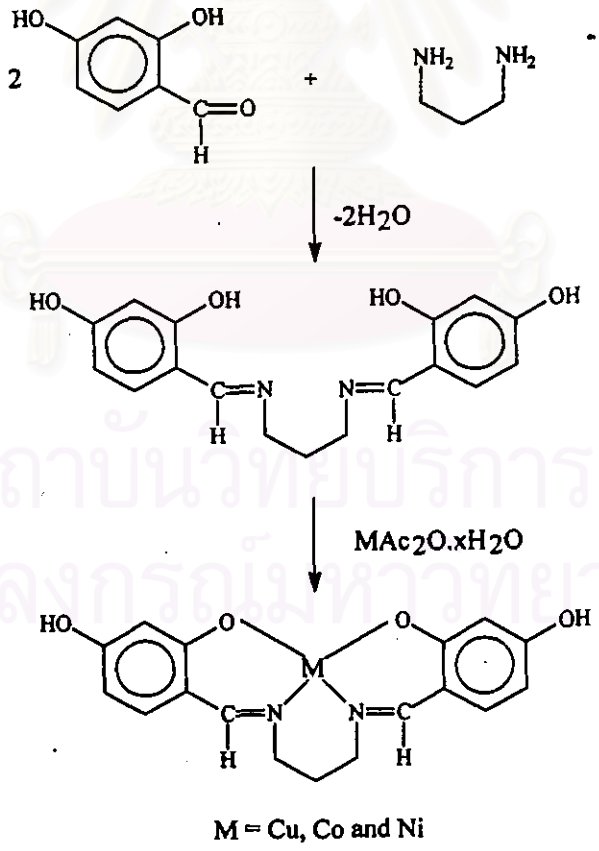
Chapter III

Results and Discussion

3.1 Synthesis of Tetradentate Schiff's Base Metal Complexes

The synthesis of tetradentate Schiff's base ligand was carried out according to the procedure described in the literature.[26] The reaction involves a condensation reaction of amine with aldehyde to give the Schiff's base ligand followed by complexation with metal ion by addition of metal acetate into methanolic solution of ligand to obtain metal complex as shown in Scheme 3.1.



Scheme 3.1 Synthesis of Schiff's base metal complexes[26]

3.2 Crosslinking Reaction of DGEBA with Tetradentate Schiff's Base Metal Complexes

Tongraung[26] studied the crosslinking reaction of DGEBA with tetradentate Schiff's base metal complexes by using DSC technique. From Figures 3.1-3.3, all thermograms show exothermic crosslinking peaks which indicated the initial temperature, the peak maximum and the final temperature of each reaction which could not be clearly identified due to the decomposition of the polymers chain at high temperature. The crosslinking temperatures for the preparation of the polymers were chosen from the peak maximum in DSC thermograms. The crosslinking temperature of DGEBA with CuL and CoL was 200^0C and crosslinking temperature with NiL was 240^0C.

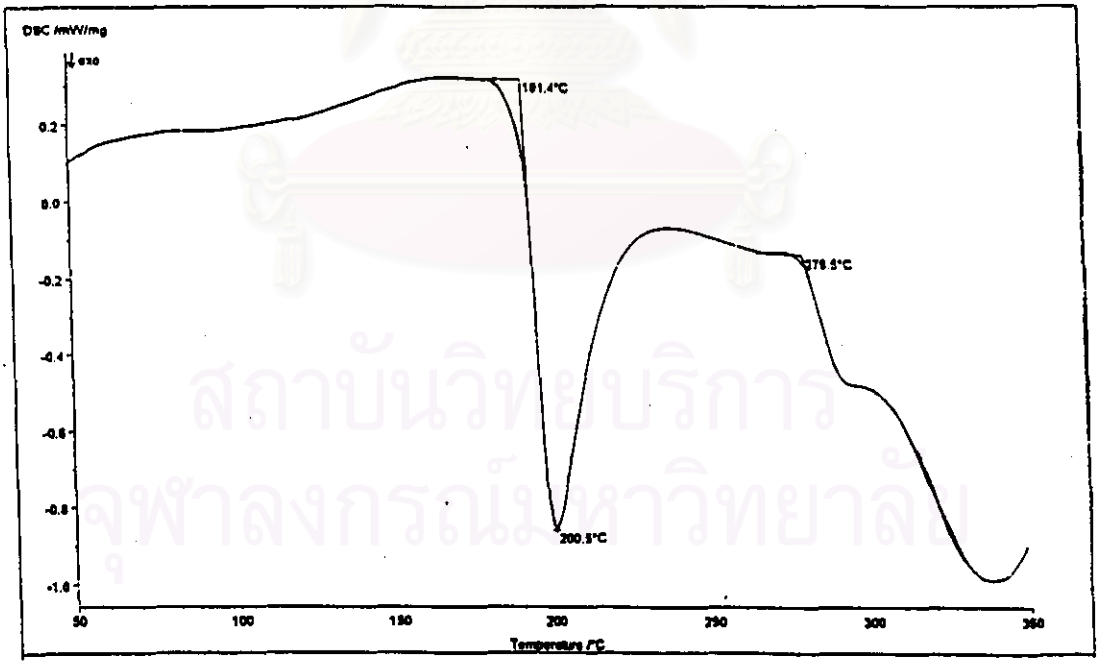


Figure 3.1 DSC thermogram of CuL:DGEBA at the equivalent weight ratio of 1:6[26]

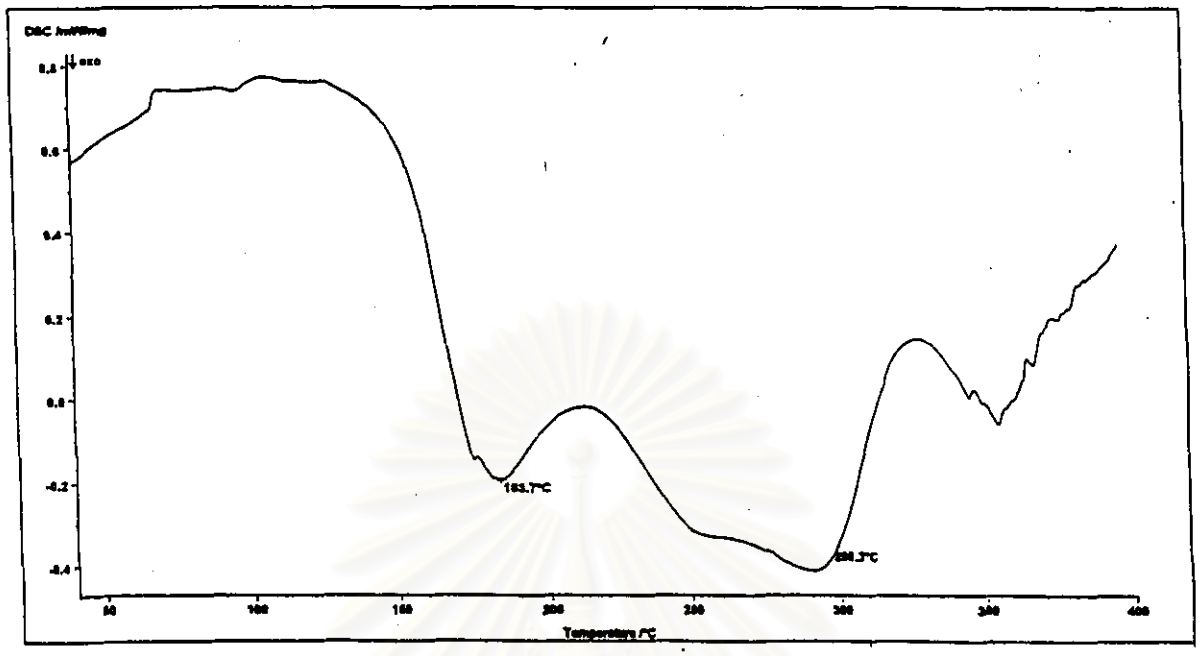


Figure 3.2 DSC thermogram of CoL:DGEBA at the equivalent weight ratio of 1:6[26]

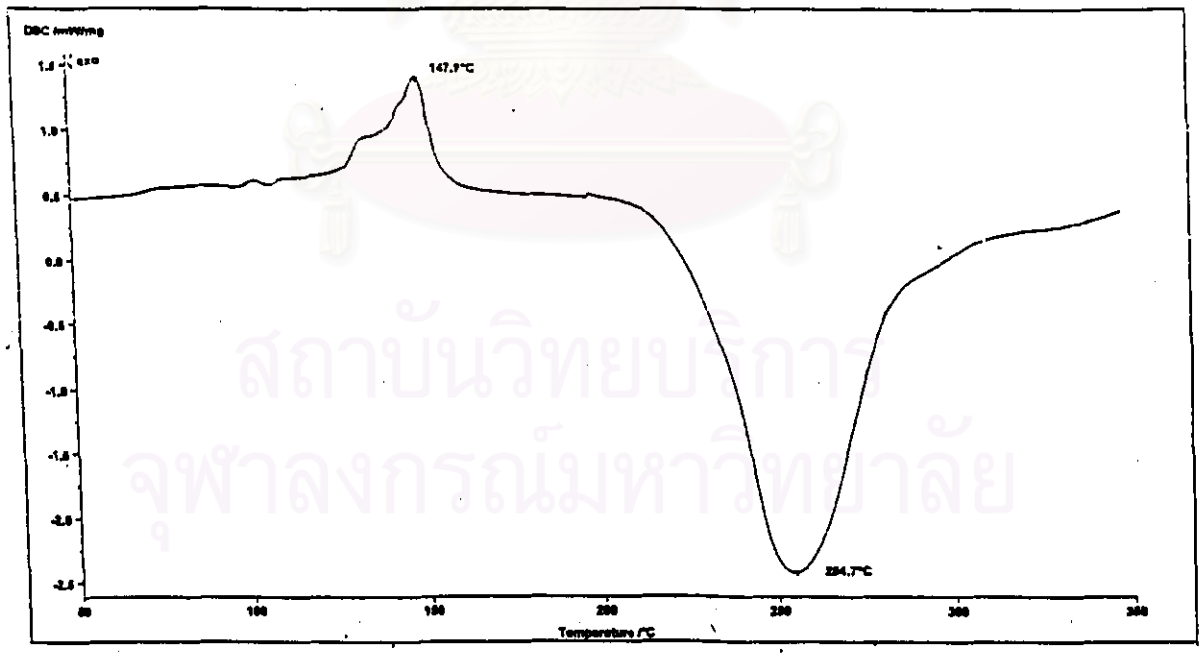


Figure 3.3 DSC thermogram of NiL:DGEBA at the equivalent weight ratio of 1:6[26]

3.3 Crosslinking Reaction of DGEBA with Tetradentate Schiff's Base Metal Complexes by Using Catalysts

Refer to Tongraung's research, the crosslinking temperature of DGEBA with the metal complex was too high. It has been known that the reaction between phenol and phenyl glycidyl ether could be catalyzed with NaOH, tertiary amines and quarternary ammonium salts. Therefore these catalysts were investigated in this work. The effect of each catalyst on the crosslinking reaction was follow by DSC. The results were shown in Figures 3.4-3.6.

From Figure 3.4, when NaOH was used as a catalyst, the DSC exothermic peak indicated the initial temperature (T_{int}), the peak maximum (T_{max}) and the final temperature (T_{end})at 158, 183 and 229^{0}C, respectively.

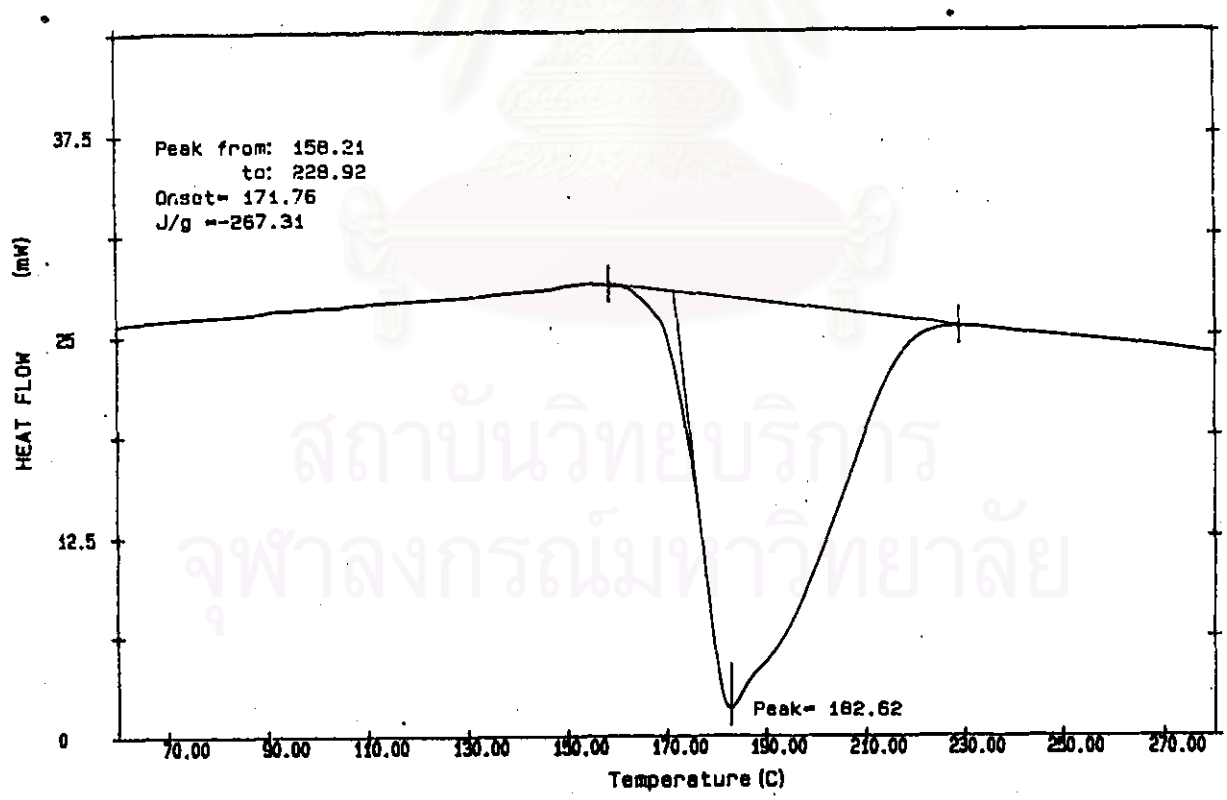


Figure 3.4 DSC thermogram of CuL:DGEBA:NaOH at the equivalent weight ratio of 1:6:0.2

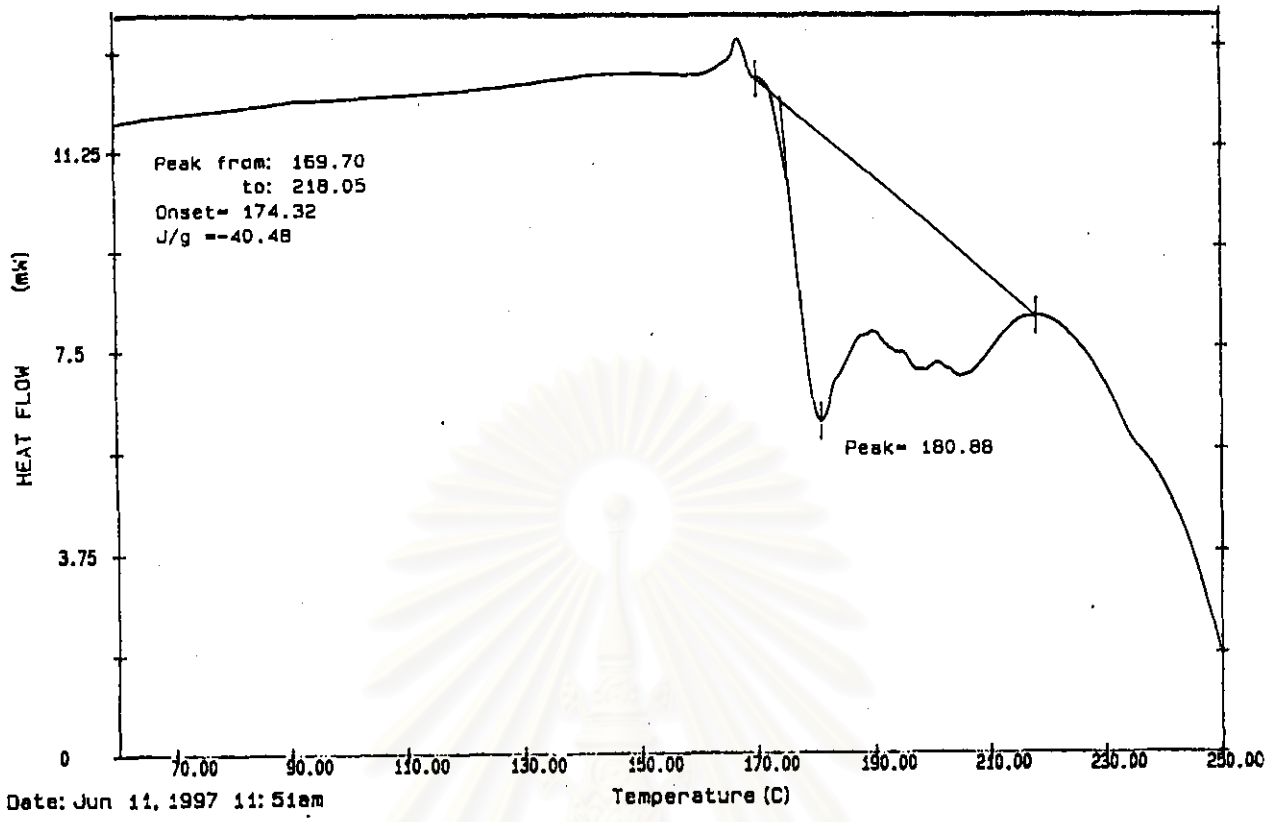


Figure 3.5 DSC thermogram of CuL:DGEBA: N,N-dimethyl aniline at the equivalent weight ratio of 1:6:0.2

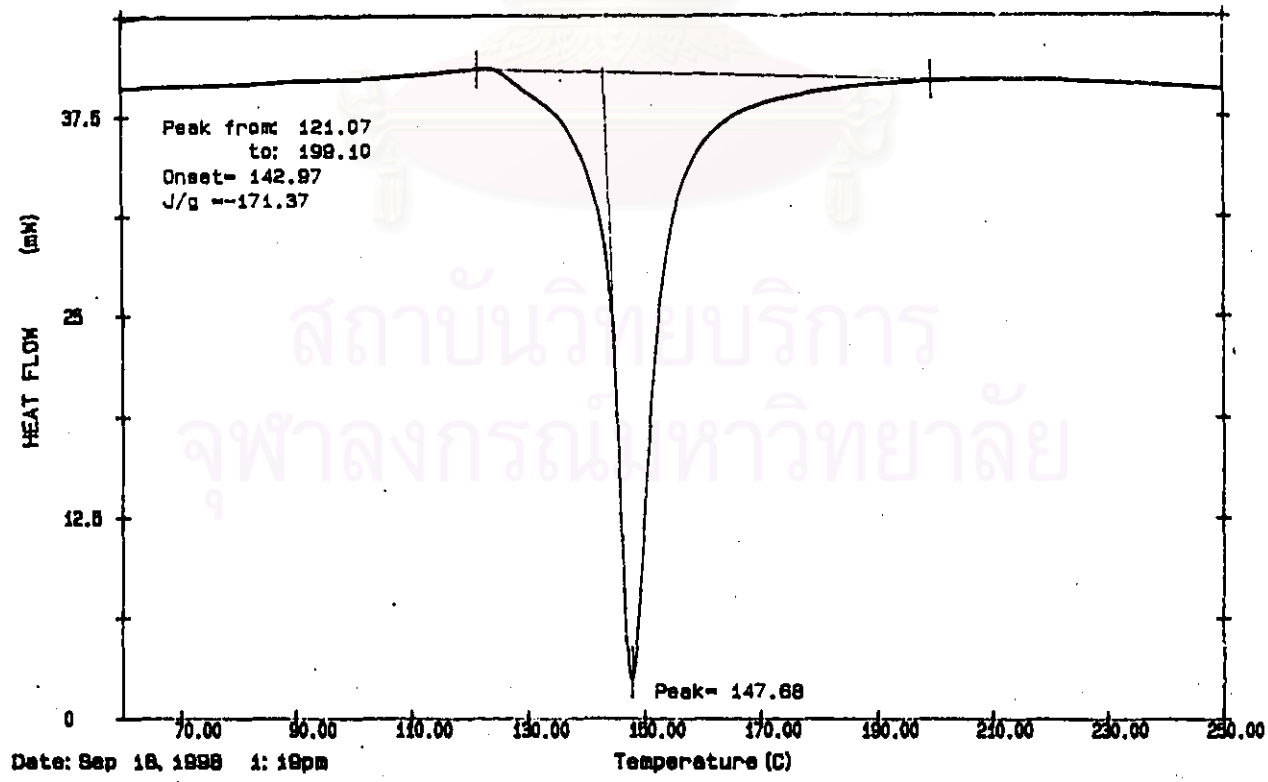
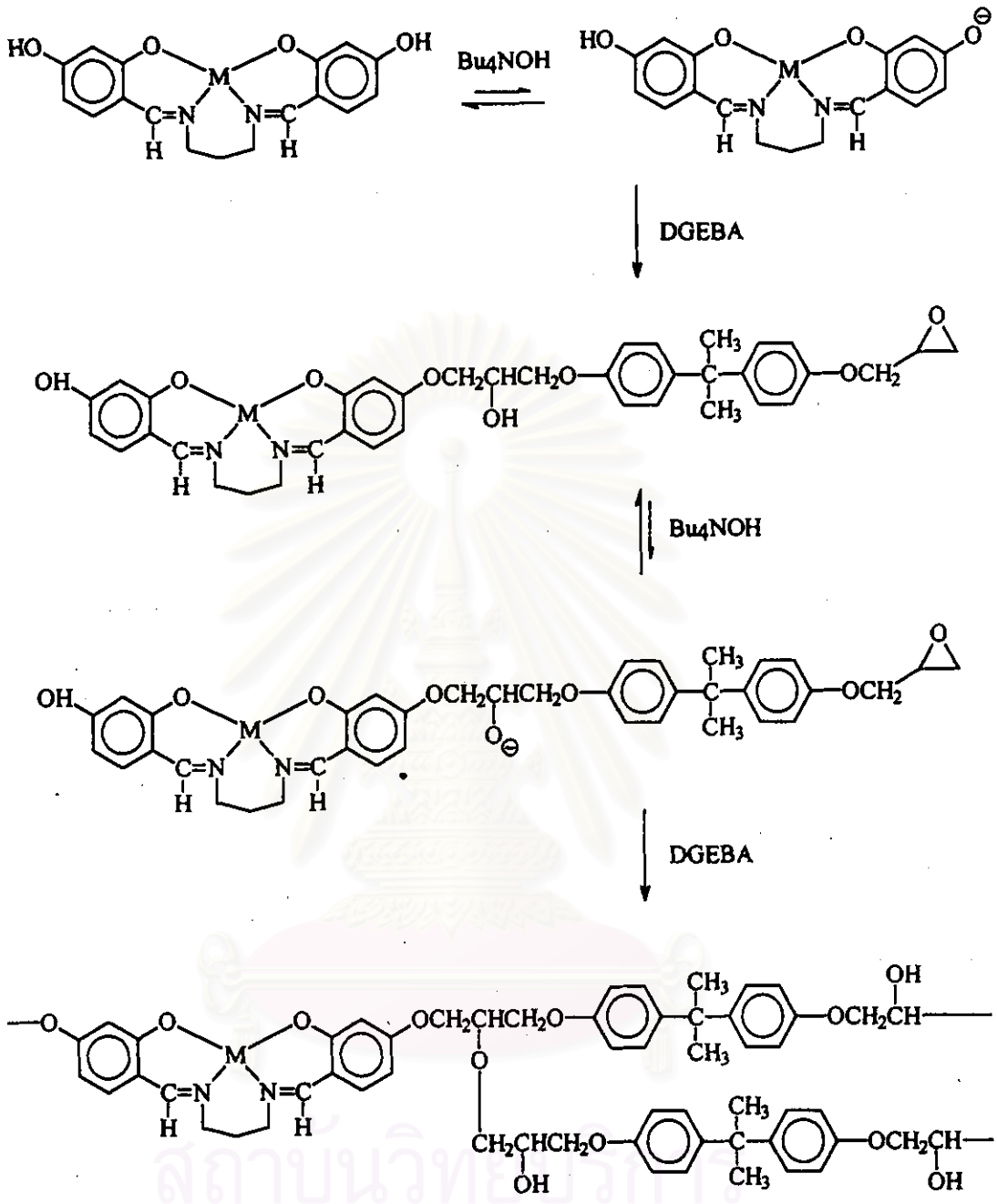


Figure 3.6 DSC thermogram of CuL:DGEBA:Bu_4NOH at the equivalent weight ratio of 1:6:0.2

From Figure 3.5, when N,N-dimethylaniline was employed, the broad DSC peak was the result of overlapping of many small peaks with the initial temperature, the peak maximum and the final temperature at 170, 181 and 218^{0}C, respectively. From Figure 3.6, when Bu_4NOH was employed the DSC exothermic indicated the initial temperature, the peak maximum and the final temperature at 121, 148 and 199^{0}C, respectively.

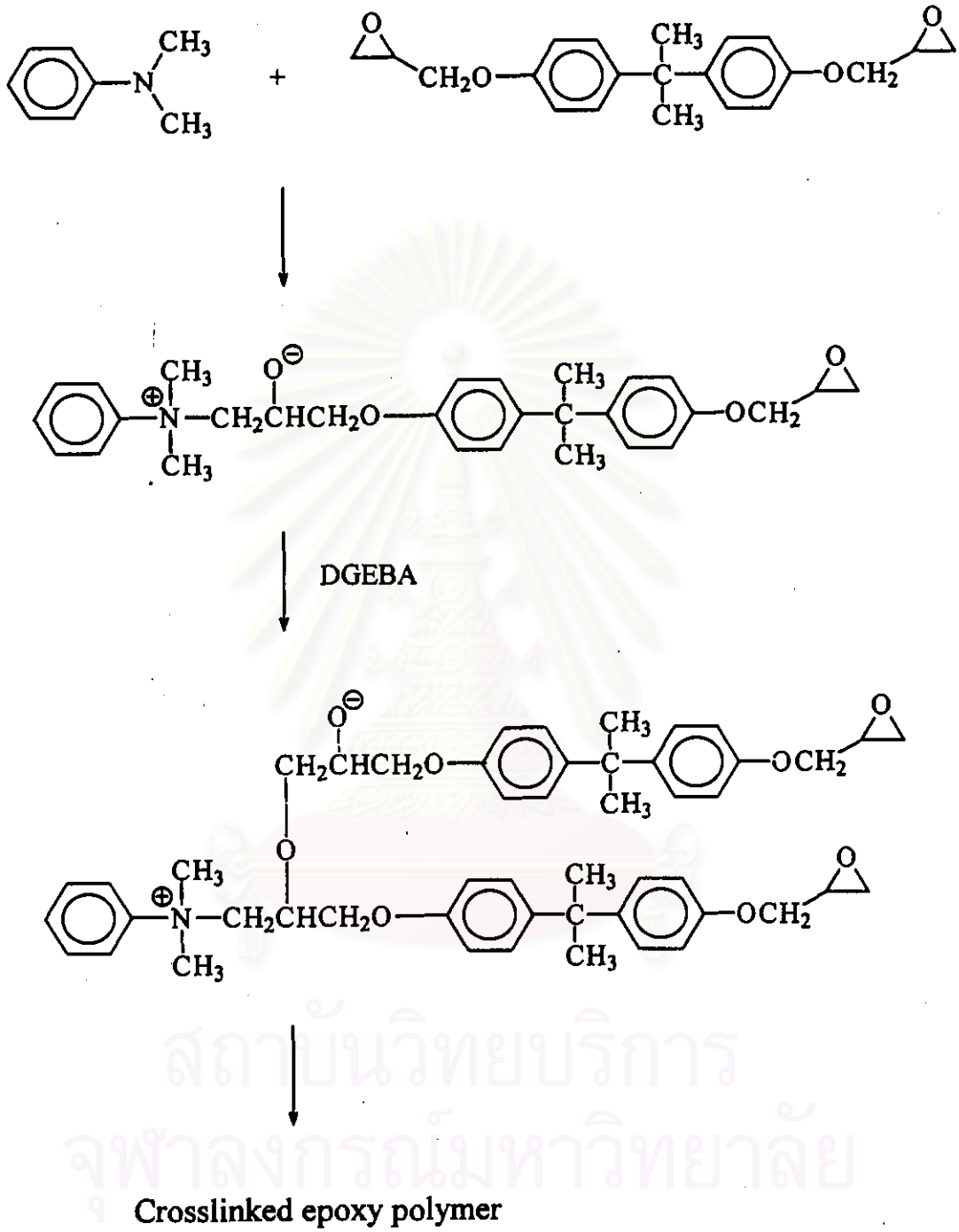
Therefore, use of Bu_4NOH resulted in narrow DSC peak with lower crosslinking temperature than NaOH and N,N-dimethylaniline. The mechanism of the crosslinking reaction of DGEBA with tetradentate Schiff's base metal complexes and Bu_4NOH was proposed to involve the abstraction of proton from the phenol group of metal complexes by Bu_4NOH to give phenoxide ion, which was more nucleophilic than phenol (Scheme 3.2). Phenoxide ion could then open the epoxide ring in DGEBA to give alkoxide ion, which could abstract a proton from another phenol group or to react with other molecules of DGEBA. The same reaction occurred repeatedly to produce metal-containing epoxy polymers. NaOH and N,N-dimethylaniline could also undergo the same reaction as Bu_4NOH. However, NaOH gave broad peak with high crosslinking temperature. This might be because NaOH is an inorganic compound which is not compatible with DGEBA. Use of N,N-dimethylaniline resulted in many overlapping DSC peaks. This might be because N,N-dimethylaniline could lead to the crosslinking of DGEBA by a chain reaction as shown in Scheme 3.3. It was therefore desirable to choose Bu_4NOH as a catalyst in this work.



Crosslinked epoxy polymer

M = Cu, Co and Ni

Scheme 3.2 Possible mechanism of the reaction of DGEBA with metal complex and Bu_4NOH



Scheme 3.3 Chain reaction between DGEBA and N,N-dimethylaniline

3.4 Effect of Bu_4NOH Quantity on the Crosslinking Reaction of DGEBA with Tetradentate Schiff's Base Metal Complexes

3.4.1 DSC Study

The chosen catalyst in this work was Bu_4NOH. The next experiment was to vary the amount of Bu_4NOH in the crosslinking reaction of DGEBA with tetradentate Schiff's base metal complexes in order to study the effect of Bu_4NOH quantity on the crosslinking temperature and to find the optimum quantity of Bu_4NOH in this work.

DSC experiments were performed by heating a mixture of metal complexes, DGEBA, and Bu_4NOH at different equivalent weight ratios. The temperature range was 25-350^{0}C at the heating rate of 20^{0}C/min. All thermograms gave exothermic crosslinking peaks which indicated the crosslinking reaction. Figures A1-A11 show the DSC thermograms and the results are summarized in Table 3.1.

As seen in Table 3.1 the temperature at the initial of the reaction at equivalent weight ratio of 1:6:0 gave the order of reactivity of metal complexes towards DGEBA are CoL > CuL > NiL. Use of Bu_4NOH resulted in the decrease of T_{max}, T_{int} and T_{end}. For example, in the case of CuL, the equivalent weight ratio of 1:6:0 gave T_{int} and T_{max} at 170 and 200^{0}C, respectively, while the equivalent weight ratio of 1:6:0.1 gave T_{int}, T_{max} and T_{end} at 136, 157 and 206^{0}C, respectively. The crosslinking temperature was also decreased with increasing amount of catalyst. For example, the equivalent weight ratio of 1:6:0.4 gave T_{int}, T_{max} and T_{end} at 112, 138 and 200^{0}C, respectively

Table 3.1 Results from DSC experiments

Metal complex	Ratio of Metal complex:DGEBA:Bu_4NOH	T_{int}[a] (^0C)	T_{max}[b] (^0C)	T_{end}[c] (^0C)
CuL	1 : 6 : 0[d]	170	200	230
	1 : 6 : 0.1	136	157	207
	1 : 6 : 0.2	121	148	199
	1 : 6 : 0.4	112	138	200
	1 : 4 : 0.2	120	147	203
	1 : 8 : 0.2	121	149	199
	1 : 10 : 0.2	121	148	221
CoL	1 : 6 : 0[d]	160	185	250
	1 : 6 : 0.1	107	179	248
	1 : 6 : 0.2	100	163	243
	1 : 6 : 0.4	91	149	223
NiL	1 : 6 : 0[d]	200	255	280
	1 : 6 : 0.1	140	167	245
	1 : 6 : 0.2	123	156	234
	1 : 6 : 0.4	107	139	210

[a]initial temperature of the reaction

[b]temperature at the peak maximum

[c]temperature at the end of the reaction

[d]results from Tongraung's work

In comparison between two DSC thermograms obtained when no Bu_4NOH was used and when Bu_4NOH was used (Figures 3.1 and 3.6), the

crosslinking peak was broad followed by decomposition of polymer chains. Therefore, T_{end} could not be identified. With the use of Bu_4NOH, the crosslinking peak was narrow and the crosslinking reaction was done before the decomposition of CuL as shown in Figure 3.6. Crosslinking with CoL and NiL gave the similar result to CuL.

3.4.2 Isothermal DSC Study

In order to compare the reaction time to obtain 100% conversion (T_c), isothermal DSC was done by chosen the constant temperature at 130^0C. The results from isothermal DSC were shown in Table 3.2 and Figures A12-A26.

In the case of CuL at the ratios of CuL : DGEBA : Bu_4NOH = 1:6:0 and 1:6:0.1, the crosslinking temperature decreased from 200^0C to 130^0C with almost equal T_c. Increase of the Bu_4NOH amount in the CuL : DGEBA : Bu_4NOH formulation to 1:6:0.2 to 1:6:0.4 resulted in further decrease of T_c to 12 and 3 min, respectively. The results of isothermal crosslinking behaviors of DGEBA with CoL and NiL were similar to that of CuL. With the use of Bu_4NOH, the order of reactivity of metal complexes towards DGEBA was CuL > NiL > CoL.

When the equivalent weight ratio of metal complex : DGEBA employed were 1:4, 1:6, 1:8 and 1:10 (with the constant Bu4NOH amount at 0.2), T_c was increased when there was less amount of metal complex to react with DGEBA.

Table 3.2 Results from isothermal DSC experiments

complex	Ratio of Metal complex: DGEBA: Bu_4NOH	Crosslinking temperature(^{0}C)	T_c[a] (min)
CuL	1 : 6 : 0[b]	200	13
	1 : 6 : 0.1	130	15
	1 : 6 : 0.2	130	12
	1 : 6 : 0.4	130	3
	1 : 4 : 0.2	130	10
	1 : 8 : 0.2	130	14
	1 : 10 : 0.2	130	16
CoL	1 : 6 : 0[b]	200	12
	1 : 6 : 0.1	130	28
	1 : 6 : 0.2	130	23
	1 : 6 : 0.4	130	12
NiL	1 : 6 : 0[b]	250	7
	1 : 6 : 0.1	130	16
	1 : 6 : 0.2	130	14
	1 : 6 : 0.4	130	6

[a]reaction time required to obtain 100% conversion

[b]results from Tongraung's work

3.5 Preparation of Metal-containing Epoxy polymers

The purpose of the preparation of metal-containing epoxy polymers was to study their physical and mechanical properties. The DSC results indicated the optimum amount of Bu_4NOH was 20 mole % of the metal complex and therefore this amount of Bu_4NOH was chosen in the

preparation of the epoxy polymers. FTIR Spectroscopy was employed to follow the disappearance of the epoxide peak at 920 cm^{-1} to ensure that the crosslinking reaction was completed. The crosslinking temperature employed were the T_{max} obtained from DSC as shown previously in Table 3.1. The curing conditions for the preparation of epoxy polymers are shown in Table 3.3.

Table 3.3 Curing conditions for the preparation of metal-containing epoxy polymers

Metal complex	Ratio of Metal complex: DGEBA: Bu_4NOH	Curing Conditions
CuL	1 : 4 : 0.2	150^0C, 4h
	1 : 6 : 0.2	150^0C, 4h
	1 : 8 : 0.2	150^0C, 4.5h
	1 : 10 : 0.2	150^0C, 5h
CoL	1 : 4 : 0.2	160^0C, 4h
	1 : 6 : 0.2	160^0C, 4h
	1 : 8 : 0.2	160^0C, 4.5h
	1 : 10 : 0.2	160^0C, 5h
NiL	1 : 4 : 0.2	155^0C, 4h
	1 : 6 : 0.2	155^0C, 4h
	1 : 8 : 0.2	155^0C, 4.5h
	1 : 10 : 0.2	155^0C, 5h

In the case of CuL, same crosslinking temperature was employed for all ratios of CuL: DGEBA: Bu_4NOH. However, longer time was required at the ratios of 1:8:0.2 and 1:10:0.2. These results agreed with these obtained from isothermal DSC as previously shown in Table 3.2

3.6 Characterization of Metal-Containing Epoxy polymers

The ratios of metal complex: DGEBA: Bu_4NOH employed were 1:4:0.2, 1:6:0.2, 1:8:0.2, 1:10:0.2 and 1:12:0.2 to determine the optimum ratio that gave the crosslinked polymers with the best physical and mechanical properties.

3.6.1 IR Spectroscopy

The obtained epoxy polymers were characterized by IR spectroscopy. An example of IR absorption bands of the polymer obtained from CuL: DGEBA: Bu_4NOH at equivalent weight ratio of 1:12:0.2 is shown in Table 3.4 and Figure A27. IR spectra bands of other metal-containing epoxy polymers synthesized by using Bu_4NOH or without using Bu_4NOH gave the similar absorption bands

Table 3.4 IR absorption characteristic of metal containing epoxy polymers

Assignment	Absorption band (cm^{-1})
O-H stretching (s)	3300-3500
aromatic C-H stretching (w)	3000-3100
aliphatic C-H stretching (w)	2800-3000
C=N stretching (s)	1600-1500
aromatic C=O stretching (m)	1400-1600
aromatic C-O stretching (s)	1241
aromatic C-H stretching (m)	831

3.6.2 Glass transition temperature (T_g)

Glass transition temperatures were obtained using DMA by observing the maximum value of the loss modulus. DMA thermograms of Cu, Co and Ni-containing epoxy polymers are shown in Figures A38-A52. The T_g values of the polymers are shown in Table 3.5.

In the case of Cu-containing epoxy polymers, use of Bu_4NOH in the synthesis resulted in higher T_g. For example, the polymers obtained from the equivalent weight ratio of 1:4:0 and 1:4:0.2 gave T_g value at 133 and 146^{0}C, respectively. The polymers obtained from the equivalent weight ratio of 1:6:0 and 1:6:0.2 gave T_g value at 78 and 153^{0}C, respectively. When Bu_4NOH was used, the first step of the reaction (Scheme 3.4) was the generation of phenoxide ion to open the epoxide ring to give alkoxide ion. The alkoxide ion could then open another epoxide ring to give crosslinked polymers with high T_g. Without using Bu_4NOH, the epoxide ring opening was mainly the reaction between phenol groups in the metal complexes which gave linear polymers with low T_g. Moreover, the crosslinking reaction was incomplete since the epoxide ring opening by secondary alcohol was difficult to occur.

Crosslinking with CoL and NiL gave the same results as in CuL case. The trend of T_g values of metal-containing epoxy polymers was Cu > Ni > Co. The ratio of Cu- and Co-containing epoxy polymers that gave the highest T_g was 1:6:0.2 with T_g of 153 and 130^{0}C, respectively. The ratio of Ni-containing epoxy polymers that gave the highest T_g was 1:8:0.2 with T_g of 140^{0}C. The T_g of Cu-containing epoxy polymer was higher than epoxy polymers synthesized by using diethylenetriamine as a crosslinking agent, which showed T_g of 96^{0}C and was comparable to the polymer obtained from DGEBA/maleic anhydride which had T_g of 146^{0}C.

Table 3.5 Glass transition temperatures of metal-containing epoxy polymers

Metal complex	Ratio of Metal complex: DGEBA: Bu_4NOH	T_g (^0C)
CuL	1 : 4 : 0[a]	133
	1 : 6 : 0[a]	78
	1 : 4 : 0.2	146
	1 : 6 : 0.2	153
	1 : 8 : 0.2	133
	1 : 10 : 0.2	138
	1 : 12 : 0.2	130
CoL	1 : 4 : 0[a]	108
	1 : 6 : 0[a]	102
	1 : 4 : 0.2	112
	1 : 6 : 0.2	130
	1 : 8 : 0.2	113
	1 : 10 : 0.2	92
	1 : 12 : 0.2	82
NiL	1 : 4 : 0[a]	120
	1 : 6 : 0[a]	95
	1 : 4 : 0.2	140
	1 : 6 : 0.2	115
	1 : 8 : 0.2	117
	1 : 10 : 0.2	121
	1 : 12 : 0.2	103
Maleic anhydride[b]		143
Diethylenetriamine[c]		96

[a]results from Tongraung's research
[b]mole ratio of DGEBA: maleic anhydride was 1:2.8 and 0.1 phr of benzyldimethylamine was employed as a catalyst
[c]mole ratio of DGEBA: diethylenetriamine was 1:1

3.6.3 Thermal stability

Another property of the metal-containing epoxy polymers investigated was the heat resistant. Isothermal study was employed to determine the thermal stability of metal-containing epoxy polymers. Table 3.6 shows % weight loss of polymers heated in air at 250^{0}C for 48 h.

From Table 3.6, the results indicated that the trend of heat resistant of the polymers was Cu > Ni > Co. The optimum ratio of Cu- and Co-containing epoxy polymers that gave the highest heat resistance was 1:10:0.2 which showed 1.9% and 3.3% weight loss, respectively. The optimum ratio of Ni-containing epoxy polymers was 1:8:0.2 with 2.0% weight loss.

Cu-containing epoxy polymers showed higher heat resistant than epoxy polymers synthesized from DGEBA/diethylenetriamine system, which possessed 9.1% weight loss within 2 h and also better than DGEBA/maleic anhydride system, which generally showed good heat resistant.

TGA of the polymer obtained from CuL: DGEBA: Bu_4NOH at the ratio of 1:10:0.2 was obtained as shown in Figure 3.7. The polymers showed 5%, 10%, 20% and 30% weight loss at 241, 291, 355 and 400^{0}C, respectively. Incomparison to another metal-containing epoxy polymer such as DGEBA / 4,4-methylenedianiline / $[Cu(R)(HOC_6H_4COO)_2]$ system[24] where R = triethylenetetramine, which possessed 10%, 20% and 30% weight loss at 343, 350 and 362^{0}C, respectively. The Cu-containing epoxy polymers in this work showed higher heat resistant.

Table 3.6 Thermal stability of Cu, Co and Ni-containing epoxy polymers

Metal Complex	Ratio of Metal complex: DGEBA: Bu_4NOH	%Weight loss at different times			
		12h	24h	36h	48h
	1 : 6 : 0[a]	-	-	3.0	3.2
	1 : 4 : 0.2	4.1	4.2	4.8	4.9
CuL	1 : 6 : 0.2	2.6	2.6	2.8	3.0
	1 : 8 : 0.2	1.2	1.4	2.0	2.1
	1 : 10 : 0.2	1.2	1.3	1.8	1.9
	1 : 12 : 0.2	0.9	1.6	2.0	2.1
	1 : 6 : 0[a]	-	-	2.6	2.8
	1 : 4 : 0.2	4.0	4.6	5.4	5.9
CoL	1 : 6 : 0.2	3.5	4.0	4.8	5.1
	1 : 8 : 0.2	2.7	3.1	3.8	4.0
	1 : 10 : 0.2	2.0	2.3	3.1	3.3
	1 : 12 : 0.2	2.1	3.8	5.1	5.3
	1 : 6 : 0[a]	-	-	2.2	2.7
	1 : 4 : 0.2	4.7	4.9	5.5	5.5
NiL	1 : 6 : 0.2	2.8	2.8	3.2	3.3
	1 : 8 : 0.2	1.5	1.6	1.9	2.0
	1 : 10 : 0.2	2.2	2.4	2.9	3.0
	1 : 12 : 0.2	2.2	3.6	4.4	4.6
Maleic anhydride[b]		1.9	2.7	3.4	4.0
Diethylene-triamine[c]		9.1 % Within 2 h			

[a]results from Tongraung's research

[b]mole ratio of DGEBA: maleic anhydride was 1:2.8 and 0.1phr of benzyldimetylamine was employed as a catalyst

[c]mole ratio of DGEBA: diethylenetriamine was 1:1

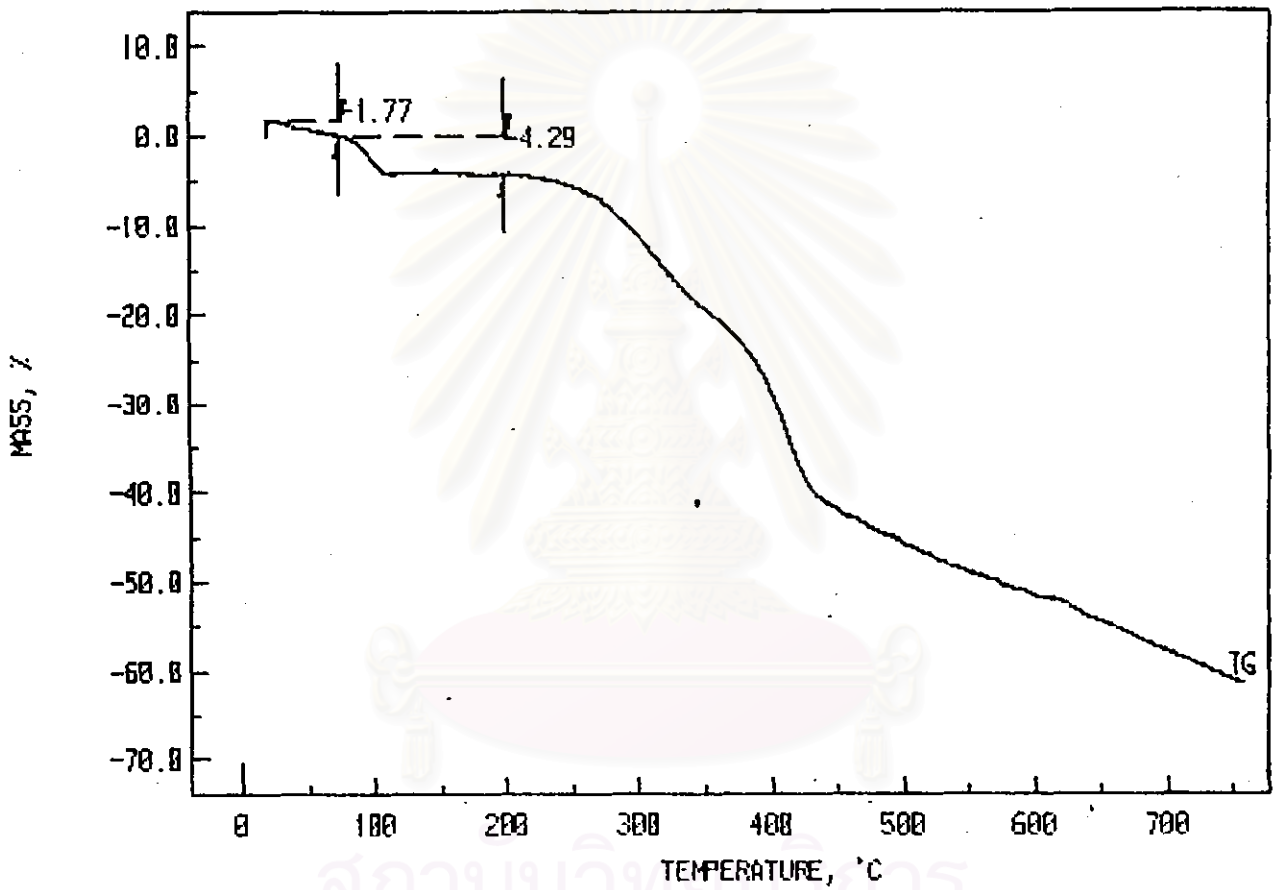


Figure 3.7 TGA thermogram of CuL:DGEBA:Bu_4NOH at the equivalent weight ratio of 1:12:0.2

3.7 Mechanical properties

Mechanical properties of the metal-containing epoxy polymers obtained from different equivalent weight ratios of metal complexes and 0.2 mole % of Bu_4NOH were studied. The properties investigated were hardness and tensile strength.

3.7.1 Tensile strength

Table 3.7 Tensile strength of metal-containing epoxy polymers

Metal complex	Ratio of Metal complex :DGEBA: Bu_4NOH	Tensile strength (MPa)
CuL	1 : 6 : 0.2	41
	1 : 8 : 0.2	53
	1 : 10 : 0.2	60
	1 : 12 : 0.2	69
	1 : 14 : 0.2	23
CoL	1 : 6 : 0.2	37
	1 : 8 : 0.2	43
	1 : 10 : 0.2	55
	1 : 12 : 0.2	44
NiL	1 : 6 : 0.2	40
	1 : 8 : 0.2	51
	1 : 10 : 0.2	59
	1 : 12 : 0.2	45
Maleic anhydride[a]	1 : 10 : 0.2	56
Diethylenetriamine[b]	1 : 12 : 0.2	44

[a]mole ratio of DGEBA: maleic anhydride was 1:2.8 and 0.1 phr of benzyldimetylamine was employed as a catalyst

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

Table 3.7 shows tensile strength of metal-containing epoxy polymers. At the same equivalent weight ratio of metal complex: DGEBA : Bu_4NOH, the trend of tensile strength of the epoxy polymers was Cu-containing polymers>Ni-containing polymers>Co-containing polymers. Consider the Cu-containing epoxy polymers obtained from the equivalent weight ratios of CuL: DGEBA : Bu_4NOH = 1:6:0.2, 1:8 :0.2, 1:10:0.2 and 1:12:0.2, the tensile strength increased when the amount of DGEBA was increased. This is because there was more DGEBA to react with hydroxyl groups to give higher degree of crosslinking in the polymers which resulted in high tensile strength. CoL and NiL gave the same trend in tensile strength as in the CuL case. The optimum ratio of Co and Ni-containing epoxy polymers that gave the highest T_g was 1:10:0.2. The optimum ratio for Cu-containing epoxy polymers was 1:12:0.2. The highest tensile strength was obtained from the Cu-containing epoxy polymer at the equivalent weight ratio of 1:12:0.2 which possessed better tensile strength than the epoxy polymers obtained from DGEBA/diethylenetriamine and DGEBA/maleic anhydride system.

3.7.2 Hardness

The metal-containing epoxy polymers possessed hardness value in the range of 81-89 shore D which was close to the hardness of the other epoxy polymers. For example, the DGEBA/triethylenetetramine system gave the hardness value of 85 shore D. The results of hardness testing were shown in Table 3.8

Table 3.8 Hardness of metal-containing epoxy polymers

Metal complex	Ratio of Metal complex :DGEBA: Bu_4NOH	Hardness (Shore D)
CuL	1 : 4 : 0.2	86
	1 : 6 : 0.2	83
	1 : 8 : 0.2	85
	1 : 10 : 0.2	85
CoL	1 : 4 : 0.2	88
	1 : 6 : 0.2	87
	1 : 8 : 0.2	89
	1 : 10 : 0.2	89
NiL	1 : 4 : 0.2	83
	1 : 6 : 0.2	81
	1 : 8 : 0.2	87
	1 : 10 : 0.2	88

3.8 Comparison of the Polymers' Properties

From the above results, Cu-containing epoxy polymers showed better properties than Co-and Ni-containing epoxy polymers. The best physical and mechanical properties of Cu-containing epoxy polymers' are summarized in Table 3.9. The equivalent weight ratio of CuL:DGEBA:Bu_4NOH that gave the highest T_g was 1:6:0.2 with T_g of 153^0C. The polymer that gave the highest thermal stability was obtained from the ratio of 1:10:0.2 with weight loss of 1.9 % after treatment at 250^0C for 48 h. The highest tensile strength was obtained from the ratio of 1:12:0.2 with tensile strength of 69 MPa. Both physical and mechanical properties of Cu-containing epoxy polymers are better than

the epoxy polymers synthesized by using diethylenetriamine or maleic anhydride as crosslinking agents.

Table 3.9 The best physical and mechanical properties of Cu-containing epoxy polymers

Ratio of CuL : DGEBA : Bu_4NOH	Tensile strength (MPa)	% Weight loss	T_g (^0C)
1 : 6 : 0.2	41	3.0	153
1 : 10 : 0.2	60	1.9	138
1 : 12 : 0.2	69	2.1	130
Maleic anhydride	56	4.0	143
Diethylenetriamine	44	9.1 within 2 h	96