Chapter 4

Results and discussion

IR studies

For each of the obtained IR spectra of HTPB, polyols standard, MDI and thin films peak in the frequency region of 4000-400 cm^{-1} are amplified respectively. Characteristic absorption peaks of urethane and urea carbonyl groups can be observed in this region. A typical IR spectra of HTPB, polyols standard, and MDI are illustrated in figures 12 to 14

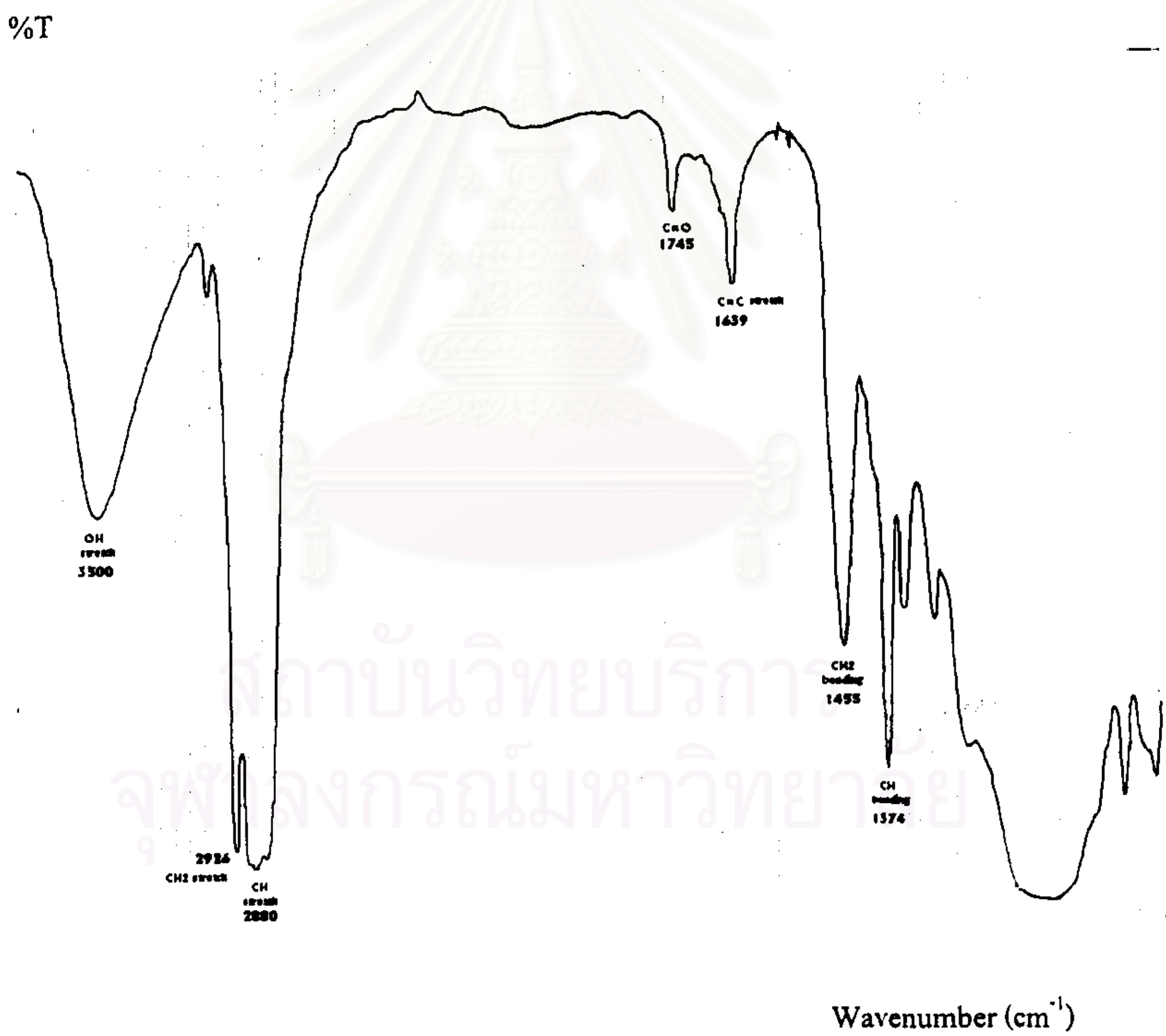

Figure 12 IR-spectra of Polyols standard

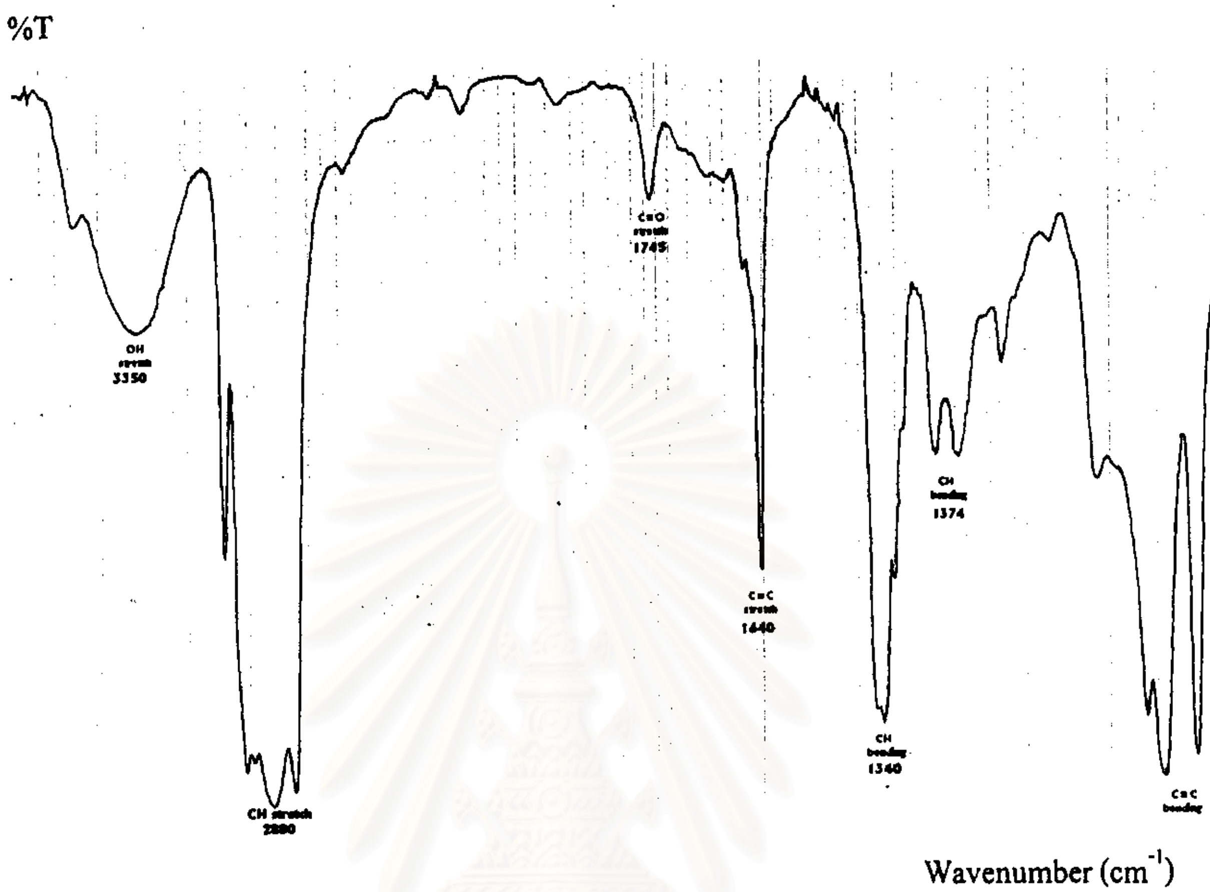

Figure 13 IR-spectra of HTPB prepolymer

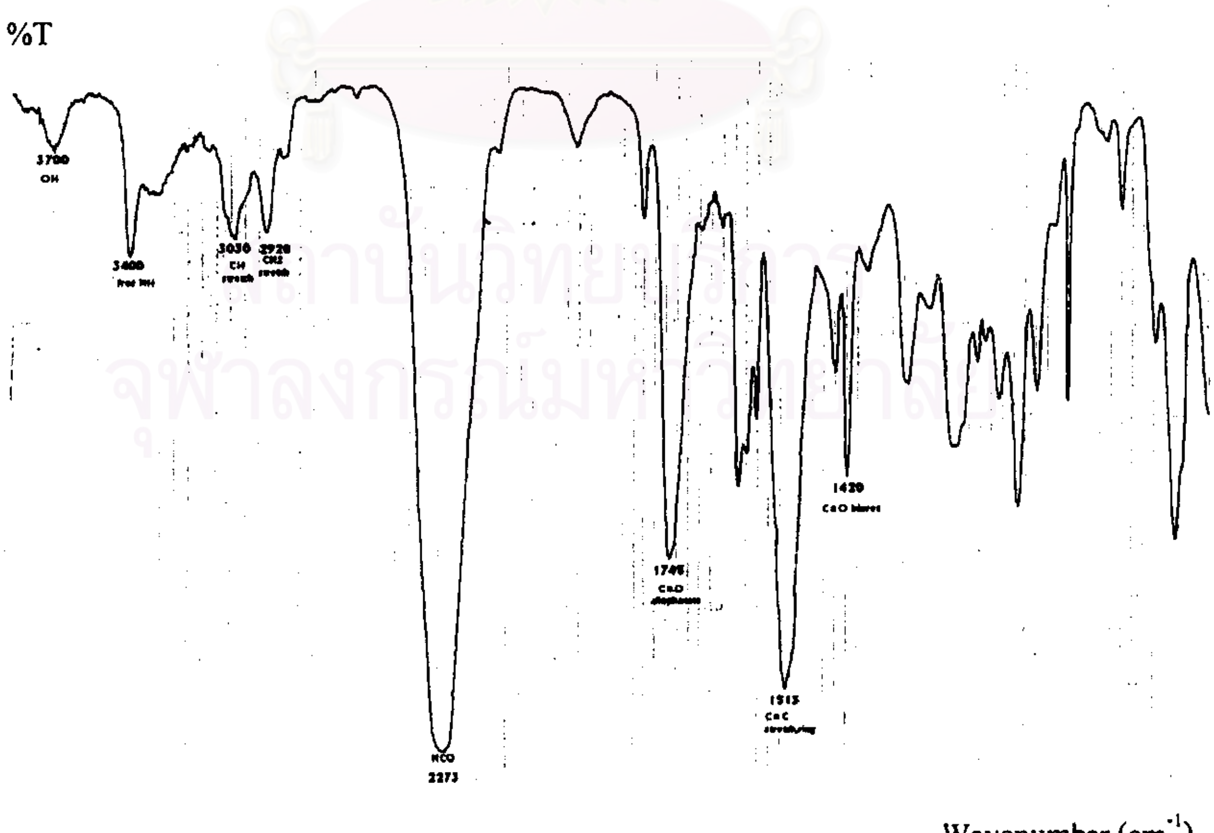

Figure 14 IR-spectra of polymeric MDI

The bands near 3330 (N-H stretch), 1745 (C= O), 1540 (C-NH bending), and 2273 cm^{-1} (NCO stretch) are attributed to the polyurethane hard segments, bands 2880 (CH stretch), 1640 (C=C stretch), 2926 (CH_2 stretch), 1640(C=C stretch), 1430 (CH bending), and 3350 (OH stretch) are attributed to the soft segments. The non-hydrogen-bonded urea carbonyl peak (1695 cm^{-1}) is not seen in both figure 15 to 23, but the broad hydrogen-bonded urea carbonyls (1720 cm^{-1}) exist in hydrogen-bonded form. Based on the NH band in the region of 3200-3500 cm^{-1}, the OH:NCO ratios not appear to be primarily hydrogen-bonded ,because the bonded NH peak at 3320 cm^{-1} predominated, whereas the free (non-hydrogen-bonded) NH peak at 3400 cm^{-1} is detectable only as a shoulder of MDI. In the carbonyl region between 1650 and 1750 cm^{-1}, the peak due to bonded C=O stretching centered at 1700 cm^{-1} predominates and that due to free C=O stretching appears as a shoulder at 1745 cm^{-1} . If it is assumed that the extinction coefficients of free and bonded C=O are approximately the same in polyurethanes, the dominance of the bonded C= O peak indicates that a large fraction of the hard segments are hydrogen-bonded.

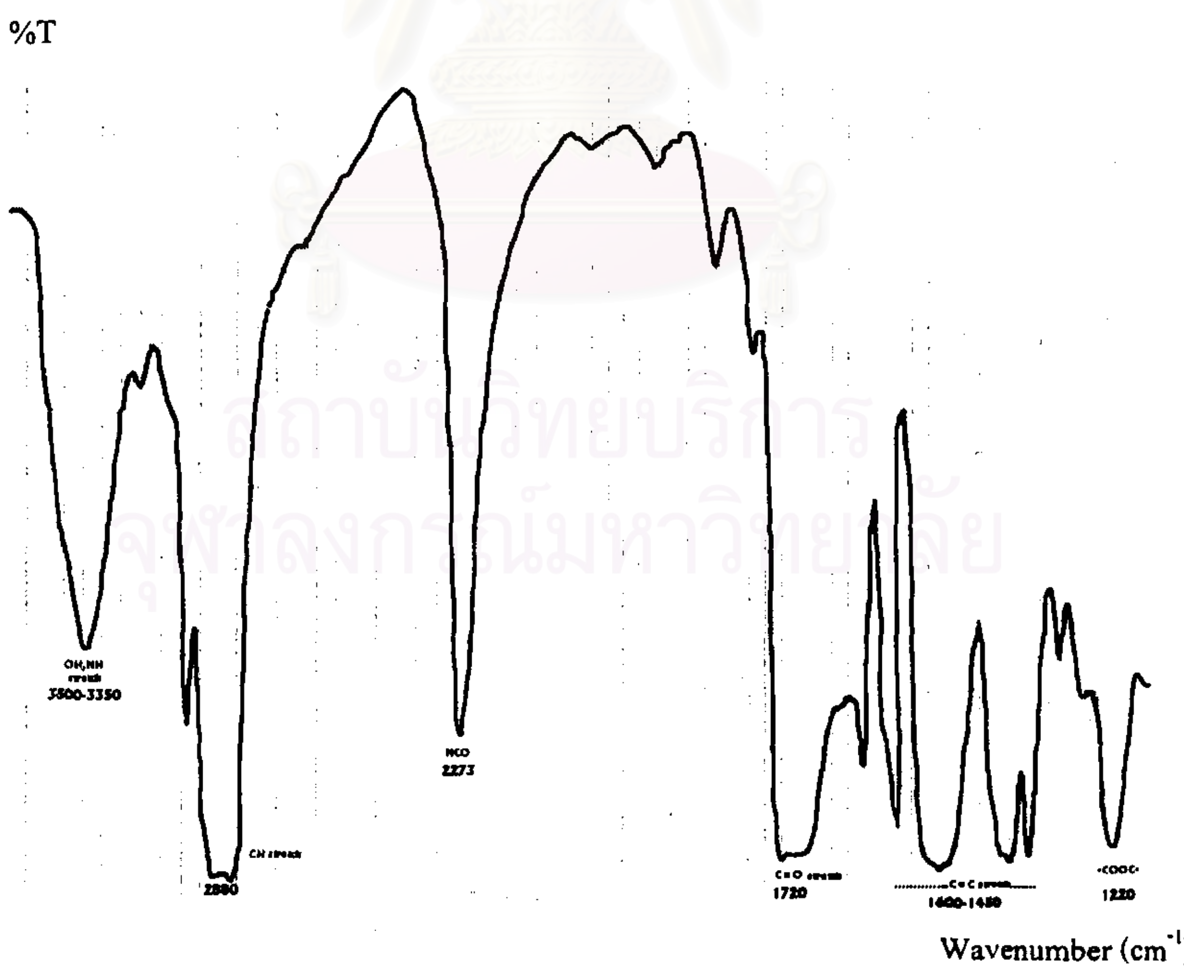

Figure 15 IR-spectra binder of OH:NCO ratio for 3:1

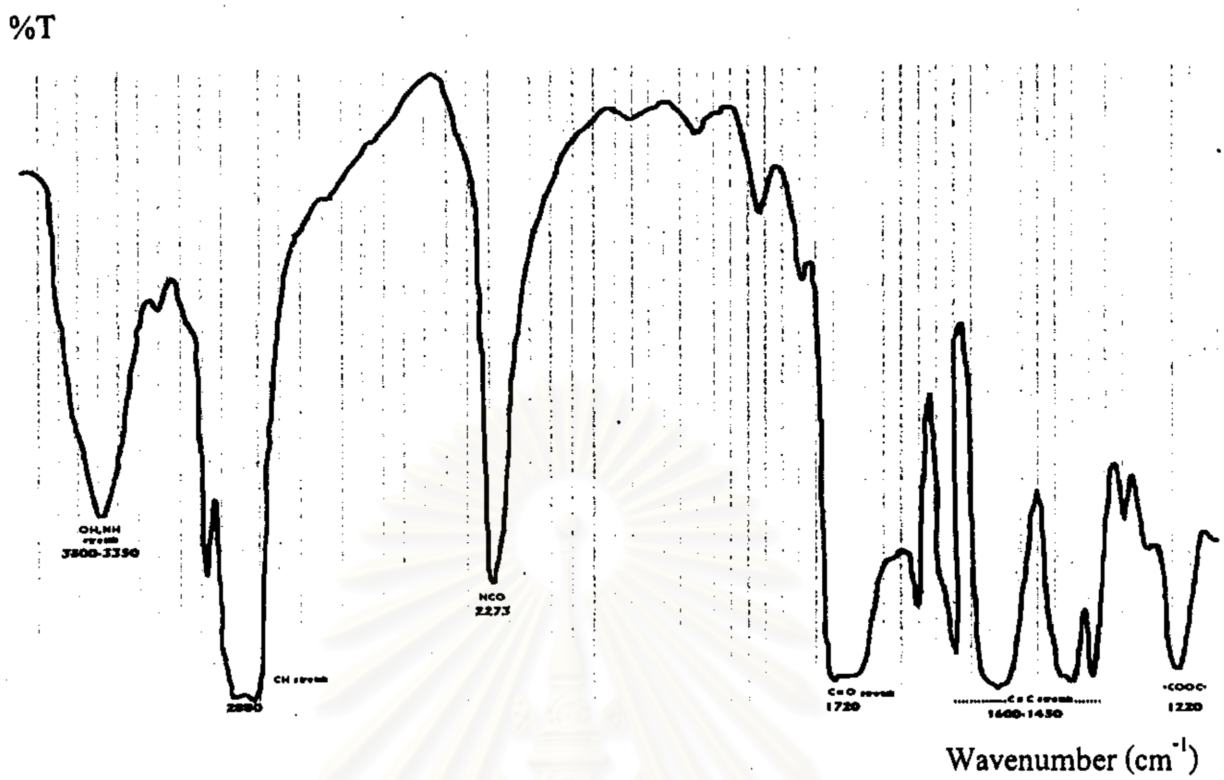

Figure 16 IR-spectra binder of OH:NCO ratio for 4:1

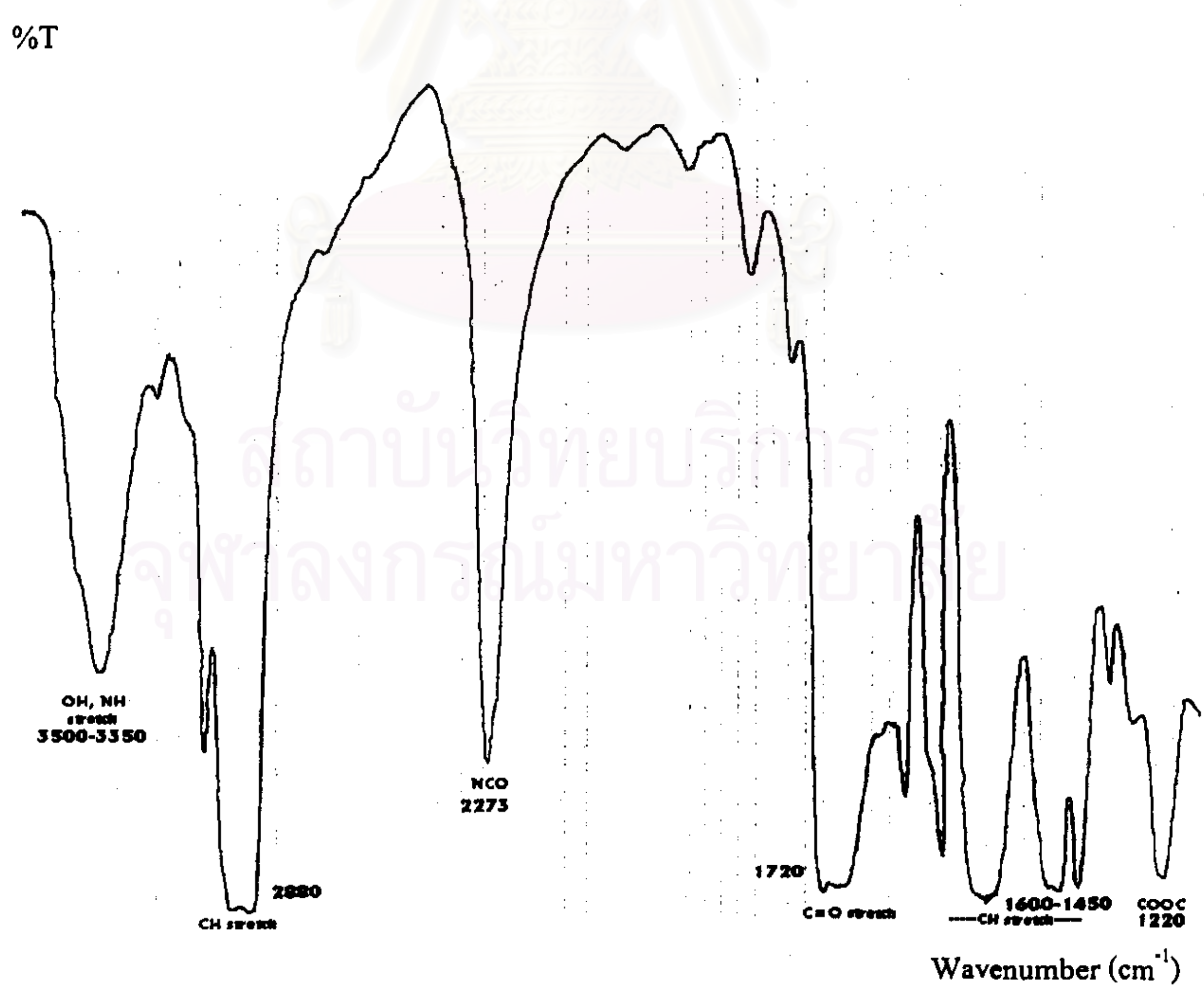

Figure 17 IR-spectra binder of OH:NCO ratio for 5:1

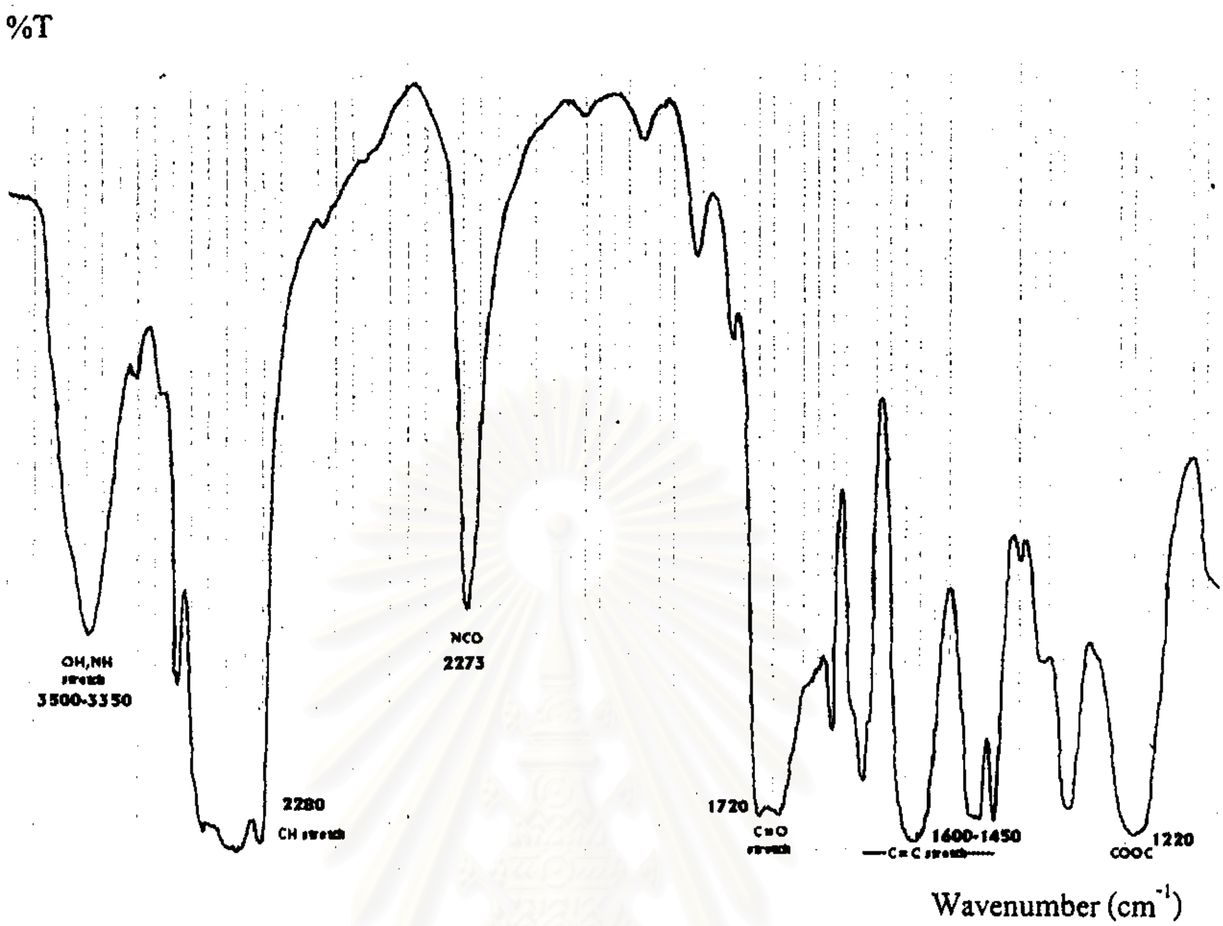

Figure 18 IR-spectra binder of OH:NCO ratio for 6:1

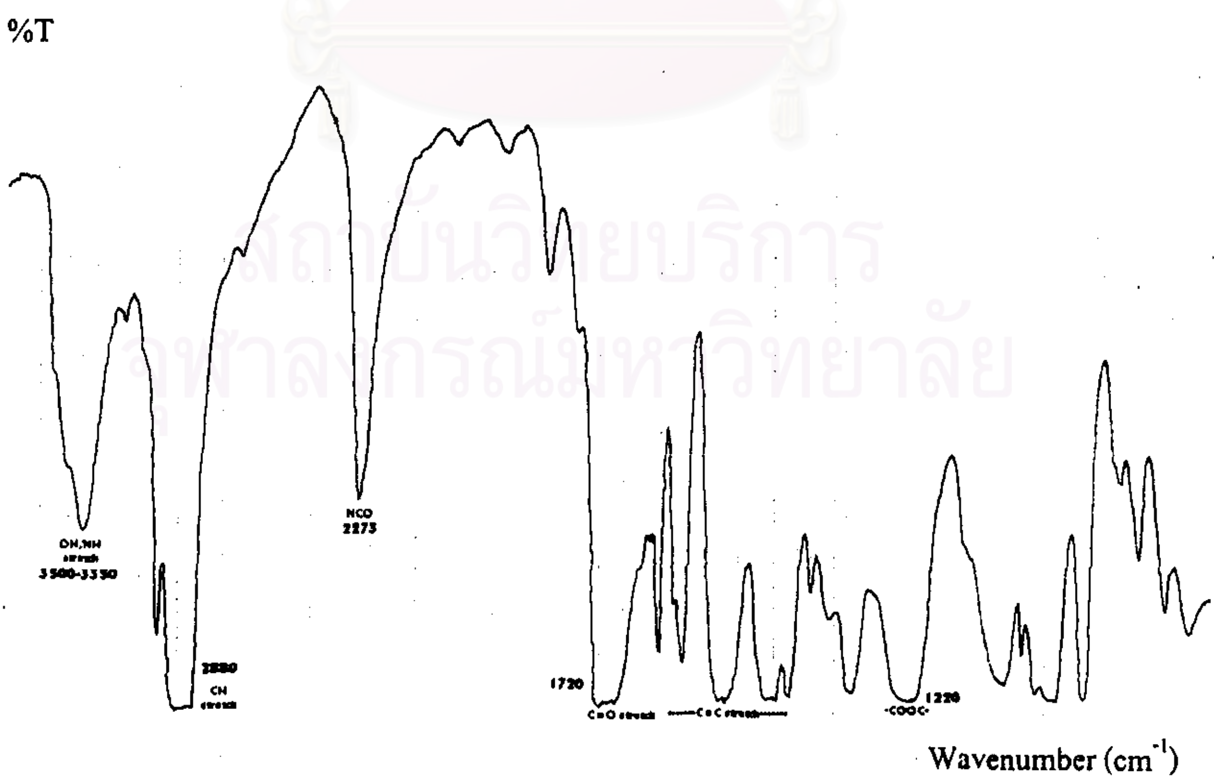

Figure 19 IR-spectra binder of OH:NCO ratio for 7:1

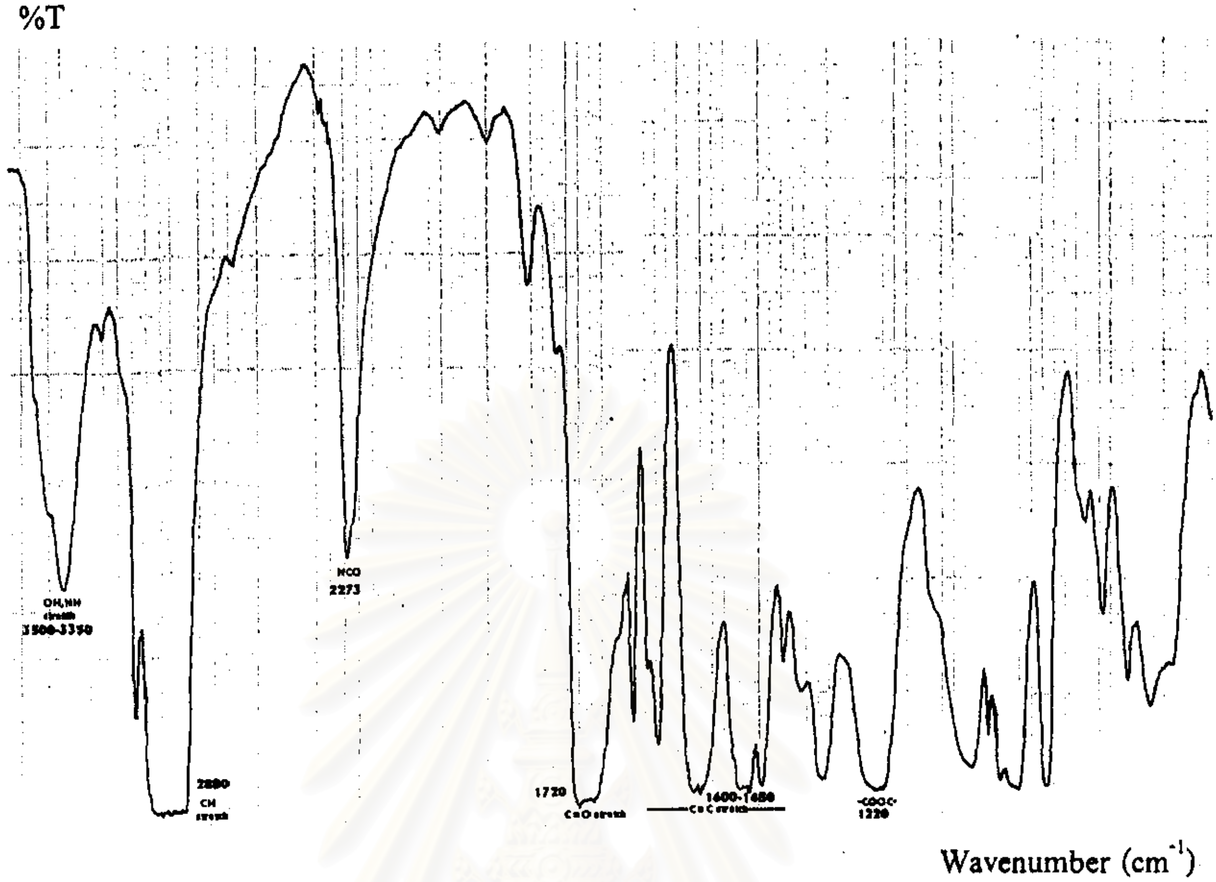

Figure 20 IR-spectra binder of OH:NCO ratio for 8:1

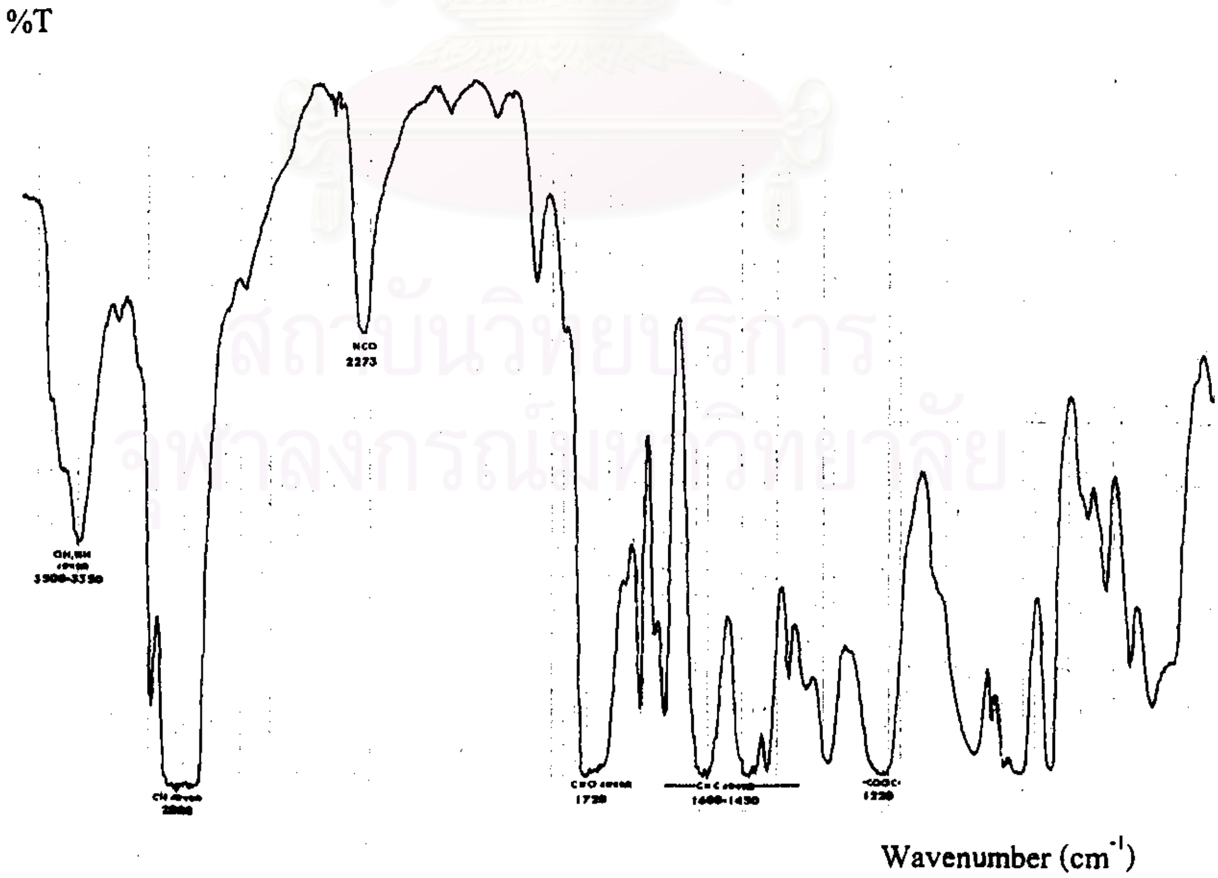

Figure 21 IR-spectra binder of OH:NCO ratio for 9:1

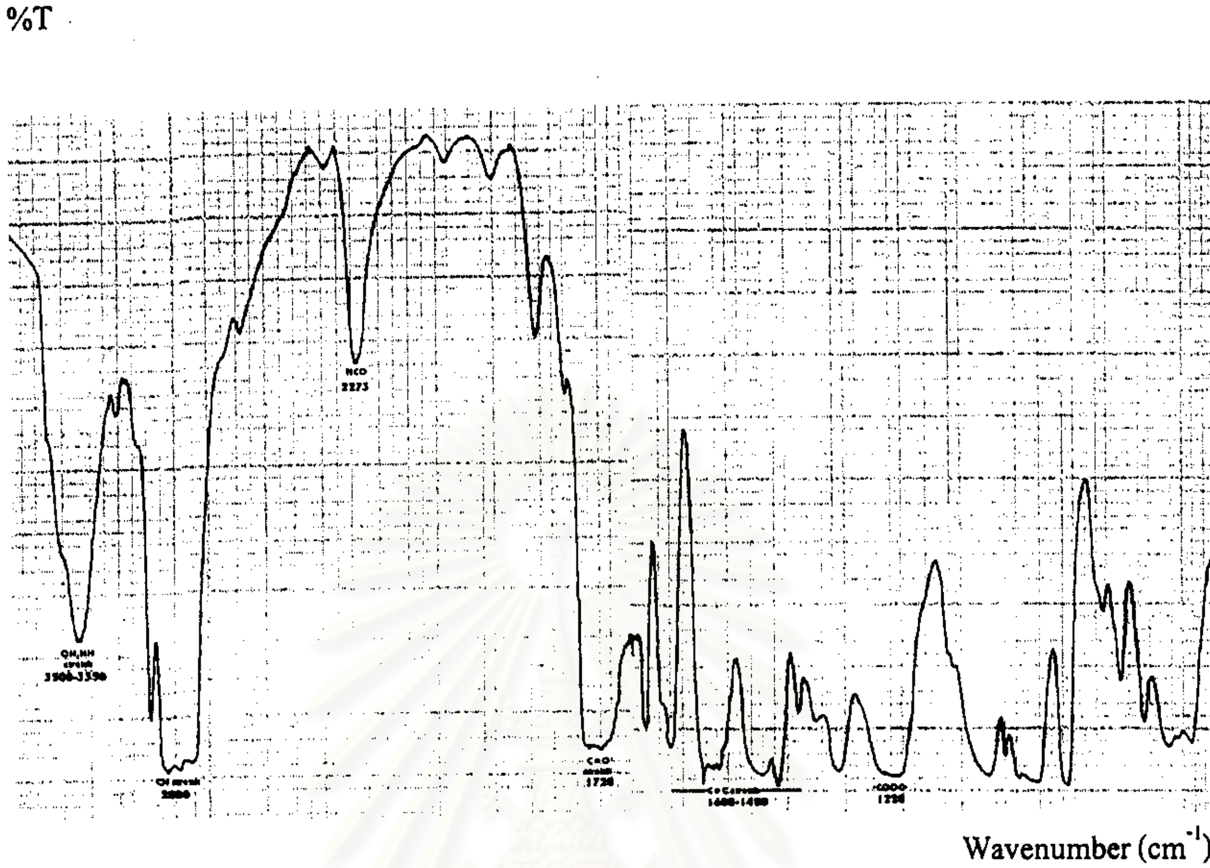

Figure 22 IR-spectra binder of OH:NCO ratio for 10:1

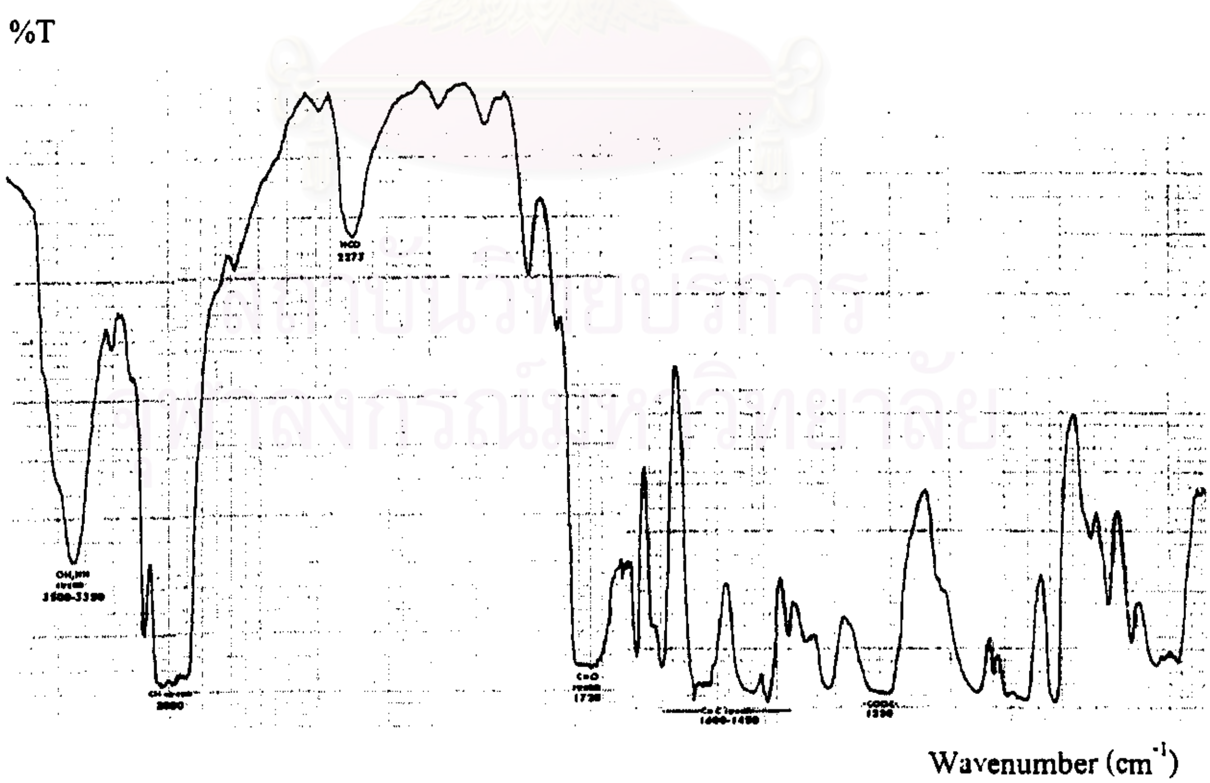

Figure 23 IR-spectra binder of OH:NCO ratio for 11:1

The IR spectra of OH:NCO 3:1 to 11:1 components were decreased of peak 3400 cm^{-1} (OH) and 2270 cm^{-1} (NCO) evidenced conversion of the OH and NCO groups but not absenced cause by steric hindrance.

GPC analysis

The HTPB and MDI were analyzed by GPC in tetrahydrofuran . The GPC traces are show in figure 24 to 25 .

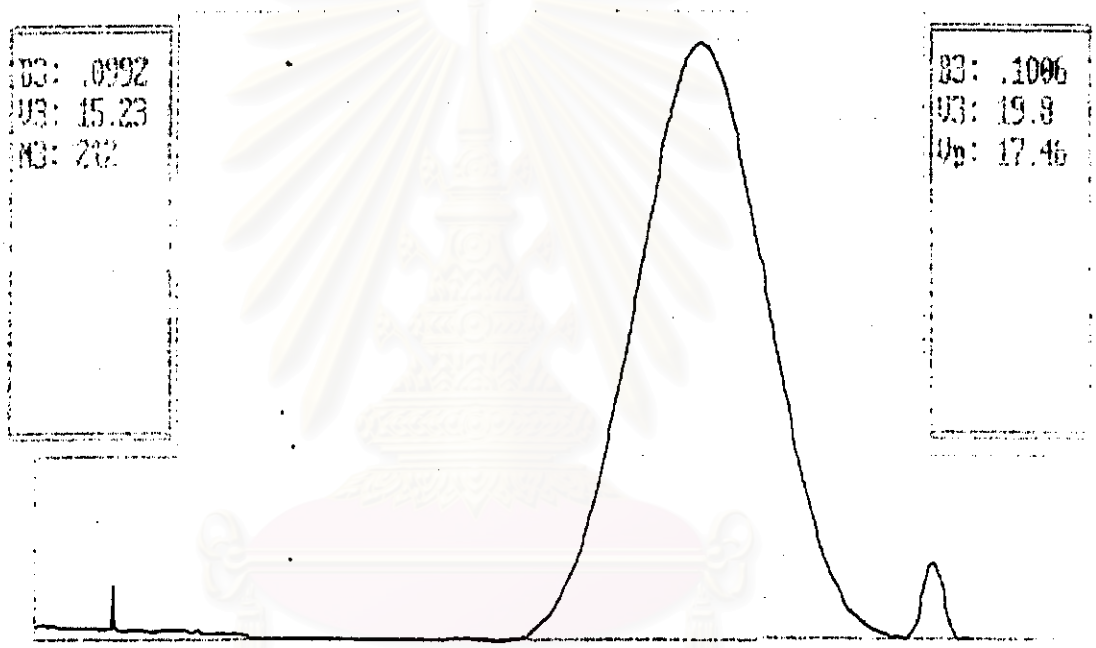

Figure 24 A typical gel permeation chromatogram of HTPB sample

The functionalities and molecular weight between crosslink calculated from GPC analysis of hydroxyl value for HTPB and NCO content for MDI.

The functionalities and molecular weight between crosslink calculated from GPC analysis of hydroxyl value for HTPB and NCO content for MDI.

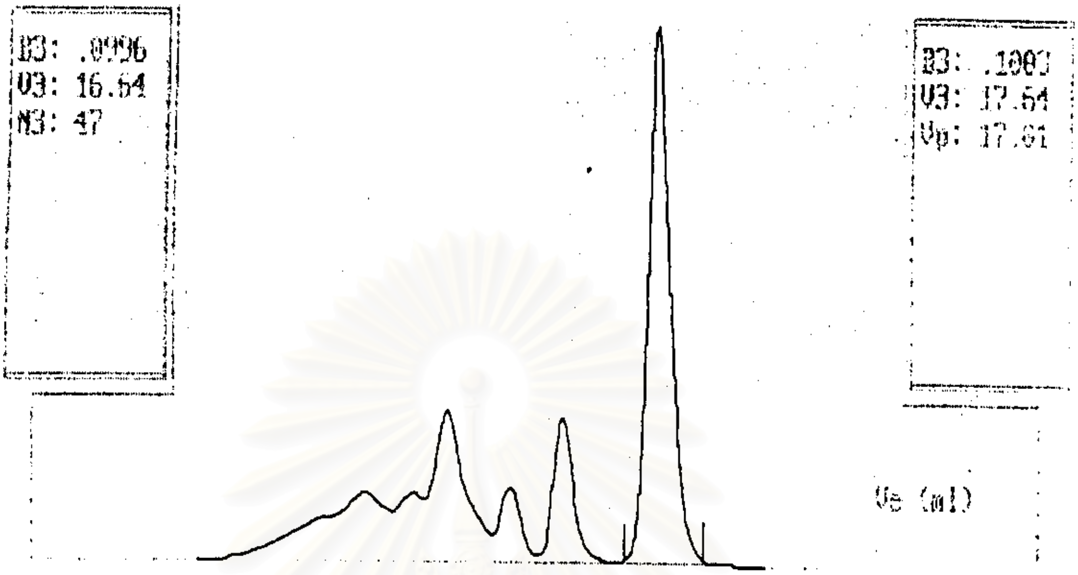

Figure 25 A typical gel permeation chromatogram of a polymeric MDI

The GPC curves indicated a molecular weight distribution for both of HTPB and MDI resin, are show in figures 26 and 27, that have effected to mechanical properties of polyurethane binders.

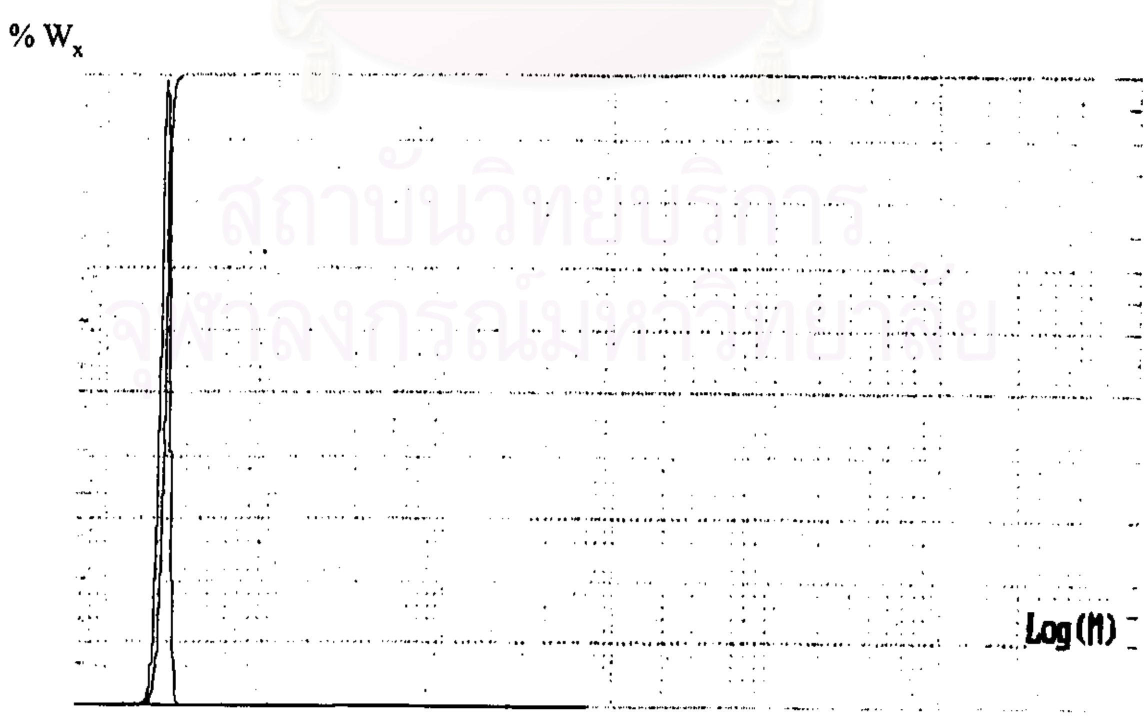

Figure 26 The distribution of molecular weights in a polymeric MDI

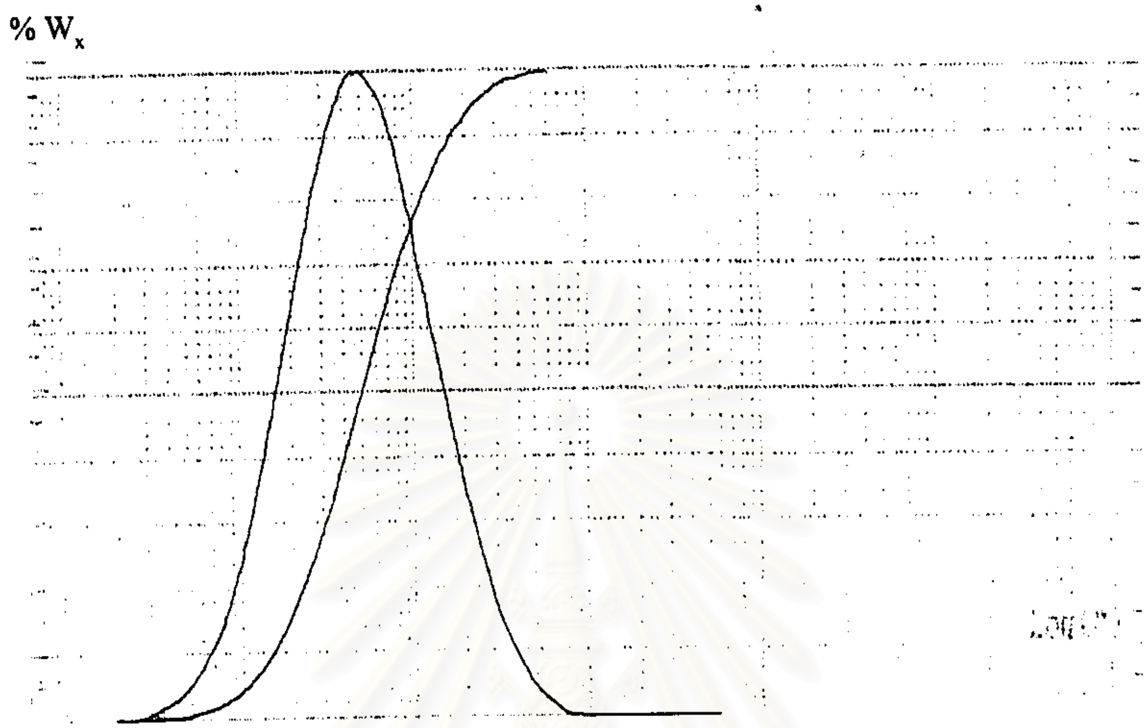

Figure 27 The distribution of molecular weights in a typical HTPB sample

Mechanical measurements

Polyurethane binders were prepared by reaction of HTPB and MDI at various OH:NCO ratio by using DBTL as catalyst at 80 °C in vacuum oven. Mechanical testings are tensile properties, peel strength (adhesive test), and shear strength.

1. Tensile properties

The modulus and stiffness of polyurethane binders are follow from high to low at OH:NCO ratio of 3:1 to 11:1, excepted in series 3 and 4 are follow from 4:1 to 10:1 ratio because the 3:1 ratio can be formed. This can be explained on the basis of the soft segments of polyol in the synthesis polyurethane binders. Therefore, these ratios lead to increase in elongation of polyurethane binders as show in figure 29

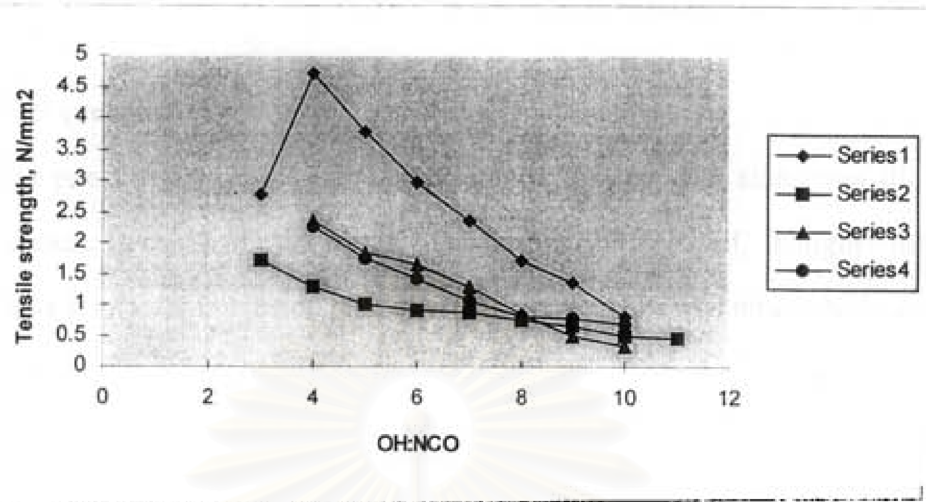

Figure 28 Plot of tensile strength versus OH:NCO ratio in series 1,2,3, and 4

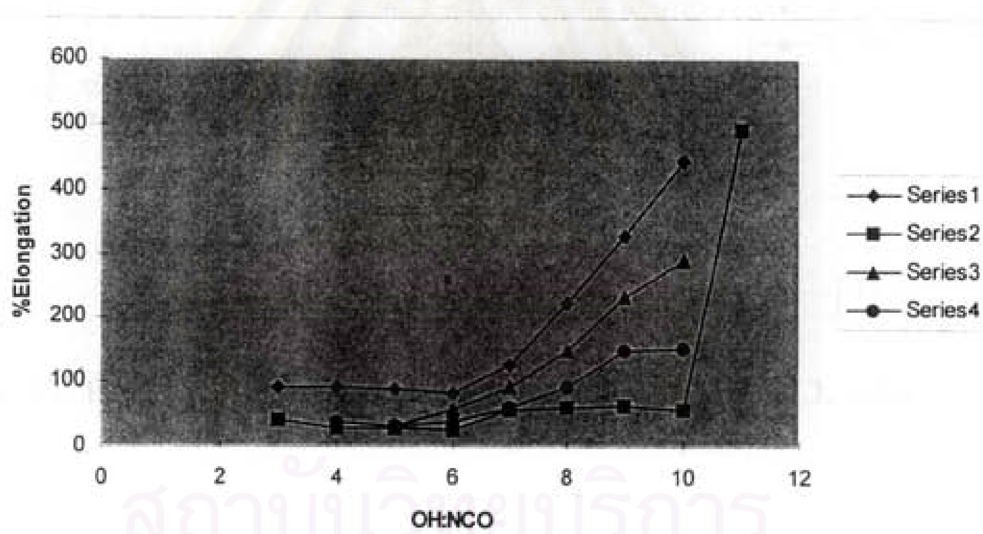

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Figure 29 Plot of percent elongation versus OH:NCO ratio in series 1,2,3, and 4

The equivalent stoichiometric amounts of the various OH and NCO were used in the experiment that keep at OH/NCO ratio of 1:1 (OH:NCO,12:1) that has been equivalent weight of HTPB and MDI. The tensile strength of series 2 is high,1.7 N/mm^2, and elongation is 489.33 %, in the other hand , series 1 (polyols standard) shows highest tensile strength and elongation, 4.72 N/ mm^2 and 444.00 % that are presented in figures 28 and 29

2. Peel strength

The peel strength is the test in adhesion of binders with aluminum alloys that use for motor rocket. Because of the better adhesion in HTPB-based, is higher than polyols-based urethane but lower in tension test. Therefore, researcher was mixed both series to form series 3 and 4.

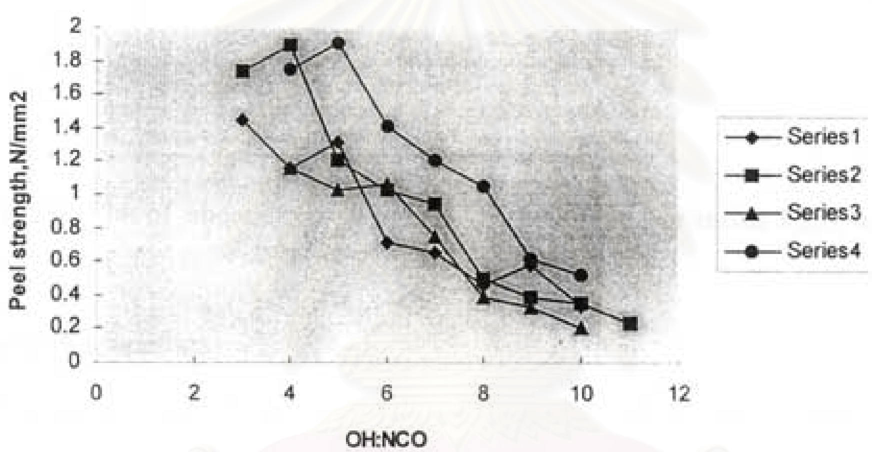

Figure 30 Plot of peel strength versus OH:NCO ratio in series 1,2,3, and 4

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3. Shear strength

The shear strength is the test in adhesion of bider force direction acts parallel to the area over while it acts, according to ASTM D 816 with aluminum alloys. polyols-based and HTPB-based approximate in tensile strength and reduce of OH:NCO ratio from 3:1 to 11:1, whereas, the mixed series, 3 and 4, are higher than polyols-based and HTPB-based in the same ratio.

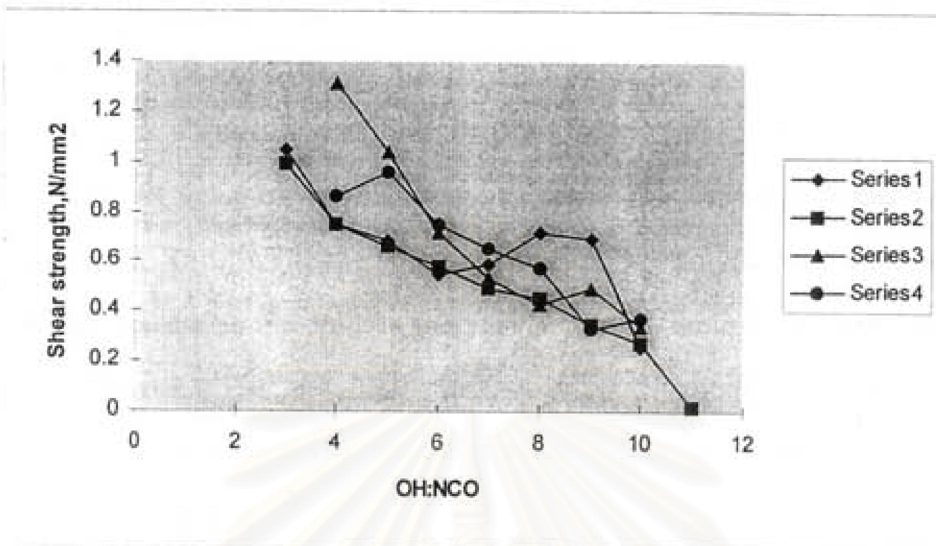

Figure 31 Plot of shear strength versus OH:NCO ratio in series 1,2,3, and 4

4. Swelling properties

Table 8 Typical values of the swelling coefficient for Polyols and HTPB-based

Solvent		Series 1	Series 2	Series 3
	ρ_1, (g/ml)	Q, (ml/g)	Q,(ml/g)	Q (ml/g)
n - hexane	0.66	0.25	0.79	0.43
Carbon tetrachloride	1.59	0.87	2.49	2.19
Toluene	0.87	0.99	2.51	2.38
2 - butanone	0.81	0.65	0.88	1.67
Benzene	0.88	1.02	2.36	2.51
Cyclohexanone	0.95	0.77	2.07	2.55
Chlorobenzene	1.11	1.15	2.68	2.85
Acetone	0.79	0.55	0.40	1.01
Tetrahydrofuran	0.89	1.27	3.06	3.24
Methanol	0.79	0.35	0.08	0.64

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The swelling properties of polyurethane binders listed in table 8 show that the swelling coefficients, (Q) of series 2 is significantly higher than series 1, polyols standard, explained that series 2 has a crosslink density lower than series 1, its effecte of functionalities and OH value of polyols are much more. This aspect is further reflected in other swell properties. Thus, while the volume fraction of the polymer and crosslink density decrease with the increase in the polyols and HTPB content, the molecular weight between the crosslinks increase. The crosslink density of the various compositions of the polyurethane binders having varied amounts of HTPB and polyols. The polyols-MDI sery gives highest crosslink density.

4.1. Effect of OH/NCO ratio

Tensile properties of the binders depend mainly on the composition of OH, NCO groups and functionalities of both resin. Variation of tensile strength and elongation are plotted as a function of OH/NCO ratios in figures 28 and 29. Generally, in all cases as OH/NCO ratio decreases, tensile strength increases and elongation decreases. This is expected because decreased OH/NCO leads to increased crosslinking of the matrix in all systems. Series 2 cures even at as low an OH:NCO ratio as 11:1, wheras, series 1 does not cure a OH:NCO ratio of 11:1. This is because the OH value of polyols standard is higher than HTPB prepolymer. In the case of series 3 and 4, curing do not take place at OH:NCO ratio of 11:1 because the main composition is polyols. Above the OH:NCO ratio of 10:1 and 11:1 of polyols and HTPB-based can not be formed.

4.2 Effect of molecular weight between crosslinks

Molecular weight between crosslink is more useful than simple functionality in evaluating the effects of prepolymer modifications on elastomer properties. Table 9 gives values of M_c calculated for the thirty-one experimental batches of binder at different OH/NCO ratios. Figure 32 gives the variation of mechanical properties with molecular weight between crosslinks.

This shows that even low M_c, leads to increased tensile strength and stiffness, in the other hand, decreased in the case of elongation of all four series (1,2,3 and 4).

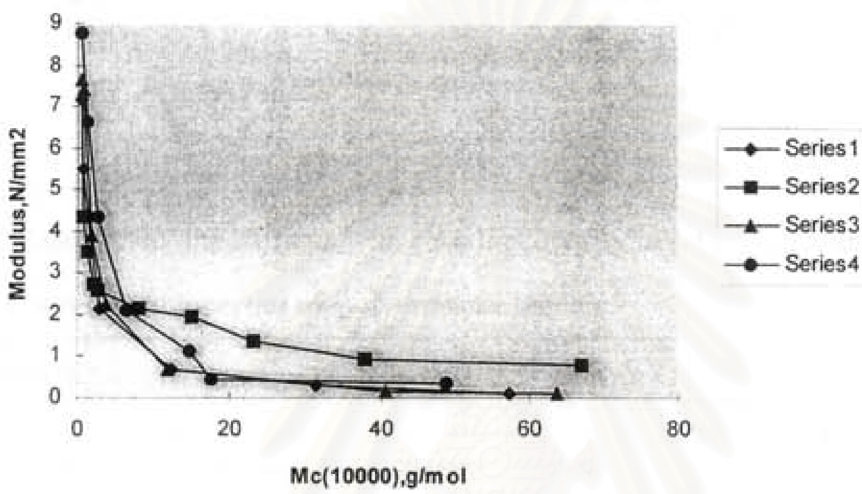

Figure 32 Plot of modulus versus molecular weight between crosslinks

4.3 Effect of crosslink density

Crosslink density is conversion of molecular weight between crosslink, has been calculated using the equation:

$$Ve = \frac{\rho_2}{Mc}$$

Where ρ_2 is the density of the polymer in g/ml and M_c is the molecular weight between crosslink in g/mol that presented in table 9. A different OH:NCO ratios of thirty-one batches give the variation mechanical properties. This shows even high Ve thus, the stiffness and tensile strength increased with increasing the Ve , whereas, the elongation decreased.

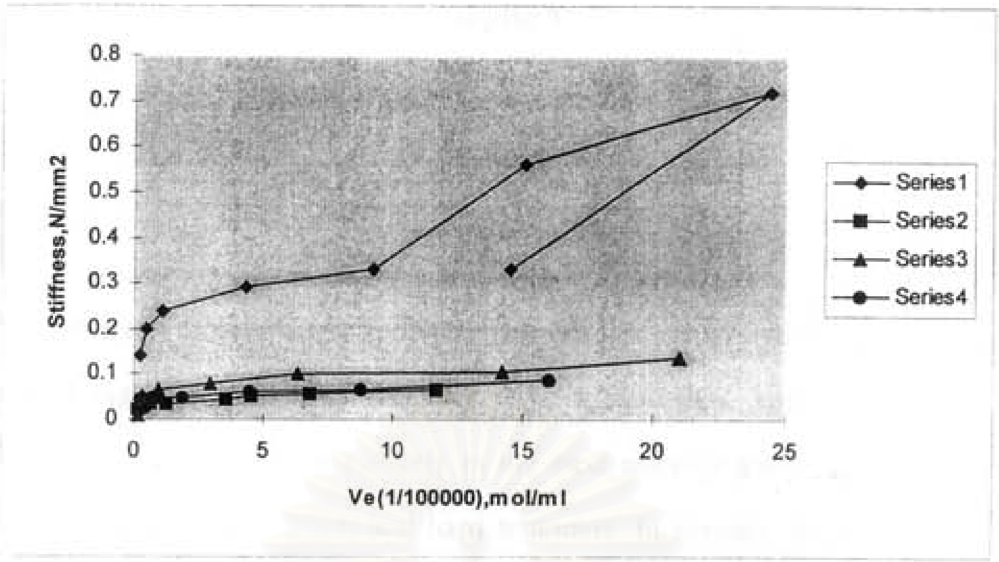

Figure 33 Variation of the stiffness with crosslink density in series 1,2,3, and 4

Table 9 The swelling[a] properties of polyurethane binders

Series / Property	OH:NCO Ratio								
	3:1	4:1	5:1	6:1	7:1	8:1	9:1	10:1	11:1
Series 1									
V_2	0.39	0.45	0.40	0.35	0.28	0.19	0.14	0.12	
Ve ($x10^{-5}$)	14.50	24.40	15.10	9.25	4.29	1.09	0.43	0.24	
M_c ($x10^4$)	0.87	0.49	0.81	1.38	3.02	12.42	31.65	57.28	
Series 2									
V_2	0.37	0.32	0.28	0.26	0.19	0.16	0.14	0.13	0.11
Ve ($x10^{-5}$)	11.70	6.75	4.52	3.56	1.21	0.64	0.41	0.26	0.14
M_c ($x10^4$)	0.74	1.41	2.18	2.70	7.91	15.05	23.30	37.91	67.12
Series 3									
V_2	-	0.43	0.39	0.31	0.25	0.18	0.13	0.11	
Ve ($x10^{-5}$)	-	21.00	14.20	6.30	2.94	0.95	0.28	0.18	
M_c ($x10^4$)	-	0.49	0.80	1.87	3.79	11.66	40.71	63.71	
Series 4									
V_2	-	0.40	0.34	0.28	0.22	0.17	0.16	0.12	
Ve ($x10^{-5}$)	-	16.00	8.78	4.45	1.88	0.80	0.66	0.24	
M_c ($x10^4$)	-	0.60	1.29	2.69	6.30	14.80	17.71	49.02	