CHAPTER 3

EXPERIMENT

3.1 Reagents and Materials

The main reactants in these work are polymeric MDI and polyester polyol, of which the specifications are present in Table 3.1 and Table 3.2, respectively. The 1,4 Butanediol was used to serve as chain extenders and its specification is presented in Table 3.3.

Other chemicals and materials used in this work are as follows :

Dibutyltin dilaurate ,	serve as	catalyst (Aldrich Chemical Company)
Calcium carbonate	"	filler (Nippon Paint Co.,Ltd.)
Silica	"	filler (Nippon Paint Co.,Ltd.)
Calcined clay (Brick)	"	filler (general)
Waste rubber tyres	"	filler (IRC. Co.,Ltd.)
Silicone	"	mold releasing agent (Bayer Co.,Ltd.)
Ethyl acetate (commercial grade)	"	solvent
Toluene (commercial grade)	"	solvent
Nitrogen	"	inert atmosphere (TIG)

Table 3.1 Specifications of polymeric MDI (Raypol C900) supplied by Thai Polyurethane Industry Co.,Ltd.

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

Table 3.2 Characteristic of polyester polyol (F113)

upplied by Thai polyurethane Industry Co.,Ltd.

Specification	F113
Acid number (mg KOH/g)	0.5-0.8
Hydroxyl number (mg KOH/g)	54-58
Viscosity at 60 °C (cps)	1,050-1200
Colour (APHA)	<100
water content (%)	<0.05
Density at 25 °C (g/cm)	1.16

Table 3.3 Characteristic of 1,4 butanediol

Specification	BDO
Boiling point at 760 mm.Hg abs.(°C)	229.5
Boiling range (°C)	2
Specific gravity at 20 °C	1.0154
Refractive Index at 20 °C	1.446
Flash point (°C)	134
Viscosity at 20 °C (cps)	90-92
Hydroxyl value	1230
Acid value	0
Freezing point (°C)	19.3-19.5
water content (%)	<0.2

3.2 Apparatus

3.2.1 Manufacturing Apparatus

Apparatus for producing polyurethane consists of the following units.

Reaction kattle (500 ml)

Vacuum pump

Water bath

Mechanical stirrer

Aluminium mold

Vacuum oven

Details of the arrangement of units are shown in Figure 3.1

3.2.2 Testing Apparatus

Tensile Testing Machine : Instron Model 4301

Shore A Durometer Hardness Tester : Swick D7900

Micrometer : Teclock 0.01 mm. Pat. No. 200959

Puncher

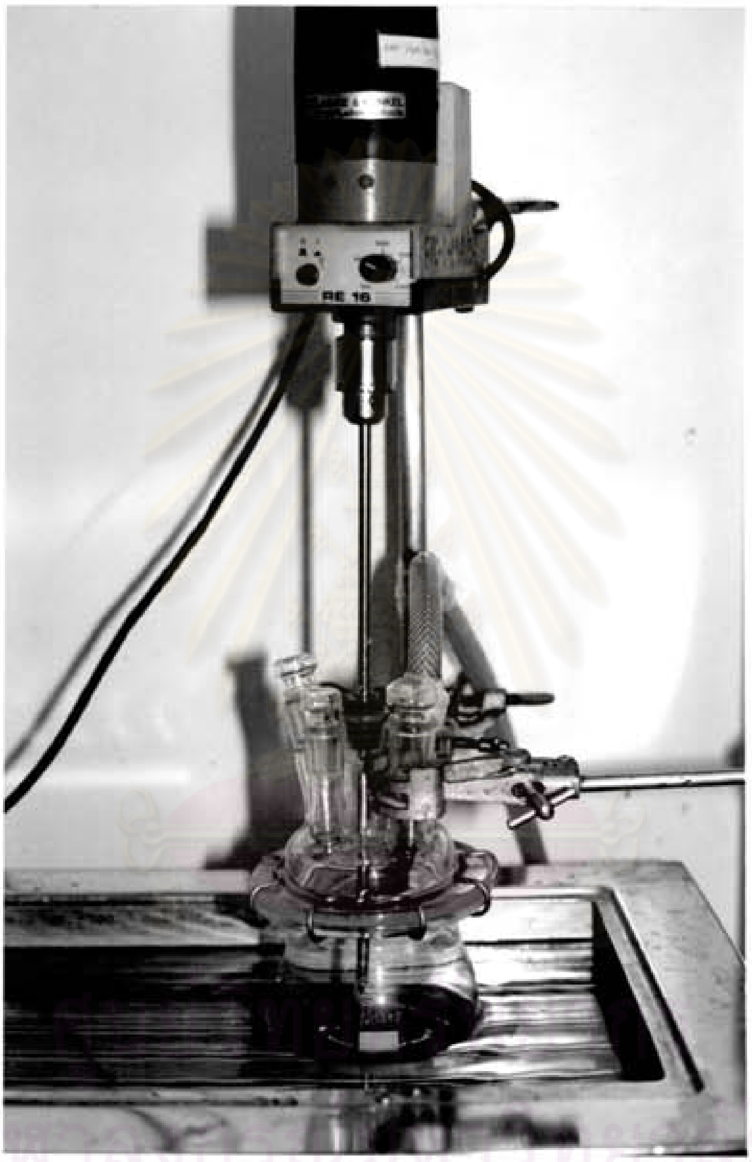

Figure 3.1 Details of the arrangement of units

3.3 Raw Material Preparation

3.3.1 Polyester polyol (F113)

Polyester polyol (F113) is hygroscopic, thus it is necessary to dehydrate under vacuum to remove absorbed water. Water levels in excess of 0.03 phr. can induce carbon dioxide generation resulting in porosity of product.

3.3.2 Waste rubber tyres

Waste rubber tyres used can be either natural or synthetic rubber as SBR (styrene butadiene rubber). To incorporate waste rubber into the final product, waste rubber tyres were cut into small particles of about 0.12 inches.

3.3.3 Mineral filler : Calcium carbonate , Silica , Calcined clay (brick)

To prevent formation of carbon dioxide bubbles in products, the mineral filers such as calcium carbonate , silica and brick must be carefully dried before it is added to polyester polyol. This was accomplished by heating open container of the fillers for 24 hours at temperature of 110 - 135 °C (R.O. Rosenberg et.al., "Vibrathane").

All the mineral fillers were passed through a US sieve No. 325.

3.4 Experimental Procedure

3.4.1 Establishing Production Procedure for unfilled polyurethane

After several trial production procedures, the best procedure and operating conditions which produced polyurethane with minimize air bubble. Figure 3.2 shows the flow diagram of this procedure.

The main unit operations of this procedure are as follows.

(a) Metering

The dried and degassed polyol were metered in the correct weight into a reaction kattle equipped with a mechanical stirrer, vacuum inlet, nitrogen inlet, septum port, thermometer and maintain under a nitrogen cover. These system was submerged in water bath at temperature around 60 °C according to Harris et.al. (1990).

(b) Mixing

The MDI was added into the reaction kattle using speed of agitator at 500 rpm. under nitrogen cover and stirred for 30 minutes. Then the kattle was evacuated to about 1 mm Hg to degas the prepolymer within 30 minutes.

(c) Curing

Catalyst (dibutyltin dilaurate, 0.02 % weight) and 1,4 butanediol were quickly added to the degassed prepolymer by using speed of agitator up to 1000 - 1500 rpm. The mixture was rapidly mixed without air entrainment (25 - 35 sec.). Then poured onto a preheat aluminium mold which was coated with silicone, the resulting product was in sheet form.

(d) Post Curing

The finished product was released out of the mold and transferred into an oven to heat at 100 °C for 24 hours in order to complete the crosslinking reaction and maintain the optimum properties.

3.4.2 Establishing Production Procedure for filled polyurethane

The production procedure for filed polyurethane is essentially the same as that of unfilled polyurethane. The procedure is shown in Figure 3.3. The main unit operations of this procedure is as follows :

(a) Metering

The dried and degassed polyol were metered in the correct weight into a reaction kattle, the set equipment was set up according to 3.4.1(a). The mineral filler was added into the reaction kattle using mechanical stirrer to agitate until it was uniform.

(b) Mixing

Procedure was identical to 3.4.1(b).

(c) Curing

Procedure was identical to 3.4.1(c).

(d) Post Curing

Procedure was identical to 3.4.1(d).

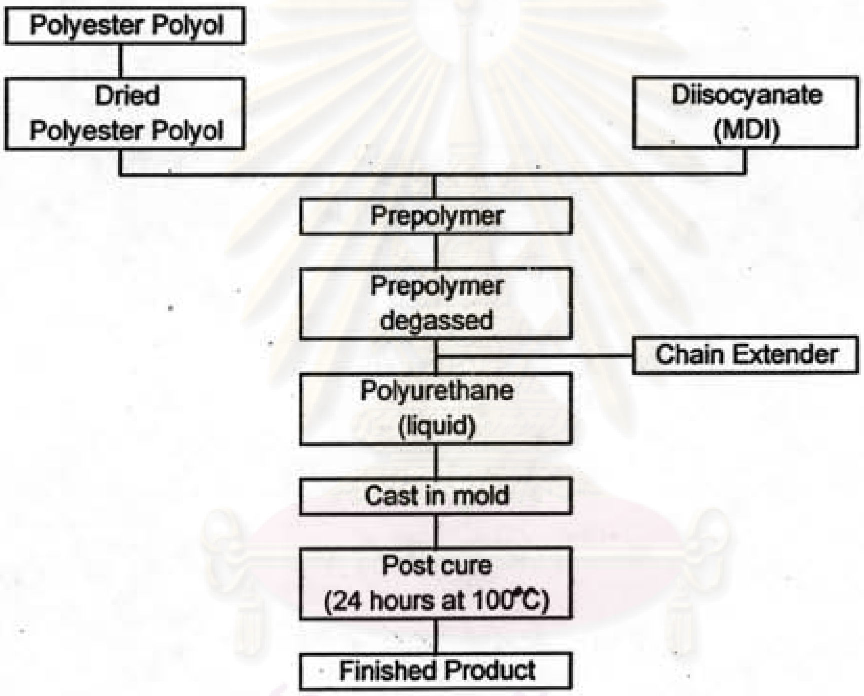

Figure 3.2 Manufacturing process for unfilled-polyurethane

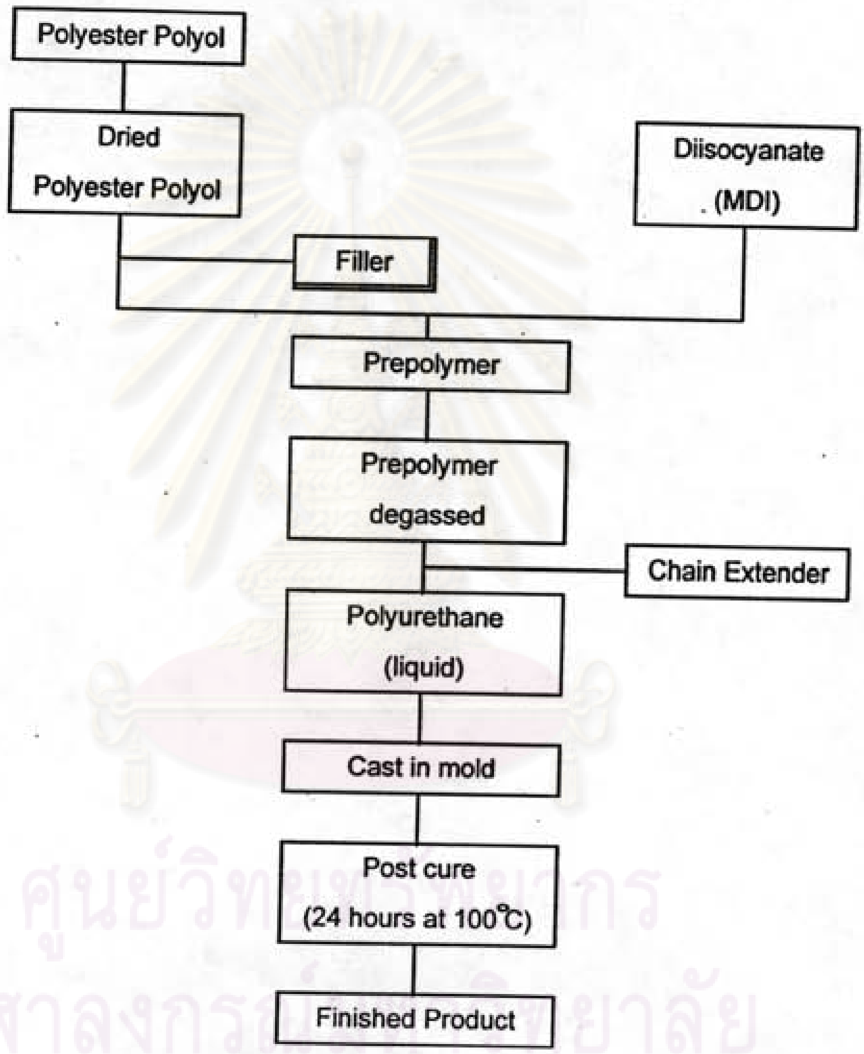

Figure 3.3 Manufacturing process for filled-polyurethane

3.4.3 Product Study Program

Guise et.al. (1980) and Korodi et.al. (1983) reported that chemical compositions are influence on mechanical properties. The strategy to obtain polyurethane product of the most suitable composition is summarized in Figure 3.4.

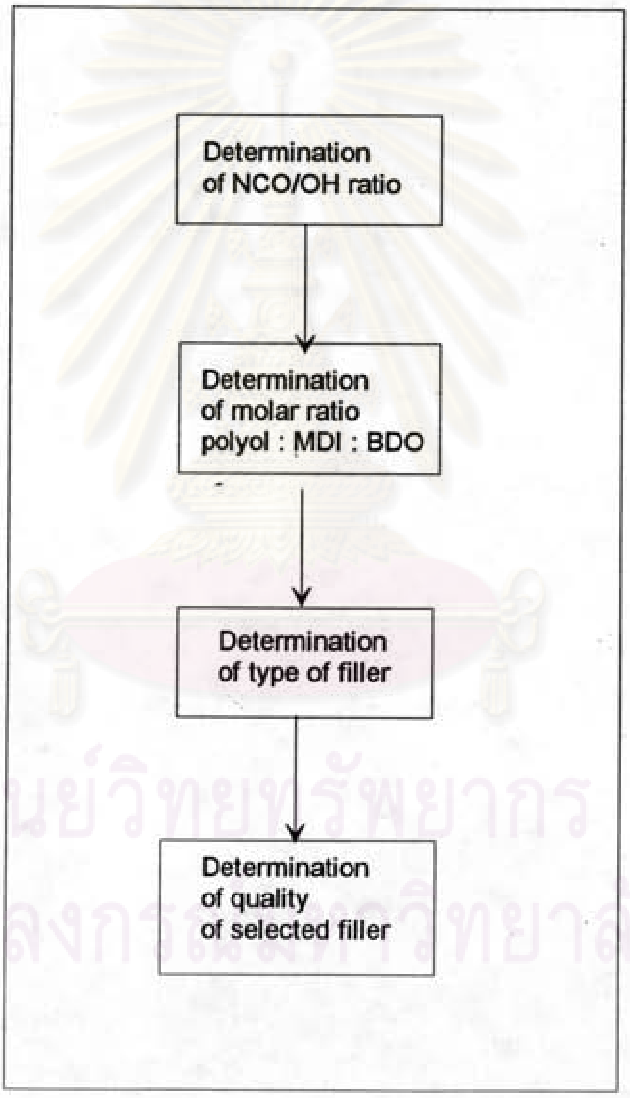

Figure 3.4 Strategy for Formulation of Product

3.4.4 Determination of NCO/OH ratio

In making polyurethane product, the relative quantities of isocyanate groups and hydroxyl groups are such that the ratio of isocyanate groups to hydroxyl groups is slightly in excess of stoichiometry ratio of 1. In this work, this ratio was varied from 0.9 to 1.15. The detail of the ratio which is used to make the polyurethane products is given in Table 3.4.

3.4.5 Determination of Molar ratio

In this part of study, the NCO/OH ratio was fixed at 1.09. For each NCO/OH ratio, sample of polyurethane were produced for various molar ratio. The molar ratio of polyester polyol : MDI : BDO was varied from 1 : 2 : 1 up to 1 : 5 : 4 (J. Fox and H. Janik, 1989). The detail of the ratio is given in Table 3.5.

3.4.6 Determination of Type of filler

Fillers investigated in this work are calcium carbonate, silica and brick powder. The first set of samples was made at fixed NCO/OH ratio of 1.09 and fixed molar ratio of polyol : MDI : BDO of 1 : 4 : 3 and fixed weight percentage of 5 for each filler. A summarize is shown in Table 3.6. The second set of samples was made of fixed NCO/OH ratio at 1.03 and fixed molar ratio of polyol : MDI : BDO of 1 : 4 : 3 and various weight percentages of each filler. A summary of this set of experiment is shown in Table 3.7.

3.4.7 Determination of Quantity of Selected Filler

From previous study in section 3.4.6, brick powder was chosen as the most suitable filler. In this part of work, the molar ratio of polyol : MDI : BDO was fixed at 1:4:3, and the NCO/OH ratio was set at 1.09 and 1.03 while the weight percentage of brick used was varied. The details of this part of work are presented in Tables 3.8 and 3.9.

Table 3.4 NCO/OH ratio of the investigated polyurethane

Ingradient	Quantity of material (pbw)							
	NCO/OH ratio							
	0.9	0.95	1.00	1.03	1.06	1.09	1.12	1.15
Polyol	100	100	100	100	100	100	100	100
MDI	47.92	50.59	53.25	54.85	56.44	58.04	59.64	64.24
BDO	13.48	13.48	13.48	13.48	13.48	13.48	13.48	13.48

Table 3.5 molar ratio of the investigated polyurethane

Molar ratio	Quantity of polyol : MDI : BDO (PBW)
1 : 2 : 1	100 : 29.02 : 4.49
1 : 3 : 2	100 : 43.53 : 8.89
1 : 4 : 3	100 : 58.04 : 13.48
1 : 5 : 4	100 : 72.55 :17.97
1 : 6 : 5	100 : 87.06 : 22.47

Table 3.6 various kinds of filler for filled-polyurethane at NCO/OH ratio1.09

Type of filler	Quantity of polyol:MDI:BDO:filler (pbw)
Brick 5 %	100 : 55.14 : 12.87 : 8.57
Calcium carbonate 5 %	100 : 55.14 : 12.87 : 8.57
Silica 5%	100 : 55.14 : 12.87 : 8.57

Table 3.7 various kinds of filler for filled-polyurethane at NCO/OH ratio 1.03

Type of filler	Quantity of polyol:MDI:BDO:filler (pbw)
Brick 5 %	95 : 52.10 : 12.81 :8.42
10 %	90 : 49.36 : 12.13 :16.83
20 %	80 : 43.88 : 10.78 : 33.66
Calcium carbonate 5 %	95 : 52.10 : 12.81 :8.42
10 %	90 : 49.36 : 12.13 :16.83
20 %	80 : 43.88 : 10.78 : 33.66
Silica 5 %	95 : 52.10 : 12.81 :8.42
10 %	90 : 49.36 : 12.13 :16.83
20 %	80 : 43.88 : 10.78 : 33.66

Table 3.8 various weight percentage of brick for filled-polyurethane at NCO/OH ratio1.09

% Brick	Quantity of polyol:MDI:BDO:brick (pbw)
0 %	100 : 58.04 : 13.48 :0
5 %	95 : 55.14 :12.87 : 8.57
9 %	91 :52.82 :12.27 : 15.44
13 %	87 : 50.49 :11.73 : 22.29
17 %	83 : 48.17 :11.19 :25.15
20 %	80 : 46.43 : 10.78 : 34.30
23 %	77 : 40.69 : 10.38 : 39.45

Table 3.9 various weight percentage of brick for filled-polyurethane at NCO/OH ratio 1.03

% Brick	Quantity of polyol:MDI:BDO:brick (pbw)
0 %	100 : 58.85 : 13.48 : 0
5 %	95 : 52.10 : 12.81 :8.42
10%	90 : 49.36 :12.13 :16.83
15%	85 :46.62 :11.46 :25.25
20%	80 :43.88 : 10.78 :33.67

Remark : In each batch, the overall reactant is not higher than 200 grams.

3.5 Mechanical Properties Analysis

All samples produced in sections 3.4.4-3.4.7 were subjected to tensile testing and hardness testing to determine the polyurethane product of the most suitable constituents.

3.5.1 Tensile Testing (ASTM D638)

The cross head speed of Instron tensile testing at 500mm./min. was used. The median of five specimen was taken 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.

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

F = Tensile force (N)

A = Cross-section area (mm^2)

Preparation of Test Specimen (D.J. David and H.B. Staley, 1969)

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 °C $\pm$ 2 °C
- 50 % $\pm$ 5% relative humidity (R.H)

Thus, the specimen 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 (3.4.1) and cut by a puncher by means 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.

3.5.2 Hardness Testing (ASTM D2240)

For characterization of the hardness of polyurethane in which spring load (for example, cone shaped) pins are press into the test specimen . The penetration depth under a standardized load is taken as a measurement of the hardness of polyurethane. The data determined with a small hand held instrument are typically single point values. In this work measurement were taken and median value represented the hardness value.