

CHAPTER IV

RESULT AND DISCUSSION

Preparation of Crosslinked Resins (4)

It has been well-known that epoxy resin undergoes crosslinking reaction at room temperature with aliphatic amine, such as ethylenediamine, therefore in this work the crosslinking reaction at ambient temperature was first investigated. The curing reactions between 2,4-diamino-6-hydroxypyrimidine (3) and epoxy resin (2) were carried out in dioxane using triethylamine as a catalyst. The mixture was stirred for 24 hours under atmospheric nitrogen. By using thin layer chromatography (TLC) to follow the reaction progress, it was found that no products obtained under this condition. The reaction was also performed at 90°C; the same result was obtained. The difficulty for the crosslinking reaction to occur is that aromatic amine (3) has less reactivity than aliphatic amines. Delocalization of an electron pair on nitrogen atom into benzene ring decreases their nucleophilicity, therefore the curing process should require higher temperature without any solvents.

To determine the suitable curing condition, DSC measurements of uncured epoxy resin at the equivalent weight ratios 3:2 of 2:1, 2:1.5 and 1:1 were carried out in closed Al pans under nitrogen atmosphere. Table 4.1 shows the glass transition temperatures (T_g) of the uncured epoxy resins obtained from DSC technique. Figures A.4-A.6 shown in Appendix are the thermograms obtained from DSC technique and relevant to the data in the table.

Table 4.1 The glass transition temperature (T_g) of uncured epoxy resins at various equivalent weight ratios 3:2 (20°C/min. heating rate, the first and the second heating cycle (loop) started from -100 -210°C).

E.W.R. 3:2	Heating cycle	T _g (°C)
2:1	1	-14.5
	2	-3.2
2:1.5	1	-14.4
	2	-4.4
1:1	1	-14.7
	2	-8.4

For the first heating cycle, it was observed that T_g's of uncured samples, i.e., T_g's of epoxy resin, were very similar. When the temperature increased from T_g to the maxima of 210°C, the crosslinking reaction should occur which one could observe from the data of T_g's of the second heatings. T_g's shifted from -3.2°C to -8.4°C that correlates to the equivalent weight ratio of 3 to 2. The surplus amount of epoxy resin (2) resulted in lower crosslinking reaction because of the lower T_g. This means that the uncomplete crosslinking reaction was obtained at the temperature lower or equal to 210°C.

The curing temperatures were then obtained carefully using the DSC technique with temperature range of -80 - 350°C and the heating rate of 10°C/min. T_g's and curing temperatures obtained are shown in Table 4.2. Figures A.7-A.9 shown in Appendix are the thermograms relevant to the data in the table.

Table 4.2 The glass transition and curing temperature of uncured epoxy resins at various equivalent weight ratios 3:2 (10°C/min. heating rate).

E.W.R.	Tg (°C)	Curing temperature (°C)	
		Onset	Peak
3:2	-16.2		
2:1	-16.2	215.9	221.9
2:1.5	-15.8	224.6	242.6
1:1	-16.2	224.5	230.4

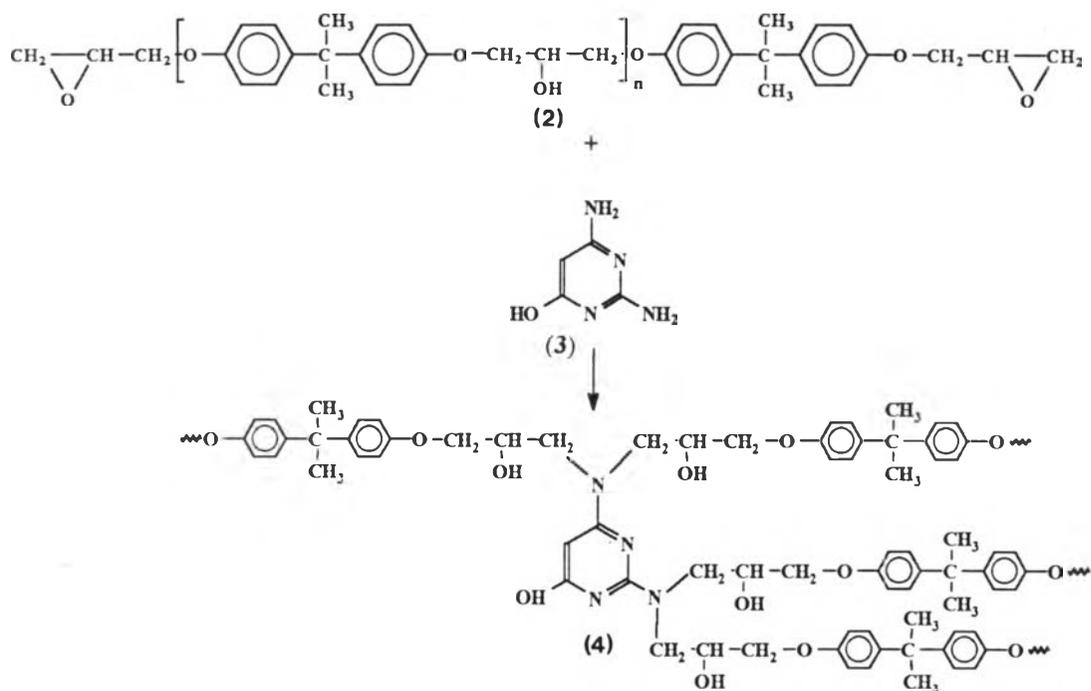
The lower Tg values obtained in comparison to those shown in Table 4.1 due to the lower heating rate at 10°C/min. instead of 20°C/min. Since the curing reaction is mostly exothermic reaction, therefore, it could be expected that an exothermic peak in thermograms would be observed. The area under peak indicates exothermic energy occurred, in the other words, the energy required for completing of the curing reactions. From Figure A.7 the exothermic peak starting at 215.9°C means the curing reaction started performing at this temperature and was peak at 221.9°C. The reaction was complete at 227°C. However, it could not observe the clear completion temperature in Figures A.8 and A.9. The uncured epoxy resin at the equivalent weight ratio of 1:1 contained more resin (2) than crosslinking agent (3), resulting in very quickly consumed of 3 (the sharp exothermic peak observed (Figure A.9)). The decomposition of crosslinked resin was at approximately over 280°C as observed from the thermograms. This result was also supported by the result obtained from TGA technique (see Figures A.16-A.20). Therefore, it could be concluded the followings:-

(1) the crosslinking reaction could be performed from 215°C to 230°C, and

(2) the decomposition reaction at approximately 280°C would exist following the completion of crosslinking reaction.

The isothermic curing behavior of these uncured epoxy resins was also investigated at the constant temperature of 190°C (Figures A.10-A.12 shown in Appendix). The uncured epoxy resin at the equivalent weight ratio of 1:1, where the resin (2) catches the crosslinking agent (3) very fast, reaches the peak maxima after 17.4 min. and develops a reaction enthalpy of -207 J/g. The uncured epoxy resin at the equivalent weight ratio of 2:1.5 requires 23.1 min. and the enthalpy amounts to -124 J/g. In contrast the equivalent weight ratio of 2:1 needs only 15 min. and the enthalpy is -260 J/g. Here the curing temperature used was at 185°C. A curing experiment was carried out at 200°C for 2 hours, the decomposition products were obtained. Therefore, the higher curing temperature over 190°C is not recommended because the decomposition reaction may be occurred.

Diamine (3) reacts with Bisphenol-A epoxy resin (2) at 185°C to yield the crosslinked resin (4). The reaction (see Scheme 4.1) involves the ring-opening of epoxide groups in 2 with the amino groups of 3. The amino groups act as nucleophiles attacking on the epoxide carbons of the resin to yield the crosslinked resin (4) having three dimensional network.



Scheme 4.1

The crosslinked resin was washed in warm dioxane to remove the unreacted epoxy resin. The pure crosslinked resin was certainly obtained because it was washed continuously until no spot of the uncured epoxy resin observed by TLC.

The yields of crosslinked resin (4) varied upon changing the equivalent weight ratio of 3 to 2 are shown in Table 4.3.

Table 4.3 Yield of crosslinked resin (4) at various equivalent weight ratios of diamine (3) to epoxy resin (2).

Equivalent weight ratio of 3:2	Crosslinked resin	Yield of 4 (%)
2:1	4a	69
2:1.25	4b	63
2:1.5	4c	50
2:1.75	4d	49
1:1	4e	42
3:1	4f	92
4:1	4g	97

The yield of 4 increased with increasing equivalent weight ratio of 3 to 2 in the reaction. These results supported that the degree of crosslinking increased when the amount of 3 greater than that of 2. The plot of equivalent weight ratio of 3 to 2 against % yield of crosslinked resin (4) is shown in Figure 4.1. It can be concluded that the yield of 4 could be obtained maxima at approximately 90 % when the E.W.R. of 3 to 2 is 3:1.

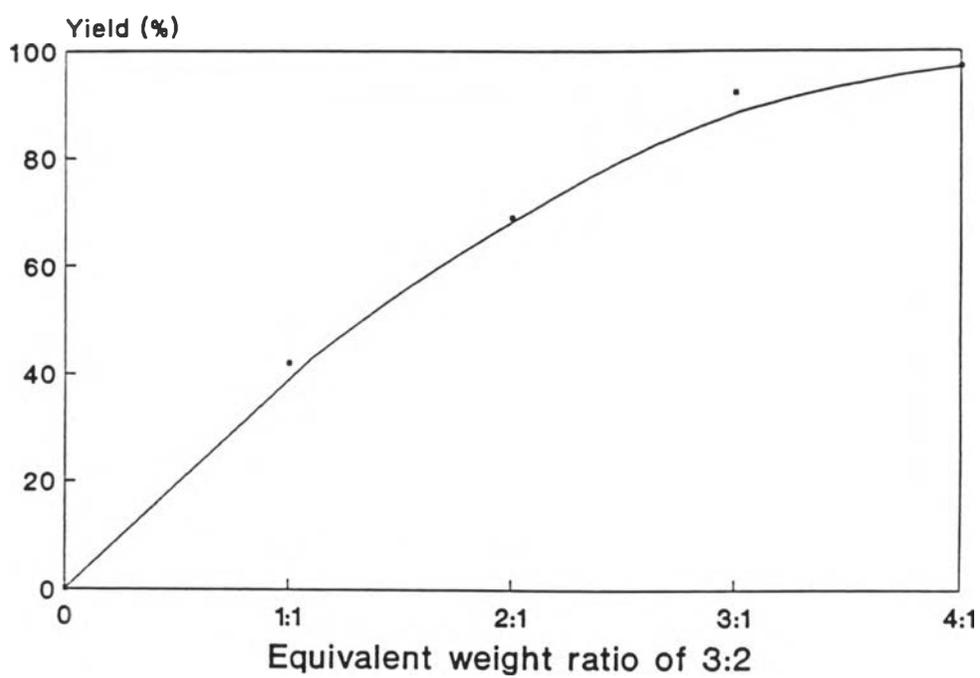


Figure 4.1 Correlation between equivalent weight ratio of 3:2 and % yield of 4

Characterization of the Crosslinked Resin (4)

1 Fourier-Transform Infrared Spectroscopy (FTIR)

The crosslinked resin (4) was insoluble in any solvents. Here the method used to confirm its chemical structure was infrared spectroscopy (IR). The IR spectrum of 4 (KBr disc) is shown in Figure A.3 (in Appendix). Consideration of the chemical structure of 4 in conjunction of those of 2 and 3, the bands at 3200-3400 and at 900-940 cm^{-1} associated to N-H stretching and epoxy terminal, respectively, should disappear due to the reaction of diamine with epoxide. The most significant band at 900-940 cm^{-1} was not observed in the spectrum indicating that the epoxide was used up. Therefore, it could be confirmed that 4 was obtained. The band assignments were 3200-3500 cm^{-1} (O-H stretching and N-H stretching), 3038 cm^{-1} (aromatic C-H stretching), 2900-3000 cm^{-1} (aliphatic C-H stretching), 1630 cm^{-1} (aromatic C=C and C=N stretching), and 1250 cm^{-1} (C-O stretching).

2 Thermal Analysis of Crosslinked Resin (4)

It is well known that processing history of polymers reflected thermal properties of polymers. Therefore properties of which derived from thermal data, such as Tg, melting point temperature (Tm), crystallinity of polymers, depend upon the processing and thermal treatment history. In this study DSC and TGA were used to obtain Tg and chemical composition of the crosslinked resin (4). Figures A.13-A.15 and A.16-A.20 shown in Appendix are DSC and TGA thermograms of the crosslinked resin (4) prepared with different ratio of 3 to 2, respectively. Table 4.4 shows the values of Tg derived from the DSC

thermograms. The first and the second heating cycles were performed using the same procedure, from which the temperature cycle started 0 to 210°C with heating rate of 20°C/min. and then from 210 to 0°C with heating rate of 10°C/min. It was observed from the DSC thermograms of the first heating cycle that a strong endothermic effect observed from approximately 60-140°C. The effect was probably due to the evaporation of dioxane remaining in the sample. This evidence was supported strongly by the results obtained from TGA. The TGA thermograms showed that 3-8% weight loss were observed at the temperature range of 60-220°C. These small amount of weight loss should be associated to small amount of chemical composition in polymers, and in this case it should be small amount of dioxane presented in the cavity of crosslinked resin (4). Tg of 4 could be obtained from the second heating cycle (DSC experiments) to be 113-117°C.

The second weight loss of 70-78% (observed at the temperature 228-510°C shown in Table 4.5) are associated to the main crosslinked resin composition. The third weight loss could also be observed at the temperature higher than 500°C, which was due to chemical decomposition of 4.

Table 4.4 The temperature of endothermic effect and glass transition temperature (Tg) of crosslinked resin (4).

Crosslinked resin	Temperature (°C)	
	Endothermic effect	Tg
4a	52.0	117.0
4c	51.3	112.7
4e	52.9	114.9

Table 4.5 Percent weight loss and temperature range of crosslinked resin (4)

Crosslinked resin	% Weight loss	Temperature range (°C)
4a	2.85	112 - 228
	77.5	228 - 491
4c	7.83	95 - 245
	73.7	245 - 504
4e	7.57	105 - 238
	78.6	238 - 494
4f	8.90	94 - 243
	72.7	243 - 510
4g	8.16	59 - 246
	69.8	246 - 518

Determination of Percent Weight Increase of Resin (4) Swollen in Dioxane

In general a crosslinked polymer with high degree of crosslinking should have less ability in absorption or holding of solvent in small amount. In this study, measurement of the percent weight increase of the crosslinked resin (4) swollen in dioxane at various equivalent weight ratios of diamine (3) to epoxy resin (2) were carried out in order to investigate the relationship of degree of crosslinking to solvent absorption ability. Table 4.6 and Figure 4.2 show the results obtained from the study, which was in good agreement in that increase in the degree of crosslinking of 4 affected on less dioxane absorption ability of the crosslinked resin (4).

Table 4.6 Percent weight increase of the crosslinked resin (4) at various equivalent weight ratios of diamine (3) to epoxy resin (2).

Equivalent weight ratio of 3:2	Crosslinked resin	% Weight increase
2:1	4a	63.20
2:1.5	4c	57.91
1:1	4e	58.16
3:1	4f	46.42
4:1	4g	35.80

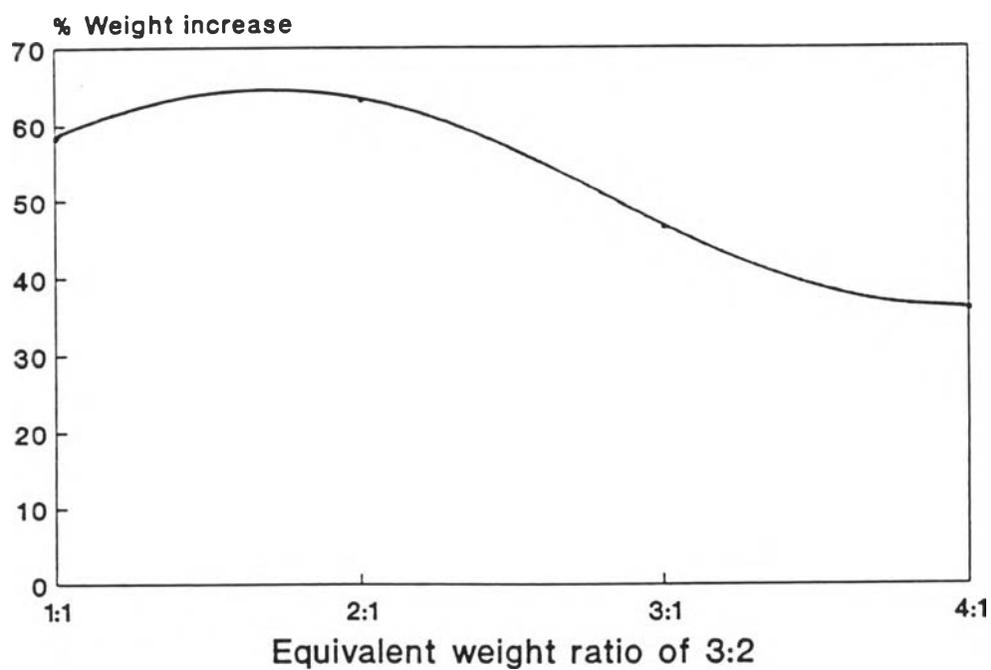


Figure 4.2 Correlation between equivalent weight ratio of 3:2 and % weight increase of 4

Measurement of Metal Ions Chelation Ability of Crosslinked Resins (4)

In order to study the chelating capacity and selectivity of metal ions by the crosslinked resin (4) (metal ions chelation ability), five metal ions including Ni(II), Pb(II), Cu(II), Co(II), Zn(II), in various solvents were employed for the studies. The crosslinked resin (4) prepared from different batches (4a-4g) used were mixed and grinded well. When water was used as solvent, the results of metal ions chelating with the resin (4) are shown in Table 4.7.

Table 4.7 The result of metal ions chelation ability of the mixture of 4 in water.

Metal ion	Chelating capacity		
	mmol/g	mg/g	meqv/g
Ni ²⁺	0.0780	4.58	0.1560
Pb ²⁺	0.1346	27.89	0.2692
Cu ²⁺	0.1216	7.73	0.2433
Co ²⁺	0.1396	8.23	0.2791
Zn ²⁺	0.1524	9.97	0.3049

The metal chelation ability was divided into two types, i.e., (1) chelating capacity and (2) chelating selectivity. The chelating capacity of the crosslinked resin was low because its swelling ability in water was poor, resulting in difficulties for metal ions in aqueous solution diffused through the resin pores. The chelating capacity reported in the table should be expected due to the loss of small amount of metal ions during filtration or dilution processes.

Since it was known that water was not appropriate for using as solvent in this study, an investigation on other suitable solvents was carried out. It was found that the crosslinked resin swelled very well in pure dioxane. However, it was necessary to use a mixture of 80% dioxane and 20% water volume by volume as solvent in this study. If dioxane exceeded 80%, the solvent mixture could not be used to dissolve metal ions, thus the chelation ability experiments could not be carried out. The word “mixed solvent” hereafter means the mixture of 80 % dioxane and 20 % water volume by volume. The result of metal ions chelation in the mixed solvent is shown in Table 4.8.

Table 4.8 Metal ions chelation with crosslinked resin (4) in mixed solvent.

Metal ion	Chelating capacity		
	mmol/g	mg/g	meqv/g
Ni ²⁺	0.1324	7.772	0.1394
Pb ²⁺	0.5921	122.68	1.1840
Co ²⁺	0.0174	1.029	0.0178
Zn ²⁺	0.0004	0.0244	0.0007

The crosslinked resin (4) showed good capacity in chelating with Pb(II), i.e., the resin had the best selectivity with Pb(II). The detail investigation of Pb(II) chelation was then carried out in various organic solvents in order to determine the optimum chelating conditions in what solvent. The experimental procedure was performed in both of batch and column methods. The results are presented subsequently.

Investigation of the Optimum Chelating Condition of Pb(II)

1 Batch Method

Various solvents including (a) 40% dioxane in water, (b) 80% dioxane in water, (c) 80% DMF in water, (d) 80% DMSO in water, and (e) 80% methanol in water were used as solvents for this investigation. The results of Pb(II) chelation with crosslinked resin in those solvents are shown in Tables 4.9-4.13.

Table 4.9 Pb(II) chelating capacity in 40% dioxane in water.

Crosslinked resin	Pb ²⁺ chelating capacity ^(a)		
	mmol/g	mg/g	meqv/g
4a	0.1278	26.48	0.2556
4b	0.1203	24.93	0.2407
4c	0.1617	33.51	0.3234
4d	0.0704	14.58	0.1408
4e	0.0538	11.15	0.1076
4f	0.0997	20.65	0.1993
4g	0.1272	26.36	0.2545

(a) = The average values obtained from three analyses

Table 4.10 Pb(II) chelating capacity in 80% dioxane in water.

Crosslinked resin	Pb ²⁺ chelating capacity ^(a)		
	mmol/g	mg/g	meqv/g
4a	0.6119	127.10	1.275
4b	0.6095	126.30	1.219
4c	0.6009	124.50	1.202
4d	0.5961	123.53	1.192
4e	0.6088	126.15	1.217
4f	0.5837	120.94	1.167
4g	0.6077	125.92	1.215

(a) = The average values obtained from three analyses

Table 4.11 Pb(II) chelating capacity in 80% DMF in water.

Crosslinked resin	Pb ²⁺ chelating capacity ^(a)		
	mmol/g	mg/g	meqv/g
4a	0.1669	34.59	0.3339
4c	0.1586	32.86	0.3171
4e	0.1523	31.56	0.3046
4f	0.1536	31.82	0.3071
4g	0.1535	31.80	0.3070

(a) = The average values obtained from three analyses

Table 4.12 Pb(II) chelating capacity in 80% DMSO in water.

Crosslinked resin	Pb ²⁺ chelating capacity ^(a)		
	mmol/g	mg/g	meqv/g
4a	0.0680	14.08	0.1359
4c	0.0442	9.150	0.0884
4e	0.0438	9.058	0.0874
4f	0.0310	6.431	0.0621
4g	0.0331	6.862	0.0662

(a) = The average values obtained from three analyses

Table 4.13 Pb(II) chelating capacity in 80% methanol in water.

Crosslinked resin	Pb ²⁺ chelating capacity ^(a)		
	mmol/g	mg/g	meqv/g
4a	0.0290	6.004	0.0580
4c	0.0199	2.748	0.0265
4e	0.0191	3.959	0.0382
4f	0.0129	2.666	0.0257
4g	0.0202	4.199	0.0406

(a) = The average values obtained from three analyses

From the results shown in Tables 4.9-4.13, the Pb(II) chelating ability of the various crosslinked resins (4a-4g) for the particular solvent were of the same trend. In comparison to the Pb(II) chelating capacity of 4 in different solvents are in the following order:-

80% dioxane solⁿ>80% DMF solⁿ>40% dioxane solⁿ>80% DMSO solⁿ>80% methanol solⁿ

1.1 The Maximum Pb(II) Chelating Capacity

The maximum Pb(II) chelating capacity of crosslinked resin (4) was studied by varying the concentrations of Pb(II) in the mixed solvent. The Pb(II) chelating capacity per gram resin against Pb(II) concentration is plotted as shown in Figure 4.3. The data relevant to the plot is shown in Table 4.14.

Table 4.14 The Pb(II) chelating capacity of the crosslinked resin (**4e**) at various concentration of Pb(II) solutions.

Pb ²⁺ Concentration		Pb ²⁺ chelating capacity		
(M)	(ppm)	mmol/g	mg/g	meqv/g
0.005	1110	0.1242	25.74	0.2484
0.01	2060	0.1709	35.40	0.3417
0.02	4520	0.2856	59.18	0.5712
0.03	7140	0.3946	81.76	0.7893
0.04	9260	0.4562	94.53	0.9124
0.05	11300	0.5531	114.59	1.1061
0.06	14200	0.6630	137.36	1.3259
0.08	18167	0.7464	154.64	1.4928
0.10	22200	0.7455	154.47	1.4911

The Pb(II) concentration exceeded 0.10 M was difficult to prepare because the solid metal salts could not be completely dissolved. The maximum Pb(II) chelating capacity of the crosslinked resin (**4e**) was approximately 0.8 mmol/g at 22,200 ppm Pb(II) solution.

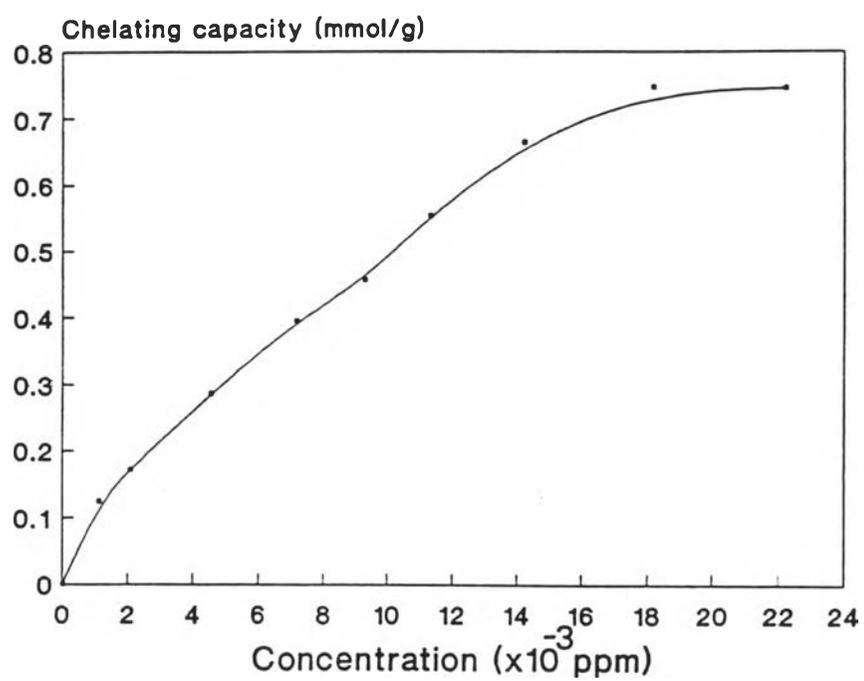


Figure 4.3 Correlation between initial Pb(II) concentration and chelating capacity



1.2 Rate of Pb(II) Chelation

The rate of Pb(II) chelation was determined to indicate the time for which chelation equilibria was achieved. The rates of Pb(II) uptake at various times are shown in Table 4.15 and Figure 4.4.

Table 4.15 Rates of Pb(II) chelation at different periods of time.

Time (min.)	Amount of Pb(II) left in solution (mmol)	Amount of Pb(II) adsorbed (mmol)	Amount of Pb(II) adsorbed/10 min.
0	0.9479	-	-
10	0.8302	0.1177	0.1177
20	0.8157	0.1322	0.0145
30	0.8012	0.1467	0.0145
40	0.7915	0.1564	0.0097
50	0.7819	0.1661	0.0097
60	0.7722	0.1757	0.0096
80	0.7674	0.1805	-
100	0.7626	0.1853	-
120	0.7578	0.1901	-
150	0.7529	0.1950	-
190	0.7481	0.1998	-

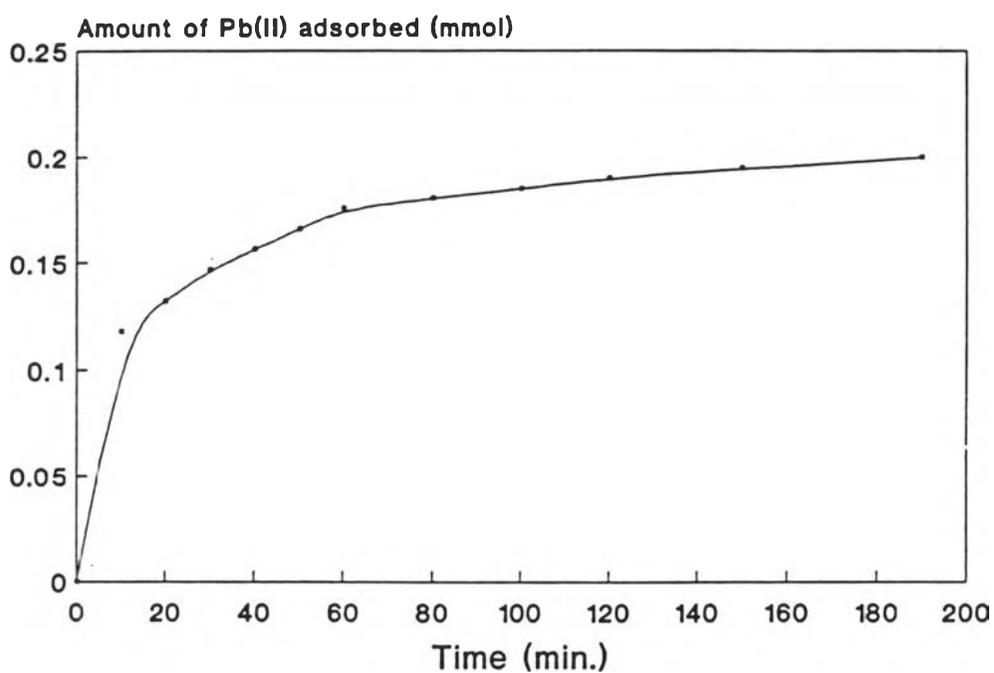


Figure 4.4 Rates of Pb(II) chelation of the crosslinked resin (4a).

The results indicated that the adsorption was initially fast, but gradually became slower with time and reached a constant value after 150 min. Therefore, the chelation of Pb(II) reached the equilibrium after 2.5 hours.

2 Column Method

The results in Pb(II) chelating ability by the crosslinked resins (4a) and (4e) by column method are shown in Table 4.16. The Pb(II) stock solution was also prepared using the mixed solvent and the same method as for the batch process.

Table 4.16 Pb(II) chelation (column method).

Crosslinked resin	Capacity of the first run			Capacity of recycle test		
	mmol/g	mg/g	meqv/g	mmol/g	mg/g	meqv/g
4a	0.1368	28.34	0.2735	0.0517	10.71	0.1034
4e	0.1259	26.09	0.2519	0.0255	5.280	0.0510

The capacity of Pb(II) chelation decreased clearly comparing with the batch method. It was due to the contact time between Pb(II) solution and the crosslinked resin (4) possibly being too fast, resulting in incompleteness of chelation.

Possibility in reusing of the resin was investigated. The resin was washed with nitric acid, and subsequently with the mixed solvent until the filtrate was neutralized. The resin was then ready for reuse in chelation experiment. It was found that the Pb(II) chelation ability of the reused resin was poorer than the original crosslinked resin according to its decomposition when

contacted with nitric acid. This was observed by changing of color of the resin from yellow to brownish red after contacting with HNO_3 . The resin (4) is therefore not recommended for reusing.

Investigation of Using the Crosslinked Resin (4) for Pb(II) Chelation in Waste Water Obtained from Battery Factory

The batch method was applied to determine the amount of Pb(II) in waste water from battery factory. The waste water was neutralized with NaOH pellets and diluted with dioxane to make the concentration of 50% v/v. The higher dilution caused the lower content of Pb(II) in the sample resulting in more difficult to analyze. The amount of Pb(II) chelation by the crosslinked resin was 0.07481 μmoles compared with the initial μmoles of 0.23167 as determined using atomic absorption spectrophotometer. Pb(II) adsorption was 33% in comparison to the initial Pb(II) amount in the waste water, which was quite low feature, making unreliable result.