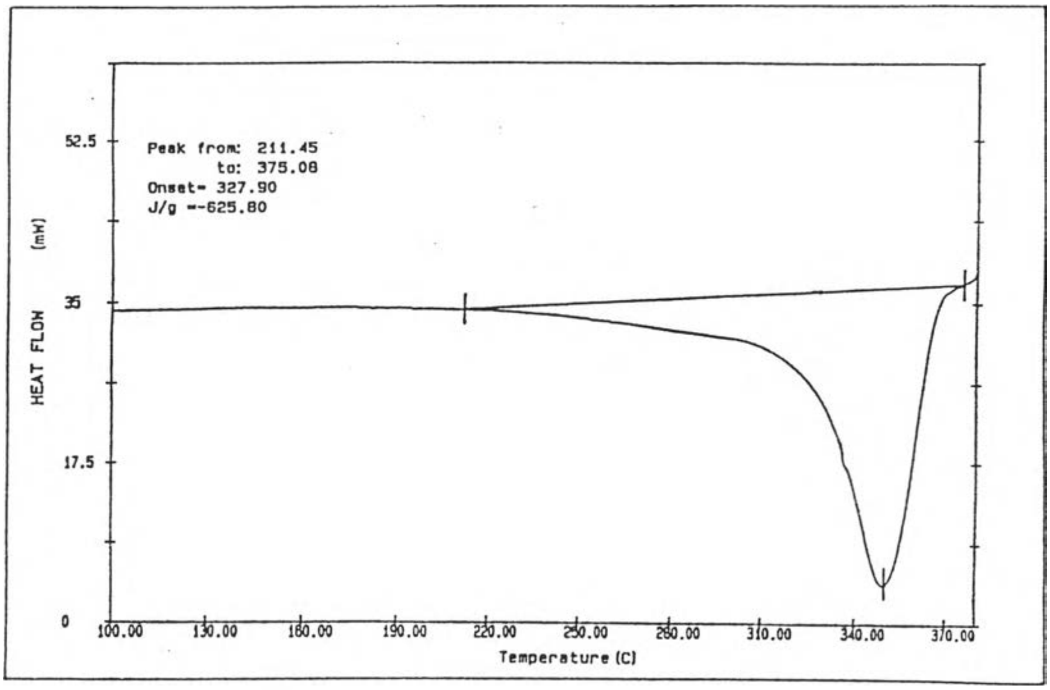
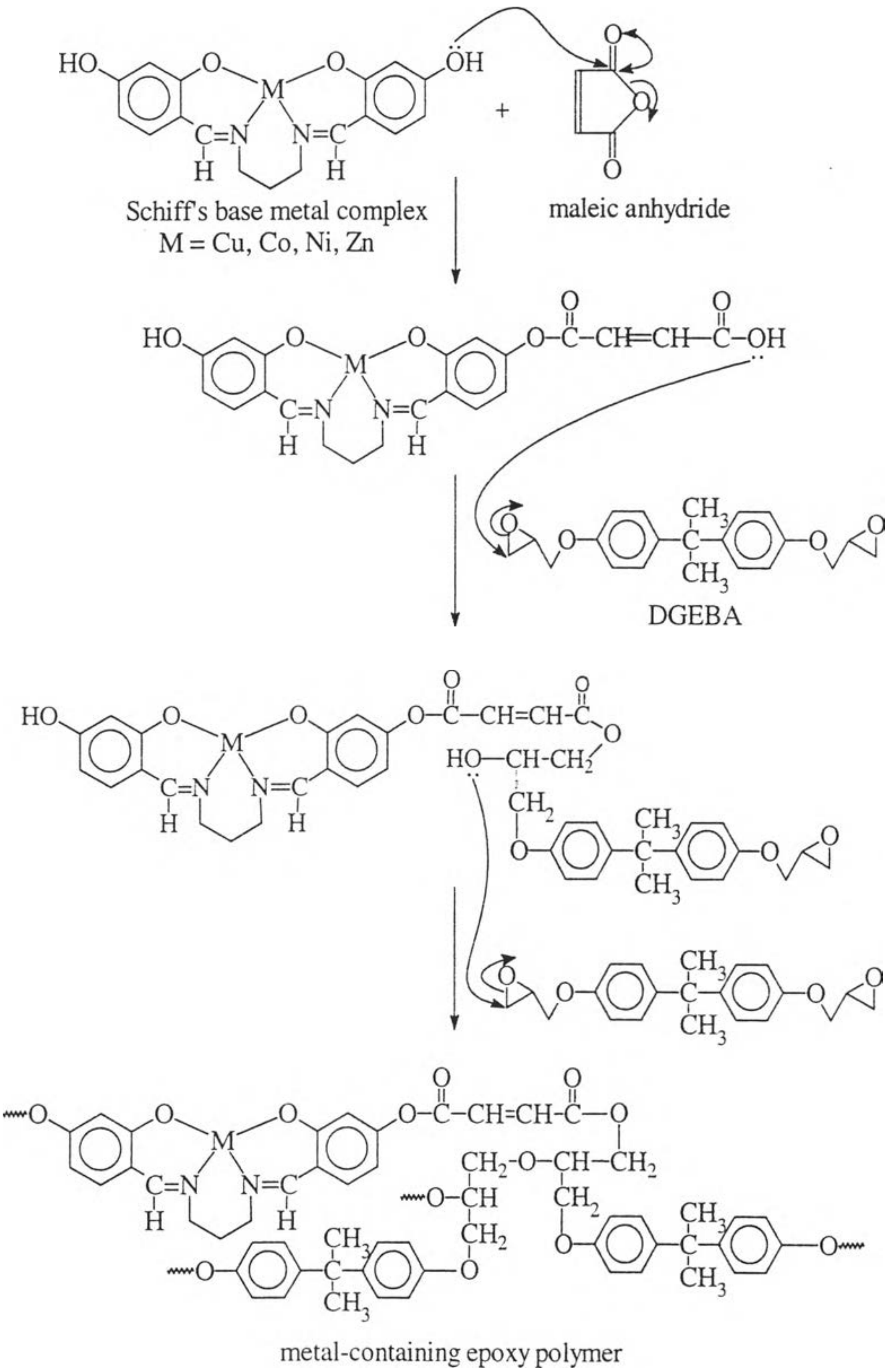


Figure 3.5 DSC thermogram of crosslinking reaction of DGEBA with ZnL

Crosslinking of DGEBA with metal complexes in the presence of maleic anhydride was more facile since the metal complexes were more reactive toward maleic anhydride than DGEBA. Therefore, the presence of maleic anhydride decreased the crosslinking temperature.

The crosslinking mechanism was proposed to involve a ring opening of maleic anhydride by the phenolic group in the metal complex to give carboxylic acid. The carboxylic acid then reacted with DGEBA to give a secondary alcohol which attacked another molecule of DGEBA. The same reaction occurred repeatedly to produce crosslinked metal-containing epoxy polymer (Scheme 3.3).



Scheme 3.3 Proposed mechanism of the crosslinking reaction of DGEBA with metal complexes and maleic anhydride

3.4 Effect of Catalysts

Basic catalysts such as NaOH, quarternary ammonium salts and tertiary amines can be used in the crosslinking reactions between DGEBA and phenolic compounds.[1] In this work, tetrabutylammoniumhydroxide (Bu_4NOH) was chosen as a catalyst in the crosslinking reaction of DGEBA to decrease the crosslinking temperature. It was found that the optimum amount was 20 mole % of the metal complex.

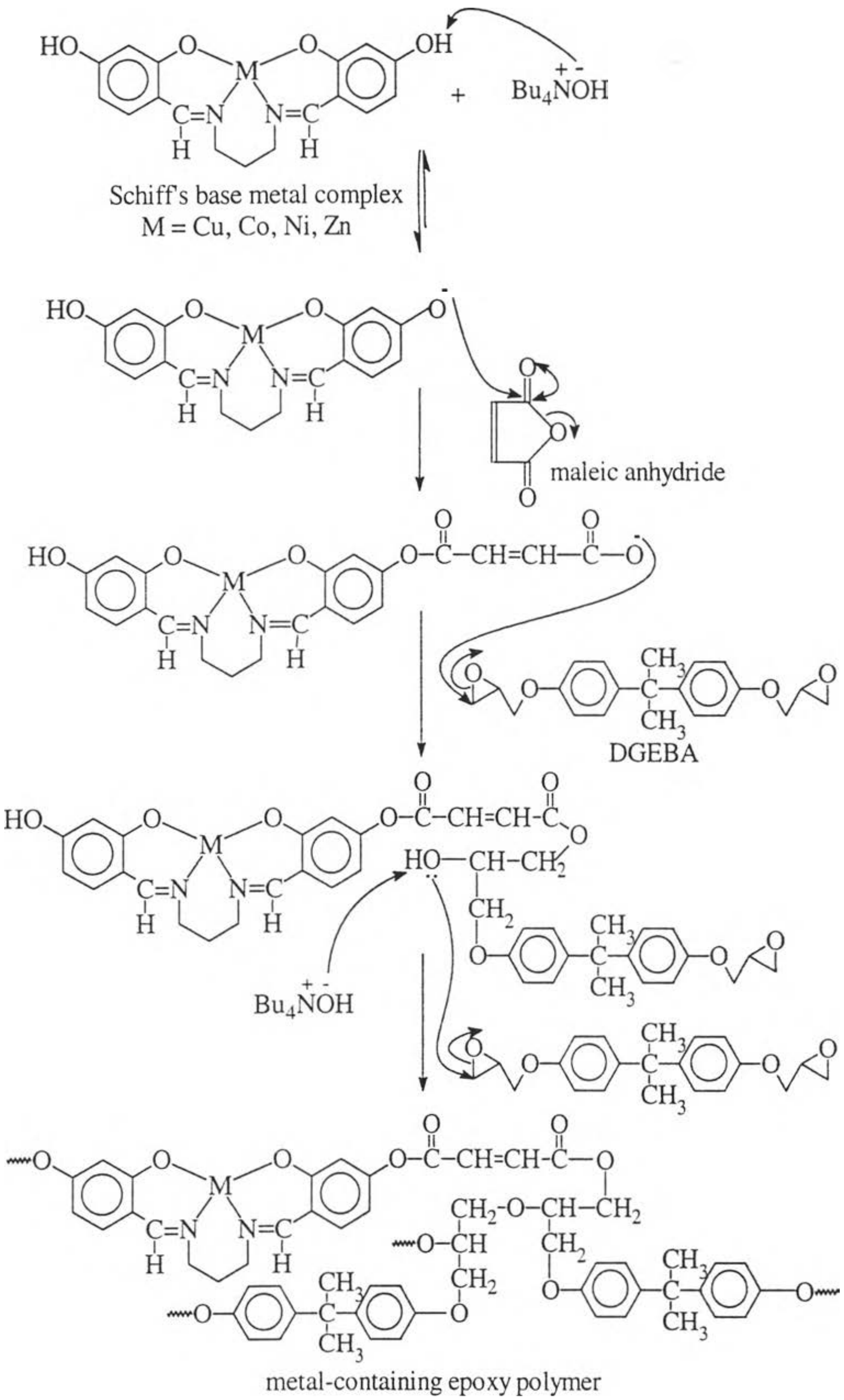
Results from isothermal DSC showed that the presence of Bu_4NOH reduced the crosslinking time at the same crosslinking temperature when Bu_4NOH was not employed. Table 3.3 showed crosslinking time when Bu_4NOH was employed at the mole ratio of ML : MA : DGEBA = 0.2 : 0.2 : 1. For example, crosslinking with CuL at 150 °C finished in 7 minutes (Figure A. 3.9) which was 4 times faster than the crosslinking reaction without Bu_4NOH. In comparison to the crosslinking reaction of DGEBA with maleic anhydride and benzyldimethylamine catalyst, crosslinking with CuL and maleic anhydride took less time (Figure A. 3.10). Crosslinking behavior of DGEBA with CoL, NiL and ZnL in the presence of Bu_4NOH gave the similar results (Figure A. 3.11-3.13).

The proposed crosslinking mechanism when Bu_4NOH was used as a catalyst is shown in Scheme 3.4. Bu_4NOH accelerated the ring opening of maleic anhydride by deprotonating a phenolic proton of the metal complex to generate a phenoxide ion which then attacked maleic anhydride. The generated carboxylate ion then, further reacted with DGEBA to give secondary alcohol which underwent ring opening reaction with another molecule of DGEBA to give metal-containing epoxy-anhydride polymers.

Table 3.3 Crosslinking temperature and time taken to complete the crosslinking of DGEBA with metal complexes and maleic anhydride when Bu_4NOH was employed as a catalyst

Metal complex (ML)	Crosslinking temperature (°C)	Time (min)
CuL	150	7
CoL	150	12
NiL	180	6
ZnL	190	3
Maleic anhydride[a]	150	13

[a] mole ratio of DGEBA : MA was 1 : 2.8 and 0.1 phr of benzyldimethylamine was employed as a catalyst



Scheme 3.4 Proposed mechanism of crosslinking reaction of DGEBA with metal complexes and maleic anhydride in the presence of Bu_4NOH

3.5 Preparation of Metal-Containing Epoxy Polymers

From the previous IR and DSC experiments, the crosslinking temperature for CuL and CoL was chosen at 150 °C. The crosslinking temperatures for NiL and ZnL were chosen at 180 and 190 °C, respectively. The time needed to complete the crosslinking reaction of DGEBA with metal complexes and maleic anhydride was obtained by observing the disappearance of the IR band of the epoxide group in DGEBA at 917 cm^{-1}. The ratios of ML : MA : DGEBA were varied to determine the optimum ratio that yielded the metal-containing epoxy polymers with the best thermal and mechanical properties. The mole ratios of ML : MA : DGEBA employed in this study were 0.1 : 0.1 : 1, 0.2 : 0.2 : 1, 0.3 : 0.3 : 1 and 0.4 : 0.4 : 1. It was found that the mole ratios of metal complexes and maleic anhydride must be equal to provide good properties. When less metal complex was used at the ratios of ML : MA : DGEBA = 0.2 : 0.4 : 1 and 0.15 : 0.3 : 1, poor polymer properties were obtained. The crosslinking reaction could be accelerated by use of Bu_4NOH. Without Bu_4NOH, it was found that the crosslinking time was 3 hours when the ratios of ML : MA : DGEBA were 0.2 : 0.2 : 1, 0.3 : 0.3 : 1 and 0.4 : 0.4 : 1, except at the mole ratio of 0.1 : 0.1 : 1, 5 hours of crosslinking followed by postcuring for 2 hours was needed. In the presence of Bu_4NOH, the crosslinking reaction took 1 hour for the ratios 0.2 : 0.2 : 1, 0.3 : 0.3 : 1 and 0.4 : 0.4 : 1. The ratio of 0.1 : 0.1 : 1 required 3 hours for crosslinking.

3.6 Characterization of Metal-Containing Epoxy Polymers

3.6.1 IR Spectroscopy

The metal-containing epoxy polymers obtained from various ratios of ML : MA : DGEBA were characterized by IR spectroscopy. All epoxy polymers gave similar spectra. Figure 3.6 showed an example of IR spectrum of a polymer obtained from a CuL : MA : DGEBA ratio of 0.2 : 0.2 : 1 and Bu_4NOH was employed as a catalyst. The IR spectrum showed the O-H absorption band of a secondary alcohol at 3300-3500 cm^{-1} and the band of C=O stretching vibration at 1730-1735 cm^{-1}. The absorption bands at 1600-1660 and 1228 cm^{-1} were due to the C=C stretching vibrations and aromatic C-O stretching vibrations and the band at 1100-1300 cm^{-1} was assigned to be C-O (ester) stretching vibration. The band at 825 and 758 cm^{-1} were assigned to be a 1,2,4-substituted benzene bending vibration.

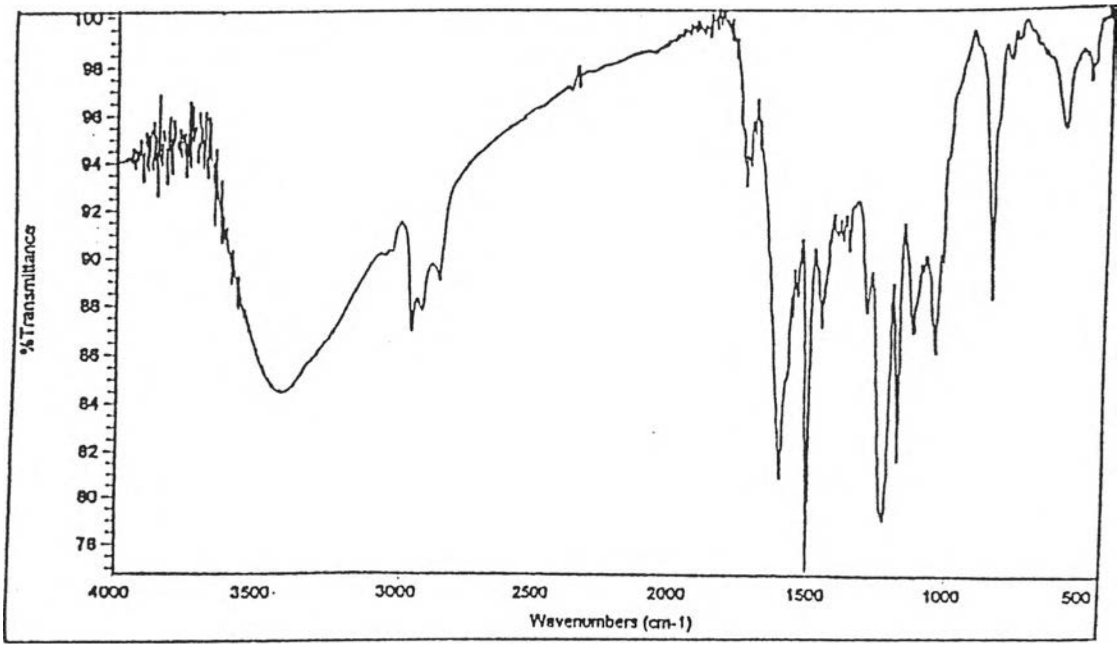
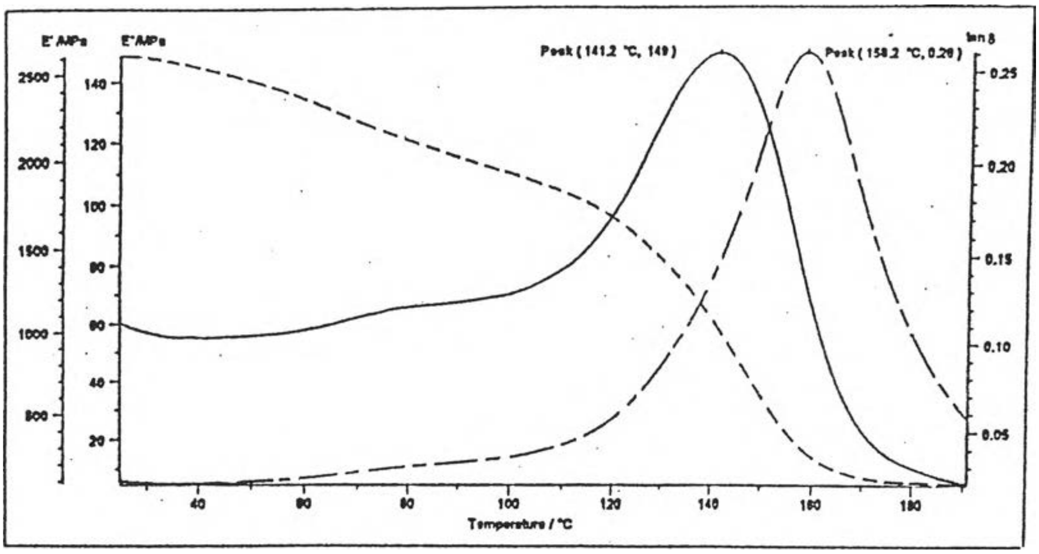


Figure 3.6 IR spectrum of Cu-containing epoxy polymers at the mole ratio of CuL : MA : DGEBA 0.2 : 0.2 : 1 and Bu_4NOH was employed as a catalyst

3.6.2 Glass Transition Temperature

DMA technique was employed to study the glass transition temperature of the epoxy polymers by observing the maximum value of the loss modulus. For instance, DMA thermogram of epoxy polymers at the ratio of CuL : MA : DGEBA = 0.2 : 0.2 : 1 showed a T_g at 141 °C (Figure 3.7). DMA thermograms of Cu-, Co-, Ni- and Zn-containing epoxy polymers are shown in Figures A. 3.14-3.28. Table 3.3 showed T_g of the epoxy polymers obtained without Bu_4NOH. It was found that the

Cu-containing epoxy polymers obtained from the ratios of 0.2 : 0.2 : 1 and 0.3 : 0.3 : 1 gave the highest T_g values.



------- = storage modulus

——— = loss modulus

——— = tan δ

Figure 3.7 DMA thermogram of Cu-containing epoxy polymer at the mole ratio of CuL : MA : DGEBA 0.2 : 0.2 : 1

When Bu_4NOH was employed as a catalyst (Table 3.5), there was almost no change in T_g. DMA thermograms of all epoxy polymers obtained from using Bu_4NOH are shown in Figures A. 3.29-3.40. The advantage of using Bu_4NOH was the reduction in crosslinking time. The use of Bu_4NOH was suitable at the mole ratio of ML : MA : DGEBA = 0.2 : 0.2 : 1. However, lower T_g was obtained at the mole ratio of 0.3 : 0.3 : 1 and it was not possible to prepare the epoxy polymers with the mole ratio of 0.4 : 0.4 : 1 since the mixture of ML : MA : DGEBA had high viscosity. Therefore, the polymers were brittle owing to the heterogeneity of the polymer matrix.

The T_g values of epoxy polymers also depended on types of metal complexes. As shown in Tables 3.4 and 3.5, the Cu-containing polymer with the mole ratio of 0.2 : 0.2 : 1 showed the highest T_g which is comparable to the T_g of DGEBA-MA system (143 °C, Figure A 3.41).

Epoxy polymers obtained from diethylenetriamine (DETA) was also prepared for a comparison. Although the crosslinking temperature was low (4 hours at 100 °C), the obtained epoxy polymer had much lower T_g (96 °C, Figure A 3.42).

Table 3.4 Glass transition temperature (T_g) of the metal-containing epoxy polymers obtained from different mole ratios of ML : MA : DGEBA

Metal complex (ML)	Mole ratio of ML : MA : DGEBA	T_g (°C)
CuL	0.1 : 0.1 : 1	108
	0.2 : 0.2 : 1	141
	0.3 : 0.3 : 1	140
	0.4 : 0.4 : 1	138
CoL	0.1 : 0.1 : 1	90
	0.2 : 0.2 : 1	114
	0.3 : 0.3 : 1	113
	0.4 : 0.4 : 1	112
NiL	0.1 : 0.1 : 1	117
	0.2 : 0.2 : 1	119
	0.3 : 0.3 : 1	123
	0.4 : 0.4 : 1	128
ZnL	0.1 : 0.1 : 1	112
	0.2 : 0.2 : 1	119
	0.3 : 0.3 : 1	126
	0.4 : 0.4 : 1	129

Table 3.5 Glass transition temperature (T_g) of the metal-containing epoxy polymers and Bu_4NOH was employed as a catalyst

Metal complex (ML)	Mole ratio of ML : MA : DGEBA	T_g (°C)
CuL	0.1 : 0.1 : 1	114
	0.2 : 0.2 : 1	143
	0.3 : 0.3 : 1	105
CoL	0.1 : 0.1 : 1	125
	0.2 : 0.2 : 1	128
	0.3 : 0.3 : 1	103
NiL	0.1 : 0.1 : 1	124
	0.2 : 0.2 : 1	125
	0.3 : 0.3 : 1	122
ZnL	0.1 : 0.1 : 1	124
	0.2 : 0.2 : 1	125
	0.3 : 0.3 : 1	123
Maleic anhydride[a]	-	143
Diethylenetriamine[b]	-	96

[a] mole ratio of DGEBA : MA was 1 : 2.8 and 0.1 phr of benzyldimethylamine was employed as a catalyst

[b] mole ratio of DGEBA : DETA was 1 : 1

3.6.3 Thermal Stability

Thermal stability of the metal-containing epoxy polymers was determined by heating the polymers at 250 °C for 48 hours. Tables 3.6 and 3.7 show weight loss of polymers at different times.

Table 3.6 Thermal stability at 250 °C of the metal-containing epoxy polymers obtained from different mole ratios of ML : MA : DGEBA

Metal complex (ML)	Mole ratio of ML : MA : DGEBA	% Weight loss at different time			
		12 h	24 h	36 h	48 h
CuL	0.1 : 0.1 : 1	1.9	2.4	2.9	3.2
	0.2 : 0.2 : 1	2.4	2.8	3.2	3.3
	0.3 : 0.3 : 1	3.7	4.2	4.6	4.8
	0.4 : 0.4 : 1	5.3	6.2	7.2	8.0
CoL	0.1 : 0.1 : 1	1.8	2.2	2.7	3.2
	0.2 : 0.2 : 1	2.1	2.6	3.1	3.3
	0.3 : 0.3 : 1	3.6	4.4	5.3	5.7
	0.4 : 0.4 : 1	4.9	6.0	7.0	7.7
NiL	0.1 : 0.1 : 1	7.6	8.7	9.7	11.0
	0.2 : 0.2 : 1	8.3	10.0	10.7	11.4
	0.3 : 0.3 : 1	8.7	9.9	11.2	12.0
	0.4 : 0.4 : 1	9.0	10.0	11.0	12.2
ZnL	0.1 : 0.1 : 1	2.5	2.9	3.2	3.6
	0.2 : 0.2 : 1	4.0	4.7	6.0	6.6
	0.3 : 0.3 : 1	4.9	6.8	7.9	8.7
	0.4 : 0.4 : 1	5.5	7.5	8.3	9.9

Table 3.7 Thermal stability at 250 °C of the metal-containing epoxy polymers obtained from different mole ratios of ML : MA : DGEBA and Bu_4NOH was employed as a catalyst

Metal complex (ML)	Mole ratio of ML : MA :DGEBA	% Weight loss at different time			
		12 h	24 h	36 h	48 h
CuL	0.1 : 0.1 : 1	1.6	2.1	2.5	2.7
	0.2 : 0.2 : 1	2.0	2.3	2.6	2.8
	0.3 : 0.3 : 1	2.5	2.7	3.0	3.2
CoL	0.1 : 0.1 : 1	1.3	1.7	2.1	2.4
	0.2 : 0.2 : 1	1.7	2.1	2.4	2.7
	0.3 : 0.3 : 1	1.8	2.2	2.7	3.1
NiL	0.1 : 0.1 : 1	4.5	5.8	7.0	8.4
	0.2 : 0.2 : 1	5.0	6.6	7.9	9.0
	0.3 : 0.3 : 1	5.3	6.5	7.8	9.3
ZnL	0.1 : 0.1 : 1	1.2	1.4	1.7	2.0
	0.2 : 0.2 : 1	1.5	1.9	2.2	2.6
	0.3 : 0.3 : 1	2.0	2.4	3.0	3.5
Maleic anhydride[a]	-	1.9	2.7	3.4	4.0
Diethylenetriamine[b]	-	9.7 % after 2 h			

[a] mole ratio of DGEBA : MA was 1 : 2.8 and 0.1 phr of benzyldimethylamine was employed as a catalyst

[b] mole ratio of DGEBA : DETA was 1 : 1

From Table 3.6, without Bu_4NOH, Ni-containing epoxy polymers showed low thermal stability. Cu-, Co- and Zn-containing epoxy polymers possessed good thermal stability. It was found that the high concentration of crosslinking agent resulted in high percentage of weight loss.

When using Bu_4NOH in the crosslinking reaction (Table 3.7), the weight loss of the metal-containing epoxy polymers decreased . This indicated that the use of Bu_4NOH improved the thermal stability of metal-containing epoxy polymers since crosslinking reaction occurred efficiently. Cu- and Zn-containing epoxy polymers obtained from the ratios 0.1 : 0.1 : 1 and 0.2 : 0.2 : 1 showed the best thermal stability which is comparable to the DGEBA-MA system and much higher than the DGEBA-DETA system.

Furthermore, thermogravimetric analysis (TGA) was also used at the heating rate of 10 °C/min to characterize the thermal property of Cu-containing epoxy polymer at the mole ratio of 0.2 : 0.2 :1 using Bu_4NOH as a catalyst. TGA thermogram (Figure 3.8) showed the thermal decomposition at the temperature range 270-400 °C which is due to decomposition of polymer chain. The decomposition resulted in 5%, 10%, 20% and 30% weight loss at 270, 305, 345 and 400 °C, respectively, which is similar to the most epoxy polymers based on DGEBA.[21]

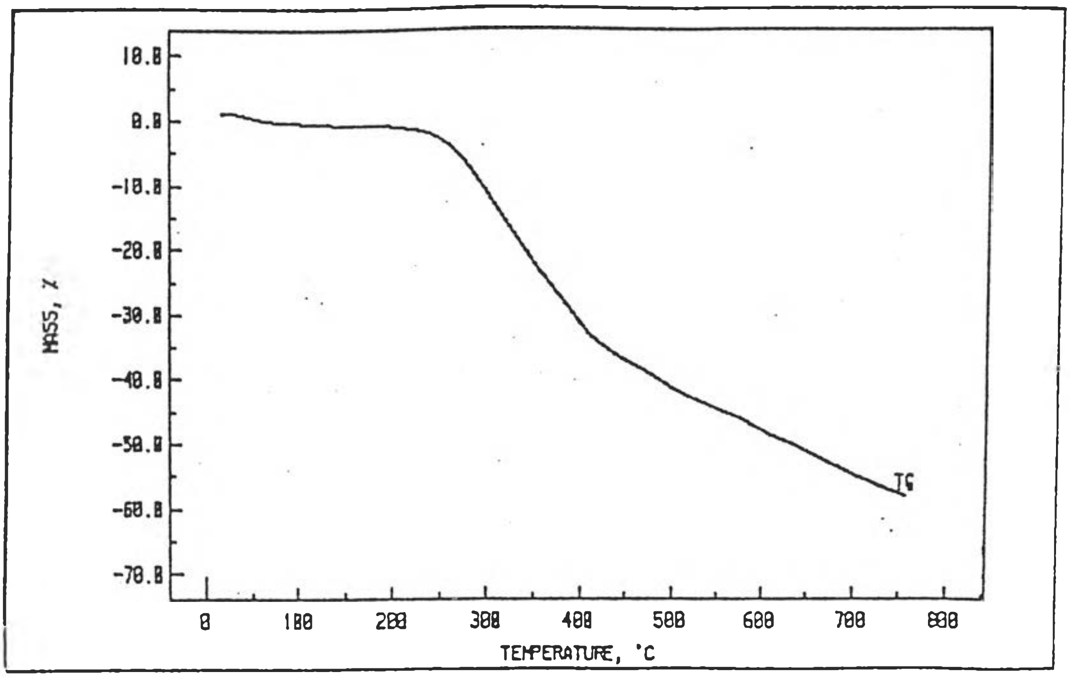


Figure 3.8 TGA thermogram of Cu-containing epoxy polymer at the mole ratio of CuL : MA : DGEBA 0.2 : 0.2 : 1 and Bu_4NOH was employed as a catalyst

3.6.4 Mechanical Properties

The next step was to prepare samples of crosslinked DGEBA for further investigation of their mechanical properties. The tensile testing was performed and the values obtained were shown in Tables 3.8 and 3.9.

Table 3.8 Tensile strength of the metal-containing epoxy polymers obtained from different mole ratios of ML : MA : DGEBA

Metal complex (ML)	Mole ratio of ML : MA : DGEBA	Tensile strength (N/mm^2)
CuL	0.1 : 0.1 : 1	41
	0.2 : 0.2 : 1	46
	0.3 : 0.3 : 1	43
	0.4 : 0.4 : 1	30
CoL	0.1 : 0.1 : 1	36
	0.2 : 0.2 : 1	42
	0.3 : 0.3 : 1	39
NiL	0.1 : 0.1 :1	38
	0.2 : 0.2 : 1	42
	0.3 : 0.3 : 1	40
ZnL	0.1 : 0.1 : 1	40
	0.2 : 0.2 : 1	50
	0.3 : 0.3 : 1	46

Table 3.9 Tensile strength of the metal-containing epoxy polymers obtained from different mole ratios of ML : MA : DGEBA and Bu_4NOH was employed as a catalyst

Metal complex (ML)	Mole ratio of ML : MA : DGEBA	Tensile strength (N/mm^2)
CuL	0.1 : 0.1 : 1	56
	0.2 : 0.2 : 1	62
	0.3 : 0.3 : 1	45
CoL	0.1 : 0.1 : 1	42
	0.2 : 0.2 : 1	51
	0.3 : 0.3 : 1	41
NiL	0.1 : 0.1 :1	43
	0.2 : 0.2 : 1	53
	0.3 : 0.3 : 1	42
ZnL	0.1 : 0.1 : 1	56
	0.2 : 0.2 : 1	60
	0.3 : 0.3 : 1	50
Maleic anhydride[a]	-	56
Diethylenetriamine[b]	-	44

[a] mole ratio of DGEBA : MA was 1 : 2.8 and 0.1 phr of benzyldimethylamine was employed as a catalyst

[b] mole ratio of DGEBA : DETA was 1 : 1

From Table 3.8, the Cu-containing epoxy polymer obtained from the ratio of 0.1 : 0.1 : 1 had tensile strength of 41 N/mm^2. The tensile strength increased to

46 N/mm^2 at the mole ratio of 0.2 : 0.2 : 1 owing to the higher crosslink density. Further increase of the mole ratio to 0.3 : 0.3 : 1 and 0.4 : 0.4 : 1 resulted in the decrease of tensile strength since the mixture of ML : MA : DGEBA had high viscosity and therefore difficult for mold casting. Since the Cu-containing epoxy polymers at the mole ratio of 0.4 : 0.4 : 1 gave very low tensile value and difficult to prepare, the Co-, Ni-, and Zn-containing epoxy polymers at this mole ratio were not investigated. The optimum ratio for all polymers was 0.2 : 0.2 : 1.

The effect of Bu_4NOH on the tensile strength was studied. From Table 3.9, crosslinking in the presence of Bu_4NOH improved the tensile strength of epoxy polymers. For example, the tensile strength of the Cu-containing epoxy polymers obtained from the mole ratio 0.2 : 0.2 : 1 increased from 41 to 56 N/mm^2. Cu- and Zn-containing epoxy polymers also gave good tensile strength at the mole ratio of 0.2 : 0.2 : 1, which is comparable to the DGEBA-MA system (56 N/mm^2) and higher than the DGEBA-DETA system (44 N/mm^2).