

Chapter 3

Experimental Procedures

Determination of the hydroxyl value of HTPB

1. Apparatus

- 1.1 Bottles pressure, borosilicate glass
- 1.2 Buret, 100 ml capacity
- 1.3 Pipet, 10ml and 25 ml capacity
- 1.4 Vacuum oven
- 1.5 Beaker, 1000 ml
- 1.6 Separatory funnel, 500 ml
- 1.7 Thermometer, 100 °C
- 1.8 Balance
- 1.9 Shaker bath

2. Reagents

2.1 Pyridine-Distilled from phthalic anhydride, discarding the fraction boiling below 114-115 °C. Store in brown glass bottle.

2.2 Phthalic anhydride (Pyridine reagent) -Weigh 28.0608 grams of phthalic anhydride into a brown bottle. Add 175 ml of pyridine, which has been distilled from phthalic anhydride, and shake vigorously until dissolved. The reagent stand overnight before use.

2.3 Phenolphthalein indicator solution-Prepare a solution of 0.2532 gram of phenolphthalein in 25 ml of pyridine.

2.4 Potassium acid phthalate-Use for standardization.

2.5 Sodium hydroxide, Standard solution (0.5 N) - Prepare a 0.5 N solution of sodium hydroxide and standardize as follows

2.5.1 Weigh 12.7592 grams of potassium acid phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) and dry it for 1-2 hour at 100 °C.

Place in a glass-stopper container, cool in a desiccator and transfer to a 250-ml conical flask. Add 125 ml of distilled water, stop the flask, and swirl it gently until the sample is dissolved.

2.5.2 Weigh 10.0972 grams of sodium hydroxide (NaOH) and transfer to a 1000 ml conical flask. Add 500ml of distilled water and swirl until it dissolved.

2.5.3 Titrate 25 ml KHP with 0.5 N sodium hydroxide solution

2.5.4 Calculate the normality of the sodium hydroxide as follows

$$N = W/(V \times 0.2042)$$

Where

N = Normality

W = $\text{KHC}_8\text{H}_4\text{O}_4$, g

V = NaOH required for titration of the $\text{KHC}_8\text{H}_4\text{O}_4$, ml

3. Procedure

3.1 Prepare a sufficient number of clean, dry bottles to make all blank and sample determinations in duplicate. Replace the rubber gaskets and make certain the caps can be fastened securely.

3.2 Accurately pipet 25 ml of the phthalic anhydride reagent in to each of bottles for blank and sample. Use the same pipette for both sample and blank determinations.

3.3 Reserve three of the bottles for the blank determination.

3.4 Cured sample at 80 °C for 24 hours.

3.5 The amount of sample calculated as follows

$$\text{Sample size, g} = 561/\text{estimated hydroxyl value}$$

3.6 Swirl to dissolve completely, cap the bottles. Keep the samples and blanks as close together as possible in the water bath, maintained at 98 °C, for 2 hours. Maintain sufficient water in the bath to cover the liquid in the bottles.

3.7 Remove the bottles from the bath and allow them to cool to room temperature.

3.8 When the bottles have cooled, uncap them carefully to release any pressure.

3.9 To each bottle, add 50 ml of redistilled pyridine and 3-4 drops of the phenolphthalein indicator solution, and titrate with standard 0.5 N NaOH solution to a pink end point that persists for 15 seconds.

3.10 Acidity correction

3.10.1 Prepare 0.1 N KHP for standardization with 0.1 N NaOH by weight 2.0418 grams KHP solute in 100 ml of distilled water and weigh 2.0896 grams of NaOH solute in 500 ml of distilled water. Two bottles for standardization and phenolphthalein indicator solution with a pink end-point

3.10.2 Normality of solutions are calculate as follow:

$$C_1 = (W_1 \times 1000) / V_1 \times 204.1$$

$$N = (C_1 \times V_1 / V_2)$$

Where

C_1 = normality of KHP

W_1 = weight of KHP, g

V_1 = volume of KHP solution, ml

N = normality of NaOH standard solution

V_2 = NaOH solution required for titration with KHP, ml

3.10.3 Weigh 12.47 grams of sample into a 400-ml flask that taken previously for the hydroxyl determination. Add to the flask 75 ml of redistilled pyridine, 75 ml of distilled water, and 3-4 drops of phenolphthalein indicator solution. The solution is colorless, titrate with standard 0.1 N NaOH solution to a pink end point that persist for 15 seconds.

3.10.4 Make a blank titration on the reagent mixture as 3.10, omitting the sample.

The acidity correction is calculate as follows:

$$\text{Acidity correction} = [(A-B) \times 56.1] / W$$

Where

A = NaOH solution required for titration of the sample, ml

B = NaOH solution required for titration of the blank, ml

W = Sample used, g

4. Results

4.1 standardization of KHP with NaOH solution

No.	NaOH required ,ml
1	21.7
2	21.5
3	21.6
4	21.5
mean	21.58

$$\begin{aligned}
 C_1 &= (W_1 \times 1000) / (V_1 \times 204.1) \\
 &= (12.7592 \times 1000) / (125 \times 204.1) \\
 &= 0.50
 \end{aligned}$$

$$\begin{aligned}
 N &= (C_1 \times V_1) / V_2 \\
 &= (0.50 \times 25) / 21.58 \\
 &= 0.58 \text{ mol/l}
 \end{aligned}$$

4.2 Blank titration

No.	NaOH solution, ml
1	96.8
2	96.6
mean	96.7

4.3 Sample titration

sample-weight, g	NaOH solution, ml
12.47	77.5
12.47	78.9
mean	78.2

4.4 Acidity

4.4.1 standardization

$$\begin{aligned}
 C_3 &= W \times 1000 / V_3 \times 204.1 \\
 &= 2.0868 \times 1000 / 100 \times 204.1 \\
 &= 0.10
 \end{aligned}$$

$$\begin{aligned}
 C_4 &= C_3 V_3 / V_4 \\
 &= 0.10 \times 25 / 26.78 \\
 &= 0.093
 \end{aligned}$$

Where

C_3 = normality of KHP

V_3 = volume of KHP

C_4 = normality of NaOH standard solution

V_4 = NaOH solution required for titration

4.4.2 Determination

	Volume NaOH, ml
Blank	0.3
Sample	0.5

$$\begin{aligned}
 \text{Acidity correction} &= [(A-B) \times 56.1] / W \\
 &= [(0.5 - 0.3) \times 56.1] / 12.38 \\
 &= 0.91
 \end{aligned}$$

4.5 Hydroxyl value

$$\begin{aligned}
 \text{Hydroxyl value} &= [(B-A) \times 56.1] / W \\
 &= [(96.7 - 78.2) \times 0.50 \times 56.1] / 12.47 \\
 &= 41.52
 \end{aligned}$$

$$\begin{aligned}
 \text{Hydroxyl value (corrected)} &= \text{hydroxyl value} + \text{acidity} \\
 &= 41.52 + 0.91 \\
 &= 42.43
 \end{aligned}$$

Functionality of HTPB

HTPB is identified by its hydroxyl value and number average molecular weight (by GPC analysis). Hydroxyl value is defined as the number of milligrams of potassium hydroxide equivalent to active functions (hydroxy content) of 1 gram of the compound or polymer.

$$\begin{aligned}
 \text{Functionality} &= \frac{(\text{hydroxy value})(M_n)}{56100} \\
 &= \frac{(41.52)(3244)}{56100} \\
 &= 2.4
 \end{aligned}$$

56100 is the molecular weight of potassium hydroxide (KOH) used in the analyses expressed in milligrams, i.e. $\text{KOH}, 39.1 + 16 + 1 = (56.1)(1000)$

$$= 56100$$

Determination of hydroxyl value of polyols

1. Apparatus

- 1.1 Bottles pressure, borosilicate glass
- 1.2 Buret, 100 ml capacity
- 1.3 Pipet, 10 ml and 25 ml capacity
- 1.4 Vacuum oven
- 1.5 Beaker, 1000 ml
- 1.6 Thermometer, 100 °C
- 1.7 Balance
- 1.8 Shaker bath

2. Reagents

2.1 Pyridine-Distilled from phthalic anhydride, discarding the fraction boiling below 114-115 °C and Stored in brown glass bottle.

2.2 Phthalic anhydride (pyridine reagent) -Weigh 25.6200 grams of phthalic anhydride into a brown bottle. Add 160 ml of pyridine, which has been distilled from phthalic anhydride, and shake vigorously until dissolved. The reagent stand overnight before use.

2.3 Phenolphthalein indicator solution-Prepare a solution of 0.1232 gram of phenolphthalein in 12.5 ml of pyridine.

2.4 Potassium acid phthalate-Use for standardization

2.5 Sodium hydroxide, Standard solution (0.5 N) - Prepare a 0.5 N solution of sodium hydroxide and standardize as follows

2.5.1 Weigh 12.7592 grams of potassium acid phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) and dry it for 1-2 hours at 100 °C. Place in a glass-stopper container, cool in a desiccator and transfer to a 250-ml conical flask. Add 125 ml of distilled water, stop the flask, and swirl it gently until the sample is dissolved.

2.5.2 Weigh 10.0983 grams of sodium hydroxide (NaOH) and transfer to a 1000-ml conical flask. Add 500 ml of distilled water and swirl until it dissolved.

2.5.3 Titrate 25 ml KHP with 0.5 N sodium hydroxide solution

2.5.4 Calculate the normality of the sodium hydroxide as follows:

$$N = W/(V \times 0.2042)$$

Where

N = Normality of sodium hydroxide

W = $\text{KHC}_8\text{H}_4\text{O}_4$, g

V = NaOH required for titration of the $\text{KHC}_8\text{H}_4\text{O}_4$, ml

3. Procedure

3.1 Prepare a sufficient number of clean, dry bottles to make all blank and sample determinations in duplicate. Replace the rubber gaskets and make certain the caps can be fastened securely.

3.2 Accurately pipet 25 ml of the phthalic anhydride reagent in to each of bottles for blank and sample. Use the same pipet for both sample and blank determinations.

3.3 Reserve three of the bottles for the blank determination.

3.4 Cured sample at 80 °C for 24 hours.

3.5 The amount of sample calculated as follows

$$\text{Sample size, g} = 561/\text{estimated hydroxyl value}$$

3.6 Swirl to dissolve completely and cap the bottles. Keep the samples and blanks as close together as possible in the water bath, maintained at 98 °C, for 2 hours. Maintain sufficient water in the bath to cover the liquid in the bottles.

3.7 Remove the bottles from the bath and allow them to cool to room temperature.

3.8 When the bottles have cooled, uncap them carefully to release any pressure.

3.9 To each bottle, add 50 ml of redistilled pyridine and 3-4 drops of the phenolphthalein indicator solution, and titrate with standard 0.5 N NaOH solution to a pink end point that persists for 15 seconds.

4. Results

4.1 standardization of KHP with NaOH solution

No.	NaOH required , ml
1	21.7
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mean	21.58

$$\begin{aligned}
 C_1 &= (W_1 \times 1000) / (V_1 \times 204.1) \\
 &= (12.7592 \times 1000) / (125 \times 204.1) \\
 &= 0.50
 \end{aligned}$$

$$\begin{aligned}
 N &= (C_1 \times V_1) / V_2 \\
 &= (0.50 \times 25) / 21.58 \\
 &= 0.579
 \end{aligned}$$

4.2 Blank titration

No.	NaOH solution, ml
1	96.8
2	96.5
3	96.2
Mean	96.5

4.3 Sample titration

No	sample-weight, g	NaOH solution, ml
1	11.01	74.8
2	11.04	75.5
3	11.02	75.0
Mean	11.023	75.1

4.4 Hydroxyl value

$$\begin{aligned}
 \text{Hydroxyl value} &= [(B-A)N \times 56.1] / W \\
 &= [(96.5 - 75.1) 0.579 \times 56.1] / 11.023 \\
 &= 63.06
 \end{aligned}$$

Determination of the isocyanate content of MDI

Method - HEATED TOLUENE-DIBUTYLAMINE

1. Apparatus

- 1.1 pH meter
- 1.2 Combine electrode
- 1.3 Pipet, 25-ml
- 1.4 Magnetic stirrer
- 1.5 Thermometer, 100 °C
- 1.6 Balance
- 1.7 Shaker bath

2. Reagents

2.1 Dibutylamine solution-Dilute 65.01 grams dibutylamine to 250 ml with dry toluene.

2.2 Hydrochloric acid (1 N)- Prepare 1 N HCl solution by standardization with 0.1 N NaOH solution, add 3-4 drops of phenolphthalein indicator solution to a pink end-point that persist for at least 15 seconds.

2.3 Isopropyl alcohol, 99.7% purity.(minimum 99%)

2.4 Dry toluene

Very high purity toluene, (bp 110.6 °C) is achieved by shaking or stirring toluene with concentrated sulfuric acid (100 ml/liter toluene), removing the acid layer and repeating until darkening becomes slight. Decant the toluene into a clean flask for distillation, however keep cool below 20 °C during H₂SO₄ treatment due to the greater reactivity of these hydrocarbons toward sulfonation. Presume that, if the boiling point keeps at 110.6 °C so the reagent is purified (from the chemist's companion)

3. Procedure

3.1 Add 50 ml of dry toluene to a dry 600-ml beaker. Pipet 25 ml of the dibutylamine solution into the beaker. Swirl the beaker to mix the contents.

3.2 Transfer to the beaker 0.02-0.03 equivalents of the sample weighed (61.5010 grams solution, and 1.5378 gram sample) to the nearest 0.001 gram. Start the magnetic stirrer carefully and rinse the sides of the beaker with an additional 10 ml of dry toluene. Cover the beaker and continue mixing for an additional 20 minutes.

3.3 Place the beaker on the hot plate with the 200 °C thermometer in the sample. Heat the sample mixture with stirring, so that the solution reaches a temperature of 95 to 100 °C in 3.5-4.5 minutes. Do not over heat. Quickly remove the beaker from the hot plate, cover it with the watch glass, and allow it to stand for 30 minutes.

3.4 Cool the beaker with water and add 225 ml of isopropyl alcohol.

3.5 Titrate potentiometrically with 1.0 N HCl to the break that occurs at approximately pH 4.2 to 4.5.

3.6 Titrate a blank exactly as described in 3.1 to 3.5, but without adding the sample.

4. Results

4.1 standardization

Dilute 41.5 ml of concentrate HCl acid with 500 ml distilled water to the beaker, this calculate the normality as follows:

$$\begin{aligned} \text{Concentration of HCl} &= [10 \times D \times X] / M \\ &= [10 \times 1.19 \times 1000 \times 37] / 1000 \times 36.5 \\ &= 12.06 \text{ mol/l} \\ C_4 V_4 &= C_5 V_5 \\ 12.06 \times 41.5 &= C_5 \times 500 \\ C_5 &= [12.06 \times 41.5] / 500 \\ &= 1.00 \text{ mol/l} \end{aligned}$$

Where

C_5 = normality required for HCl

D = density of HCl

X = percentage, w/w

M = molecular weight of HCl

Add 5 ml of HCl and 3-4 drops of phenolphthalein indicator solution to the flask at a pink end-point as results :

No	NaOH required, ml
1	48.3
2	48.5
mean	48.4

$$\begin{aligned} \text{Normality, HCl} &= (48.4 \times 0.093) / 5 \\ &= 0.90 \end{aligned}$$

4.2 Determination

Blank	HCl required, ml
1	45.6
2	45.3
3	45.7
mean	45.53

No	Sample weight, g	HCl required, ml
1	1.5378	27.7
2	1.5628	27.5
3	1.5626	30.4
mean	1.5544	28.53

4.3 Calculations

$$\begin{aligned}
 \%NCO &= [4.202(B-S)N]/W \\
 &= [4.202(45.53-28.53)0.90]/1.5544 \\
 &= 41
 \end{aligned}$$

Where:

B = HCl required for titration of blank, ml

S = HCl required for titration of sample, ml

N = normality of HCl

W = sample used, g, and

4.202 = constant combining the equivalent weight of NCO, conversion of gram to 1000 milligram and conversion to 100 %

Functionality of MDI

MDI is identified by its NCO content and number average molecular weight (by GPC analysis). Also, active isocyanate content of MDI decreases with storage, a decrease of about 0.05 % per month being normal. For these reasons it is necessary to measure the amount of isocyanate available for reaction at any specific time. It can be calculated from NCO content as follows:

$$\begin{aligned}
 \text{Functionality} &= \frac{(\text{NCO content})(M_n)}{\text{Molecular weight of NCO}} \\
 &= \frac{(0.4136)(218.4)}{42} \\
 &= 2.1
 \end{aligned}$$

Determination of the moisture of HTPB and MDI

1. Apparatus

- 1.1 Potentiometric automatic titrator, (T 80/20)
- 1.2 Magnetic stirrer
- 1.3 Syringe, 10 μ l
- 1.4 Balance

2. Reagents

2.1 Karl Fischer (KF) reagent (mixture of iodine, sulfur dioxide, pyridine and methanol)

2.2 Distilled water

3. Procedure

- 3.1 Turn on switch the T 80/20 and end point detector
- 3.2 Clean vessel with methanol and turn on the magnetic stirrer (TM 120)
- 3.3 Feed the KF reagent into the burette
- 3.4 Turn the knob to T position (T = titration, F = feed)

4. Results

4.1 Determination of equivalent weight of water by titration KF with 10 μ l of distilled water (C- factor)

No	C-factor, mg H ₂ O/ml
1	2.5
2	3.36
3	3.24
mean	3.05

4.2 Determination of the percentage of moisture in HTPB prepolymer:

$$\% \text{H}_2\text{O} = V \times E / 10 \times W_s$$

where

V = KF required for titration, ml

E = water equivalent of KF reagent, mg/ml

W_s = weight of samples, g

V_s = Volume of samples, ml

No	W _s , g	V _s , ml	%H ₂ O
1	3.1518	0.18	0.017
2	1.4390	0.19	0.040
3	1.4493	0.40	0.084
4	3.0410	0.96	0.096
Mean			0.059

4.3 Determination of the percentage of moisture in polymeric MDI

No	Ws, g	Vs, ml	%H ₂ O
1	3.1106	0.160	0.012
2	3.1183	0.150	0.014
3	3.1227	0.240	0.022
4	3.0807	0.089	0.0088
5	3.3300	0.170	0.1557
Mean			0.0425

Apparatus

1. Glass plates
2. Beakers
3. Vacuum pump
4. Stainless stirrer
5. Vacuum oven
6. Hygrometer
7. Vernier caliper
8. Gel permeation chromatography
9. Instron universal testing machine
10. Infrared spectrophotometer

Materials

Polyurethane binder based on MDI and HTPB were prepared. HTPB synthesized by the free radical polymerization of butadiene was supplied by Science and Weapon System Development Center, RTAF. It has an average number molecular weight, 3244 by GPC; functionality 2.4; hydroxyl value, 41; and viscosity, 6500 cp at 30 °C.

MDI synthesized by condensation of aniline with formaldehyde to form diaminodiphenylmethane and derived by phosgenation of diaminodiphenylmethane.

It has number-average molecular weight, 218 ; functionality, 2.1 ; and % NCO content, 42.

Dibutyltin dilaurate, (0.001 wt %), was used as the catalyst

Table 5 Characteristics of HTPB (at 30 ± 2 °C)

Properties	
Hydroxyl value (mg KOH/g)	41
Acid value (mg KOH/g)	0.91
Molecular weight (\bar{M}_n by GPC)	3244
Average functionality	2.4
Polydispersity (M_w/M_n by GPC)	2.32
Percent H ₂ O content (%)	0.06

Table 6 Characteristics of MDI (at 30 ± 2 °C)

Properties	
Percentage NCO content (%)	42
Molecular weight (\bar{M}_n by GPC)	218
Average functionality	2.1
Polydispersity (M_w/M_n by GPC)	1
Percent H ₂ O content (%)	0.04

GPC analysis

GPC was used to separate and measure the concentrations of the species in prepolymer. The retention time versus molecular weight of the GPC system was calibrated with a narrow-molecular weight PPG (Poly propylene glycol) standards by the same procedures as given for the Voranol PPG.

A calibration curve plotted from the data on the Voranol PPG samples. The molecular weight distribution of MDI and HTPB prepolymer were measured by the gel permeation chromatography in THF at 40 °C, equipped with the three columns of porosities in the rang 1000, 500, 100 Å and consisting of two units: a 600 E pump system and 490 E UV differential refractometer.

The carrier solvent was THF (IR grade) and the elution rate was 0.1 ml/min. The HTPB and MDI were contained 0.3 g/ml of THF and the peak molecular weight was show at 17.46 and 17.01 ml. of elution volume in figure 24 for HTPB and figure 25 for MDI.

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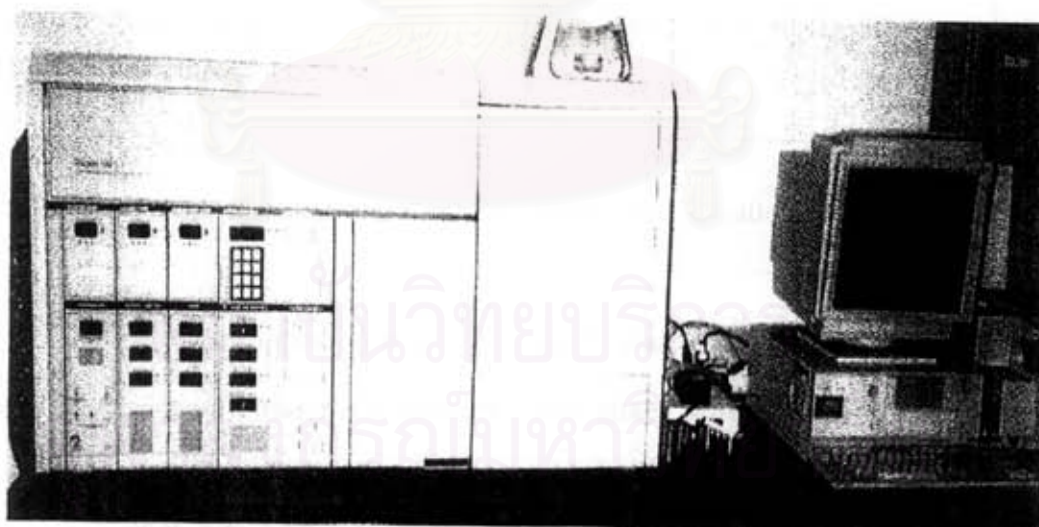


Figure 7 The schematic of Gel permeation chromatography model 150- CV

GPC distributions were investigated as a function of dose by styragel. It was removed from the distribution by carefully filtering the solutions that cause a narrowing of the wing at high molecular weights.

Preparation of samples

The copolyurethane binders based on HTPB and MDI were prepared by mixing the two polymers in several different component ratios with a high speed, 450-500 rpm, for 2 minutes and the polyols standard binder were prepared the same one as follows :

Series	Ratios by weight									
1 (Polyols:MDI)	3:1	4:1	5:1	6:1	7:1	8:1	9:1	10:1	-	
2 (HTPB:MDI)	3:1	4:1	5:1	6:1	7:1	8:1	9:1	10:1	11:1	
3 (Polyols:HTPB:MDI)	-	3:1:1	4:1:1	5:1:1	6:1:1	7:1:1	8:1:1	9:1:1	-	
4 (Polyols:HTPB:MDI)	-	2:2:1	3:2:1	4:2:1	5:2:1	6:2:1	7:2:1	8:2:1	-	

OH/NCO = equivalent ratio, OH:NCO = stoichiometric ratio

Before preparing the samples, the HTPB was dried at 80 °C for 24 hours and degassed with vacuum pump for 2 minutes , then mixed with DBTDL 0.001 % by weight with a speed stirrer for a further 5 minutes . Add the liquid MDI to blend and continuously stirred under relative humidity below 40 %, after the mixing for about 15 seconds the mixture was poured into the glass and aluminum moulds, kept the samples in the vacuum oven at 80 °C,400 mbar for 24 hours. The samples were post-cured at ambient temperature for at least 7 days before testing and swelling studies.

Film preparation

Films were prepared by casting from polyurethane binders on clean glass plates, with preparing as the binders preparation procedure.

IR-spectra

The IR spectra of the thin polymer films were obtained with a infrared spectrophotometer (Jasco IR-810). The data were taken using KBr pellets for liquid and thin polymer films by scanning with $4000-400\text{ cm}^{-1}$.



Figure 8 The schematic of infrared spectrophotometer (Jasco IR-810).

Mechanical properties

The tensile, shear, adhesive strength and percentage elongation at break of the cast polyurethanes elastomer were determined using an instron universal testing machine model LR 100 K (LLOYD, UK.) using dumb-bell shaped specimens as described in ASTM D 638-90. The shear and adhesive strength were measured according to ASTM D 816-82. The aluminum surface treatments were prepared according to ASTM D 2651.

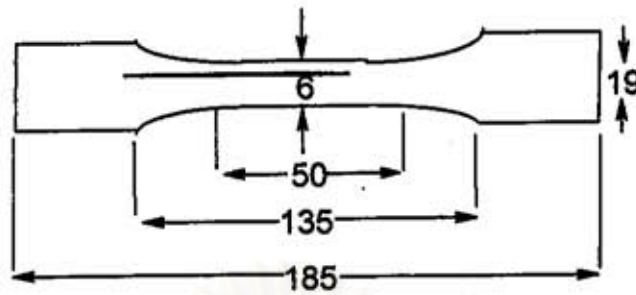


Figure 9 Schematic of test specimen dimensions in mm. for the polyurethane binder

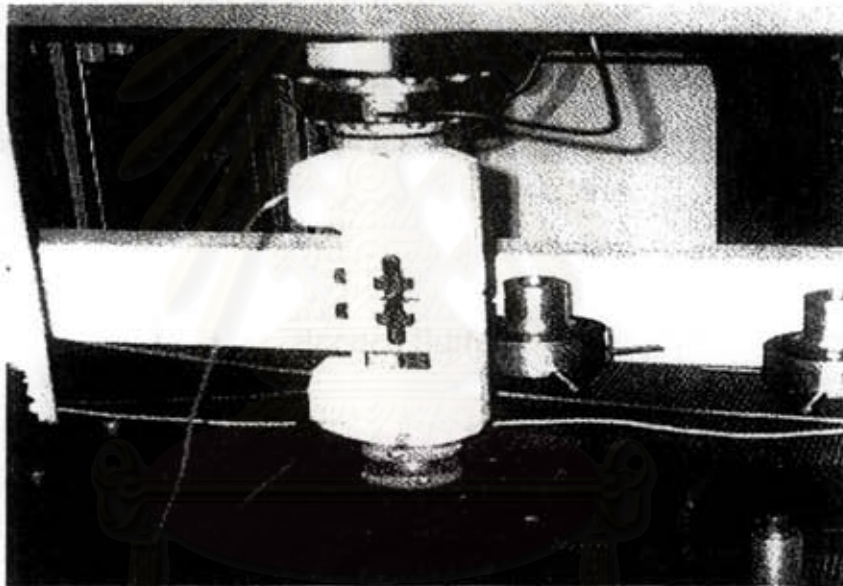


Figure 10 The instron universal testing machine model LR 100 K (LLOYD,UK.)

Surface treatment of aluminum alloys

Typical pretreatments are refer to the appropriate literature for details on cleaning techniques and procedures

1. Alkaline degreasing solutions may be used instead of, or in addition to, vapor degreasing. A common degreasing method is to immerse for 10 minutes at 70°C .
2. Mechanical preparation- Surface which are scaled should be abraded using a glass-bead blasting. Abrasive should be water rinsed from the surface.

3. Acid etching solutions typically used are the following:

Sulfuric acid	27 % by weight
Sodium dichromate	135 g/l
Temperature	66 °C
Immersion time	15 min.

4. A final rinse with warm-to-hot water.

5. Drying, The surface dried in the oven at 100 °C for 1 hour and then left in ambient condition for about 1 hour before the adhesive is applied. Longer dwell times should be avoided.

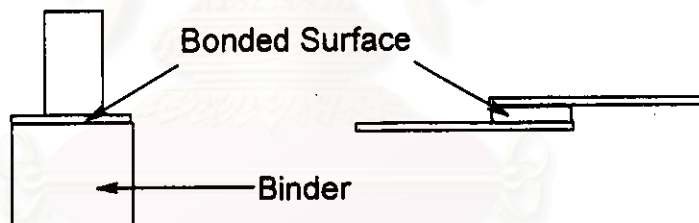


Figure 11 The schematic of specimen for peel and shear test with aluminum alloys

Crosslink density and \bar{M}_n between crosslinks

Crosslink density, defined as moles of effective network chain per cubic centimeter, was obtained by calculating the volume fraction of the swollen polymer. For this, the swelling coefficient, (Q) was obtained experimentally by placing the polymer specimens 7x7 mm.size in toluene for 24 hours. The specimens were removed from the solvent and weighed after gently wiping off the solvent. Subsequently, the solvent absorbed was driven off by placing the specimens in an oven for 2 hours at 100 °C, and the weight of the deswollen specimens were determined.

From the weights of the swollen (W_s), deswollen (W_{ds}) specimens and density of the swelling agent (ρ_1), the swell coefficient is given by

$$Q = (W_s/W_{ds} - 1) / \rho_1$$

The weight fraction of the polymer (W_2) and the solvent (W_1) can then be calculated by the relation,

$$W_2 = 1/(1+Q) \quad \text{and}$$

$$W_1 = 1 - W_2$$

The volume fraction of the polymer (V_2) in the swollen specimen is given by

$$V_2 = \frac{W_2/\rho_2}{W_2/\rho_2 + W_1/\rho_1}$$

Where ρ_1 and ρ_2 are the densities of the solvent and the polymer, respectively. From the volume fraction data under equilibrium swollen condition, the crosslink density (V_c) and molecular weight between crosslink points ($\overline{M_c}$) were calculated by the Flory-Rehner relation,

$$V_c = \frac{\rho_2}{M_c} = \frac{-[\ln(1-V_2) + V_2 + X V_2^2]}{V_s (V_2^{1/3} - V_2/2)}$$

Where V_s is the molar volume of the solvent, and X is the polymer-solvent interaction parameter which is related to the solubility parameters of the polymer (δ_p) and the solvent (δ_s), as,

$$X = 0.34 + V_s/RT(\delta_p - \delta_s)^2$$

Determination of the solubility parameter of samples

1. Apparatus

1.1 Beaker, 20 ml

1.2 Cutter

1.3 Vernier caliper

1.4 Balance

1.5 Vacuum oven

Table 7 Typical values of the solubility parameter and density for some solvents

2. Reagents	δ (J/cm ³) ^{1/2}	ρ_1 (g/cm ³)
n - hexane	14.8	0.660
Carbon tetrachloride	17.6	1.590
Toluene	18.3	0.870
2 - butanone	18.5	0.805
Benzene	18.7	0.880
Cyclohexanone	19.0	0.946
Chlorobenzene	19.4	1.106
Acetone	19.9	0.790
Tetrahydrofuran	20.3	0.890
Methanol	29.7	0.790

(Textbook of polymer science, Fred W. Billmeyer, Jr., pp.153)

3. Procedure

The solubility parameter was obtained by calculating the volume fraction of the swollen polymer. For this, the swelling coefficients were obtained experimentally by replacing the polymer specimens 7x7 mm size in ten different solvents ranging in solubility parameter, δ from 14.8 (J/cm³)^{1/2} (n-hexane) to 29.7 (J/cm³)^{1/2} (methanol) for 24 hours. The specimens were removed from the solvent and weighed after gently wiping off the solvent. Subsequently, the solvent absorbed was driven off by placing the specimens in a vacuum oven for 2 hours at 100 °C, and the weights of the deswollen were determined. The swelling coefficients were evaluated using equation $Q=(W_s/W_{ds}-1)/ \rho_1$. According to this experiment the solubility of polyurethane binders in series 1, 2, 3, and 4 are 20.3 (J/cm³)^{1/2} because its better swell in tetrahydrofuran.