CHAPTER III

EXPERIMENTAL

3.1 General

Reagents and raw materials were obtained from various suppliers as shown in Table 3.1.

Table 3.1 Source of chemicals

Materials	Company
Acetone	J.T. Baker
Allyl glycidyl ether	Fluka
2-Butanone peroxide (Methyl ethyl ketone peroxide, MEKP)	Fluka
Chloroform-d	Fluka
Cobalt Naphthenate (Co)	Sigma
Diallylamine	Fluka
Dibutyltin dilaurate	Fluka
Diglycidyl ether of bisphenol A (D. E. R. 331)	Dow Chemical Thailand Co., Ltd.
Ethyl acetate	J.T. Baker
Ethylene diamine	Merck
Hexane	J.T. Baker
Polyester polyol	Thai Polyurethane Co., Ltd.
Polymeric MDI	Thai Polyurethane Co., Ltd.
Potassium permanganate	Fluka
Silica gel $60F_{254}$	Merck
Sodium hydroxide	Carlo Erba
Sodium sulfate anhydrous	Fluka
Styrene monomer	Siam Polystyrene Co., Ltd.

Specification of polymeric MDI and polyester polyol used in the preparation of polyurethane are shown in Table 3.2 and Table 3.3, respectively. The polymeric MDI and polytester polyol were melted and preheated to 70-80 °C, and degassed under vacuum for at least 30 minutes until any vigorous foaming and bubbling ceases.

The styrene monomer was used to serve as copolymer and its specification is presented in Table 3.4. A trace of hydroquinone in styrene monomer was removed by washing with 1.0 % NaOH solution followed by washing with distilled water and then dried with anhydrous Na_2SO_4. The dried styrene monomer was distilled under reduced pressure and stored under nitrogen atmosphere at 5-10 °C.

Table 3.2 Specification of polymeric MDI (Raypol C900) supplied by Thai Polyurethane Industry Co., Ltd.

Specifications	Polymeric MDI (Raypol C900)
Physical state at room temperature	Liquid
Color	Fawn to dark brown
Odor	None to aromatic at room temperature
Density at 25°C (g/ml)	1.24
Viscosity at 25°C (cps)	200-500
% Free NCO (by weight)	31.5
Flash point (°C)	>200
Crystallization temperature (°C)	<10
Shelf life at 20 °C (month)	6
Average functionality	2.7

Table 3.3 Specification of polyester polyol (F113) supplied by Thai Polyurethane Industry Co., Ltd.

| Specifications	Polyester polyol (F113)
Acid number (mg KOH/g)	0.5-0.8
Hydroxyl number (mg KOH/g)	54-58
Viscosity at 60°C (cps)	1,050-1,200
Color (APHA)	<100
Water content (%)	<0.05
Density at 25°C (g/cm)	1.16

Table 3.4 Specification of styrene monomer supplied by Siam Polystyrene Co., Ltd.

| Specifications	Styrene monomer
Molecular weight	104.14
Inhibitor	para-ter-butylcatechol (< 0.01%)
Form	Liquid
Color	Colorless
Odor	Strong penetrating aromatic hydrocarbon
Boiling point (°F)	293
Freezing point (°F)	-23
Specific gravity (H_2O) at 77°F	0.901
Vapor pressure at 68°F (mmHg)	5
Soluble in	Ethyl alcohol, ethyl ether, Carbon disulfide, methanol, and acetone
Flash point (°F)	88

3.2 Experimental Procedure [5,12]

3.2.1 Preperation of Bis-(3-N,N'-diallylamino-2-propanol) diphenylolpropane (BDPD, **3**)

(BDPD,3)
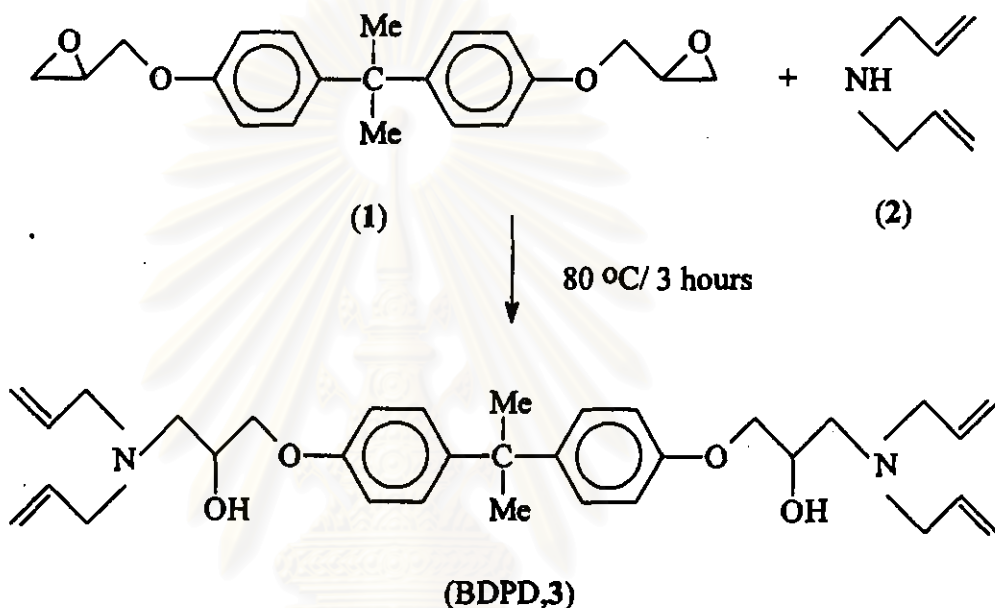
BDPD was synthesized by employing the procedure in the literature as follows : Diglycidyl ether of bisphenol A (**1**) (10.0 g, 1.0 mole) and diallylamine (**2**) (5.72 g, 2.0 mole) were placed in a round-bottomed flask fitted with drying tube. The reaction mixture was left stirring at 80°C for 3 hours to give a crude product (15.72 g) which contained (**3**) as a major component ; ^{1}H NMR 7.12 (4H, d, J=8.9, H12), 6.81 (4H,d, J=8.9, H11), 5.80 (4H, tdd, J=10.9, J=17.3, H3), 5.20 (4H, tdd, J=1.4, J=2.6, J=17.4, H2), 5.12 (4H, tdd, J=1.4, J=2.7, J=10.7, H1), 3.90-4.03 (6H, m, H8, H9, H10), 3.24 (4H, dd, J=5.9, J=14.0, H5), 3.08 (4H, dd, J=7.2, 14.0, H4), 2.61 (4H, d, J=6.6, H6, H7), 1.60 (6H, s, H13). The crude product was used in preparation of polyurethane elastomer without purification.

3.2.2 Preperation of N,N,N',N'-tetrakis-(3-allyloxy-2-propanol) ethylenediamine (TAPE, 6)

(TAPE,6)
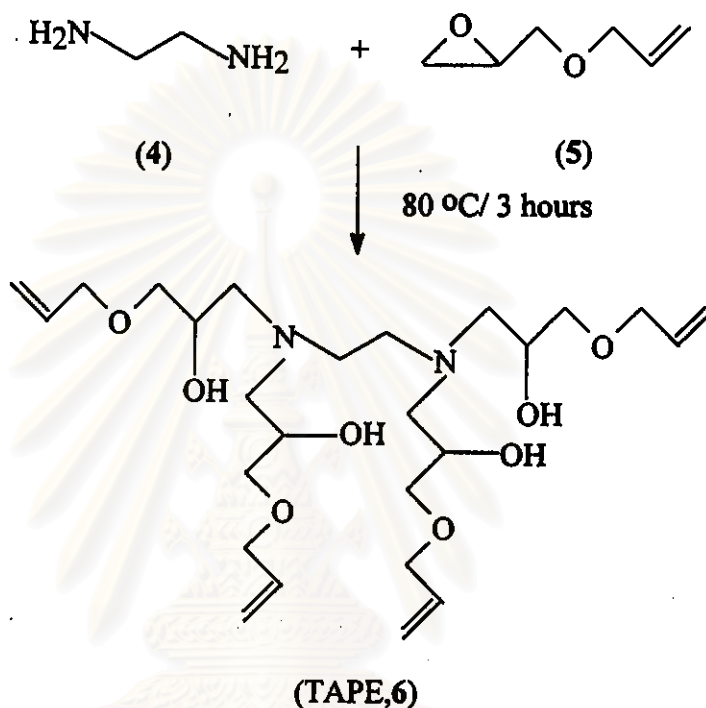
TAPE was synthesized by employing the procedure in the literature as follows : Ethylene diamine (4) (1.32 g, 1.0 mole) and allyl glycidyl ether (5) (10.0 g, 4.0 mole) were placed in a round-bottomed flask fitted with a drying tube. The reaction mixture was left stirring at 80°C for 3 hours to yield a crude product (11.32 g) which contained (6) as a major component ; ^{1}H NMR 5.79-5.88 (4H, m, H3), 5.01-5.27 (8H, m, H1, H2), 3.75-3.99 (12H, m, H6, H7, H8), 3.37-3.39 (8h, m, H4, H5), 2.05-3.02 (12H, m, H9, H10, H11, H11, H12). The crude product was used in preparation of polyurethane elastomer without purification.

3.3 Calculations [1-2]

3.3.1 Equivalent weights

The equivalent weight of a molecule is its molecular weight divided by the number of reactive groups available.

$$\text{Equivalent weights} = \frac{\text{Molecular weight}}{\text{Number of reactive groups or functionality}}$$

3.3.2 Percentage Free NCO

The amount of NCO available in a pure or impure mixture of diisocyanates for reaction is the percentage free NCO

$$\% \text{ NCO} = \frac{\text{Molecular weight of NCO}}{\text{Molecular weight of MDI}}$$

Polyols and polymeric isocyanates are often used whose molecular weight and functionality are not known and in these instances their equivalent molecular weights are determined by isocyanate (NCO) or hydroxyl (OH) group analysis.

3.3.3 Equivalent Weight of an Isocyanate

Many of the commercial reactants used in urethane synthesis are impure materials, for example MDI may be used as pure MDI, a low melting-

point (38°C) solid; polymeric or 'crude' MDI, which is a dark-coloured low viscosity liquid. Also, active isocyanate content of a prepolymer decreases with storage, a decrease of about 0.05% per month being normal. For these reason it is necessary to measure and specify the amount of isocyanate available for reaction at any specific time, and this is done by calculation of the isocyanate equivalent weight of the mixture using the following procedure:

$$\frac{\text{Molecular weight of NCO group}}{\text{Equivalent weight of the reactant}} = \% \text{ available (free) NCO}$$

$$\frac{42}{\text{Equivalent weight of the reactant}} = \% \text{ NCO}$$

$$\frac{42}{\% \text{ available (free) NCO}} = \text{Equivalent weight of the reactant}$$

3.3.4 Hydroxy Content

Polyols are identified by their hydroxyl numbers. Hydroxyl number is defined as the number of milliweights (or milligrams) of potassium hydroxide equivalent to the active functions (hydroxyl content) of 1 g of the compound or polymer.

$$\text{Hydroxyl number} = \frac{56,100}{\text{Equivalent weight}}$$

Note: 56,100 is the molecular weight of potassium hydroxide (KOH) used in the analyses expressed in milligrams, i.e. KOH, 39.1+16+1 = 56.1, 56.1 x 1,000 = 56,100.

If the analysis of polyol indicates that the hydroxyl number is 48.3, then

$$\text{Equivalent weight} = \frac{56,100}{48.3} = 1,162$$

Note:

$$\text{Hydroxyl number} = \frac{(\text{Functionality})(56,100)}{\text{MW polyol}} = \frac{56,100}{(\text{MW polyol})/(\text{Functionality})}$$

3.3.5 Isocyanate Index

The amount of isocyanate used relative to the theoretical equivalent amount, is known as the Isocyanate index.

$$\text{NCO index} = \frac{\text{Isocyanate equivalents}}{\text{polyol equivalents}}$$

Note: Normally excess isocyanate is used to compensate for allophanate and biuret readings.

As the chemical reaction on a 1:1 equivalent weight basis, the polyol would react with the polymeric MDI. This 1:1 equivalent weight is called the isocyanate index.

3.4 Preparation of Polyurethane Elastomer [1-2,4,6]

The major components used in this study are polymeric MDI, polyester polyol, and crosslinking agents. BDPD or TAPE were used as crosslinking agents. The term MDI/POLYOL/BDPD and MDI/POLYOL/TAPE were used to indicate specific chemical composition that used to prepare polyurethane elastomer (PU).

3.4.1 MDI /POLYOL/BDPD Formulation

The NCO/OH ratio employed was constant at 1.04. The equivalent weight ratio of MDI:POLYOL:BDPD was 2:1.8:0.2 (Table 3.5). Methyl ethyl ketone peroxide (MEKP) and Cobalt naphthenate (Co) were used as initiator and accelerator, respectively.

Table 3.5 Composition of starting materials in MDI:POLYOL:BDPD formation

Equivalent weight ratio MDI:POLYOL:BDPD	Weight of starting materials (g)				
	MDI	POLYOL	BDPD	MEKP	Co
2:1.8:0.2	7.54	50	1.48	0.0111[a]	0.0037[a]

[a] 1 wt% MEKP/Co, the content of Co was 25 wt% of MEKP

3.4.2 MDI/POLYOL/TAPE Formulation

The NCO/OH ratio employed was constant at 1.04. The equivalent weight ratios of MDI:POLYOL:TAPE were varied from 2:1.8:0.2, 2:1.6:0.4 and 2:1.4:0.6 (Table 3.6). Methyl ethyl ketone peroxide (MEKP) and Cobalt naphthenate (Co) were used as initiator and accelerator, respectively.

Table 3.6 Composition of starting materials in MDI:POLYOL:TAPE formation

Equivalent weight ratio MDI:POLYOL:TAPE	Weight of starting materials (g)				
	MDI	POLYOL	TAPE	MEKP	Co
2:1.8:0.2	7.54	50	0.72	0.0054[a]	0.0018[a]
2:1.6:0.4	8.49	50	1.61	0.0120[a]	0.0040[a]
2:1.4:0.6	9.70	50	2.77	0.0208[a]	0.0069[a]

[a] 1 wt% MEKP/Co, the content of Co was 25 wt% of MEKP

3.5 Preparation of Polyurethane/Polystyrene Elastomer [1-2,4,6]

3.5.1 MDI/POLYOL/BDPD and Polystyrene Formulation

The NCO/OH ratio employed was constant at 1.04. Dibutyltin dilaurate was used as catalyst (0.02% by weight of PU).The equivalent weight ratio of MDI:POLYOL:BDPD was 2:1.8:0.2 .The weight composition of MDI/POLYOL/BDPD and styrene monomer was varied and shown in Table 3.7. Methyl ethyl ketone peroxide (MEKP) and Cobalt naphthenate (Co) were used as initiator and accelerator, respectively.

Table 3.7 Composition of starting materials in MDI:POLYOL:BDPD (PU) and PS formulation

Equivalent weight ratio MDI:POLYOL:BDPD	% Styrene monomer (w/w)	Weight of styrene monomer (g)	MEKP (g)	Co (g)
2:1.8:0.2	10	6.0	0.0450[a]	0.0150[a]
			0.0900[b]	0.0300[b]
	20	12.0	0.0900[a]	0.0300[a]
			0.1800[b]	0.0600[b]

[a] 1.wt% MEKP/Co, the content of Co was 25 wt% of MEKP

[b] 2 wt% MEKP/Co, the content of Co was 25 wt% of MEKP

3.5.2 MDI/POLYOL/TAPE and Polystyrene formulation

The NCO/OH ratio was constant at 1.04. Dibutyltin dilaurate was used as catalyst (0.02% by weight of PU). All the equivalent weight ratios of MDI:POLYOL:TAPE were used. The weight composition of MDI/POLYOL/TAPE and styrene monomer was varied and shown in Table3.8. Methyl ethyl ketone peroxide (MEKP) and Cobalt naphthenate (Co) were used as initiator and accelerator, respectively.

Table 3.8 Composition of starting materials in MDI:POLYOL:TAPE (PU) and PS formulation

Equivalent weight ratio MDI:POLYOL:TAPE	% Styrene monomer (w/w)	Weight of Styrene monomer (g)	MEKP (g)	Co (g)
2:1.8:0.2	10	5.83	0.0437[a]	0.0146[a]
			0.0875[b]	0.0292[b]
	20	11.65	0.0874[a]	0.0291[a]
			0.1748[b]	0.0582[b]
2:1.6:0.4	10	6.01	0.0450[a]	0.0150[a]
			0.0902[b]	0.0300[b]
	20	12.02	0.0902[a]	0.0300[a]
			0.1803[b]	0.0600[b]
2:1.4:0.6	10	6.25	0.0469[a]	0.0156[a]
			0.0938[b]	0.0312[b]
	20	12.50	0.0938[a]	0.0313[a]
			0.1875[b]	0.0626[b]

[a] 1 wt% MEKP/Co, the content of Co was 25 wt% of MEKP.

[b] 2 wt% MEKP/Co, the content of Co was 25 wt% of MEKP

Procedures for the preparation of PU elastomer and PU/PS elastomer were shown in Figure 3.1 and 3.2, respectively. The details of these procedures were explained as follows :

Metering

The dried polyester polyol were metered in the correct weight into a round bottom flask equipped with a vacuum inlet and was heated by at 70°C for 30 minutes.

Mixing

The dried polymeric MDI, dibutyltin dilaurate and MEKP/Co were added into the dried polyol. The mixture was rapidly mixed and stirred for 30 seconds then degassed under reduced pressure.
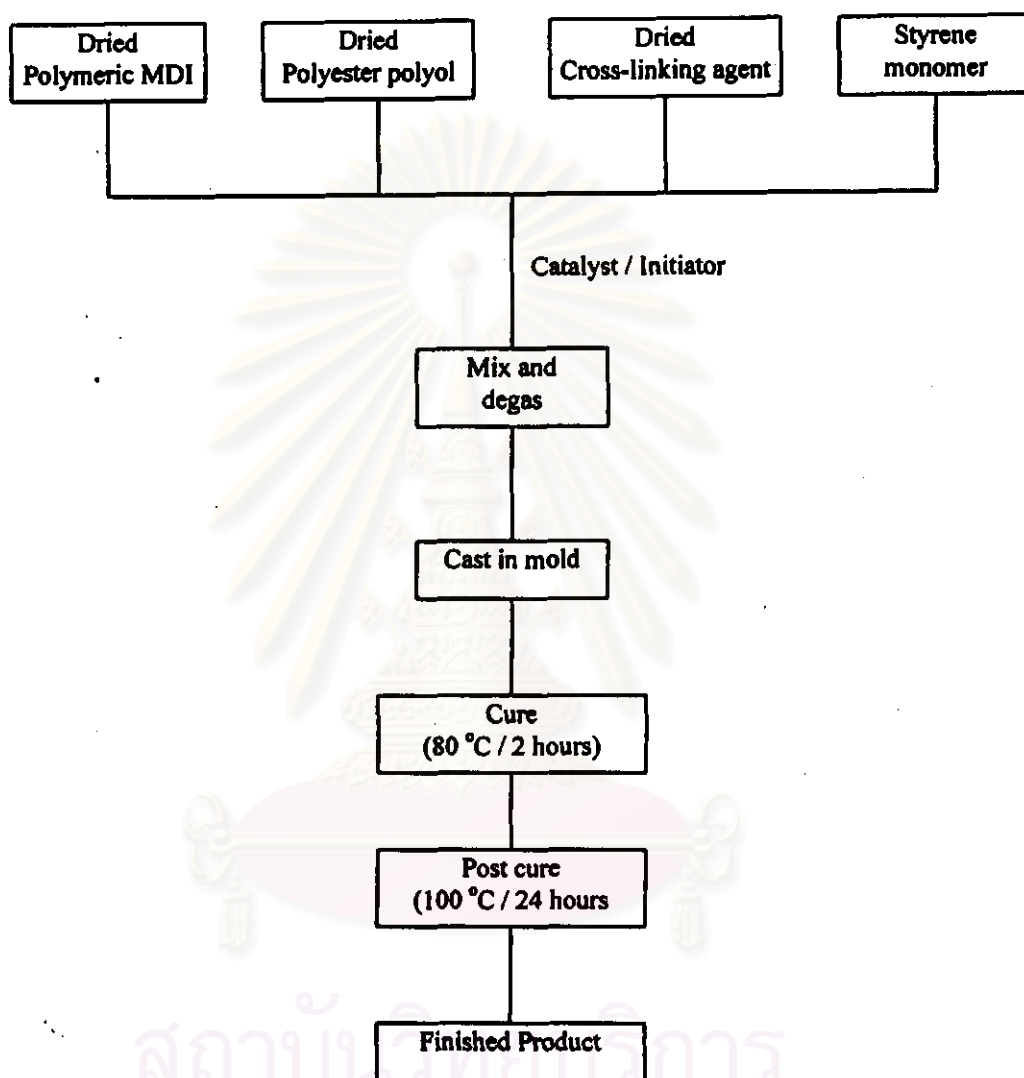
Curing

The degassed mixture was poured onto a preheated mold and heated in an oven at 80°C for 2 hours.

Post curing

The PU sheet was post cured at 100°C for 24 hours in order to complete the crosslinking reaction.
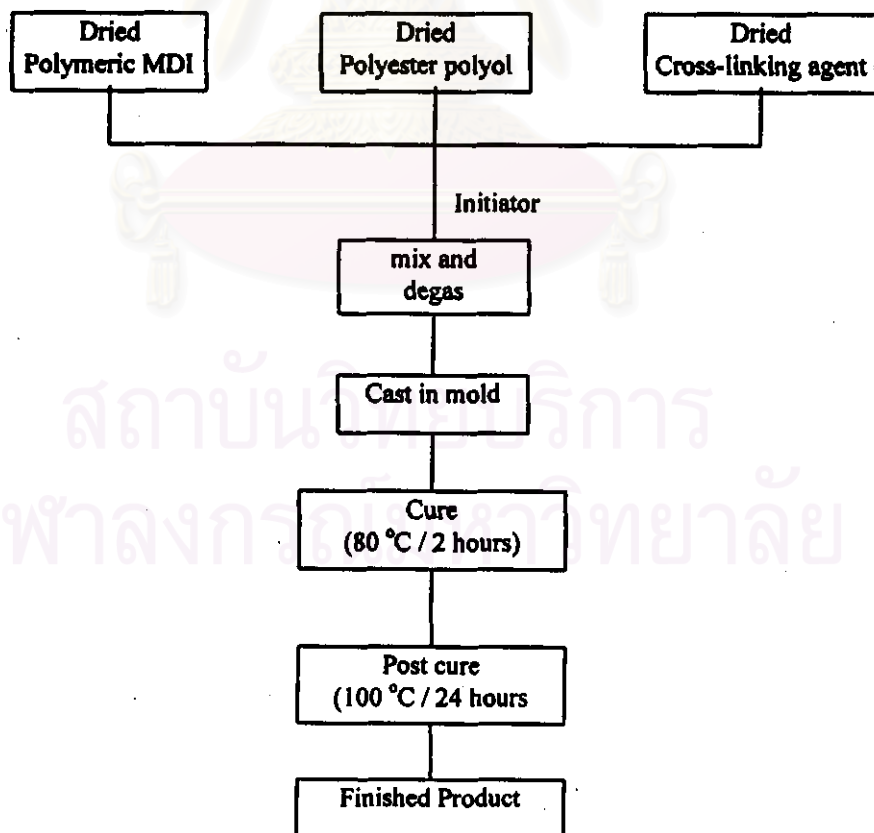
Figure 3.1 Procedure for the preparation of polyurethane elastomer.

Figure 3.2 Procedure for the preparation of polyurethane/polystyrene elastomer.

3.6 Characterization of Crosslinking Agents and Polyurethane Elastomer

3.6.1 Nuclear Magnatic Resonance Spectrosocopy

Nuclear magnatic resonance (NMR) spectra were recorded on a Bruker Model ACF200 Fourier-transform NMR Spectrometer. The chemical shift (δ) reported are given in part per million.

3.6.2 Tensile Testing (ASTM D638)

Tensile testing was performed by used of Instron Model 4301. The cross head speed of Instron tensile testing at 500 mm./min. was used. The median of five specimen was take as the characteristic of the material tested. The load at rupture was record and divided by the original area of cross-section to express tensile strength in N/mm^2 using the following equation.

Tensile strength = F/A

F = Tensile force (N)
A = Cross-section area (mm^2)

The elongation at break or the ultimate elongation is the maximum extension of the specimen at the point of rupture.

Elongation at break (%) = $[(L-L_o)/ L_o]$ x 100

where L-L$_o$ = Change of length
L$_o$ = Original length
L = Final length at the point of rupture.

The plot of stress against strain yields the modulus of elasticity. This is the initial, straight-line portion of the stress-strain curve.

Stress-strain curves can also provide information on toughness of a material. An integration of the area under stress-strain curve is proportional to the energy-to-break per unit volume, which is a measure of the toughness of the specimen under the conditions of the test.

Preparation of Test Specimen

Polyurethane was cured in a mold of cavity size 50 mm X 150 mm X 3 mm (WxLxH). The specimen was cut by plastic sample cutting mechine (Yasuda Seiki No. 189 PAL).

Polyurethane, containing hydrophilic groups such as amino groups and polyoxyethylene segments, have reduced secondary intermolecular bonding when the amount of water vapour present in the atmosphere is high. The physical properties as measured change significantly with humidity and specimen for testing must be allowed to reach equilibrium with a standard atmosphere at conditions :

$23\ ^{\circ}C \pm 2\ ^{\circ}C$

$50\ \% \pm 5\ \%$ relative humidity (R.H.)

Thus, the specimen was condition was conditioned for at least 3 hours at the above standard conditions.

Specimen of polyurethanes for tensile testing are produced by moulding in sheet form and cut by a puncher by mean of dies in dumbbell shape.

Thickness was then measured by a thickness micrometer. Three measurements of thickness were taken and the median value was used for calculating the cross-section area. Width of specimen is considered to be the width of the die used.

3.6.3 Hardness Testing (ASTM D785)

Hardness testing was performed by used of Swick 3102. The thickness of the test specimen should be at least 6 mm. Hardness test usually measures the amount of penetration of an indentor into a plastic speciment. This test method is based on the penetration of a specific type of indentor when forced into the material under specified conditions. The indentation hardness is inversely related to the penetration and is depent on the elastic modulus and viscoelastic behavior of material. In this work a durometer type 'shore A' was used. Shore A is a scale of shore hardness used for soft materials, such as an elastomer. The indentor for the shore A has a flat face of diameter of 0.8 mm. It is connected to a coiled spring. When a PU or PU/PS specimens were tested. the indentor was forced into the surface of the specimens and exerted the force of the coiled spring. The depth of penetration of indentor was a measurement of the hardness of specimens.

3.6.4 Compression Set (ASTM D395)

Compression set testing was performed by use of CEAST 6425/0000. The specimen having a cavity of 6.0 mm in thickness and 13 mm in diameter. Compression set tests are intended to measure ability of rubber compounds to retain elastic properties prolonged action of compressive stresses. Compression device was shown in Figure 3.3. Place the test specimen between the plates of

the compression device with the spacers on each side. Tighten the bolts so that the plates are drawn together uniformly until they are in contact with the spaceres. The suitable temperature and time for the compression set in this studied were 24 hours at 70°C. It is suggested that the test temperature be chosen from thoses listed in Practice ASTM D1349.
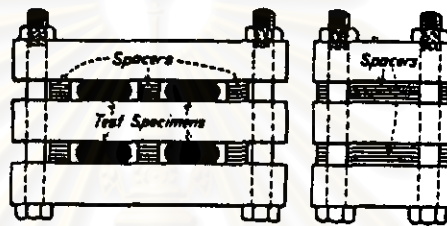
Figure 3.3 Device for compression set test under constant deflection.

Calculation the compression set expressed as percentage of the original deflection as follows :

$$C_B = [(t_o - t_i)/(t_o - t_n)] \times 100$$

where:

C_B = compression set expressed percentage of the original deflection

t_o = original thickness of specimen

t_i = final thickness of specimen

t_n = thickness of the spacer bar used

3.6.5 Dynamic Mechanical Analysis (DMA)

The dynamic response of a material to oscillatory loading, often sinusoidal wave, is usually carried out using a Dynamic Mechanical Analyzer. A sinusoidal stress is applied to a viscoelastic polymer. Its response correspondent to sinusoidal strain is out-of-phase behind the applied stress. Figure 3.4 shows the sinusoidal stress (σ) with the sinusoidal strain response (ε), and the lagging phase angle (δ).
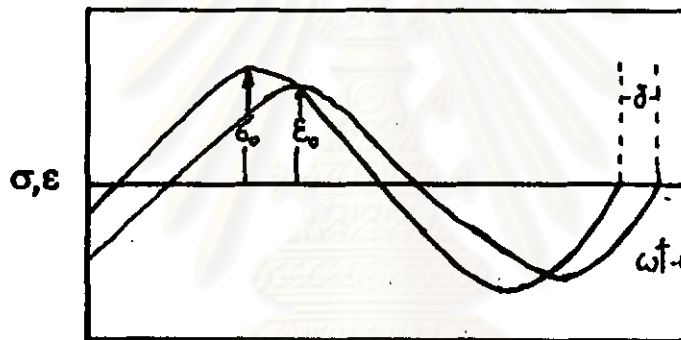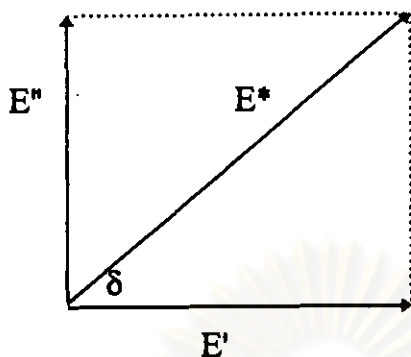

Figure 3.4 Sinusoidal stress with the strain response.

A complex modulus, E^*, is definded by σ_o / ε_o with the real and imaginary components, E' and E'', which are also named respectively as the storage and loss modulus.

$$E^* = \sigma_o / \varepsilon_o$$
$$E^* = E' + E''$$

The relationship between these quantities is summarised in the Argand diagram shown below.

The ratio of the energy lost to the energy stored per deformation cycle, i.e., E''/E' or tan δ, is the most useful parameter. It exhibits peaks over a wide range of temperature. Each peak corresponds to a specific relaxation process, e.g., primary T_g (or α-T_g) of the measured polymer.

In the present work, Netzch DMA242 with the compression/penetration mode was used. The maximum force of 4.0 N was applied to sample with the frequency of 1.0 Hz. and the amplitude of 120 μm.. The temperature was varied from -70 to 200 °C, the heating rate was 5.0 K/min..

3.6.6 Thermogravimetric Analysis (TGA)

TGA is a technique used to measure the mass change with respect to a known total mass of determined material while the temperature is increased at constant rate. Weight losses occur when volatiles absorbed by the polymer are driven off, and at higher temperatures when degradation of the polymer occurs with the formation of volatile products.

In this work, Perkin Elmer TGA 7 was used. The heating rate was 20 °C/min. The measured temperature ranges were 20 to 800 °C.

3.6.7 Scanning Electron Microscopy (SEM)

The morphology of polyurethane was studied by SEM. In the SEM, a fine beam of electrons is scanned across the specimen surface and an appropriate detector was used to collect the electrons emitted from each point. The amplified current from the detector is then displayed on a cathode-ray tube, which is scanned synchronously with the electron probe. In this way the image is built up, line by line. In this work, JSM 35 CF was used to examine compatibility between PU and PU/PS elastomer.

3.6.8 Differential Scanning Calorimetry (DSC)

The glass transition temperature, T_g was measured using Netzch DSC200. Data were record at scanning rate of 20 $^{\circ}$C/min, temperature ranges of the scan were -100 to 200 under nitrogen atmosphere. The weight of specimens used were 20-30 mg.