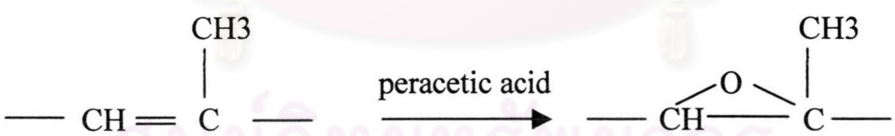
CHAPTER IV

RESULTS AND DISCUSSIONS

In this research, amine crosslinked membranes were prepared by reaction of neutralized epoxidised natural rubber latex (ENR) and amines. The compression molding was used for preparing the membranes. Then the compatibility of amine quantity, gel content, solvent swelling, temperature and compression time were determined. Also, the machanical properties of the membrane were investigated.

4.1 Characterization of epoxidised natural rubber (ENR)

25% and 50% Epoxidised natural rubber were obtained from a reaction between stabilized natural rubber latex and calculated amount peracetic acid (7.2% and 10% V/V of natural rubber, respectively). A reaction temperature of 20-25°C was maintained for 2.5 hours. The chemical equation of the reaction was represented as follows:



Scheme 4.1 The formation of epoxidesed natural rubber

Epoxidised natural rubber products were characterized by IR and NMR Spectroscopies and percentage of epoxidation of ENR was calculated from ^{1}HNMR.

4.1.1 ^{1}H-NMR spectra [10]

The ^{1}H-NMR spectra of natural rubber and ENR were determined in $CDCl_3$ as shown in Figure 4.1-4.3. The NMR spectrum showed the presence of a proton of the epoxide group at δ_H 2.68-2.69, methyl group adjacent to epoxide group at δ_H 1.28 [33]. The ^{1}H-NMR spectrum of epoxidised natural rubber is shown in Figure 4.1. The percentage of epoxidation of ENR was calculated using the equation

$$\text{mol \% epoxidation} = \frac{100 * [A_{2.70}]}{A_{5.14}+A_{2.70}}$$

From this equation, the calculation of 25% and 50% ENR as shown below

25% ENR, $A_{2.70} = 1.2114$

$A_{5.14} = 3.5889$

$$\text{mol \% epoxidation} = \frac{100 * [1.2114]}{3.5889+1.2114} = 25\%$$

50% ENR, $A_{2.70} = 2.7781$

$A_{5.14} = 2.8213$

$$\text{mol \% epoxidation} = \frac{100 * [2.7781]}{2.8213+2.7781} = 50\%$$

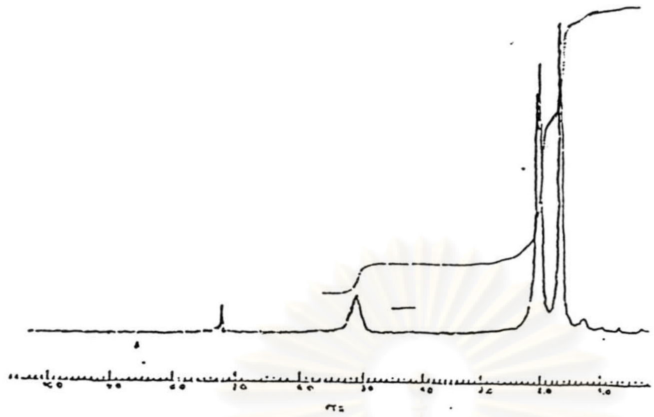


Figure 4.1 [1]H-NMR spectrum of natural rubber

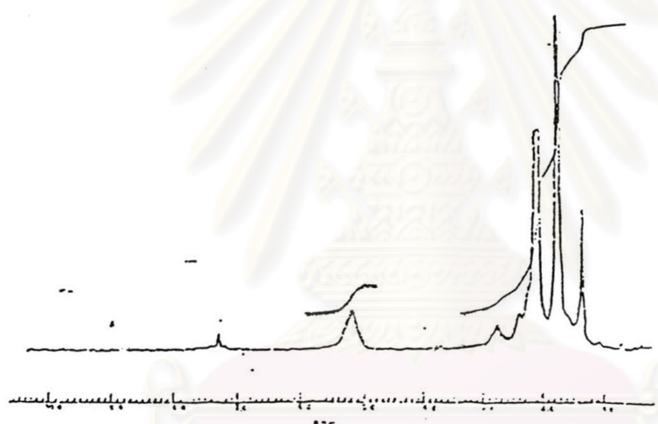


Figure 4.2 [1]H-NMR spectrum of 25% epoxidised natural rubber

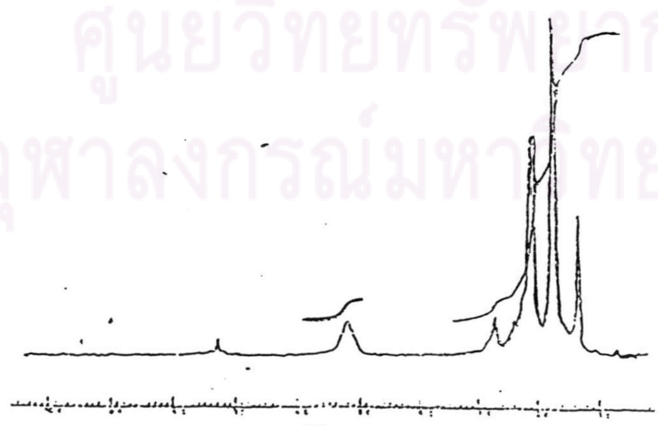


Figure 4.3 [1]H-NMR spectrum of 50% epoxidised natural rubber

4.1.2 Infrared spectra [10]

The IR spectra of epoxidised natural rubber and natural rubber are shown in Figure 4.4-4.6. Table 4.1 provides the important peaks and their assignments.

Table 4.1 Infrared spectral data of natural rubber and ENR

Vibration Assignments	Absorption Frequency (cm^{-1})	
	Natural rubber	ENR
cis-alkene (H-C=)	3040	3040
CH-aliphatic	2850-2965	2850-2965
C-O epoxy ring	-	875

From IR spectrum of ENR compared with natural rubber, the *cis*-alkene vibration of ENR at approximately 3040 cm^{-1} was decreased and indicated the presence of a specific epoxide band at 875 cm^{-1}.

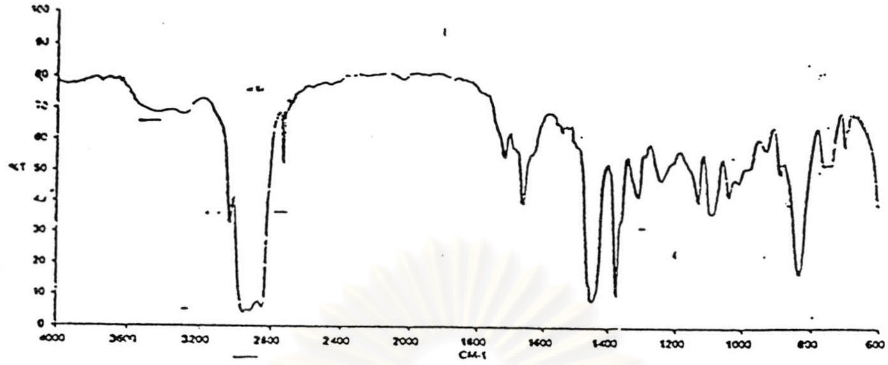


Figure 4.4 IR spectrum of natural rubber

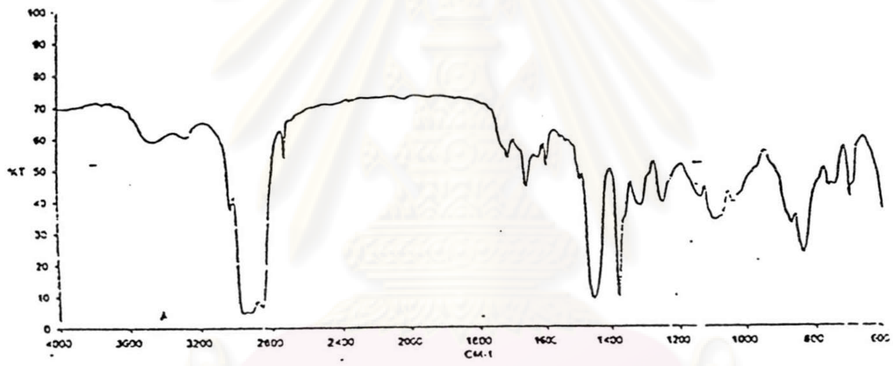


Figure 4.5 IR spectrum of 25% epoxidised natural rubber

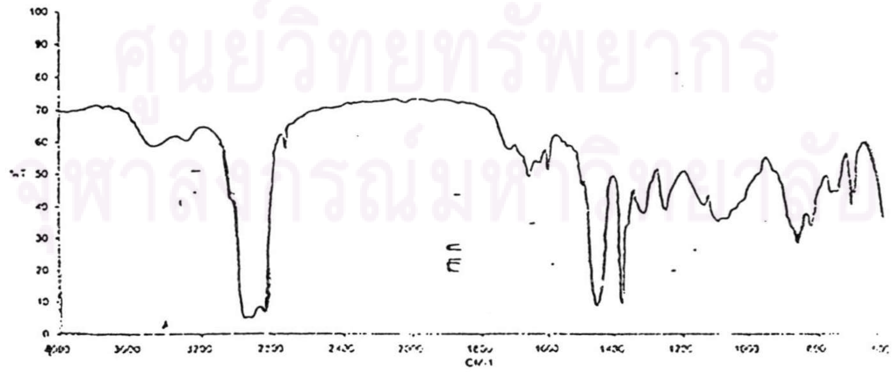


Figure 4.6 IR spectrum of 50% epoxidised natural rubber

4.2 Preparation of membrane

The membranes were prepared by reaction of 25% and 50% ENR with amines for investigating the effects of amine types, amines concentrations, curing times and curing temperatures on membrane properties including mechanical properties, solvent swelling and permeability. The *p*-phenylenediamine crosslinked epoxidised natural rubber was prepared using Hashim's method [30]. The *p*-phenylenediamine compounding rubbers were cured at 120 ^{o}C under 24 N/cm^2 for 30 min to give *p*-phenylenediamine cured rubber sheets. Two linear aliphatic amines, ethylenediamine and diethylenetriamine were used. Linear amine crosslinked epoxidised natural rubber were prepared using modified Lye's method [31]. All amine cured rubber sheets were subjected to characterize their properties cured results were discussed following.

4.2.1 Effect of various amines and amine concentration

In this experiment, ethylenediamine, diethylenetriamine and *p*-phenylenediamine were used. The effect of amine types and their concentrations were studied by varying the amine concentrations to 0, 1, 2, 3, 4 and 5 phr (part per hundred of rubber). The amine cured rubber sheets were prepared for studying the effect of amine and amine concentrations on mechanical properties and solvent swelling of amine crosslinked 25% and 50% ENR cured rubber sheets. Mechanical properties, including tensile strength, elongation and modulus and solvent swelling were determined. The results are shown in Table 4.2 and 4.3, respectively.

Table 4.2 The mechanical properties of amine cured ENR sheets with various amine concentrations.

Amine concentrations (phr)	Tensile strength (MPa)		Elongation (%)		Modulus 300% (MPa)	
	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR	Amine crosslinke 25% ENR	Amine crosslinke 50%ENR	Amine crosslinke 25% ENR	Amine crosslinked 50%ENR
Ethylenediamine [a]						
0%	7.41	7.44	938.8	949.5	0.8023	0.8018
1%	12.59	130.1	982.4	979.8	0.9975	0.998
2%	14.12	14.53	974.3	970.3	1.0916	1.092
3%	15.43	15.64	964	969.1	1.0984	1.0984
4%	14.01	14.29	981.7	972	1.1149	1.1289
5%	13.28	13.4	988.5	971.2	1.2771	1.2841
Diethylenetriamine [b]						
0%	7.41	7.44	938.8	949.5	0.8023	0.8018
1%	13.18	13.58	985.1	974.3	0.9975	0.9978
2%	14.38	14.93	975.3	968.5	1.0923	1.093
3%	15.59	15.89	962.4	956.1	1.0991	1.1002
4%	14.1	14.38	979.8	967.1	1.1189	1.1293
5%	13.61	13.72	983	969.8	1.254	1.2561
p-phenylenediamine [c]						
0%	7.41	7.44	938.8	949.5	0.8023	0.8018
1%	13.63	14.02	978.1	973.8	0.9981	0.9993
2%	14.74	15.44	989	966	1.0934	1.0958
3%	16.01	16.38	955.4	953.2	1.0996	1.125
4%	14.22	14.71	968.2	964.6	1.1289	1.1295
5%	13.57	13.92	973.5	967.5	1.1421	1.261

Note:

[a] The membranes were cured at 105 °C for 10 min under 24 N/cm^2.

[b] The membranes were cured at 110 °C for 10 min under 24 N/cm^2.

[c] The membranes were cured at 120 °C for 10 min under 24 N/cm^2.

Table 4.3 The solvent swelling of amine cured ENR sheets with various amine concentrations.

Amine concentrations (phr)	Solvent swelling (%)									
	Hexane		$CHCl_3$		EtOH		Acetone		Toluene	
	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR
Ethylenediamine [a]										
0%	642.86	634.21	450.23	447.83	261.33	250.02	331.02	315.72	674.58	656.03
1%	593.57	579.64	517.48	492.61	334.45	288.3	362.15	332.05	501.24	502.43
2%	540.32	531.47	530.27	522.85	342.16	294.43	375.62	359.14	497.83	483.44
3%	490.01	481.25	538.14	533.05	364.43	331.02	384.16	367.13	486.94	470.15
4%	482.53	463.46	544.06	540.26	376.21	354.41	388.47	374.13	475.71	458.74
5%	479.78	438.71	548.63	542.06	380.45	360.11	394.52	390.42	469.95	442.8
Diethylenetriamine [b]										
0%	642.86	634.21	450.23	447.83	261.33	250.02	331.02	315.72	674.58	656.03
1%	591.5	574.35	503.14	471.08	274.54	269.31	319.55	314.9	498.29	487.32
2%	529.61	531.06	514.38	493.55	288.35	276.43	324.58	321.84	472.1	461.05
3%	483.52	490.33	525.04	524.66	302.89	288.67	341.06	336.44	461.92	450.78
4%	451.03	450.98	528.27	527.41	334.51	294.53	355.29	341.29	440.3	435.94
5%	429.81	421.69	533.48	530.34	341.05	311.03	368.1	359.41	421.59	401.2
p-phenylenediamine [c]										
0%	642.86	634.21	450.23	447.83	261.33	250.02	331.02	315.72	674.58	656.03
1%	551.45	512.3	463.48	459.51	254.82	252.32	310.8	308.94	461.54	454.89
2%	496.88	461.47	477.41	463.2	262.03	258.47	317.48	315.87	435.11	424.58
3%	412.51	400.14	497.52	472.14	274.94	264.58	326.41	320.04	419.94	407.61
4%	390.67	374.82	506.16	477.53	279.83	269.84	334.07	326.85	388.65	391.93
5%	385.24	368.7	511.48	481.24	286.55	274.64	346.5	334.15	379.92	387.72

Note:

[a] The membranes were cured at 105 °C for 10 min under 24 N/cm^2.

[b] The membranes were cured at 110 °C for 10 min under 24 N/cm^2.

[c] The membranes were cured at 120 °C for 10 min under 24 N/cm^2.

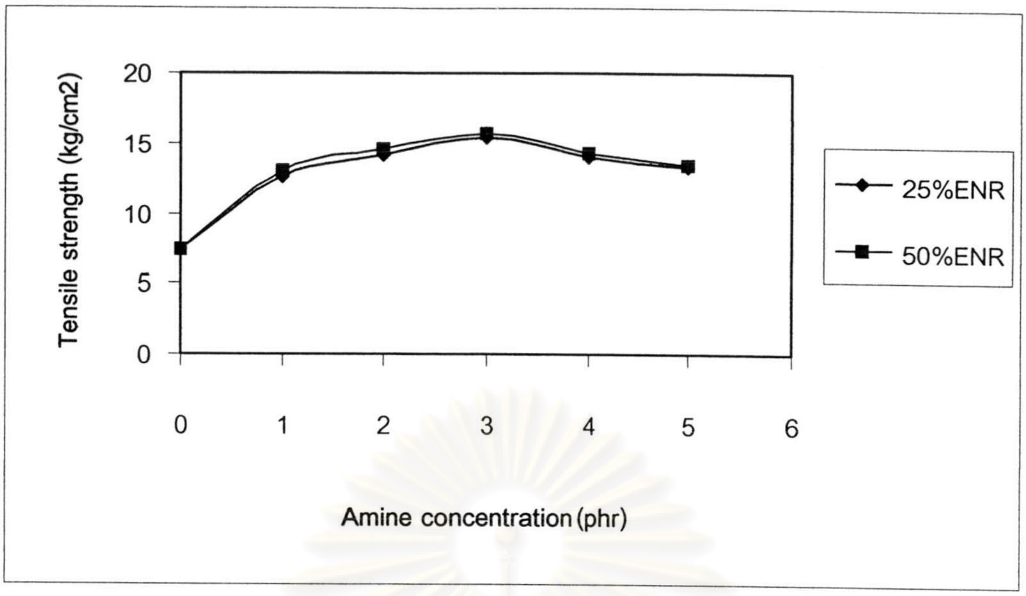


Fig 4.7 Tensile strength of the ethylenediamine crosslinked 25% and 50% ENR

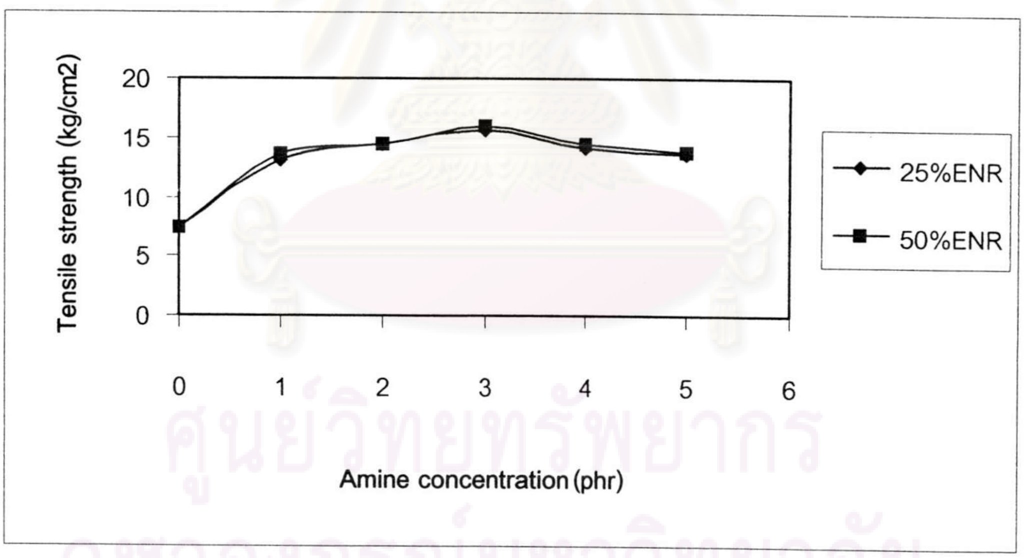


Fig 4.8 Tensile strength of the diethylenetriamine crosslinked 25% and 50% ENR

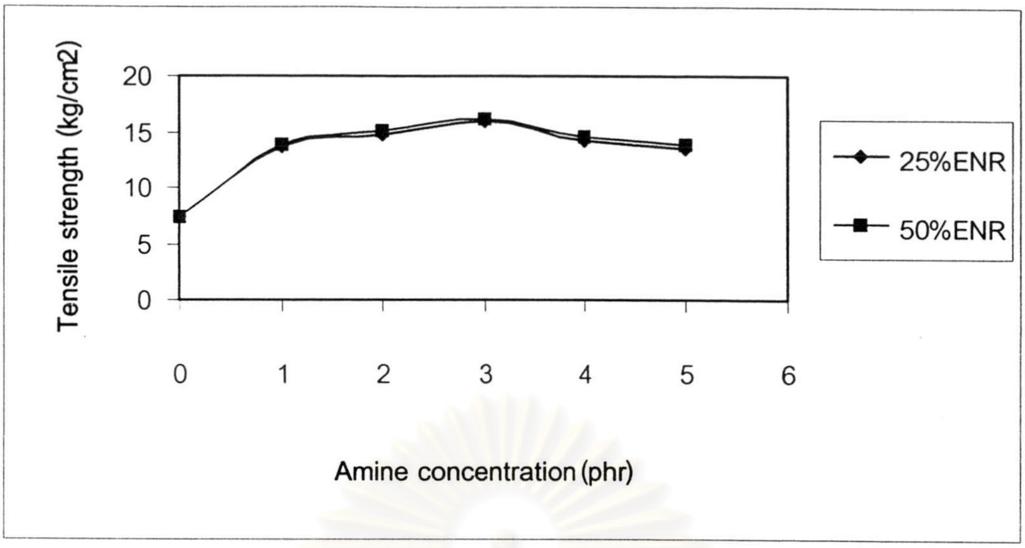


Fig 4.9 Tensile strength of the *p*-phenylenediamine crosslinked 25% and 50% ENR

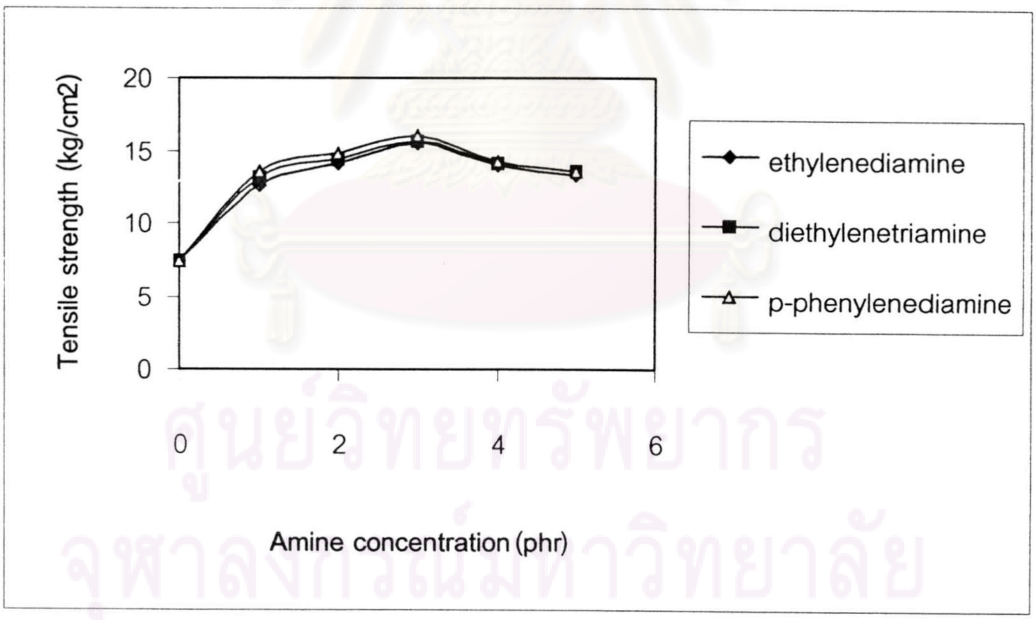


Fig 4.10 Tensile strength of the amine crosslinked 25% ENR

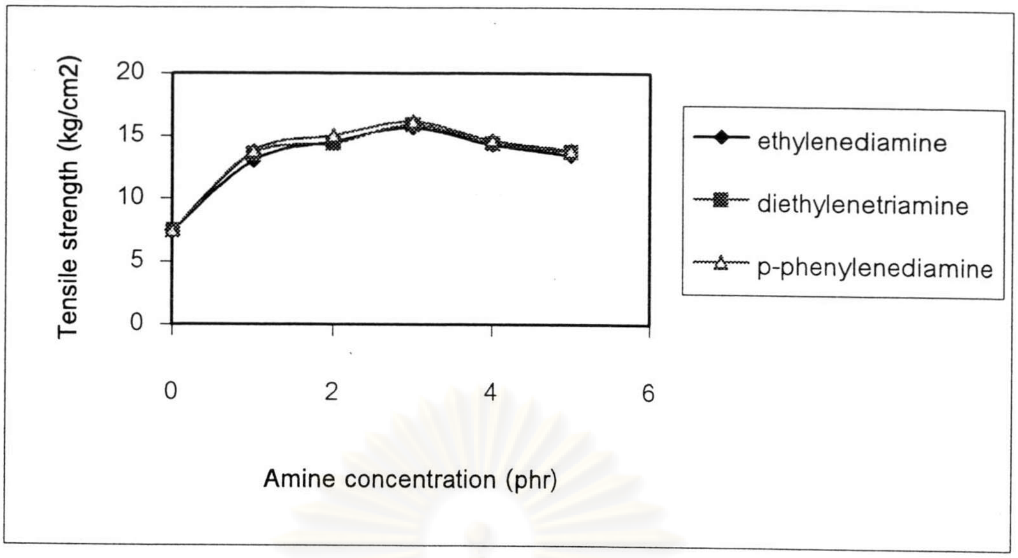


Fig 4.11 Tensile strength of the amine crosslinked 50% ENR

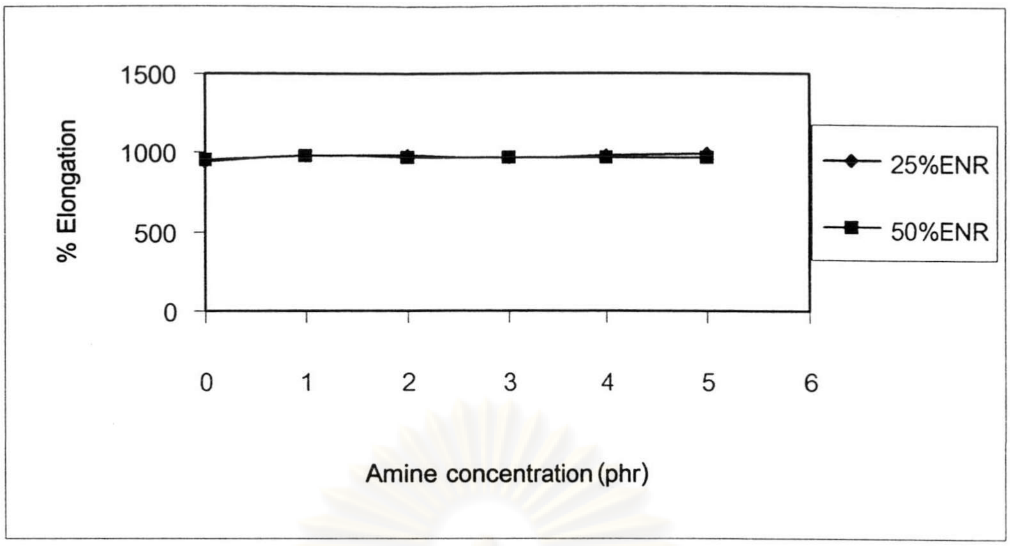


Fig 4.12 % Elongation of the ethylenediamine crosslinked 25% and 50% ENR

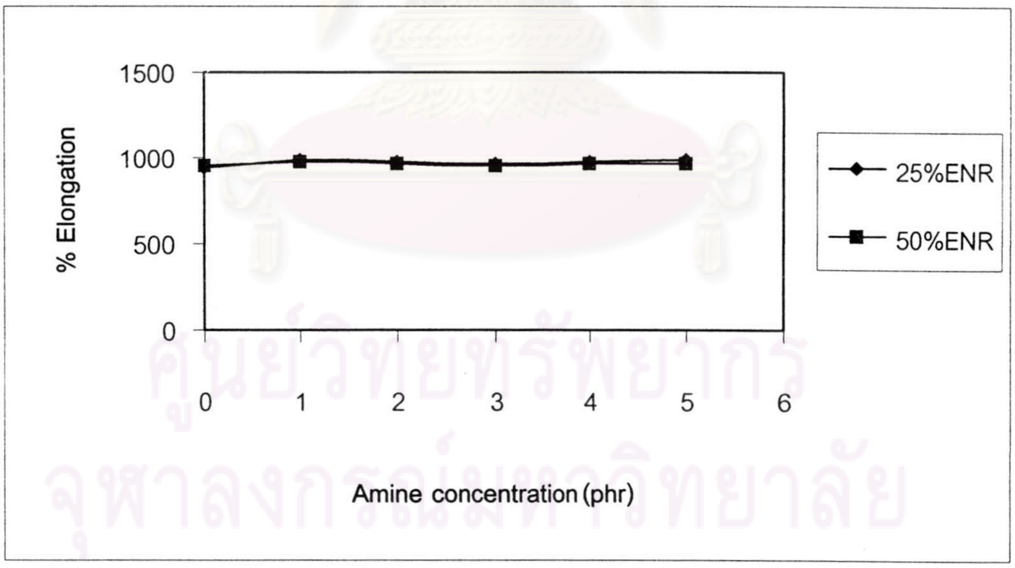


Fig 4.13 % Elongation of the diethylenetriamine crosslinked 25% and 50% ENR

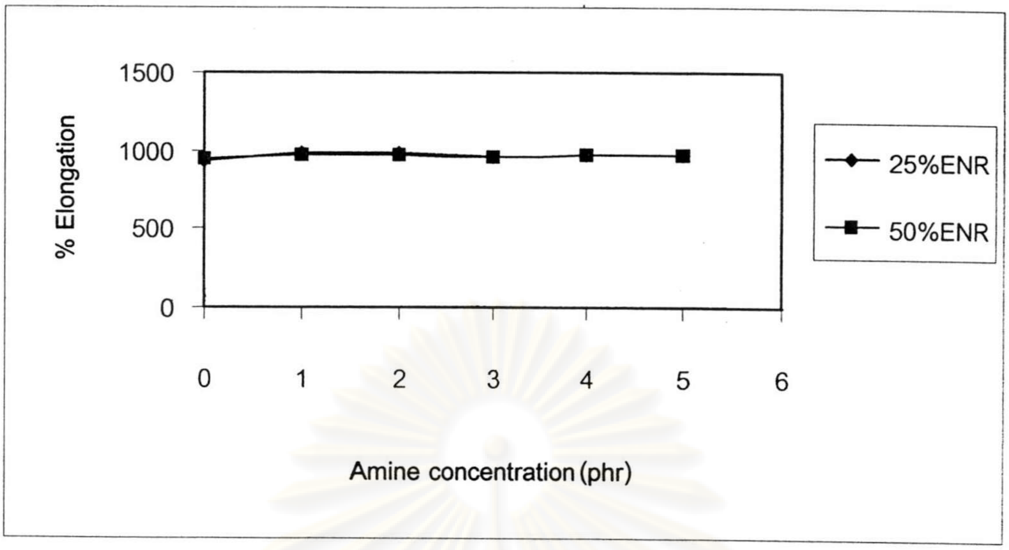


Fig 4.14 % Elongation of the *p*-phenylenediamine crosslinked 25% and 50% ENR

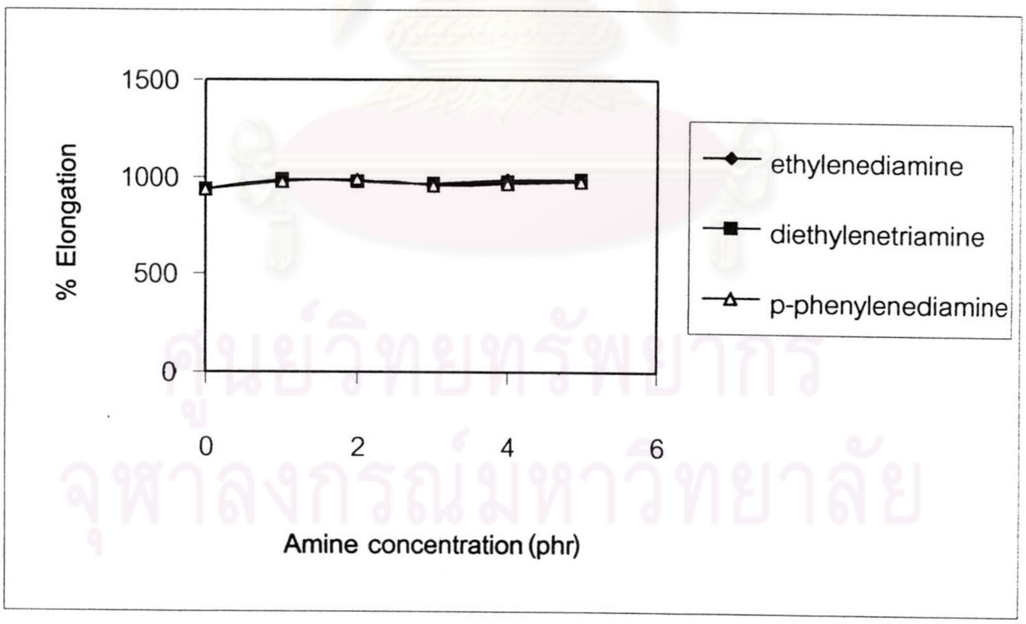


Fig 4.15 % Elongation of the amine crosslinked 25% ENR

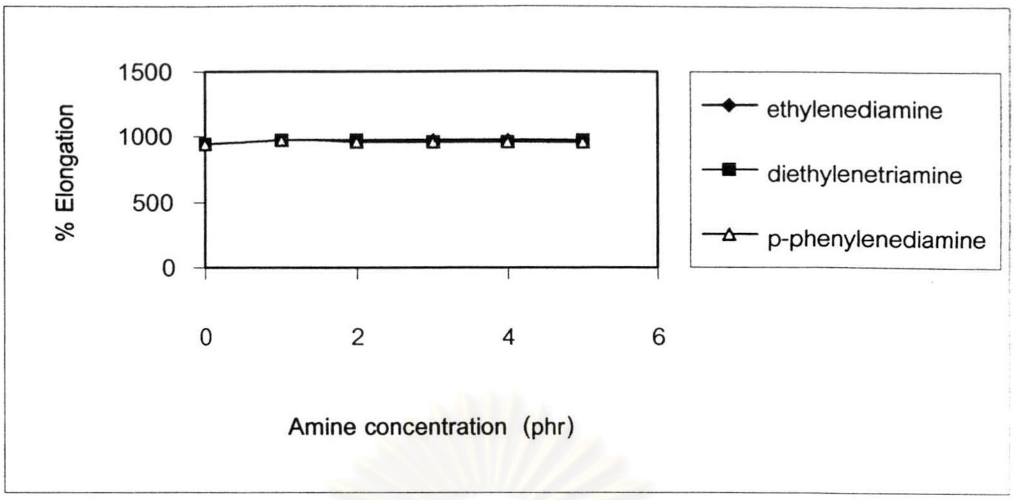


Fig 4.16 % Elongation of the amine crosslinked 50% ENR

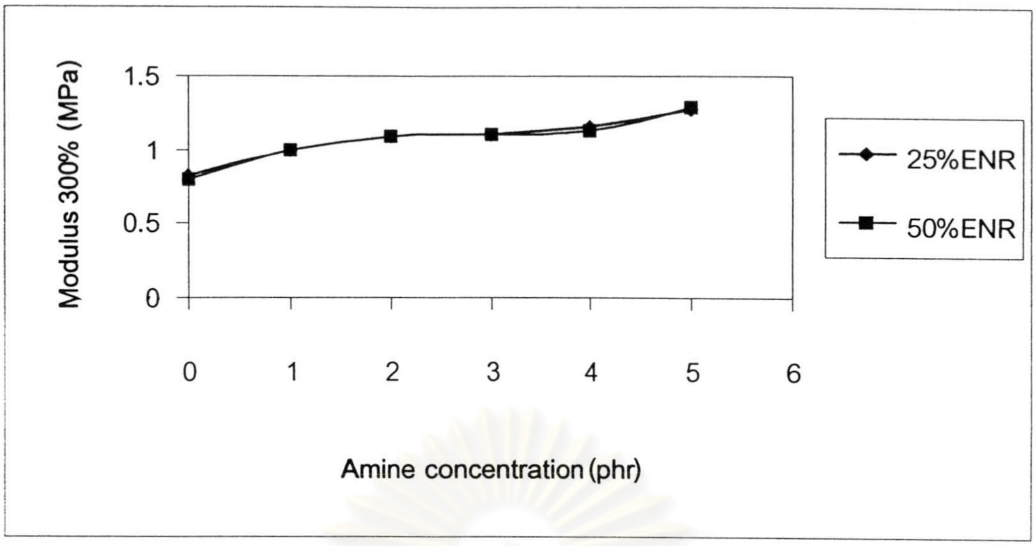


Fig 4.17 Modulus 300% of ethylenediamine crosslinked 25% and 50% ENR

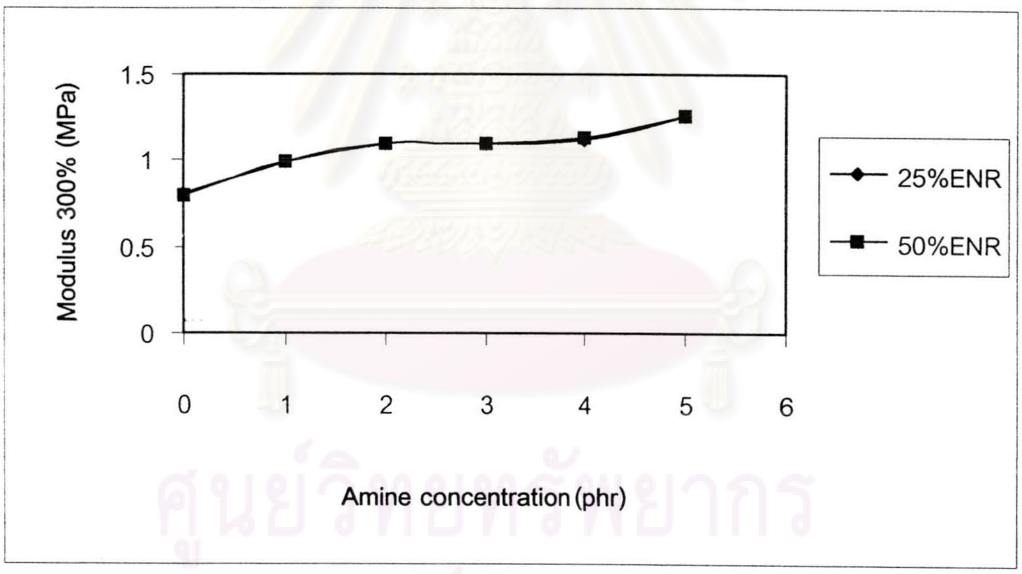


Fig 4.18 Modulus 300% of the diethylenetriamine crosslinked 25% and 50% ENR

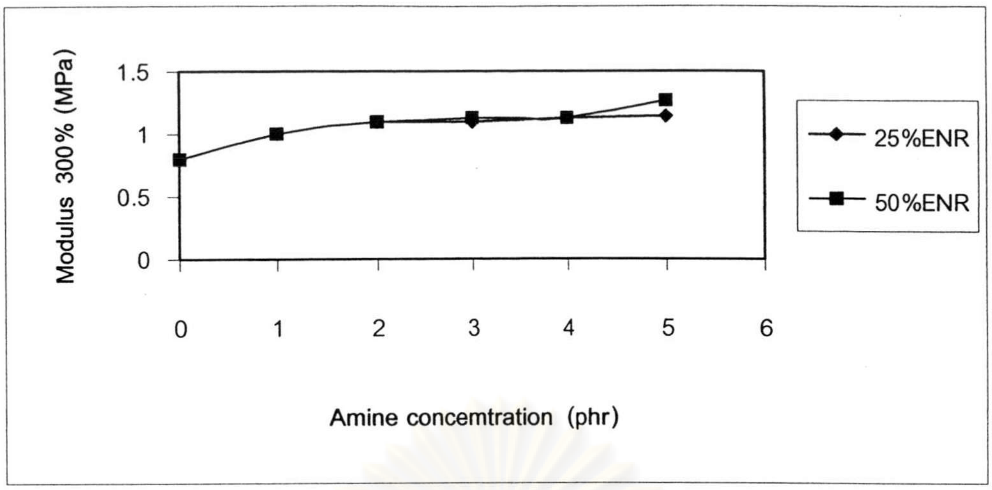


Fig 4.19 Modulus 300% of the *p*-phenylenediamine crosslinked 25% and 50% ENR

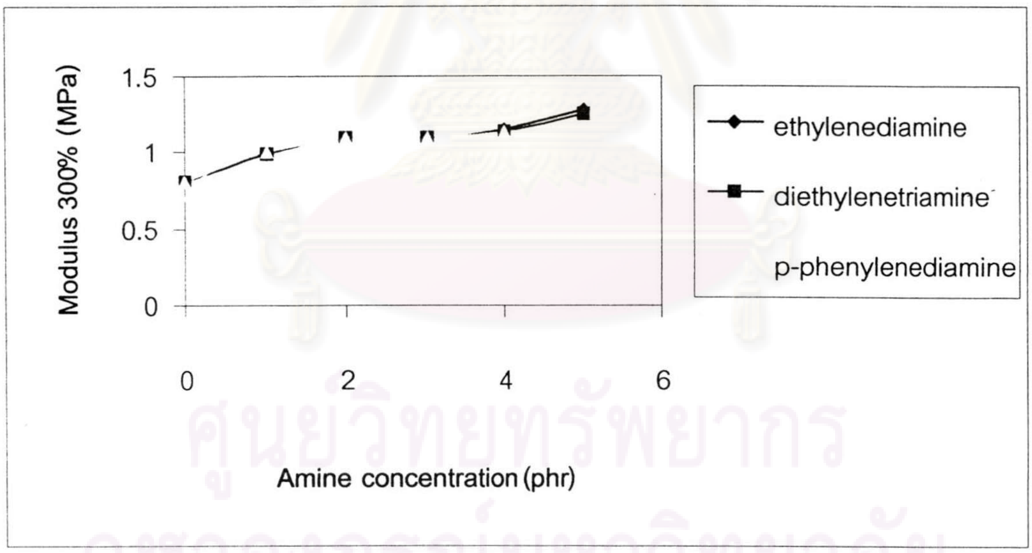


Fig 4.20 Modulus 300% of the amine crosslinked 25% ENR

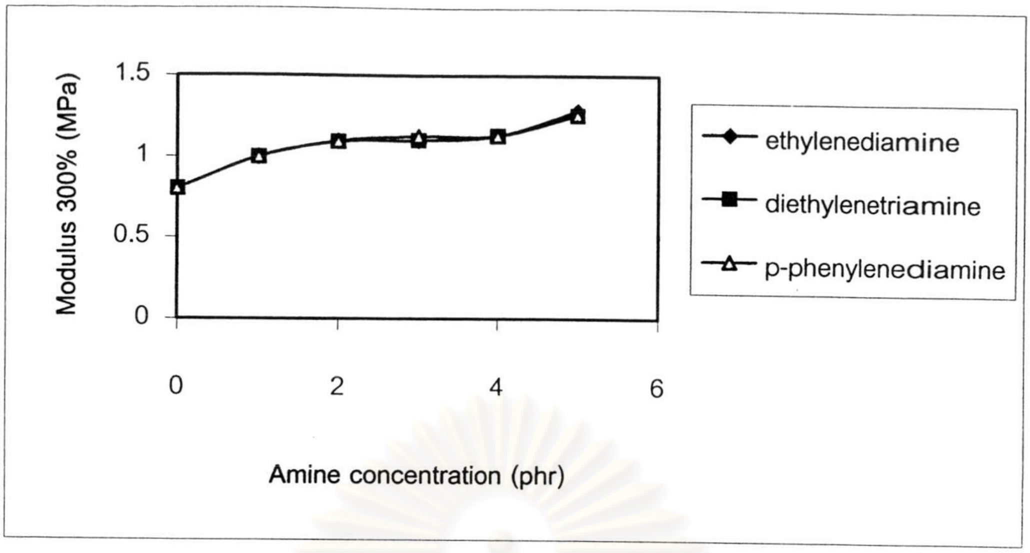


Fig 4.21 Modulus 300% of the amine crosslinked 50% ENR

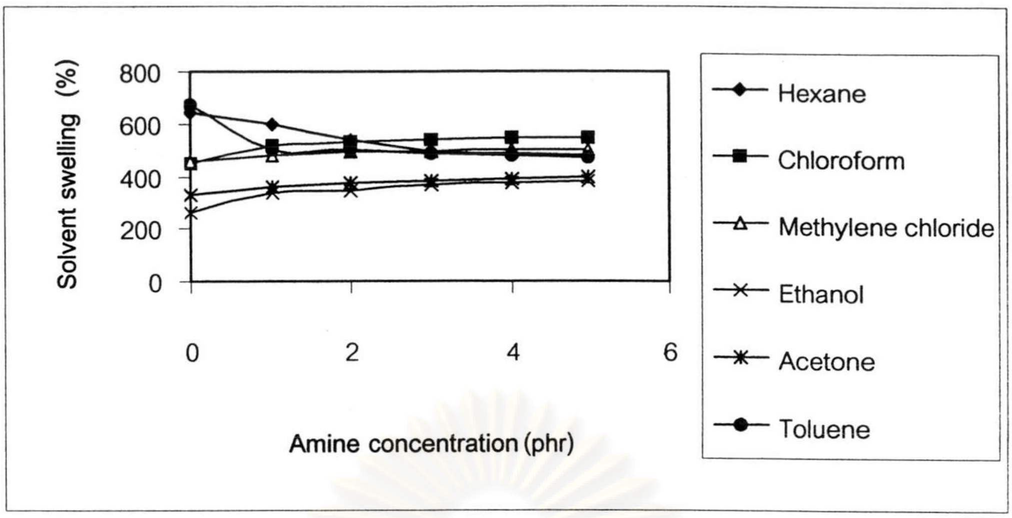


Fig 4.22 Solvent swelling of the ethylenediamine crosslinked 25% ENR in toluene

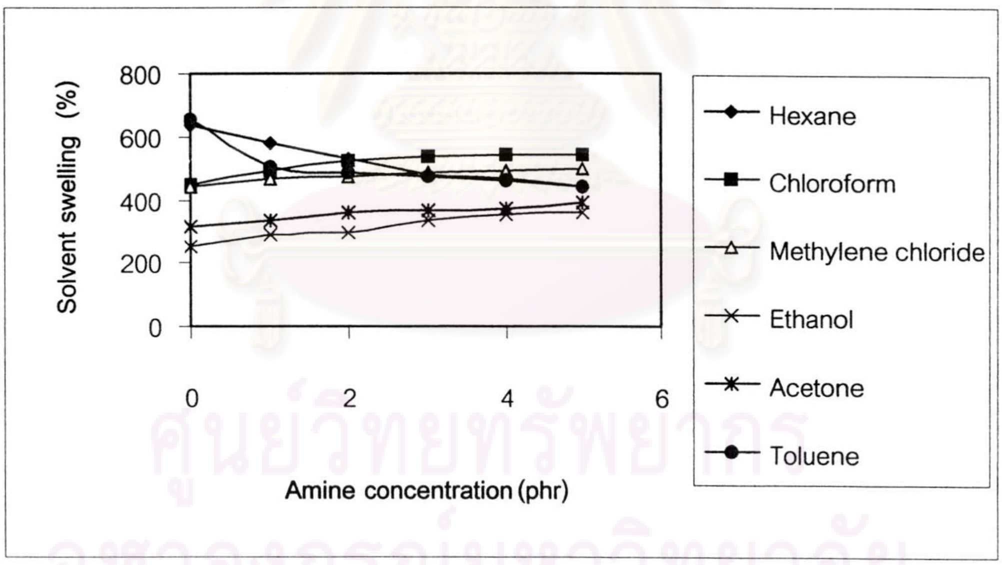


Fig 4.23 Solvent swelling of the ethylenediamine crosslinked 50% ENR in toluene

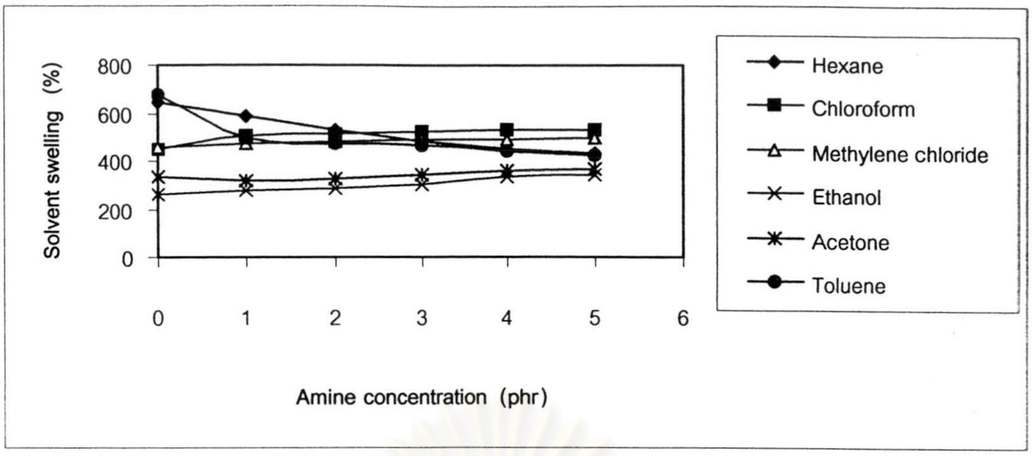


Fig 4.24 Solvent swelling of the diethylenetriamine crosslinked 25% ENR in toluene

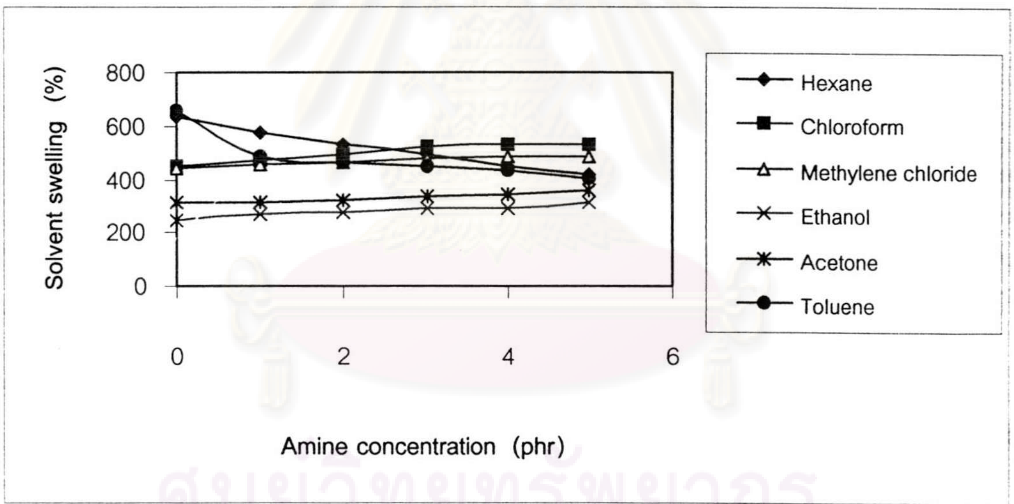


Fig 4.25 Solvent swelling of the diethylenetriamine crosslinked 50% ENR in toluene

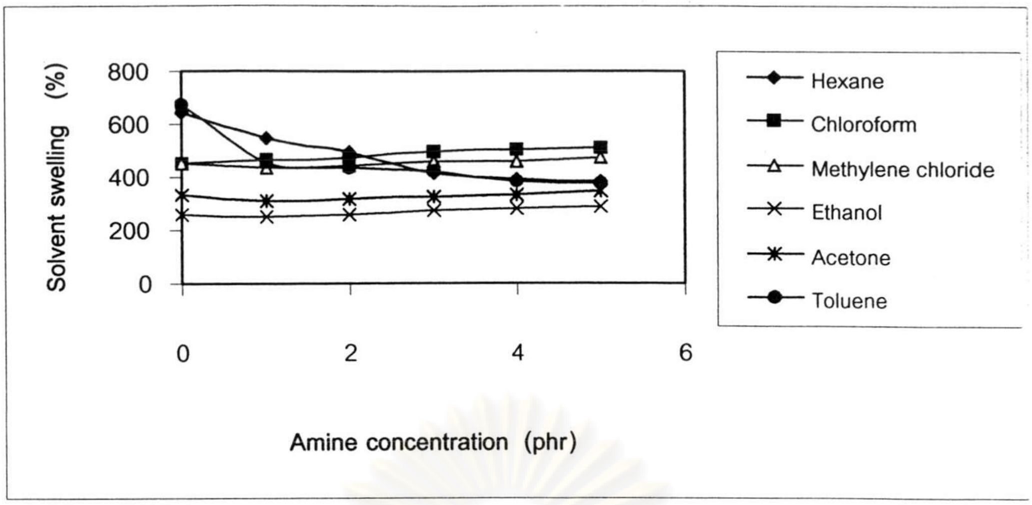


Fig 4.26 Solvent swelling of the *p*-phenylenediamine crosslinked 25% ENR in toluene

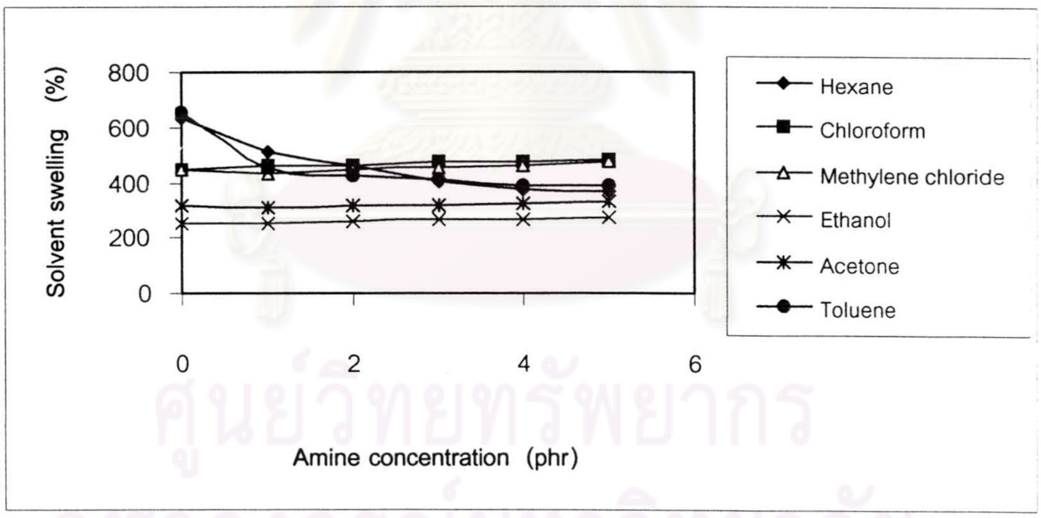


Fig 4.27 Solvent swelling of the *p*-phenylenediamine crosslinked 50% ENR in toluene

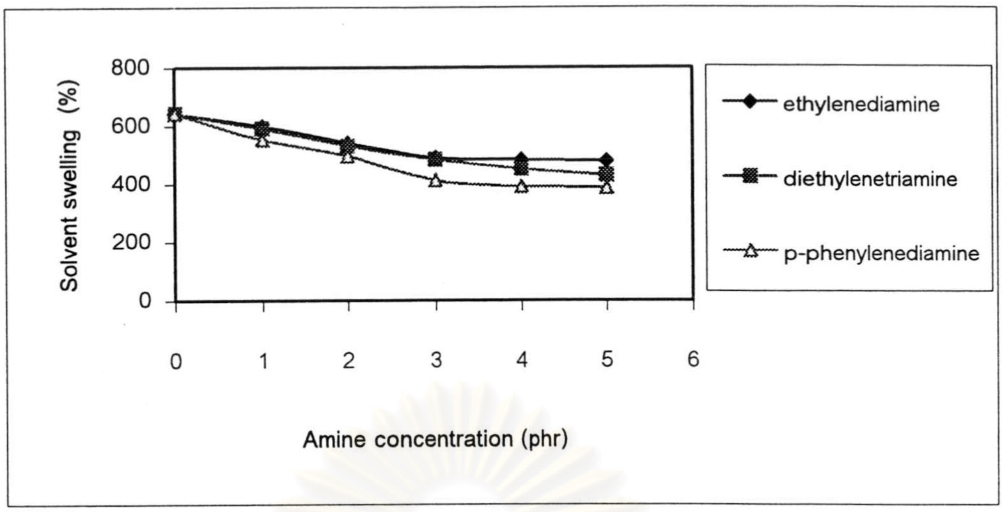


Fig 4.28 Solvent swelling of the amine crosslinked 25% ENR in ethanol

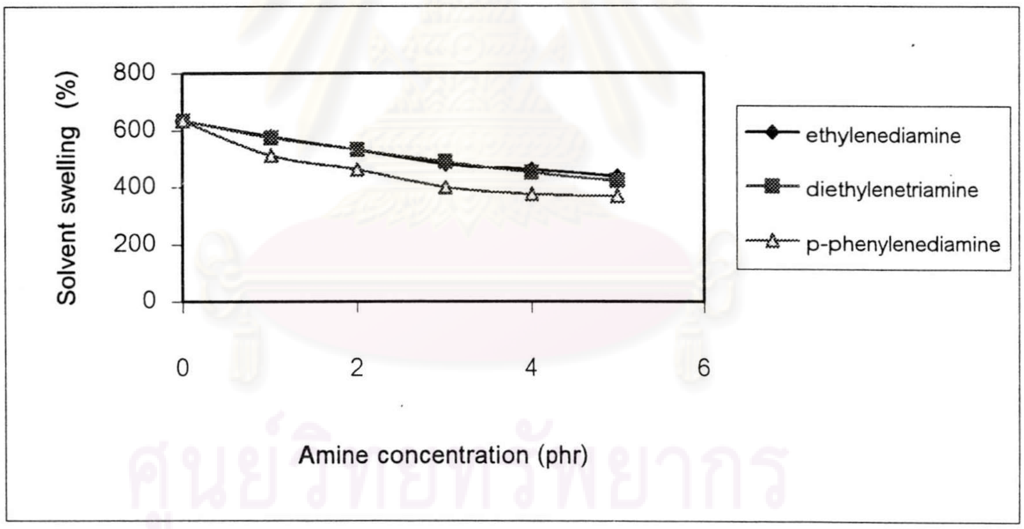


Fig 4.29 Solvent swelling of the amine crosslinked 50% ENR in ethanol

Figures 4.7-4.11 illustrated the effect of ethylenediamine, diethylenetriamine and *p*-phenylenediamine concentration on the tensile strength of amine cured rubber sheets. It was found that when ethylenediamine, diethylenetriamine and *p*-phenylenediamine contration were at 1 phr the tensile strength rapidly increased to about 14 MPa and when amine concentration of three amines was at 3 phr gave highest tensile strength. The amine concentration of more than 3 phr caused the slightly decreased tensile strength due to the increasing of amine concentration in the compounding system may affect gel formation and structure of crosslinked rubber sheet.

The effect of amines concentration on the elongation of the amine cured 25% and 50% ENR sheets are presented in Figures 4.12-4.16. The elongation significantly at the concentration of ethylenediamine, diethylenetriamine and *p*-phenylenediamine between 0-5 phr were approximately 1000.

The modulus 300% were studied. The results are shown in Figure4.17-4.20. It was found that increasing amine concentration resulted in slightly increase of the modulus 300% until 3 phr of amine concentration. These should the efficiency of amines in crosslinking which caused increasing the stiffness of the amine cured ENR.

The mechanical properties of amine cured rubber membranes were investigated in various amine concentrations. The amines could improve the mechanical properties of the amine cured rubber membrane in a limited range of amine concentrations. The optimum ethylenediamine, diethylenetriamine and *p*-phenylenediamine concentration were 3 phr which the highest mechanical properties for the membranes.

The solvent swelling of the amine crosslinked membrane in non-polar solvent (hexane and toluene) showed that increasing of amine concentration resulted in decreasing of the swelling of the membrane. In contrast, the solvent swelling in polar solvent was increased when increased amine concentration. The swelling of the membrane in EtOH and acetone was slightly increased while the membrane could swell in $CHCl_3$ and CH_2Cl_2 more than in other solvent. Additionally, ethylenediamine crosslinked ENR membrane was the highest percent solvent swelling in $CHCl_3$ and the solvent swelling of this membrane was nearly constant at the amine concentration of more than 3 phr.

4.2.2 Effect of curing time

The curing time of the membrane was another important factor. Usually the production property depends on a period of curing time. In this work, the curing time for preparing the membrane was investigated using 3 phr of the amine concentration, 105 °C for ethylenediamine, 110 °C for diethylenetriamine and 120 °C for *p*-phenylenediamine by varying the curing time to 5, 10, 15 and 20 minutes.

The mechanical properties of the amine cured rubber sheets were observed to obtain the appropriate time for membranes. Tables 4.4-4.5 illustrate the effect of curing time on the mechanical properties of the amine cured rubber membranes.

Table 4.4 The mechanical properties of amine cured ENR sheets with various curing times [a]

Curing Time	Tensilt strength (MPa)		Elongation (%)		Modulus (MPa)	
(min)	25% ENR	50%ENR	25% ENR	50%ENR	25% ENR	50%ENR
Ethylenediamine [b]						
5	13.87	13.98	991.2	988.1	1.097	1.0972
10	15.43	15 .64	980.5	979.8	1.0984	1.0984
15	15.42	15.69	982	977.9	1.099	1.0989
20	14.78	15.74	985.4	977	1.0993	1.0991
25	14.61	15.8	987.9	976.8	1.0998	1.0995
Diethylenetriamine [c]						
5	13.99	14.03	990.5	987.4	1.0974	1.098
10	14.64	14.7	987.2	984.8	1.098	1.0997
15	15.59	15.89	985.1	974.3	1.0991	1.1002
20	15.63	15.93	984.8	971	1.0994	1.1012
25	15.67	15.99	984.2	966 .5	1.0999	1.1022
p-phenylenediamine [d]						
5	14.59	14.63	993.2	989.1	1.0979	1.1076
10	15.80	15.92	978.1	973.8	1.0996	1.125
15	16.24	16.38	975.4	97 1.2	1.091	1.1281
20	16.35	16. 42	974.8	9 68.7	1.0913	1.1288
25	16.41	16.49	974	960	1.0917	1.1295

Note:

[a] all membranes were contained 3 phr of amine.

[b] The membranes were cured at 105 °C under 24 N/cm^2.

[c] The membranes were cured at 110 °C under 24 N/cm^2.

[d] The membranes were cured at 120 °C under 24 N/cm^2.

Table 4.5 The solvent swelling of amine cured rubber sheets with various curing times[a]

Curing Time (min)	Solvent swelling (%)			
	$CHCl_3$		EtOH	
	25% ENR	50%ENR	25% ENR	50%ENR
Ethylenediamine[b]				
5	584.06	576.26	365.21	348.41
10	500.14	516.05	331.45	328.3
15	513.27	510.85	324.16	320.43
20	508.48	504.61	320.45	314.3
25	500.23	499.83	317.33	306.02
Diethylenetriamine[c]				
5	554.27	542.41	334.51	314.53
10	500.04	471.66	274.54	263.67
15	487.38	453.55	265.35	256.43
20	480.14	449.8	258.54	248.67
25	476.23	445.83	250.53	242.02
p-phenylenediamine[d]				
5	528.16	526.53	295.83	289.84
10	498.52	482.14	258.61	268.58
15	450.41	438.2	202.35	198.52
20	445.44	429.51	198.01	194.58
25	443.23	427.53	192.47	190.84

Note:

[a] all membranes were contained 3 phr of amine.

[b] The membranes were cured at 105 °C under 24 N/cm^2.

[c] The membranes were cured at 110 °C under 24 N/cm^2.

[d] The membranes were cured at 120 °C under 24 N/cm^2.

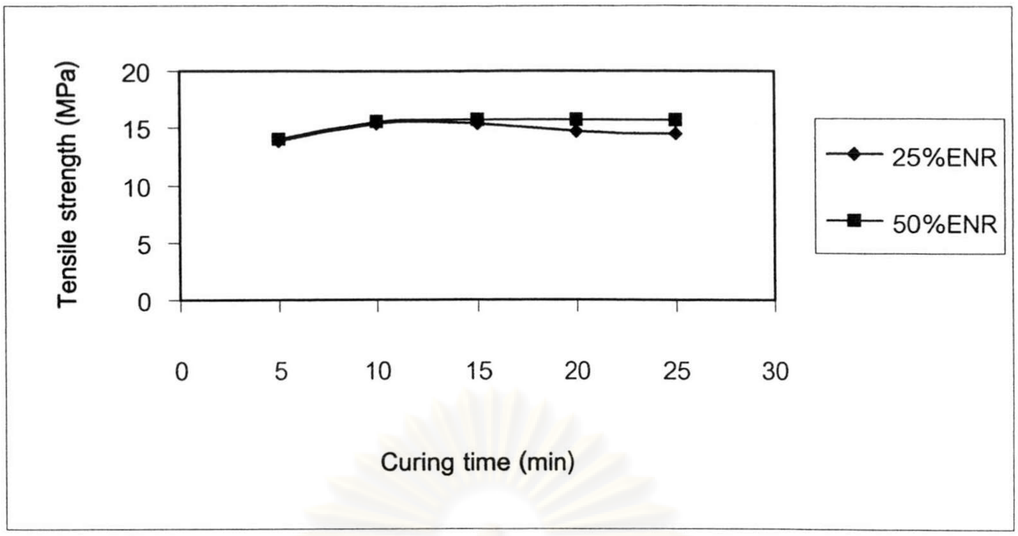


Fig 4.30 Tensile strength of the ethylenediamine crosslinked 25% and 50% ENR

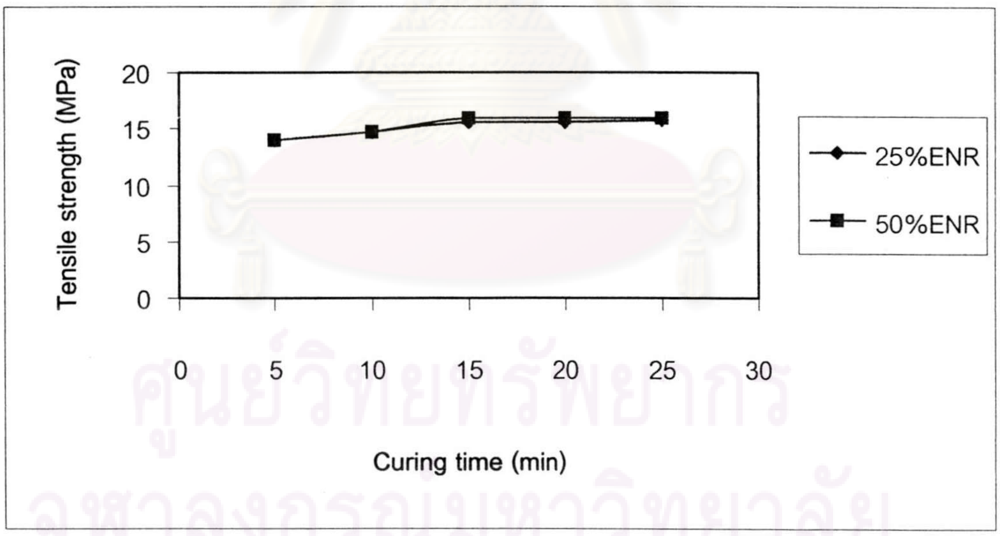


Fig 4.31 Tensile strength of the diethylenetriamine crosslinked 25% and 50% ENR

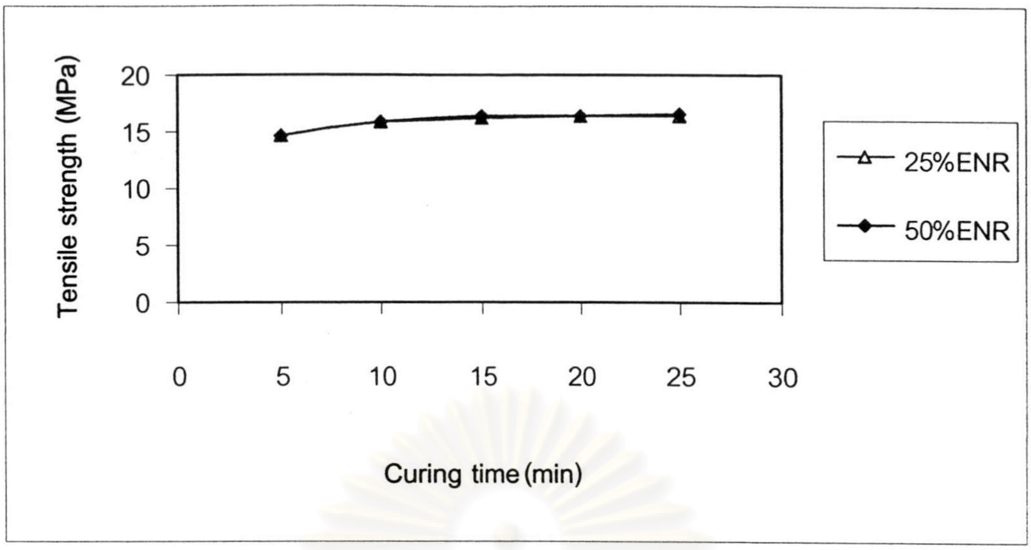


Fig 4.32 Tensile strength of the *p*- phenylenediamine crosslinked 25% and 50% ENR

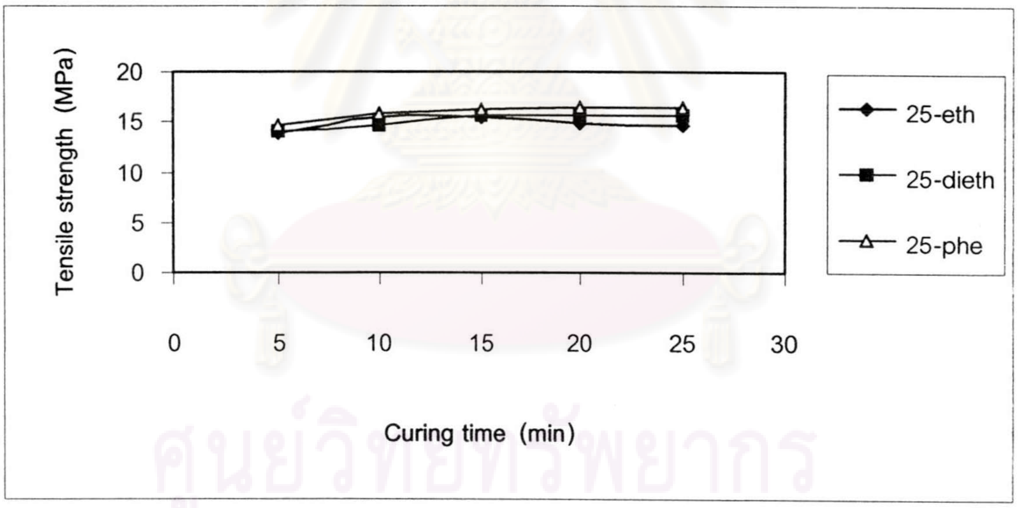


Fig 4.33 Tensile strength of the amine crosslinked 25% ENR

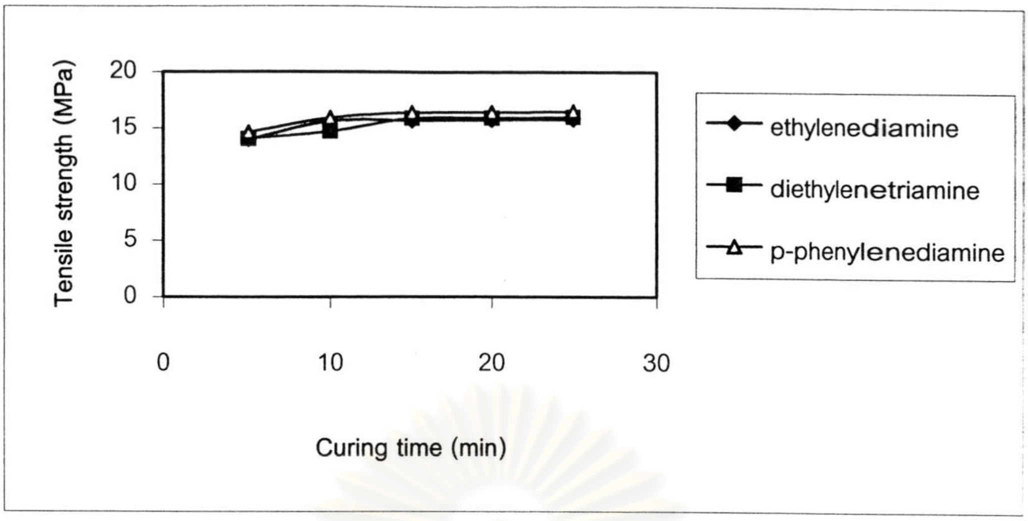


Fig 4.34 Tensile strength of the amine crosslinked 50% ENR

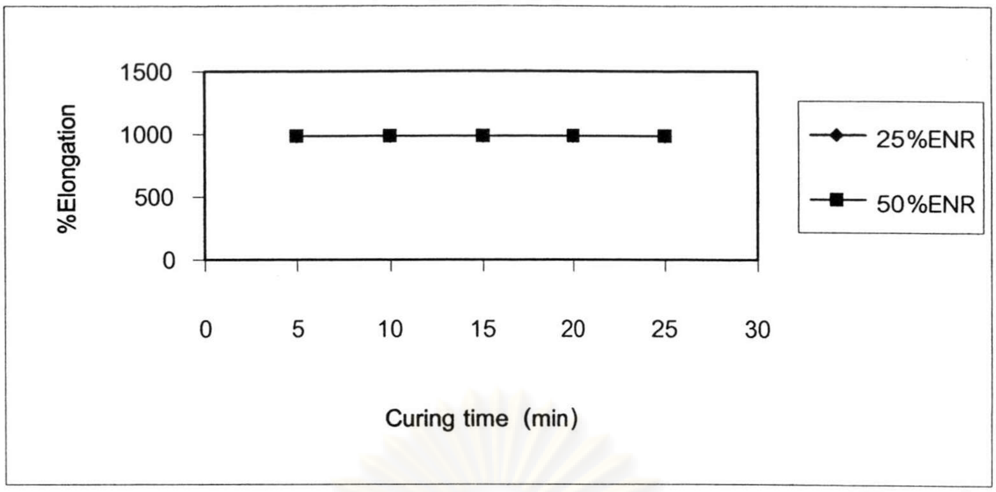


Fig 4.35 % Elongation of the ethylenediamine crosslinked 25% and 50% ENR

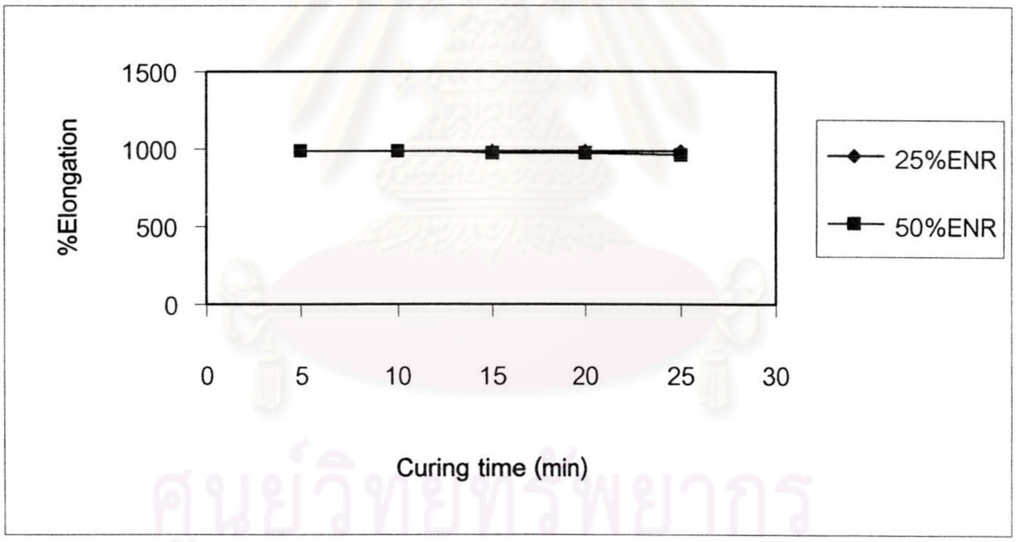


Fig 4.36 % Elongation of the diethylenetriamine crosslinked 25% and 50% ENR

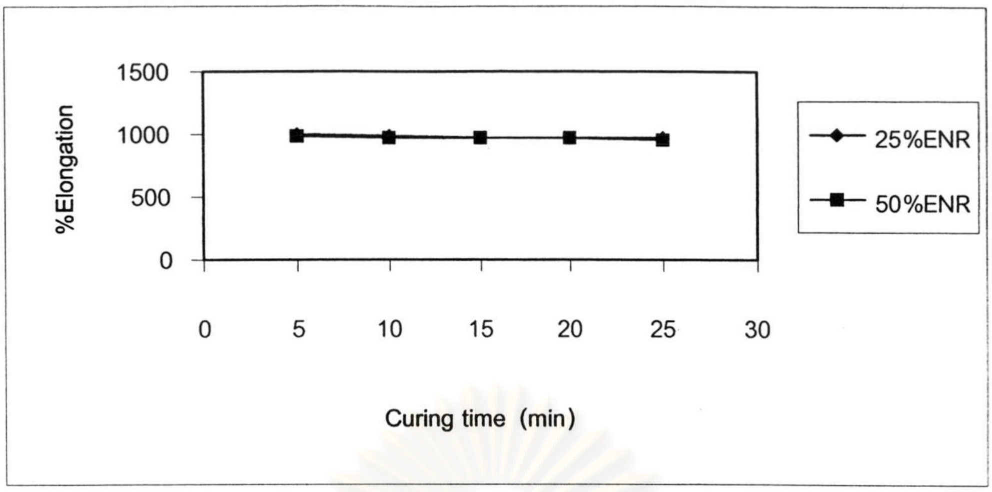


Fig 4.37 % Elongation of the *p*-phenylenediamine crosslinked 25% and 50% ENR

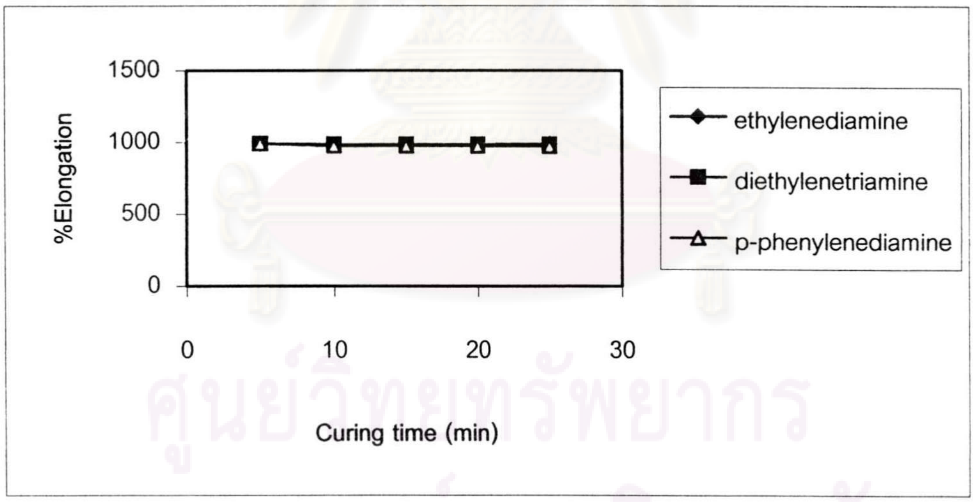


Fig 4.38 % Elongation of the amine crosslinked 25% ENR

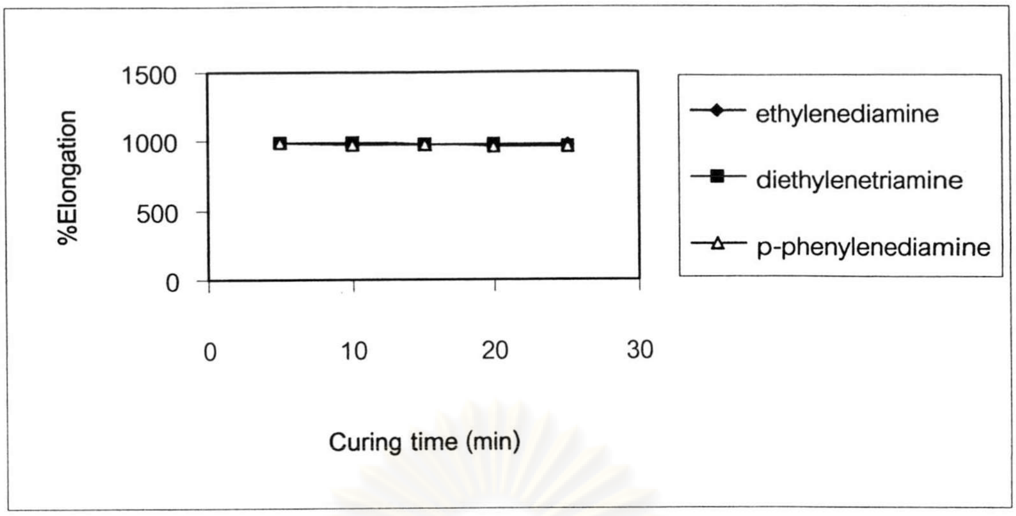


Fig 4.39 % Elongation of the amine crosslinked 50% ENR

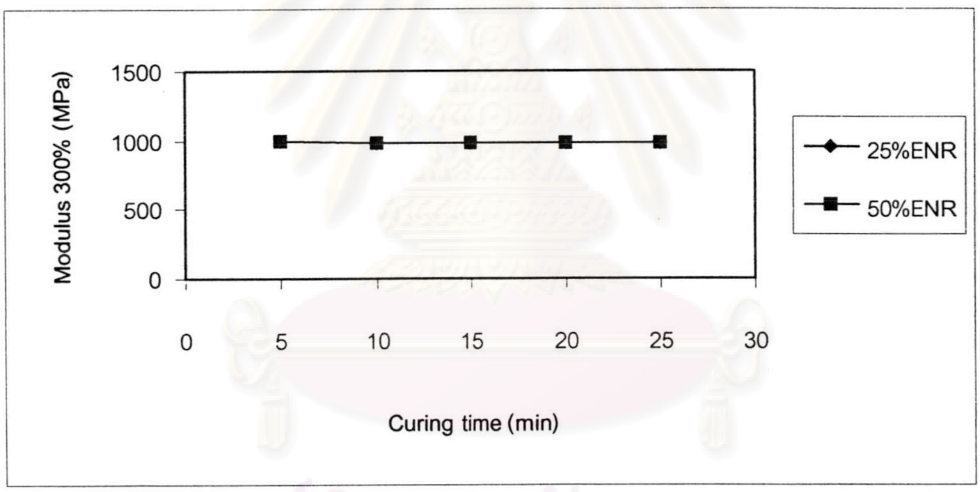


Fig 4.40 Modulus 300% of the ethylenediamine crosslinked 25% and 50% ENR

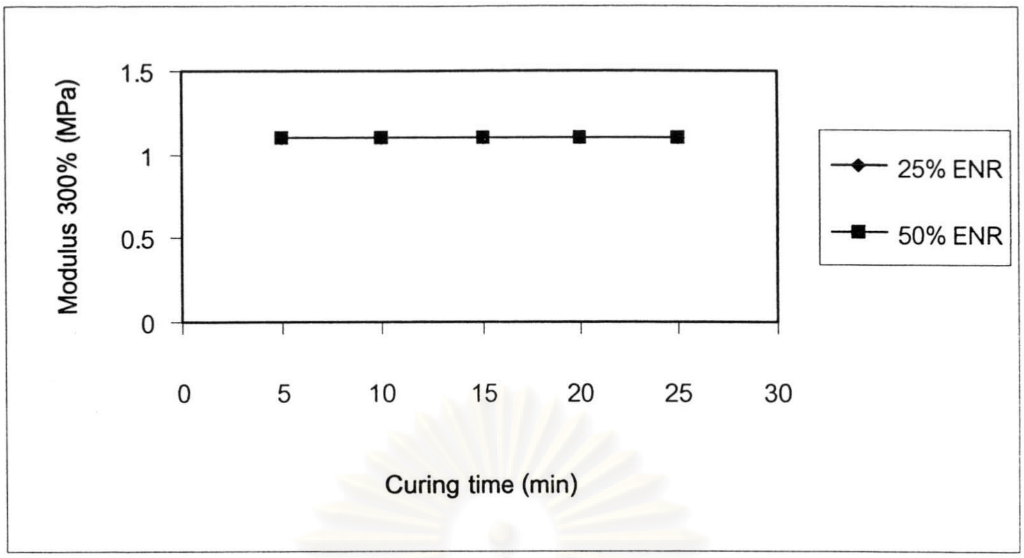


Fig 4.41 Modulus 300% of the diethylenetriamine crosslinked 25% and 50% ENR

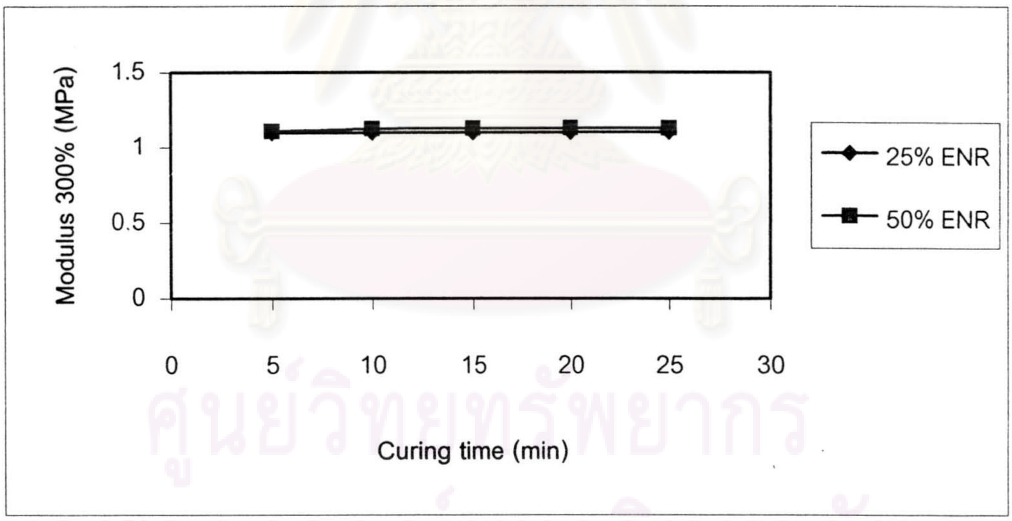


Fig 4.42 Modulus 300% of the *p*-phenylenediamine crosslinked 25% and 50% ENR

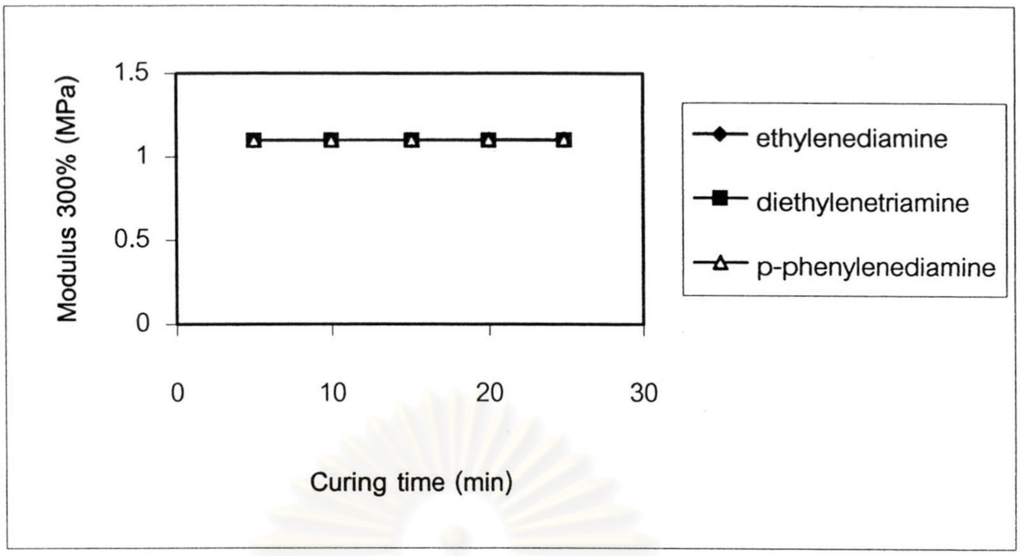


Fig 4.43 Modulus 300% of the amine crosslinked 25% ENR

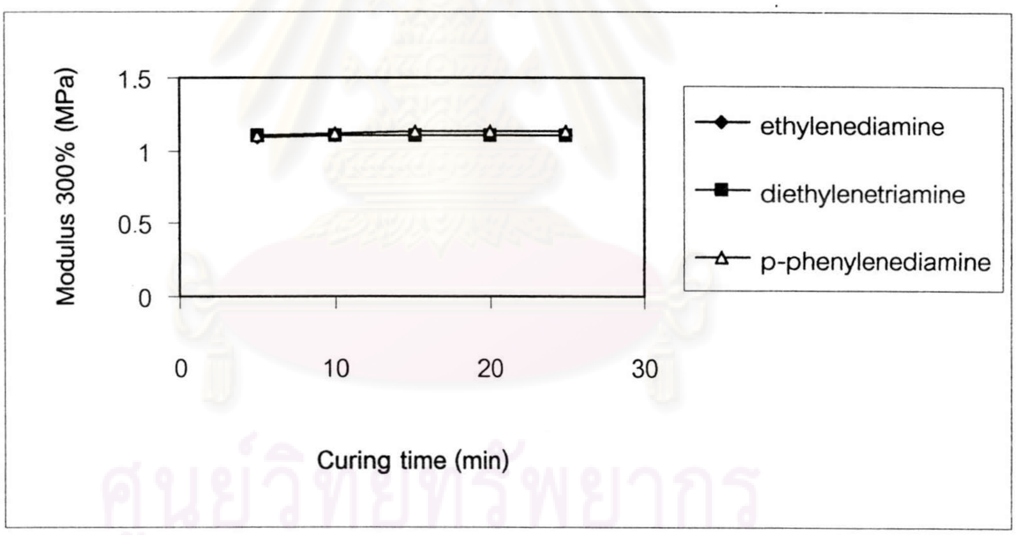


Fig 4.44 Modulus 300% of the amine crosslinked 50% ENR

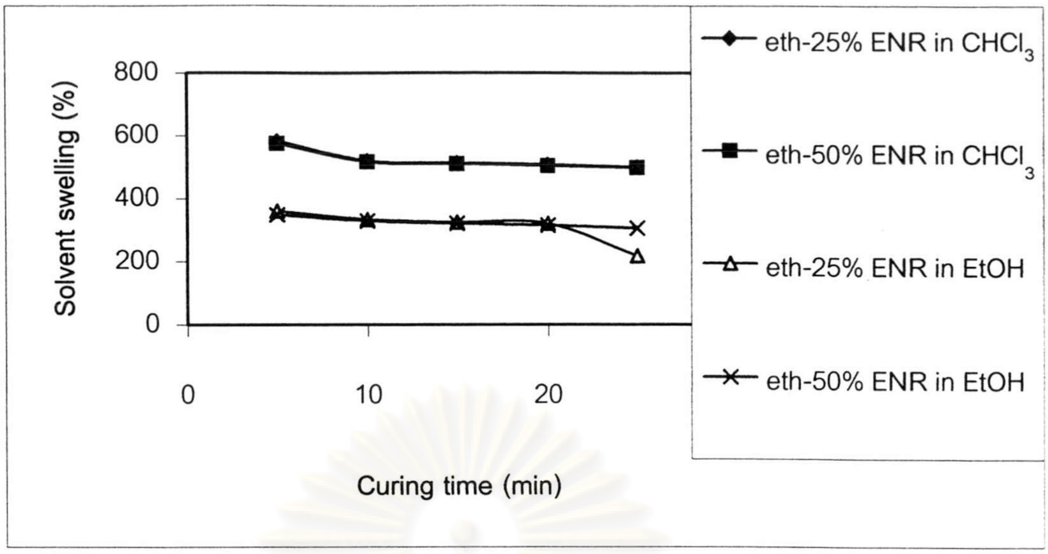


Fig 4.45 Solvent swelling of the ethylenediamine crosslinked 25% and 50% ENR

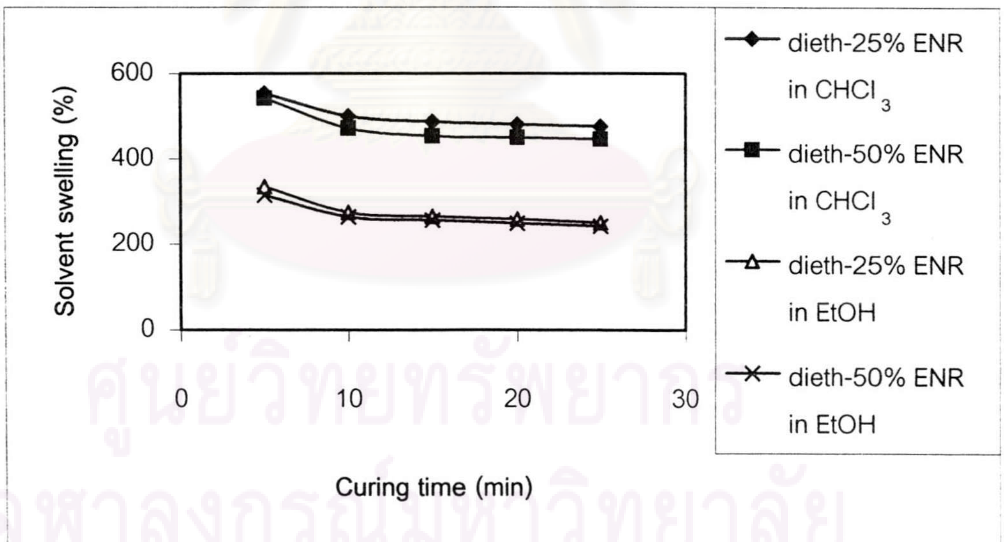


Fig 4.46 Solvent swelling of the diethylenetriamine crosslinked 25% and 50% ENR

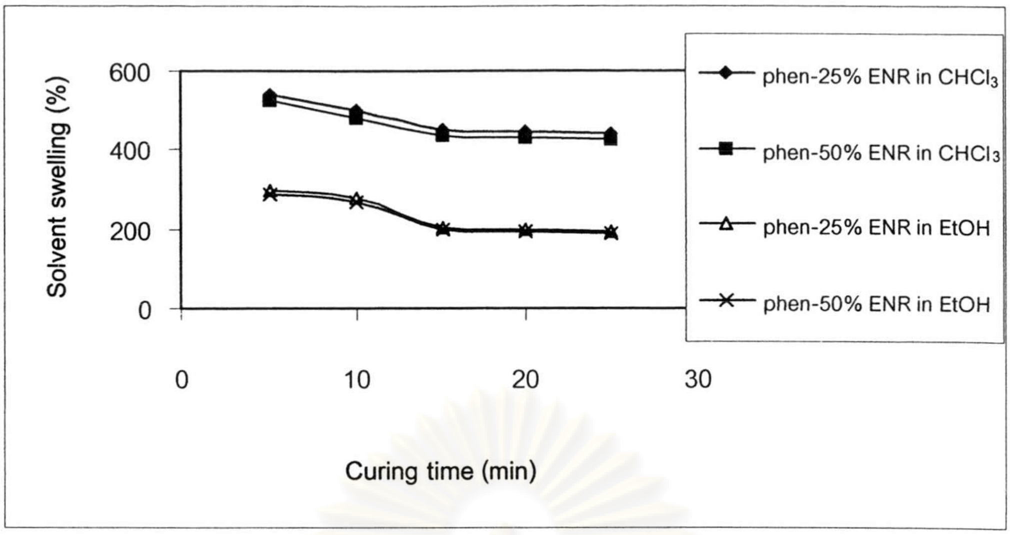


Fig 4.47 Solvent swelling of the *p*-phenylenediamine crosslinked 25% and 50% ENR

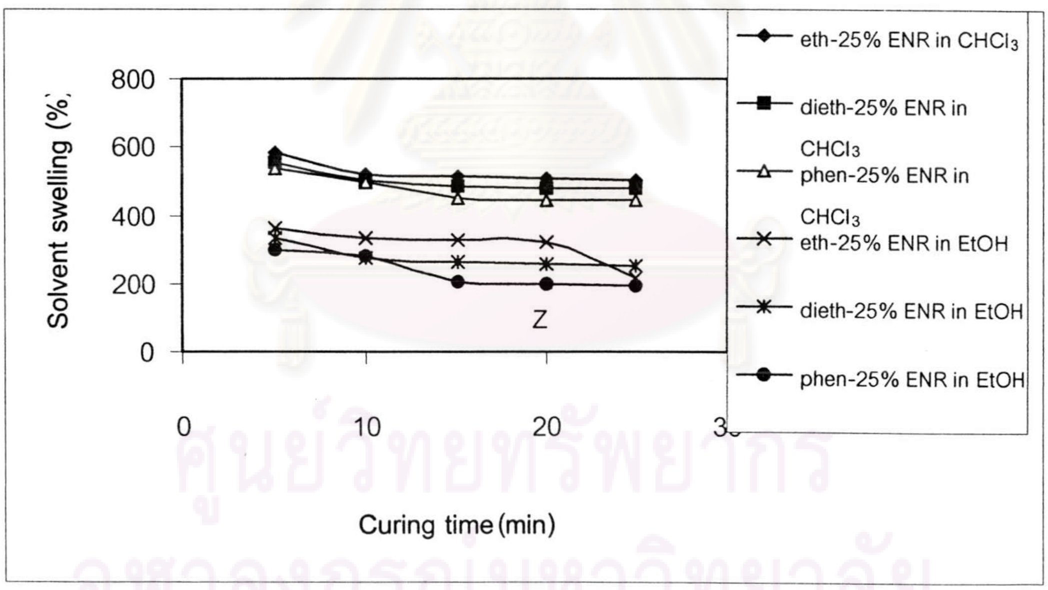


Fig 4.48 Solvent swelling of the amine crosslinked 25% ENR

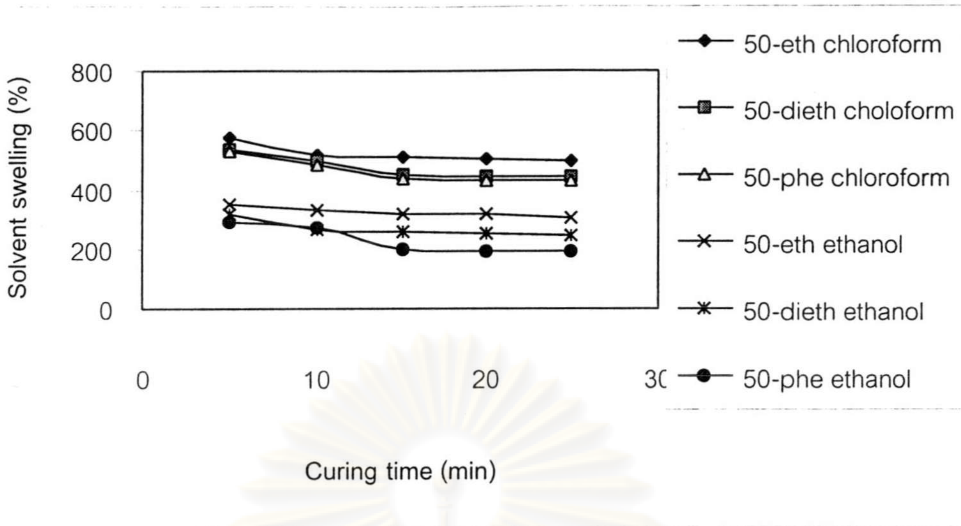


Fig 4.49 Solvent swelling of the amine crosslinked 50% ENR.

From the mechanical properties of the amine cured ENR membranes in various curing time, the tensile strength and elongation increased with increasing curing time from 5 to 10 minutes for ethylenediamine, from 5 to 15 minutes for diethylenetriamine and *p*-phenylenediamine. When the time of curing was increased to 10 minutes for ethylenediamine and to 15 minutes for diethylenetriamine and *p*-phenylenediamine, the tensile strength and the elongation were decreased. The modulus 300 % of the amine cured rubbers were slightly increased with increasing the curing time. The optimum curing times were of 10 and 15 minutes for the preparation of the compounded rubber latex using ethylenediamine, diethylenetriamine and *p*-phenylenediamine as crosslinking agent, respectively. The effect of curing time on solvent swelling was found to highly increase from 5 to 10 min and slightly increase from 10 to 20 min for ethylenediamine and diethylenetriamine but highly increase from 5 to 15 min and slightly increase from 15 to 25 min for *p*-phenylenediamine. In addition, high crosslinking membranes decrease swelling and retard permeability [25]. Thus these curing times were appropriated for crosslinked condition.

4.2.3 Effect of curing temperature

The curing temperature of the membrane was another important factor. Usually the product property depends on a period of curing temperature. In this work, the temperature for preparing the membrane was investigated using 1 phr of the amine concentration and 10 to 15 min by varying the curing temperature to 105, 110, 115, 120 and 125°C for ethylenediamine, diethylenetriamine and *p*-phenylenediamine.

The mechanical properties of amine cured rubber sheets were observed to obtain the appropriate temperature for membranes. Tables 4.6-4.7 illustrate the effect of curing temperature on the mechanical properties of amine cured rubber membranes.

Table 4.6 The mechanical properties of amine cured ENR sheets with various curing temperature [a]

Curing Temperature (°C)	Tensilt strength (MPa)		Elongation (%)		Modulus (MPa)	
	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR
Ethylenediamine [b]						
105	13.64	13.87	997.6	993.2	1.0968	1.0970
110	15.43	15.64	988.5	979.8	1.0984	1.0984
115	15.50	15.71	982.0	976.9	1.0989	1.0990
120	14.07	13.97	974.5	974.0	1.0971	1.0975
125	13.48	13.24	969.7	971.8	1.0962	1.0964
Diethylenetriamine [c]						
105	12.98	13.04	998.9	991.4	1.0954	1.0961
110	13.70	13.68	993.4	988.0	1.0969	1.0972
115	14.14	14.66	989.0	987.5	1.0978	1.0987
120	15.59	15.89	985.1	974.3	1.0991	1.1002
125	15.67	15.93	984.8	973.6	1.0999	1.1014
p-phenylenediamine [d]						
105	12.23	12.54	994.0	992.8	1.0958	1.0966
110	14.05	14.16	993.2	991.3	1.0968	1.0979
115	15.36	15.42	988.7	990.7	1.0974	1.1012
120	16.46	16.63	978.1	973.8	1.0996	1.1250
125	16.58	16.74	977.8	971.6	1.1012	1.1254

Note:

[a] all membranes were contained 3 phr of amine.

[b] The membranes were cured at various curing temperature for 10 min under 24 N/cm^2.

[c] The membranes were cured at various curing temperature for 10 min under 24 N/cm^2.

[d] The membranes were cured at various curing temperature for 10 min under 24 N/cm^2.

Table 4.7 The solvent swelling of amine cured rubber sheets with various curing temperature[a]

Curing Temperature (°C)	Solvent swelling (%)			
	$CHCl_3$		EtOH	
	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR	Amine crosslinked 25% ENR	Amine crosslinked 50%ENR
Ethylenediamine[b]				
105	450.23	447.83	261.33	250.02
110	533.48	518.61	338.45	298.30
115	540.27	521.85	342.16	331.43
120	548.14	533.05	354.43	340.02
125	554.06	540.26	360.21	348.41
Diethylenetriamine[c]				
105	450.23	447.83	261.33	250.02
110	517.14	501.08	274.54	269.31
115	534.38	528.55	288.35	276.43
120	541.04	532.66	302.89	288.67
125	544.27	536.41	334.51	294.53
p-phenylenediamine[d]				
105	450.23	447.83	261.33	250.02
110	486.48	479.51	274.82	252.32
115	493.41	485.20	282.03	258.47
120	530.52	510.14	288.94	264.58
125	538.16	516.53	295.83	269.84

Note:

[a] all membranes were contained 3 phr of amine.

[b] The membranes were cured at various temperature for 10 min under 24 N/cm^2.

[c] The membranes were cured at various temperature for 10 min under 24 N/cm^2.

[d] The membranes were cured at various temperature for 10 min under 24 N/cm^2.

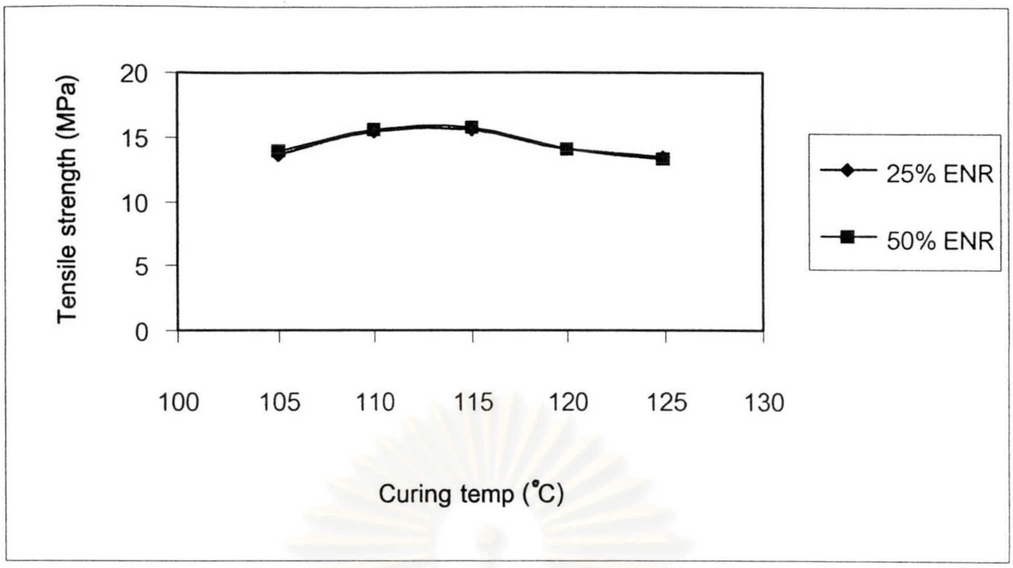


Fig 4.50 Tensile strength of the ethylenediamine crosslinked 25% and 50% ENR

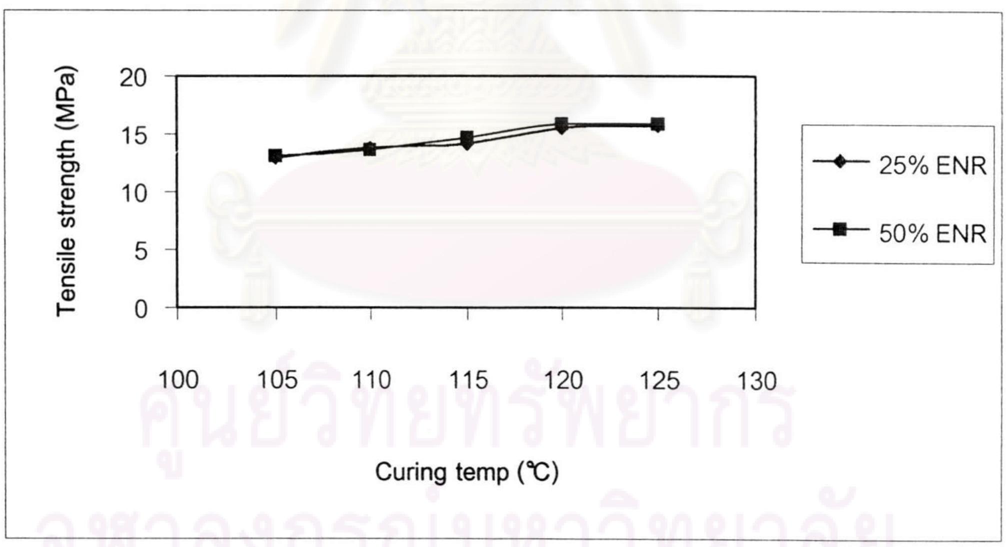


Fig 4.51 Tensile strength of the diethylenetriamine crosslinked 25% and 50% ENR

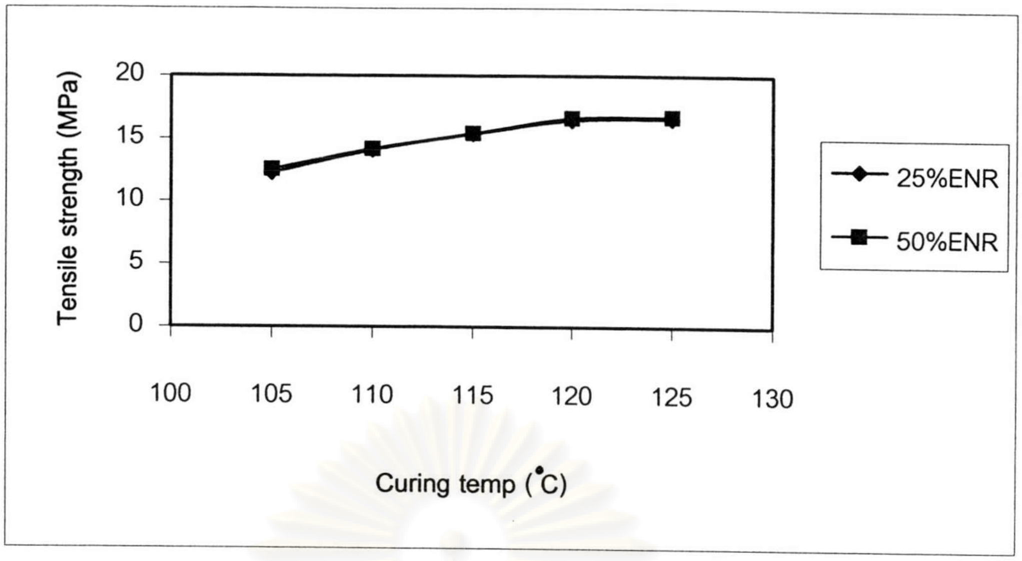


Fig 4.52 Tensile strength of the *p*-phenylenediamine crosslinked 25% and 50% ENR

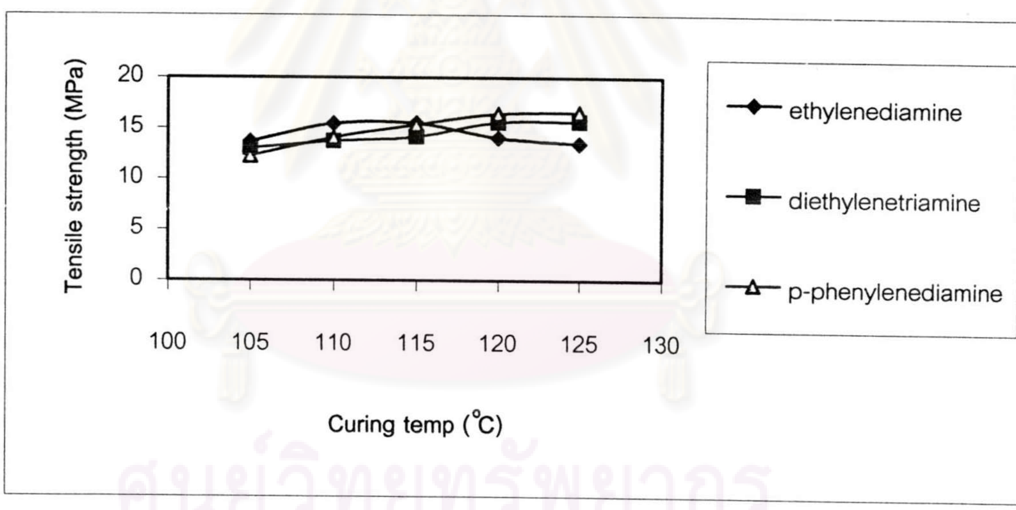


Fig 4.53 Tensile strength of the amine crosslinked 25% ENR

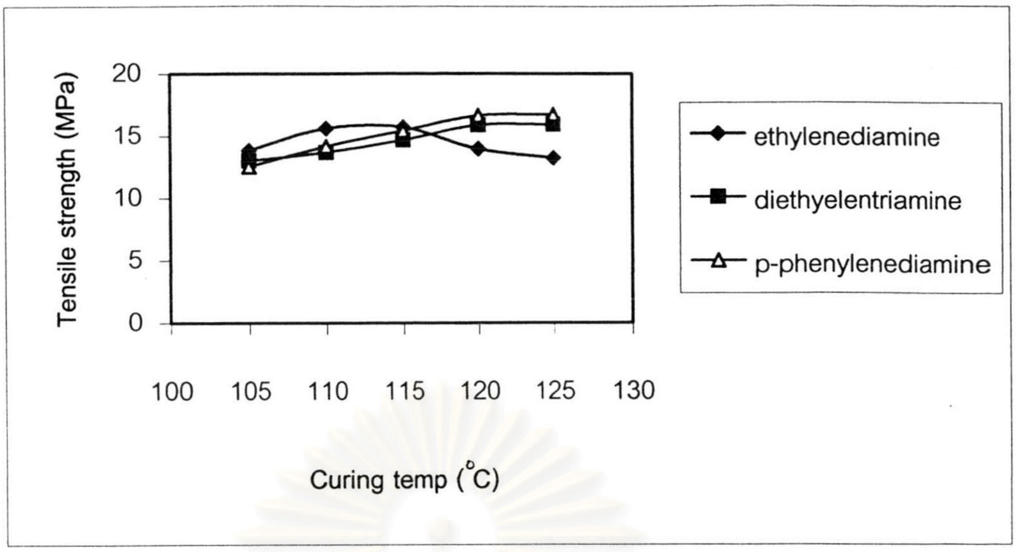


Fig 4.54 Tensile strength of the amine crosslinked 50% ENR

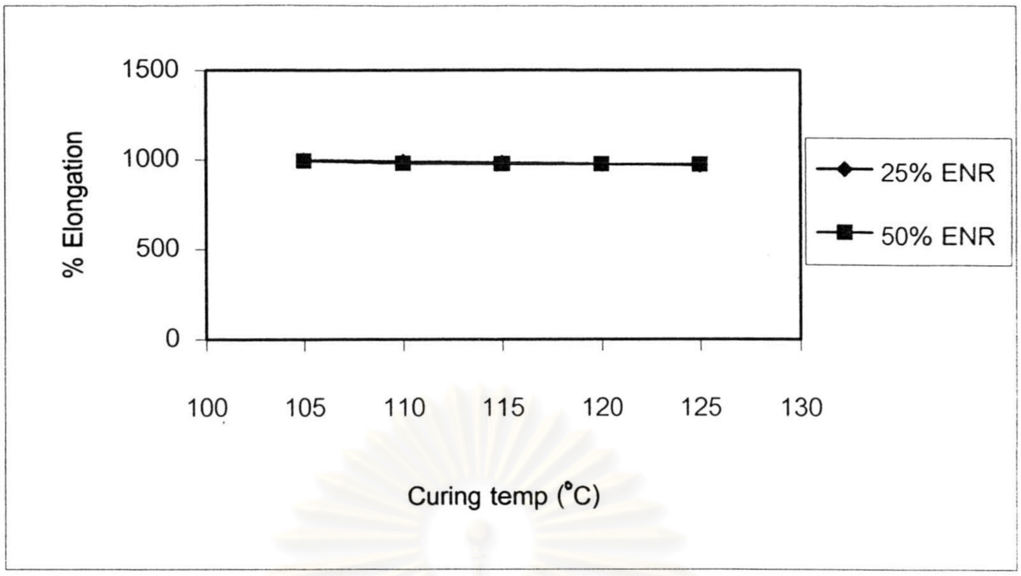


Fig 4.55 % Elongation of the ethylenediamine crosslinked 25% and 50% ENR

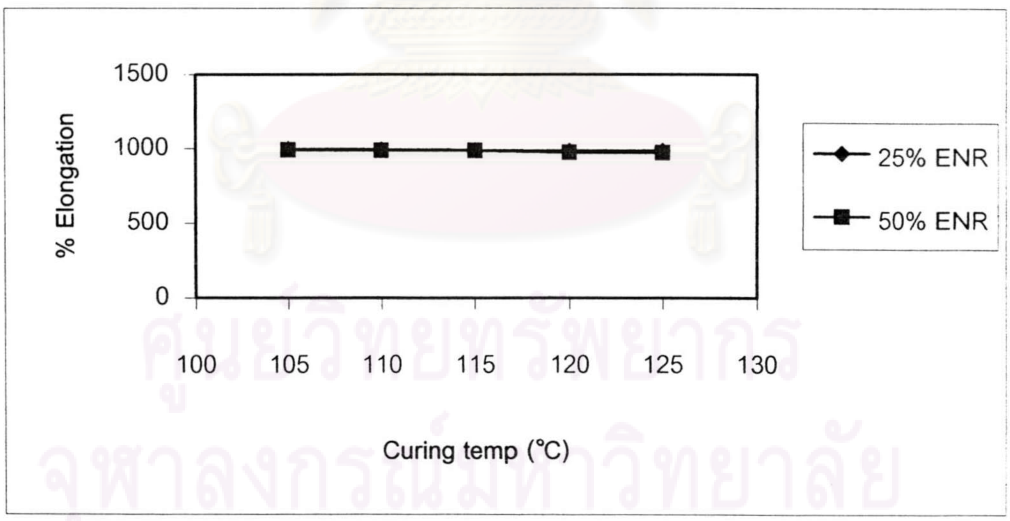


Fig 4.56 % Elongation of the diethylenetriamine crosslinked 25% and 50% ENR

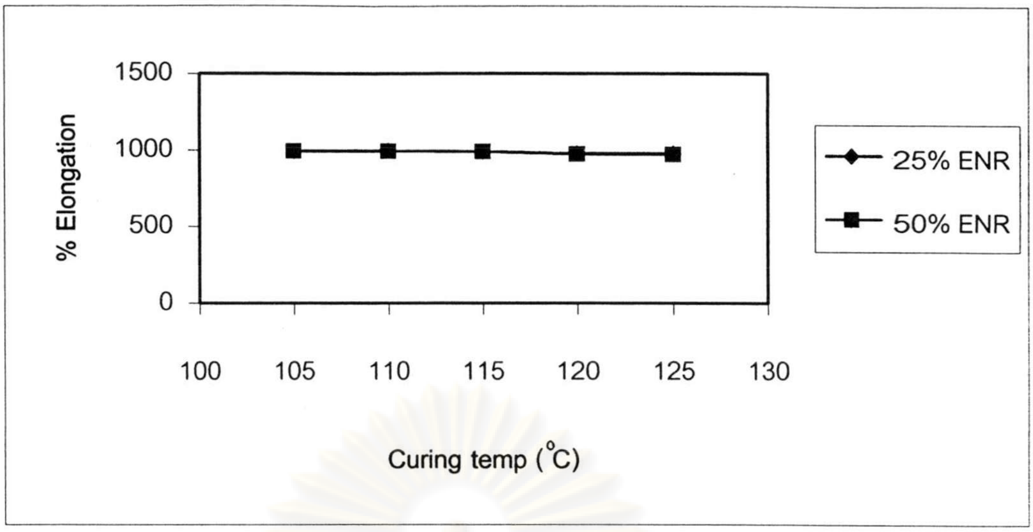


Fig 4.57 % Elongation of *p*-phenylenediamine crosslinked 25% and 50% ENR

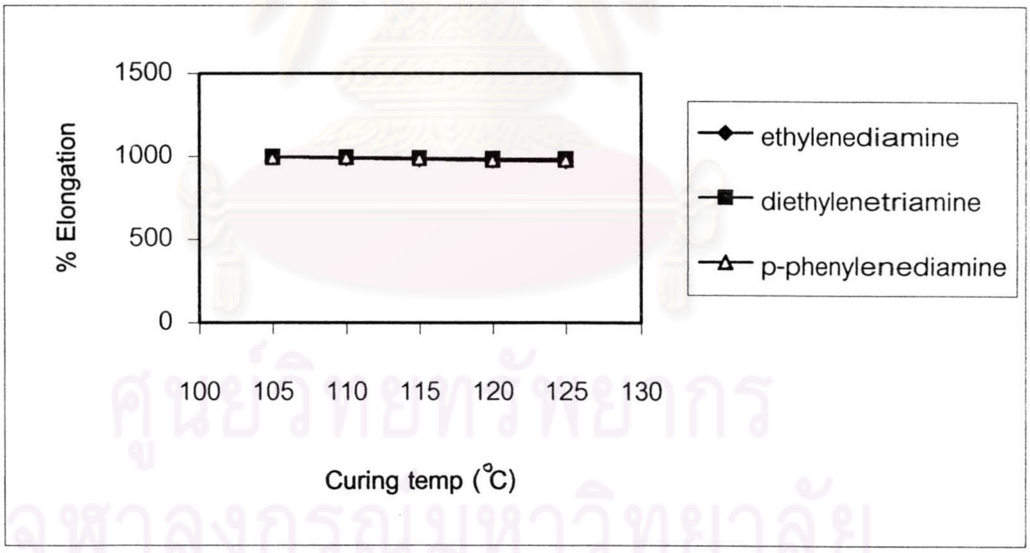


Fig 4.58 % Elongation of the amine crosslinked 25% ENR

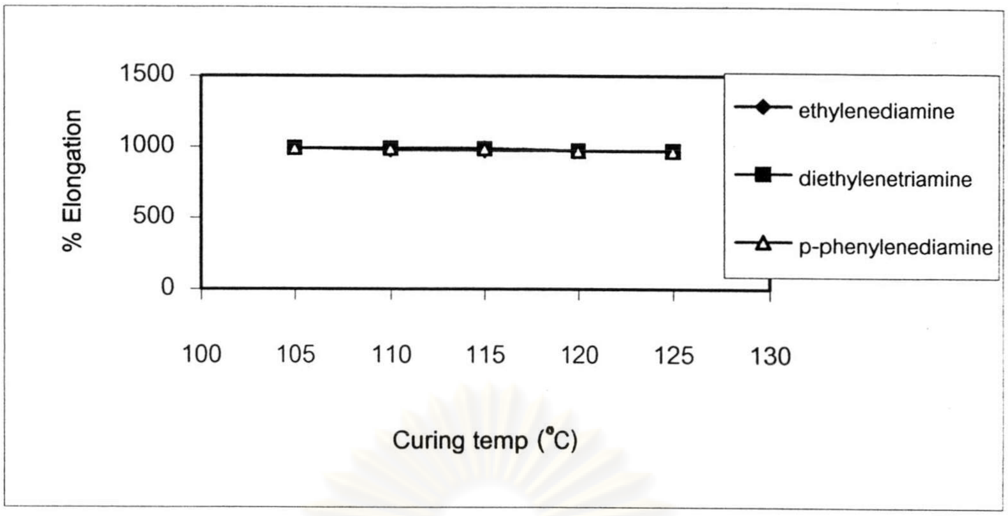


Fig 4.59 % Elongation of the amine crosslinked 50% ENR

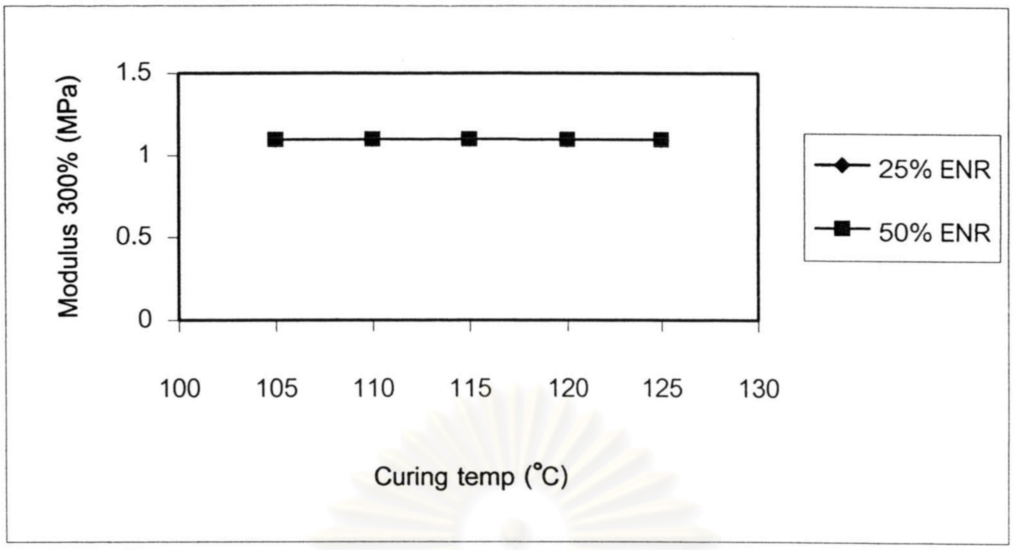


Fig 4.60 Modulus 300% of the ethylenediamine crosslinked 25% and 50% ENR

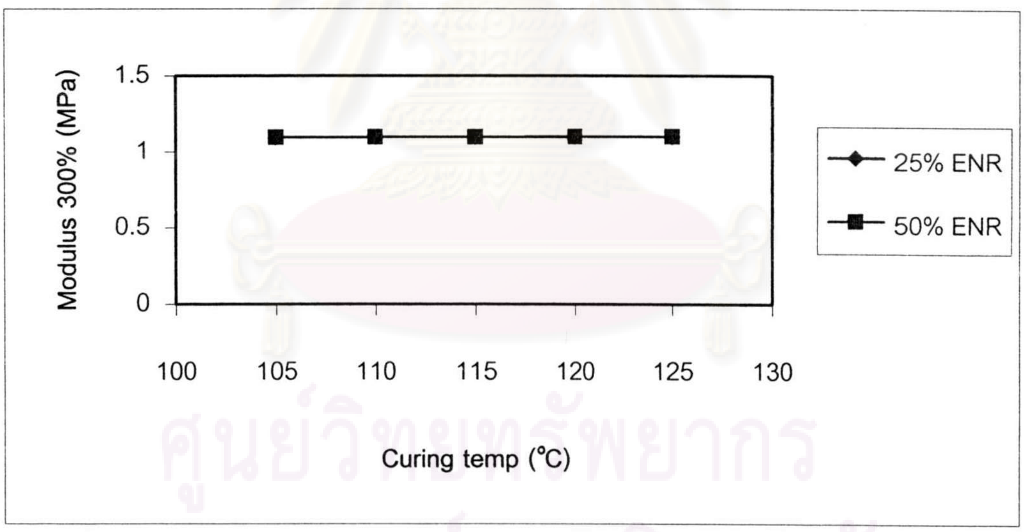


Fig 4.61 Modulus 300% of the diethylenetriamine crosslinked 25% and 50% ENR

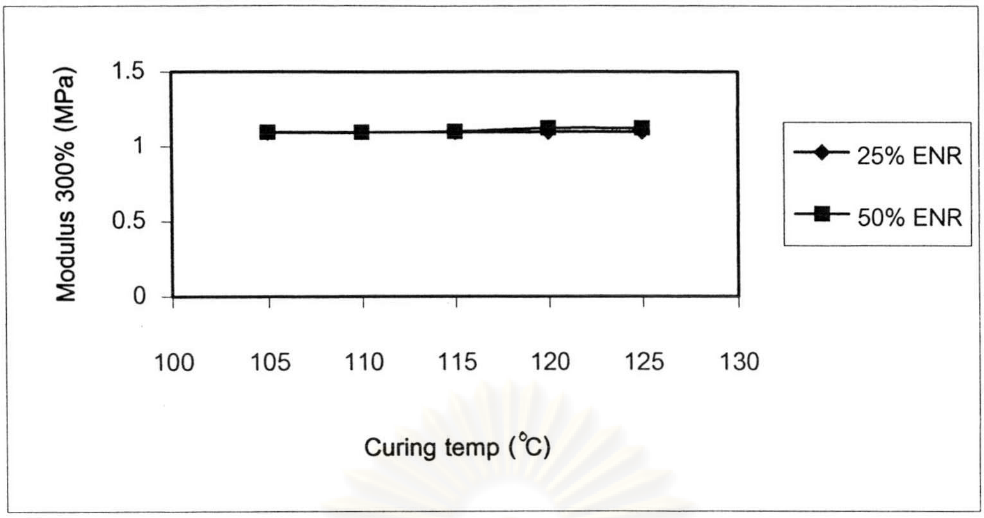


Fig 4.62 Modulus 300% of the *p*- phenylenediamine crosslinked 25% and 50% ENR

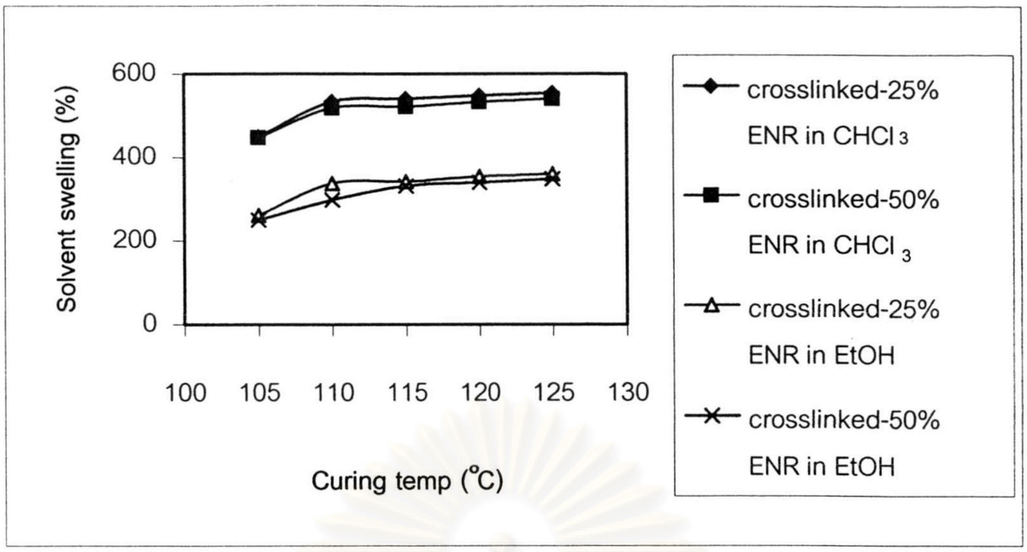


Fig 4.63 Solvent swelling of the ethylenediamine crosslinked 25% and 50% ENR

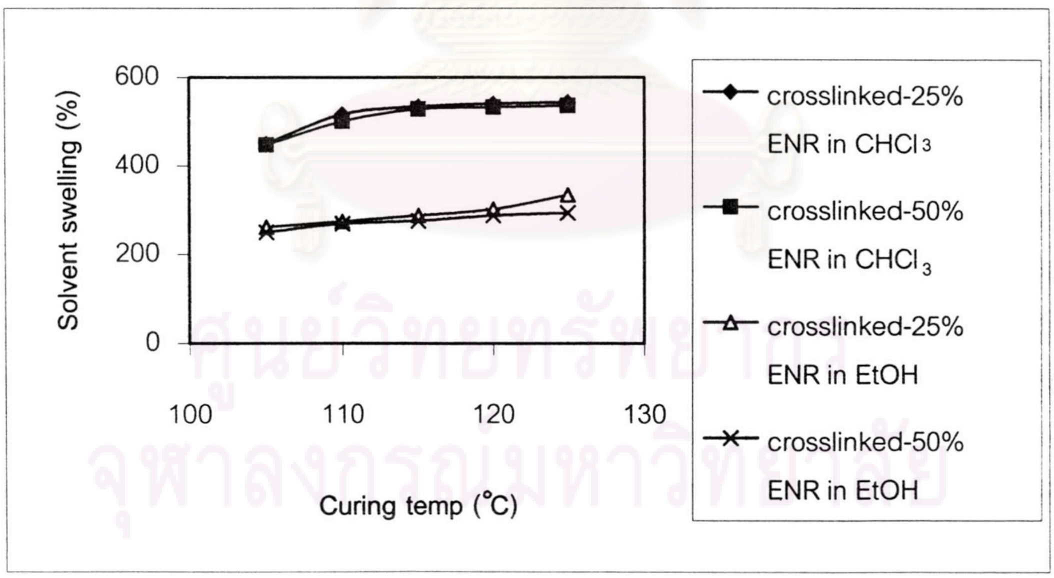


Fig 4.64 Solvent swelling of the diethylenetriamine crosslinked 25% and 50% ENR

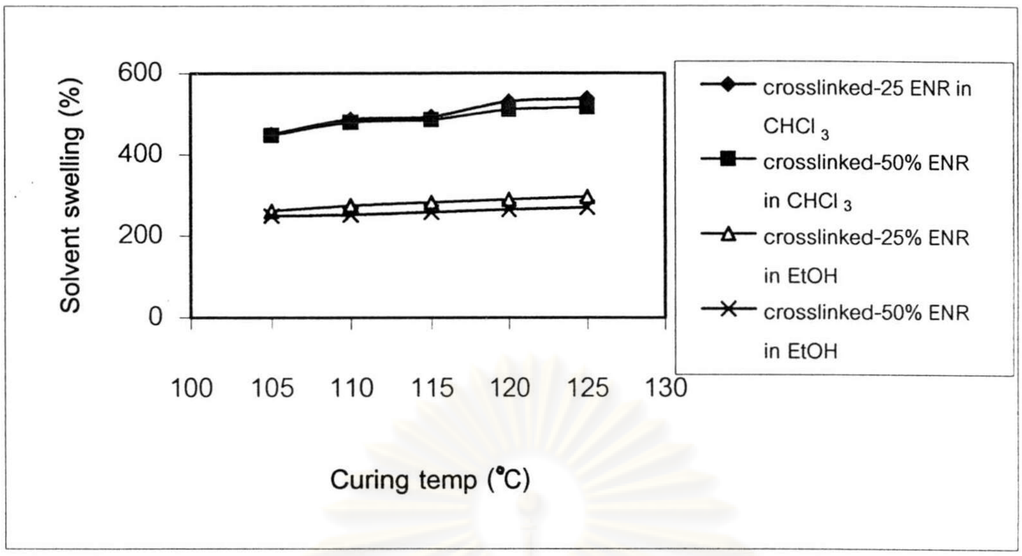


Fig 4.65 Solvent swelling of the *p*-phenylenediamine crosslinked 25% and 50% ENR

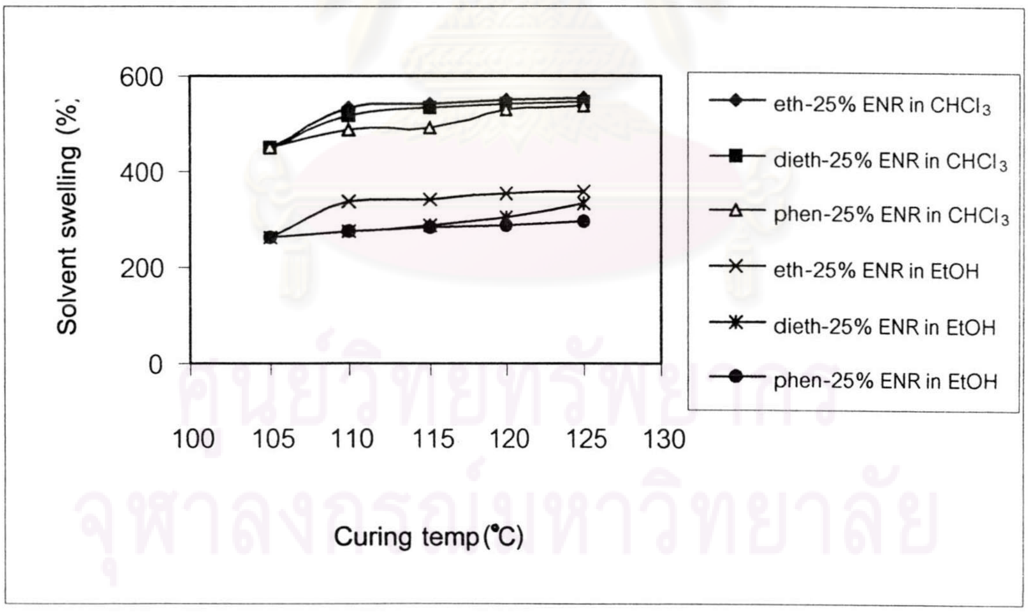


Fig 4.66 Solvent swelling of the amine crosslinked 25% ENR

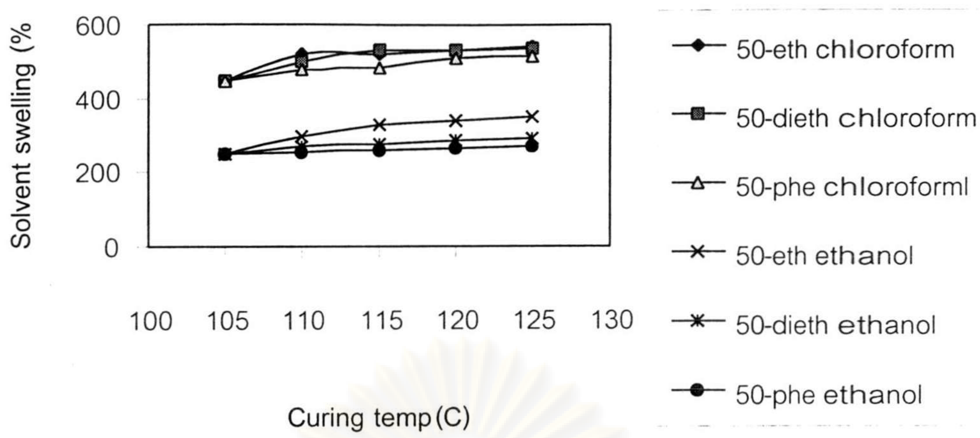


Fig 4.67 Solvent swelling of the amine crosslinked 50% ENR.

From the mechanical properties of the amine cured ENR membranes in various curing temperature, the tensile strength and elongation increased with increasing curing temperature from 105 to 110 °C for ethylenediamine, from 105 to 110 °C for diethylenetriamine and 110 to 120 °C and slightly increase to 125 °C for *p*-phenylenediamine. When the curing temperature were increased to higher than 110 °C for ethylenediamine, 120 °C for diethylenetriamine, the tensile strength and the elongation were decreased. The modulus 300 % of the vulcanized rubber were slightly increased with increasing the curing time. The effect of curing temperature on solvent swelling was found that solvent swelling highly increased from 105 to 110°C and slightly increased from 110-125°C for ethylenediamine and diethylenetriamine but highly increased from 105 to 120°C and slightly increased from 120-125 °C for *p*-phenylenediamine due to these time were appropriated for crosslinked condition. The high crosslink decreased swelling and retarded permeability [25]. Thus, the curing temperature of 105, 110 and 120 °C were used as the optimum curing time for preparation of the compounded rubber latex for crosslinking with ethylenediamine, diethylenetriamine and *p*-phenylenediamine, respectively.

4.2.4 The gel content.

Determination of the crosslinking level was investigated using the gel content method. The results are illustrated in Table 4.8 and Figure 4.68 – 4.70. It was found that the gel content of the amine crosslinked ENR membrane was decrease when the amine concentration increased. The results also showed that the amine crosslinking was properly achieved at the amine concentration of 3 phr.

Table 4.8 The gel content of the determination of amine crosslinked membrane[a]

Membrane	The gel content (%)					
	0 phr	1 phr	2 phr	3 phr	4 phr	5 phr
Ethylenediamine[b]						
25%ENR	200	120	95	90	85	78
50%ENR	180	104	93	86	81	75
Diethylenetriamine[c]						
25%ENR	200	100	93	86	79	75
50%ENR	180	96	90	82	76	73
p-phenylenediamine[d]						
25%ENR	200	97	92	84	76	74
50%ENR	180	92	87	80	73	70

Note:

[a] all membranes were contained 3 phr of amine.

[b] The membranes were cured at 105 °C for 10 min under 24 N/cm^2.

[c] The membranes were cured at 110 °C for 10 min under 24 N/cm^2.

[d] The membranes were cured at 120 °C for 10 min under 24 N/cm^2.

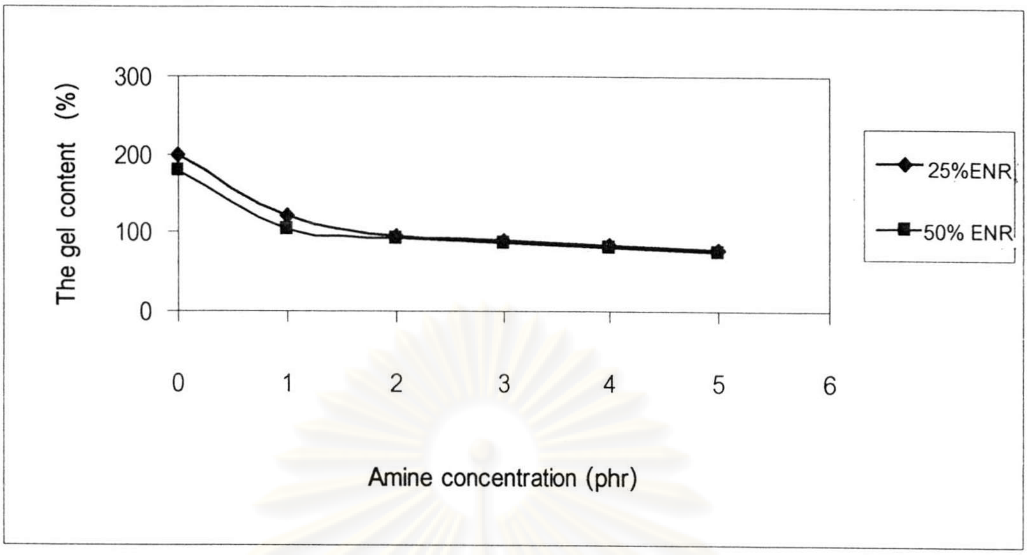


Fig 4.68 The gel content of the ethylenediamine crosslinked 25% and 50% ENR

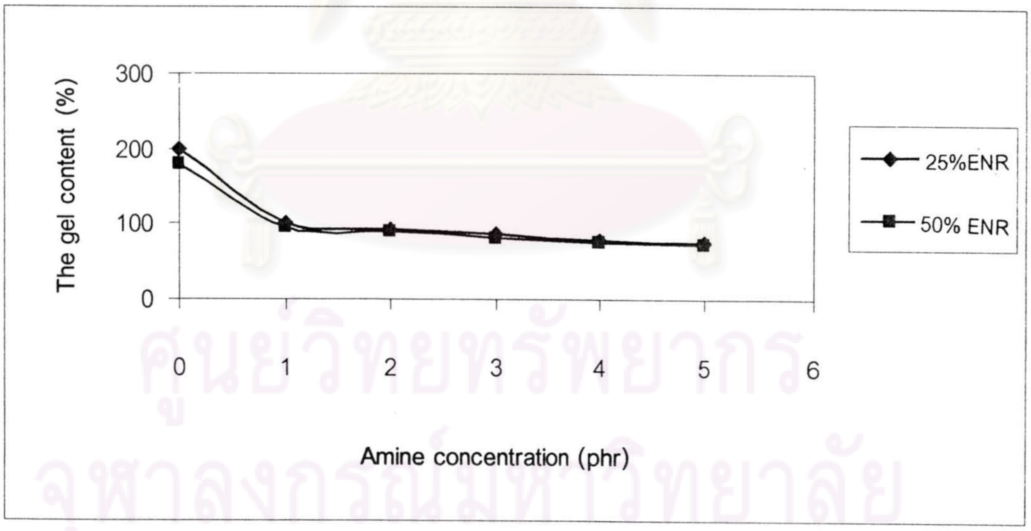


Fig 4.69 The gel content of the diethylenetriamine crosslinked 25% and 50% ENR

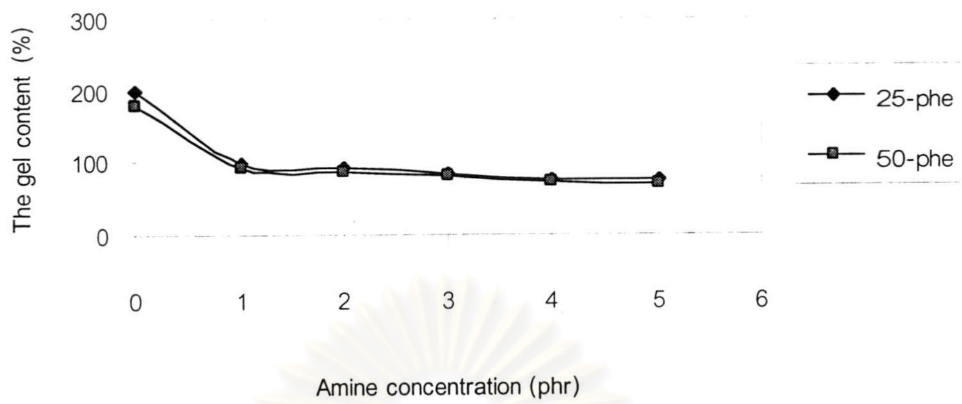


Fig 4.70 The gel content of the *p*-phenylenediamine crosslinked 25% and 50% ENR

From the results was showed decreas the gel content when increas amine concentration due to amine was crosslinking agent.

4.2.5 Effect of Thickness

The thickness of the membrane was another important factor. In this work, the thickness for preparing the membrane was investigated by varying from 0.1, 0.2, 0.3, 0.4 to 0.5 mm. for ethylenediamine, diethylenetriamine and *p*-phenylenediamine

The thickness of amine cured sheets were observed to obtain the appropriate thickness for membranes. Table 4.8 illustrates the effect of thickness on the swell ratio and selectivity of vulcanized membranes.

Table 4.9 The effect of thickness of amine cured rubber membranes on chloroform solvent swelling.

Solvent swelling membrane (%)	Thickness (mm)				
	0.01	0.02	0.03	0.04	0.05
Ethylenediamine cured 25% ENR membrane	540.02	536.41	533.26	531.05	529.75
Ethylenediamine cured 50% ENR membrane	525.64	521.35	518.72	516.87	515.38
Diethylenetriamine cured 25% ENR membrane	530.29	528.76	525.64	523.43	521.09
Diethylenetriamine cured 50% ENR membrane	520.34	517.65	515.48	513.92	511.94
p-phenylenediamine cured 25% ENR membrane	525.66	524.81	522.93	521.08	520.71
p-phenylenediamine cured 50% ENR membrane	510.03	508.49	507.86	506.95	505.06

From the membrane properties of the amine cured ENR membranes in various thickness, the % chloroform swelling decreased when thickness increased from 0.01 to 0.05 mm for ethylenediamine, diethylenetriamine and *p*-phenylenediamine. The results indicated that the separation efficiency is independent of the thickness of the membrane. Then the thickness of 0.1 mm was used as the optimum condition for preparation of the compounded rubber latex from crosslinked with ethylenediamine, diethylenetriamine and *p*-phenylenediamine, respectively.

4.2.6 Permeability of pure chloroform and pure ethanol [Johnson's method]

The permeability study was carried out in two bottles containing 50 g of chloroform and 50 g of ethanol in each bottle. The bottles were covered with membrane (thickness 0.01 mm) and crapped tightly with aluminium cap. After the bottles were left for 1, 6, 12, 24 and 48 hrs at room temperature, the percentage of permeability was calculated equation :

$$\text{Permeability (\%)} = \frac{\text{wt. of solvent-containing bottle at various times} \times 100}{\text{wt. of solvent-containing bottle at initial}}$$

The results are shown in Table 4.10

Table 4.10 The permeability of the amine crosslinked ENR membranes on pure chloroform and pure ethanol[a]

Membrane	Permeability of the solvent at various times (%)									
	1hr		6hrs		12hrs		24 hrs		48 hrs	
	$CHCl_3$	EtOH	$CHCl_3$	EtOH	$CHCl_3$	EtOH	$CHCl_3$	EtOH	$CHCl_3$	EtOH
Ethylenediamine[b]										
25% ENR	100	100	100	100	93.1	98.0	62.0	84.2	55.4	79.5
50% ENR	100	100	100	100	93.8	98.4	64.5	86.3	58.2	81.0
Diethylenetriamine[c]										
25% ENR	100	100	100	100	94.0	99.2	62.8	92.1	59.0	86.4
50% ENR	100	1003	100	100	95.8	99.7	67.1	94.2	61.6	89.0
p-phenylenediamine[d]										
25% ENR	100	100	100	100	97.4	100	74.8	94.8	69.5	90.1
50% ENR	100	100	100	100	98.5	100	78.1	96.6	72.4	92.0

Note:

[a] all membranes were contained 3 phr of amine.

[b] The membranes were cured at 105 °C for 10 min under 24 N/cm^2.

[c] The membranes were cured at 110 °C for 10 min under 24 N/cm^2.

[d] The membranes were cured at 120 °C for 10 min under 24 N/cm^2.

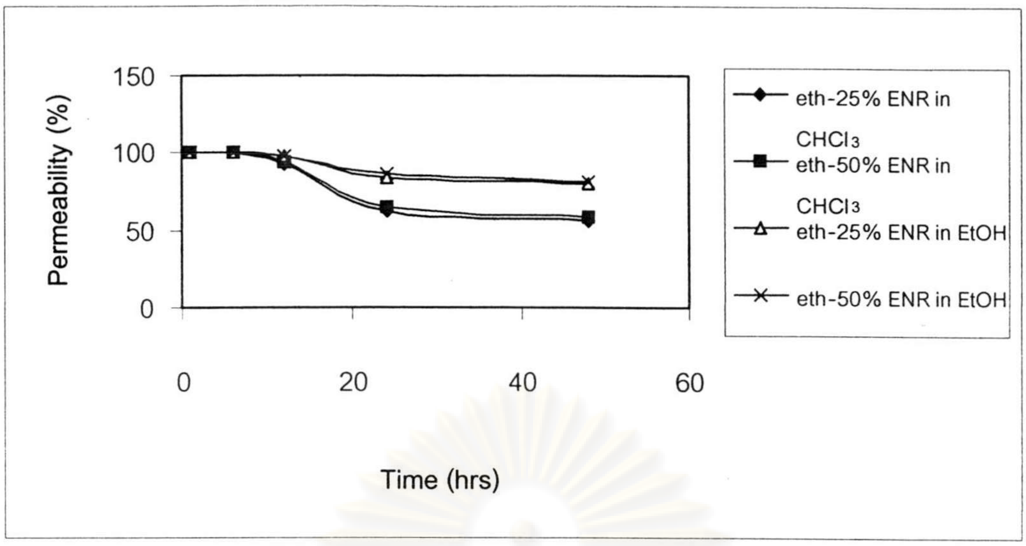


Fig 4.71 Percentage of chloroform and ethanol permeability of the ethylenediamine crosslinked 25% and 50% ENR

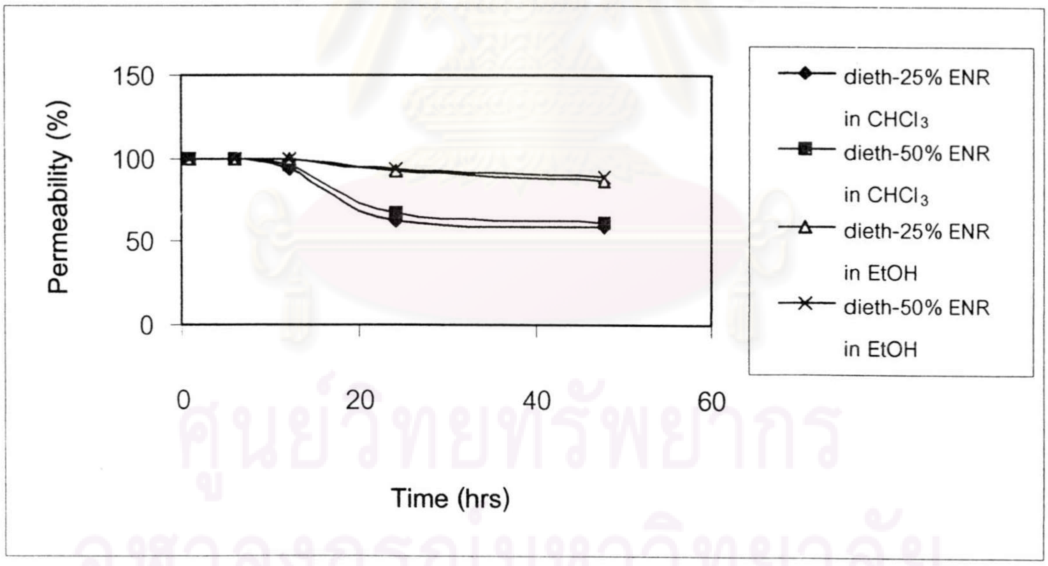


Fig 4.72 Percentage of chloroform and ethanol permeability of the diethylenetriamine crosslinked 25% and 50% ENR

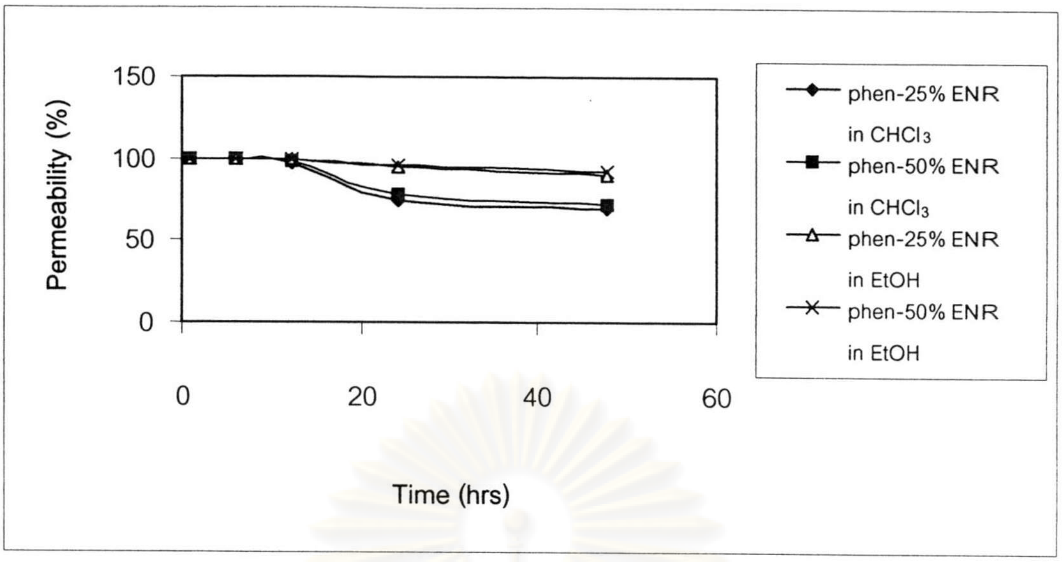


Fig 4.73 Percentage of chloroform and ethanol permeability of the *p*-phenylenediamine crosslinked 25% and 50% ENR

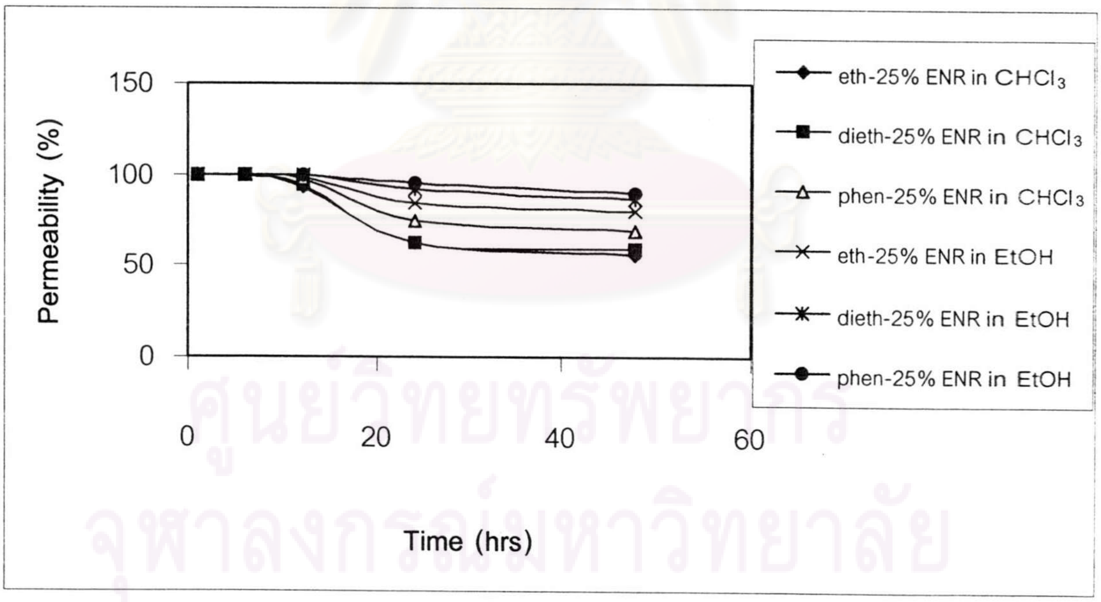


Fig 4.74 Percentage of chloroform and ethanol permeability of the amine crosslinked 25% ENR

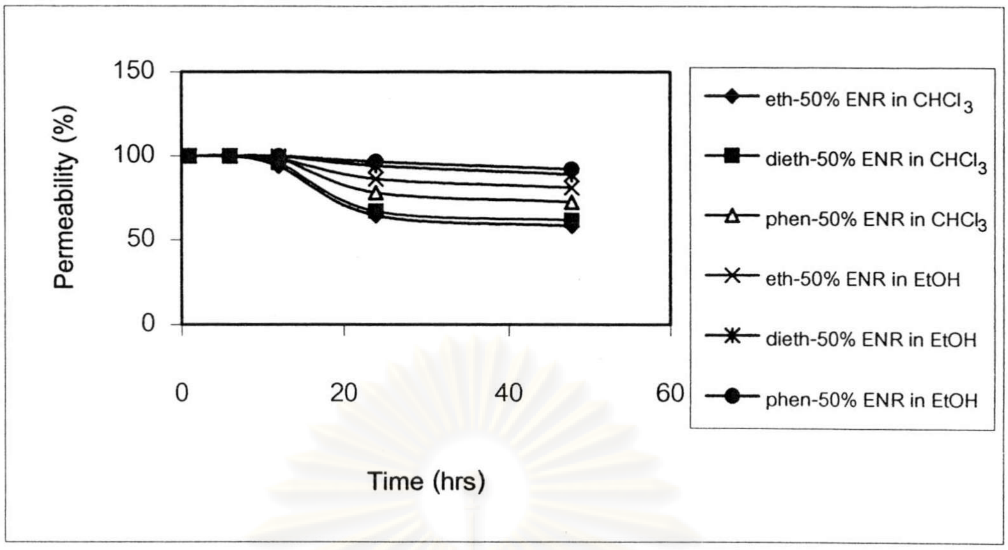


Fig 4.75 Percentage of chloroform and ethanol permeability of the amine crosslinked 50% ENR

From Table 4.10 and Figure 4.71 to 4.75, the membrane permeability in various solvents was shown that

1. % Permeability of chloroform was more than ethanol due to the permeability through the membranes were found to decrease with increase in the polarity of the predominantly permeating species. So these membrane appropriates for less polarity solvent. [31].
2. Permeability of the crosslinked 25% ENR was more than the crosslinked 50% and permeability of ethylenediamine, diethylenetriamine and *p*-phenylenediamine decreased respectively due to the differences in the permeability of membranes was explained in terms of the different degree of crosslinking as well as the different physicomechanical nature of the crosslinks in the membranes [31]

Comparison of permeability in term of permselectivity, it was found that the crosslinked membrane using ethylenediamine, diethylenetriamine and *p*-phenylenediamine as crosslinking agent showed chloroform permeation was more than ethanol permeation through the membrane.

4.2.7 Permeability of chloroform and ethanol mixture

The permselective properties of membranes were determined by solubility and diffusivity of the permeating components in the membrane. Because both sorption and diffusion phenomena are dependent on the composition of the liquid mixture, permeation characteristics of membranes are usually strongly influenced by the concentration of mixed solvent [27]. Thus, permeability of chloroform and ethanol mixtures with various ratio was investigated. The results are shown in Table 4.11.

Table 4.11 The permeability of the amine crosslinked ENR membranes[a] on chloroform and ethanol mixture

Membrane	Permeability of the solvents at various times (%)									
	1 hr		6 hrs		12 hrs		24 hrs		48 hrs	
	$CHCl_3$	EtOH	$CHCl_3$	EtOH	$CHCl_3$	EtOH	$CHCl_3$	EtOH	$CHCl_3$	EtOH
Ethylenediamine [b]										
$CHCl_3$: EtOH (75:25)										
25% ENR	75	25	75	25	73	27	55	45	51	49
50% ENR	75	25	75	25	73	27	57	43	53	47
$CHCl_3$: EtOH (50:50)										
25% ENR	50	50	50	50	50	50	38	62	35	65
50% ENR	50	50	50	50	50	50	39	61	36	64
$CHCl_3$: EtOH (25:75)										
25% ENR	25	75	25	75	25	75	18	82	16	84
50% ENR	25	75	25	25	25	75	20	80	18	82
Diethylenetriamine [c]										
$CHCl_3$: EtOH (75:25)										
25% ENR	75	25	75	25	74	26	59	41	57	43
50% ENR	75	25	75	25	75	25	61	39	59	41
$CHCl_3$: EtOH (50:50)										
25% ENR	50	50	50	50	50	50	40	60	38	62
50% ENR	50	50	50	50	50	50	42	58	39	61
$CHCl_3$: EtOH (25:75)										
25% ENR	25	75	25	75	25	75	20	80	18	82
50% ENR	25	75	25	25	25	75	22	78	20	80
p-phenylenediamine [d]										
$CHCl_3$: EtOH (75:25)										
25% ENR	75	25	75	25	75	25	65	35	63	37
50% ENR	75	25	75	25	75	25	68	32	65	35

Membrane	Permeability (%)									
	1 hr		6 hrs		12 hrs		24 hrs		48 hrs	
	$CHCl_3$	EtOH	$CHCl_3$	EtOH	$CHCl_3$	EtOH	$CHCl_3$	EtOH	$CHCl_3$	EtOH
$CHCl_3$: EtOH (50:50)										
25% ENR	50	50	50	50	50	50	46	54	42	58
50% ENR	50	50	50	50	50	50	47	53	44	56
$CHCl_3$: EtOH (25:75)										
25% ENR	25	75	25	75	25	75	24	76	24	76
50% ENR	25	75	25	25	25	25	25	75	25	75

Note:

[a] all membranes were contained phr of amine.

[b] The membranes were cured at 105 °C for 10 min under 24 N/cm^2.

[c] The membranes were cured at 110 °C for 10 min under 24 N/cm^2.

[d] The membranes were cured at 120 °C for 10 min under 24 N/cm^2.

From Table 4.11, it was found that the selectivity increased with increase of chloroform concentration in the mixture. When the concentration of ethanol increased, the selectivity values was lower and chloroform permeated slower through the membranes. This is because of decreased swelling with increasing ethanol concentration. The decreased swelling hinders the passage of ethanol molecules, thereby increasing the selectivity.