CHAPTER 3

EXPERIMENTAL

3.1 Raw materials

3.1.1 α, ω-Hydroxyl polycaprolactone or polycaprolactone glycol (PCL)

PCL was supplied by Aldrich Chemical Co., Ltd. It is solid at room temperature with a melting point of 50 °C. A number- average molecular weight was 2000 g mol^{-1}. It has the chemical structure as shown below.

$$R \begin{cases} -[O-\overset{O}{\overset{\|}{C}}(CH_2)_5-]_n OH \\ -[O-\underset{O}{\underset{\|}{C}}(CH_2)_5-]_m OH \end{cases}$$
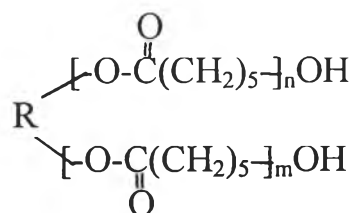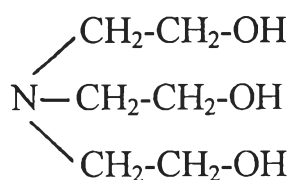
PCL was dried upon heating at 90 °C for 6 h under vacuum in order to remove a trace of moisture. It was stored in a desiccator prior to uses.

3.1.2 Modified 4,4'-diphenylmethane diisocyanate (Modified MDI or MMDI)

Modified MDI used in this study was cordinally supplied by Thai Polyurethane Industry Co., Ltd. (TPU). It is yellow to light brown liquid and contains a small amount of isocyanates having higher functionality. In this work, modified MDI was dried under vacuum for 1 h before uses.

3.1.3 Triethanolamine (TEA)

TEA, having a mild ammoniacal odour, is a colourless liquid at room temperature. In this study it was used to serve as a crosslinking agent and also cordinally supplied by Thai Polyurethane Industry Co., Ltd. It is completely soluble in water and alcohol and slightly soluble in ether or chloroform. TEA chemical structure is shown below.

$$
N \begin{cases} CH_2\text{-}CH_2\text{-}OH \\ CH_2\text{-}CH_2\text{-}OH \\ CH_2\text{-}CH_2\text{-}OH \end{cases}
$$

TEA was dried upon heating at 90 °C under a vacuum for 6 h and then stored in a desiccator before uses.

3.1.4 Poly(vinyl Chloride) (PVC)

PVC resin (produced by suspension polymerization), having a molecular weight of 50,625 g mol^{-1}, was cordinally supplied by Thai Plastic and Chemicals Co., Ltd. It was dried upon heating at 90 °C under vacuum for 6 h and stored in a desiccator before uses.

3.1.5 Tetrahydrofuran (THF)

THF, having a boiling point of 66 - 67 °C, was used to serve as a solvent for PVC resin. It was dried over 4A type molecular sieves before uses.

3.2 Raw materials characterisation

3.2.1 Determination of Hydroxyl Number of PCL

Hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of the polyol. The method for determination of the hydroxyl groups of PCL was by acetic anhydride acetylation. The known amount of PCL was acetylated with a solution of acetic anhydride in pyridine. The excess acetic anhydride was hydrolyzed with water and the acetic acid obtained from hydrolyzation was titrated with sodium hydroxide solution. The

hydroxyl content was calculated from the difference in titration of the blank and PCL solution. Acid number of PCL would be added to hydroxyl number of PCL for correction of the hydroxyl number (see Section 3.2.2).The average-hydroxyl number of PCL reported in Table 3.1 was averaged from three determinations. (ASTM D4274-88)

Table 3.1   Average-Hydroxyl number of PCL

Sample	Hydroxyl number (mg KOH / g)
1	55.54
2	55.00
3	54.98
Average	55.17±37

3.2.2 Determination of Acid Number of PCL

Acid number is an essential data to measure the residual amount of carboxyl end groups presented in PCL. They reacts with isocyanates to form acidamides with the release of CO_2, resulting in the cause of bubble formation.

Acid number is defined as the quantity of base, expressed in mg of KOH, required to titrate with acidic constituents present in 1 g of sample. In this work, the known amount of PCL was dissolved in a mixture of toluene and ethyl alcohol. The resulting single-phase solution was titrated at room temperature with alcoholic KOH solution, to the end point indicated by the color change of the added phenolphthalein. The acid number less than 1 mg KOH/g is accepted, and frequently even an acid number less than 0.5 mg KOH/g. The average-acid number of PCL, average from three determinations, is shown in Table 3.2.(ASTM D4662-93)

Table 3.2   Average-Acid number of PCL

Sample	Acid number (mg KOH / g)
1	0.169
2	0.178
3	0.172
Average	0.173 ± 0.005

After adding of the average-acid number to the hydroxyl number of PCL, the correct average-hydroxyl number was 55.34 mg KOH/g.

3.2.3 Determination of Hydroxyl Number of TEA

A test method for determination of hydroxyl number of TEA was as same as that for PCL. The average-hydroxyl number shown in Table 3.3 was obtained from the average of three determinations.

Table 3.3   Average-Hydroxyl Number of TEA

Sample	Hydroxyl number (mg KOH / g)
1	1,116.55
2	1,116.66
3	1,116.71
Average	1,116.64 ± 0.09

3.2.4 Determination of the Isocyanate Content of MMDI

NCO content is defined as the weight percent of the NCO groups presented in the isocyanate compound. It can be determined by the titration of the functional groups as was done for the polyols.

In the present work, the NCO content was determined from the amount of dibutylamine consumed in the reaction. The MMDI was added to an excess dibutylamine in toluene and allowed to stand at room

temperature for 15 min. The isocyanate reacts with dibutylamine to form urea. The reaction mixture was diluted with isopropyl alcohol, and the excess dibutylamine was back-titrated with HCl aqueous solution to the end point using bromcresol green indicator. Table 3.4 shows the average percentage of NCO groups of modified MDI after three determinations. (ASTM D5155-91)

Table 3.4   Average-Isocyanate Content of Modified MDI

Sample	Isocyanate Content (%)
1	30.02
2	30.08
3	30.27
Average	30.12±0.15

3.3 Calculation

The amount of Modified MDI required to react with PCL and TEA, was calculated to obtain the chemically stoichiometric equivalents. For the calculation the equivalent weight (E_n) of reagents are used, by which

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

The equivalent weight relates to the hydroxyl number and the isocyanate content according to the following equations.

$$\text{Hydroxyl number (mg KOH/g)} = \frac{56.1 \times \text{functionality} \times 1000}{\text{Molecular weight}}$$

$$\text{or Equivalent weight} = \frac{56.1 \times 1000}{\text{Hydroxyl number}}$$

$$\text{Isocyanate Content} = \% \text{-NCO groups} = \frac{42 \times \text{functionality} \times 100}{\text{Molecular weight}}$$

$$\text{or Equivalent weight} = \frac{42 \times 100}{\% \text{ NCO groups}}$$

The hydroxyl number of PCL, TEA and the isocyanate content of MMDI determined from the previous section were used to calculate E_n, and the values are shown in Table 3.5.

Table 3.5   Equivalent weight of PCL, TEA and MMDI.

Chemicals	E_n (g mol^{-1})
PCL	1,013.64
TEA	50.23
Modified MDI	139.43

In order to obtain the stoichiometric equivalents, the ratio of equivalents of isocyanate to the total hydroxyl groups was calculated from the equation shown below.

$$r = \frac{\text{isocynate equivalents}}{\text{polyol equivalents} + \text{crosslinker equivalents}}$$

$$\text{where equivalents} = \frac{\text{weight of reagents}}{\text{equivalent weight}}$$

In making polyurethane product, an excess isocyanate should be used because it can also react with moisture as well as with the carbamate group of the polyurethane product.

3.4 Formulation of Polyurethane and Semi-IPN

Polyurethane synthesized in these studies was a crosslinked polymer. The reactions of MMDI with PCL and MMDI with TEA gave the soft and the hard segments of the resulting PU. In order to and evoid ambiguity which may occured from now on the term "PCL/MMDI/TEA-based PU" is used to indicate specific chemical compositions that used to prepare PU.

3.4.1 PCL/MMDI/TEA-based PU formulation : Variation of the equivalent ratio of PCL:MMDI:TEA

The NCO/OH ratio was constant at 1.05. The equivalent ratios of PCL : Modified MDI(MMDI) : TEA were varied resulting in the variation of weight of materials for each equivalent ratio (see also Table 3.6). (Nongluck, 1994)

Table 3.6 Weights of reagents for various equivalent ratio of PCL/MMDI/TEA-based PU

equivalent ratio	Weight of chemicals (g)		
PCL: MMDI: TEA	PCL	MMDI	TEA
2 : 3 : 1	100.00	21.74	2.49
1 : 2 : 1	100.00	28.99	4.97
1 : 3 : 2	100.00	43.48	9.95

3.4.2 <u>PCL/MMDI/TEA-based PU formulation :Variation of</u>

<u>NCO/OH ratio</u>

The stoichiometric ratio of NCO to OH groups was varied from 0.95 to 1.20, while the equivalent ratio of PCL:MMDI:TEA was fixed at 1:3:2. Table 3.7 shows the values of NCO/OH ratio and the weight of reagents used for the particular formulations.

<u>Table 3.7</u> Weight of reagents for various NCO/OH ratio of PCL/MMDI/TEA-based PU

NCO/OH ratio	Weight of chemicals (g)		
	PCL	MMDI	TEA
0.95	100.00	39.34	9.95
1.00	100.00	41.41	9.95
1.05	100.00	43.48	9.95
1.10	100.00	45.55	9.95
1.15	100.00	47.62	9.95
1.20	100.00	49.69	9.95

3.4.3 Semi-IPN of PCL/MMDI/TEA-based PU and PVC formulation

: Variation of NCO/OH ratio

In this study, the constant composition of PU and PVC was set at 90 to 10% by weight. For the PU component, the equivalent ratio of PCL:MMDI:TEA was also kept constant at 1:3:2. Only the NCO/OH ratio was varied from 0.95 to 1.20 as described in Section 3.4.2. The weight of all of the reagents used for particular ratios of NCO to OH for preparation of semi-IPNs is given in Table 3.8.

Table 3.8 Weight of reagents for various NCO/OH ratio for the
preparation of Semi-IPNs of PCL/MMDI/TEA-based PU
and PVC.

NCO/OH	Weight of chemicals (g)			
ratio	PCL	MMDI	TEA	PVC
0.95	100.00	39.34	9.95	14.93
1.00	100.00	41.41	9.95	15.14
1.05	100.00	43.48	9.95	15.34
1.10	100.00	45.55	9.95	15.55
1.15	100.00	47.62	9.95	15.76
1.20	100.00	49.69	9.95	15.96

3.4.4 Semi-IPNs of PCL/MMDI/TEA-based PU and PVC formulation

:Variation of the weight composition of PCL/MMDI/TEA-based

PU and PVC

The PCL/MMDI/TEA-based PU component having the equivalent ratio of PCL:MMDI:TEA equal to 1:3:2 and the NCO/OH ratio equal to 1.05 was fixed for every formulations. The weight composition of PCL/MMDI/TEA-based PU and PVC was varied and shown in Table 3.9.

Table 3.9 Weights of PVC for various weight composition of Semi-IPNs of PCL/MMDI/TEA-based PU and PVC.

Composition	% PVC (w/w)	Weights of PVC (g)
PU 95/ PVC 5	5	7.67
PU 90/ PVC 10	10	15.34
PU 85/ PVC 15	15	23.01
PU 80/ PVC 20	20	30.69
PU 70/ PVC 30	30	46.03

3.5 Preparation of PCL/MMDI/TEA-based PU and Semi-IPN

3.5.1 PCL/MMDI/TEA-based PU

In these studies one-shot process was employed for the preparation of PCL/MMDI/TEA-based PU. All polyols were mixed together and followed by the mixing isocyanate. The experimental was detailed the followings.

1) The known amount of dried PCL and TEA (see Tables 3.6 and 3.7) were mixed in a reaction kettle equipped with a mechanical stirrer and a vacuum inlet. The system was maintained in a water bath at 60°C.

2) The reagents from 1) were mixed together while stirring at the speed of 500 rpm. for 30 min. The mixture was subsequently subjected to vacuum for 30 min.

3) The known amount of MMDI subjected to vacuum for 30 min., was added into the mixture from 2) which was maintained in the reaction kettle. They were suddenly mixed using a high speed stirrer at 1300 rpm. for 10 sec.

4) Pouring the mixture into an aluminium mould coated with silicone-based releasing agent.

5) The mould was placed in a vacuum oven at 70°C for 20 min. Subsequently it was pressed additionally under a hydraulic press at 70°C for 15 min. It is noted that the resulting polymer prior to pressing would be soft unless otherwise it was hard to press if the mixture was kept too long in the oven. (Xiao, 1983)

6) Then the mould was placed in an oven at 70°C for additional 24 h without any pressing. The samples were then conditioned in a desiccator for a week prior to further analysis and characterization. (Dickie, 1988)

3.5.2. Semi-IPN of PCL/MMDI/TEA-based PU and PVC

In preparation of the semi-IPN, one-shot process and prepolymer process were employed.

a) One-shot process

The experiment procedure was as same as that described in section 3.5.1. The known amount of dried PVC (see Tables 3.8 and 3.9) was

dissolved in THF (PVC ~15 g / THF 100 ml) to obtain the PVC solution, which was subsequently mixed with PCL and TEA.

b) Prepolymer process

First, PCL was mixed together with isocyanate (MMDI) to give a prepolymer. Then PVC solution in THF was mixed together with the prepolymer, finally followed by the mixing of the crosslinking agent, TEA. Details of the experimental were the followings.

1) The stoichiometric amount (see also Table 3.8) of dried PCL and modified MDI were prepared and then were mixed in a reaction kattle equipped with a mechanical stirrer and vacuum inlet. These system was maintain in water bath at $60^{\circ}C$.

2) The reagents from 1) were mixed well using a mechanical stirrer at the speed of 500 rpm for 30 min to obtain prepolymer, which was subsequently subjected to vacuum for approximately 30 min.

3) The exact amount of dried PVC (see Table 3.8 and 3.9) dissolved in THF (PVC ~15g / THF 100 ml.) to obtain PVC solution, which was

mixed while stirring at the speed of 500 rpm with the prepolymer for 30 min. Then the mixture was subjected to vacuum for 15 min. in order to remove a large portion of THF.

4) The known amount of dried TEA (see Tables 3.8 and 3.9) was added into the mixture from 3) and suddenly mixed quickly using a high spped stirrer of 1500 rpm. for about 15 sec.

5) The experimental was subsequently followed 4) to 6) of Section 3.5.1.

3.6 Materials Characterisation

All of the synthesized samples in these studies were characterised their physical and mechanical properties using various test techniques including tensile testing, hardness testing, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Details for each test are given subsequently.

3.6.1 Tensile testing

The tensile property is important characteristics of material strength. The specimen is stretched at a constant rate until it breaks.

The tensile strength is the maximum stress that the material withstands before rupture.

$$\text{Tensile strength} = F / A$$

$$F = \text{Breaking force (N)}$$

$$A = \text{Cross-sectional area (mm}^2)$$

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

$$\text{Elongation at break (\%)} = ((L - L_0) / L_0) \times 100$$

$$\text{where } L - L_0 = \text{Change of length,}$$

$$L_0 = \text{Original length,}$$

$$L = \text{Final length at the point of rupture.}$$

The plot of stress against strain yields the modulus of elasticity. This is the slope of 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. (Wood, 1987)

In the present work, LLOYD 500 was used. The speed of testing was constant at 500 mm/min. Tensile strength and ultimate elongation were measured. Material specimens in sheet forms were cut using a die-cut in dumbbell shape having size equal to type IV specimen conformed to ASTM D638. Width and thickness of specimens were measured using a micrometer. Five measurements were taken and the median value was used for calculation of the cross-sectional area.

3.6.2 Hardness testing

Hardness test usually measures the amount of penetration of an indentor into a plastic specimen. 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

polyurethane or semi-IPN 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 the indentor was a measurement of the hardness of specimens. (ASTM D785)

3.6.3 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 3.1 shows the sinusoidal stress (σ) with the sinusoidal strain response (ε), and the lagging phase angle (δ).

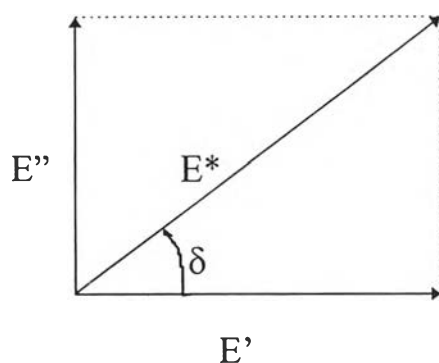Figure 3.1 Sinusoidal stress with the strain response
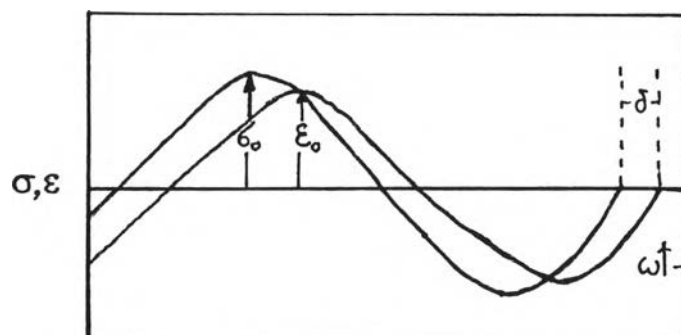
A complex modulus, E^*, is definded by σ_o / ε_o with the real and imaginary components, E' and E", which are also named respectively as the storage and loss modulus.

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

$$E^* = E' + E"$$

The relationship between these quantities is summarised in the Argand diagram shown below. (Hunt, 1993)

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, Netzsch DMA242 with the compression mode was used. The maximum force of 4.0 N was applied to sample with the

frequency of 1Hz. and the amplitude of 120 μm.. The temperature was varied from -30 to 100 °C, the heating rate was 2.0 K/ min.

3.6.4 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 a 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 50 to 700 °C.

3.6.5 Scanning Electron Microscopy (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, SEM was used to examine compatibility between PCL/MMDI/TEA-based PU and PVC in the semi-IPNs.