CHAPTER 4
EXPERIMENT

4.1 Reagent nd Raw Materials

4.1.1 Polyol

The type of polyol used in this study is polyester polyol and its tradename is F 113. F 113 was donated by Thai Polyurethane Industry Co.,Ltd.. The specifications of F 113 are presented in Table 4.1.

Table 4.1 Specifications of polyester polyol (F 113)

Specifications	Polyester polyol : F 113
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
Colour (APHA)	< 100
Water content (%)	< 0.05
Density at 25 °C (g/cm^3)	1.16

4.1.2 Isocyanate

The type of isocyanate used in this study is polymeric MDI and its tradename of polymeric MDI is Raypol C 900. The specifications of Raypol C 900 are presented in Table 4.2. Raypol C 900 was supplied by Thai Polyurethane Industry Co.,Ltd..

Table 4.2 Specifications of polymeric MDI (Raypol C 900)

Specifications	Polymeric MDI : Raypol C 900
Physicalstate at room temperature	Liquid
Colour	Fawn to dark brown
Odour	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
Crystallisation temperature (°C)	< 10
Shelf life at 20 °C (month)	6
Average functionality	2.7

4.1.3 Chain-extender

Chain-extender used in this study is diethylene glycol(DEG). It was supplied by Thai Polyurethane Co.,Ltd.. The structure and specifications of diethylene glycol are presented in Figure 4.1 and Table 4.3, respectively.

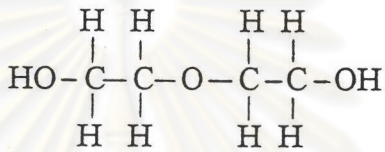

Figure 4.1 Structure of diethylene glycol

Table 4.3 Characteristic of diethylene glycol (DEG)

Specifications	Diethylene glycol
Specific Gravity (20/20°C)	1.1188
Acidity (Wt % as HAo)	0.0016
Water content (Wt %)	0.047
Ash (Wt %)	0.0002
Colour (Pt-Co)	10
Odour	Mild
Hydroxyl value	1,057

4.1.4 Other chemical

Other chemical used in this work are as follows:

Dibuthyltin diluarate	serve as	catalyst
Brick powder	serve as	filler
Silicone	serve as	mold releasing agent
Ethylacetate	serve as	solvent

4.2 Apparatus

This study consisted of two parts: batch experiment and continuous experiment.

4.2.1 Manufacturing Apparatus (Batch Experiment)

Apparatus for producing polyurethane consists of the following units: mechanical stirrer, beaker (250 ml), aluminuim mold and vacuum oven.

Details of the arrangement of units are shown in Figure 4.2.

4.2.2 Manufacturing Apparatus (Continuous Experiment)

Apparatus for producing polyurethane consists of the following units: gear pump, static mixer (1026 cm^3), container, aluminuim mold and vacuum oven.

Details of the arrangment of units are shown in Figure 4.3.

4.2.3 Testing Apparatus

Tensile Testing Machine : Tensometer T 10 (Figure 4.4)

Shore A Durometer Hardness Tester : Durometer 473 (Figure 4.5)

Micrometer : Mitutoyo (Figure 4.6)

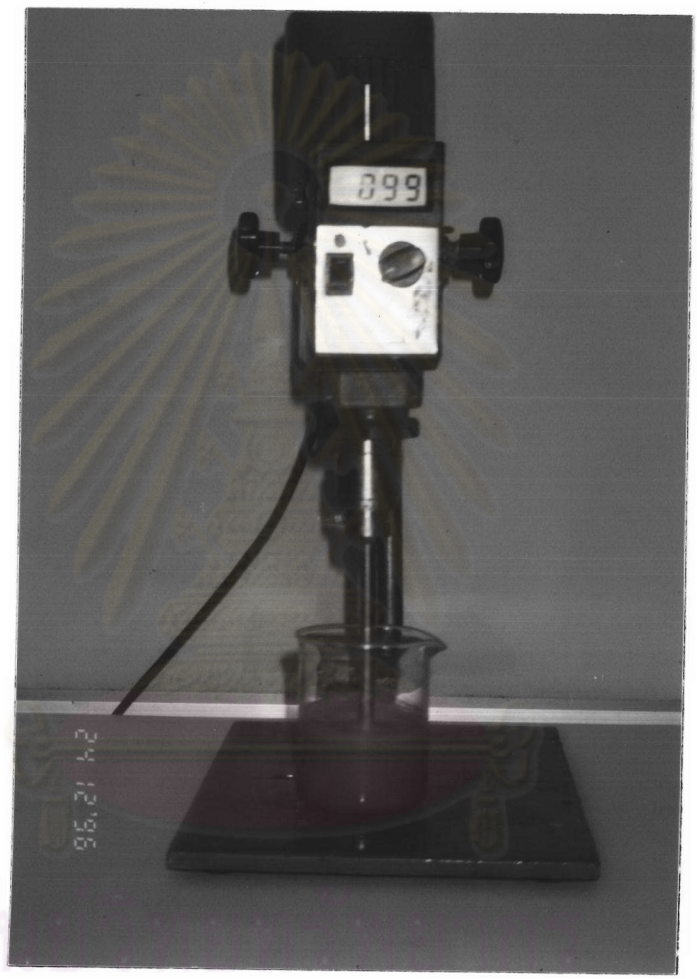

Figure 4.2 Details of the arrangement of units(Batch experiment)

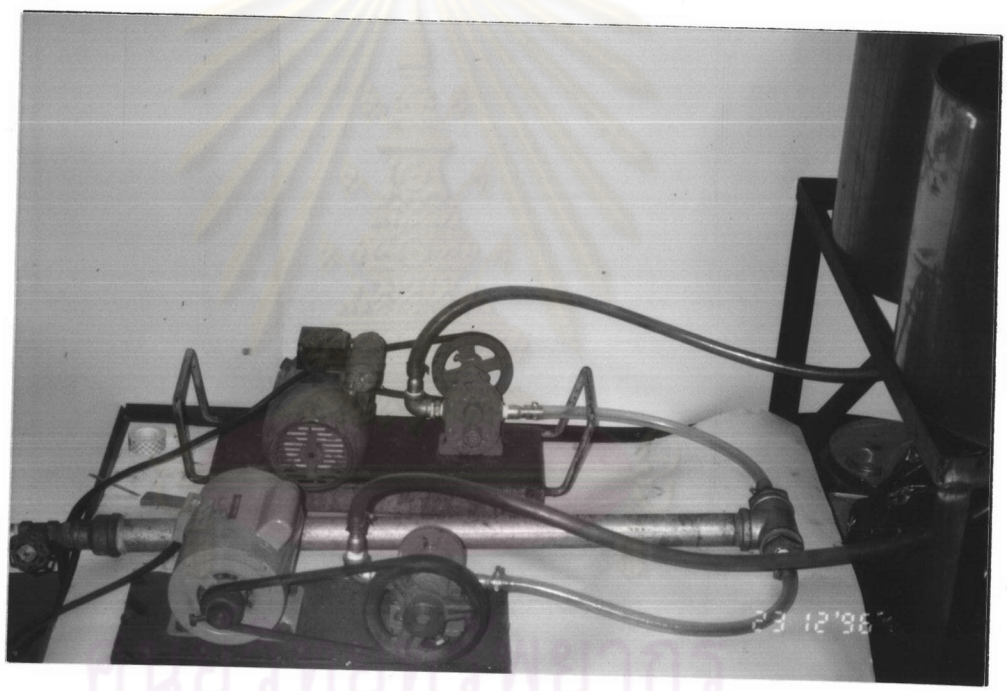

Figure 4.3 Details of the arrangement of units(Continuous experiment)

Figure 4.4 Tensile testing machine: Tensometer T10

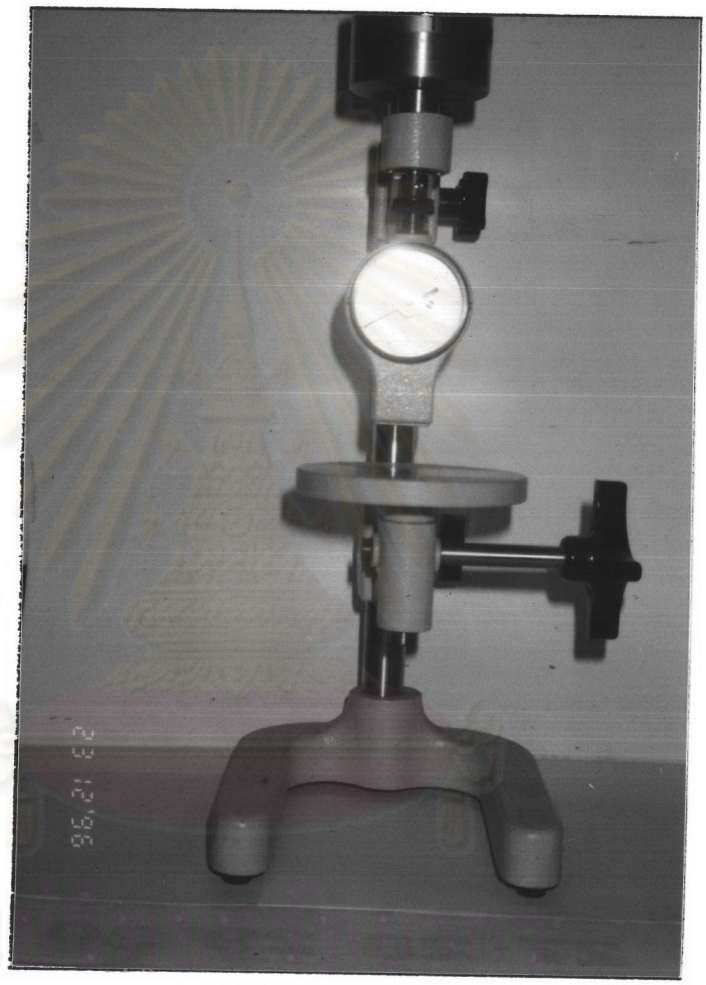

Figure 4.5 Shore A Durometer Hardness Tester: Durometer 473

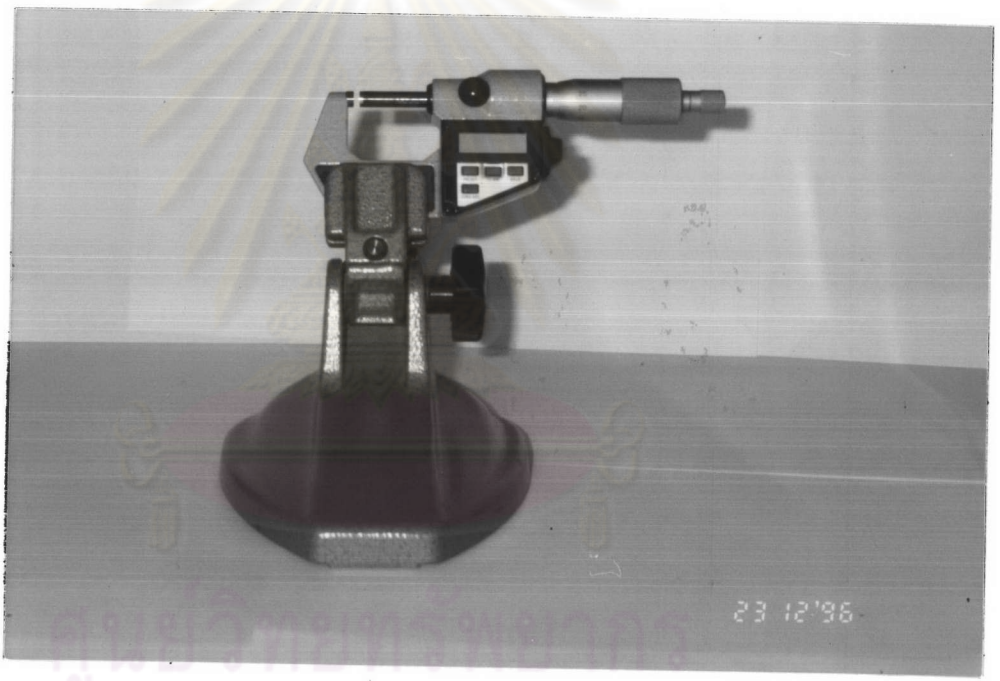

Figure 4.6 Micrometer: Mitutoyo

4.3 Batch Experiment

4.3.1 Establishing Production Procedure for unfilled- polyurethane

Figure 4.7 shows the flow diagram of this procedure.

(a) Raw Material Preparation

Polyester polyol is hydroscopic, thus it is necessary to dehydrate to remove absorbed water. Water levels in excess of 0.03 part per hundred resin(phr.) can induce carbondioxide generation resulting in porosity of product. The dried polyester polyol, diethylene glycol and dibuthyltin dilaurate were metered in the correct weight in the beaker and mixed for 5 minutes. Then the beaker was kept in vacuum oven for 24 hours.

(b) Polymerization

The MDI was added to the polyol mixture in the beaker and mixed for 6 minutes. Then the liquid polyurethane was poured onto aluminuim mold which was coated with silicone. The resulting product was in sheet form.

(c) Post curing

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

4.3.2 4.3.1 Establishing Production Procedure for filled- polyurethane

The production procedure for filled polyurethane is essentially the same as that of unfilled polyurethane. The procudure is shown in Figure 4.8.

(a) Raw Material Preparation

Brick powder must be carefullydried before added to the dried polyester polyol. The dried polyester polyol, diehtylene glycol, brick powder and dibuthyltin dilaurate were metered in the correct weight in the beaker and mixed for 5 minutes. Yhen the beaker was kept in vacuum oven for 24 hours.

(b) Polymerization

The MDI was added to the polyol mixture in the beaker and mixed for 6 minutes. Then the liquid polyurethane was poured onto aluminuim mold which was coated with silicone. The resulting product was in sheet form.

(c) Post curing

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

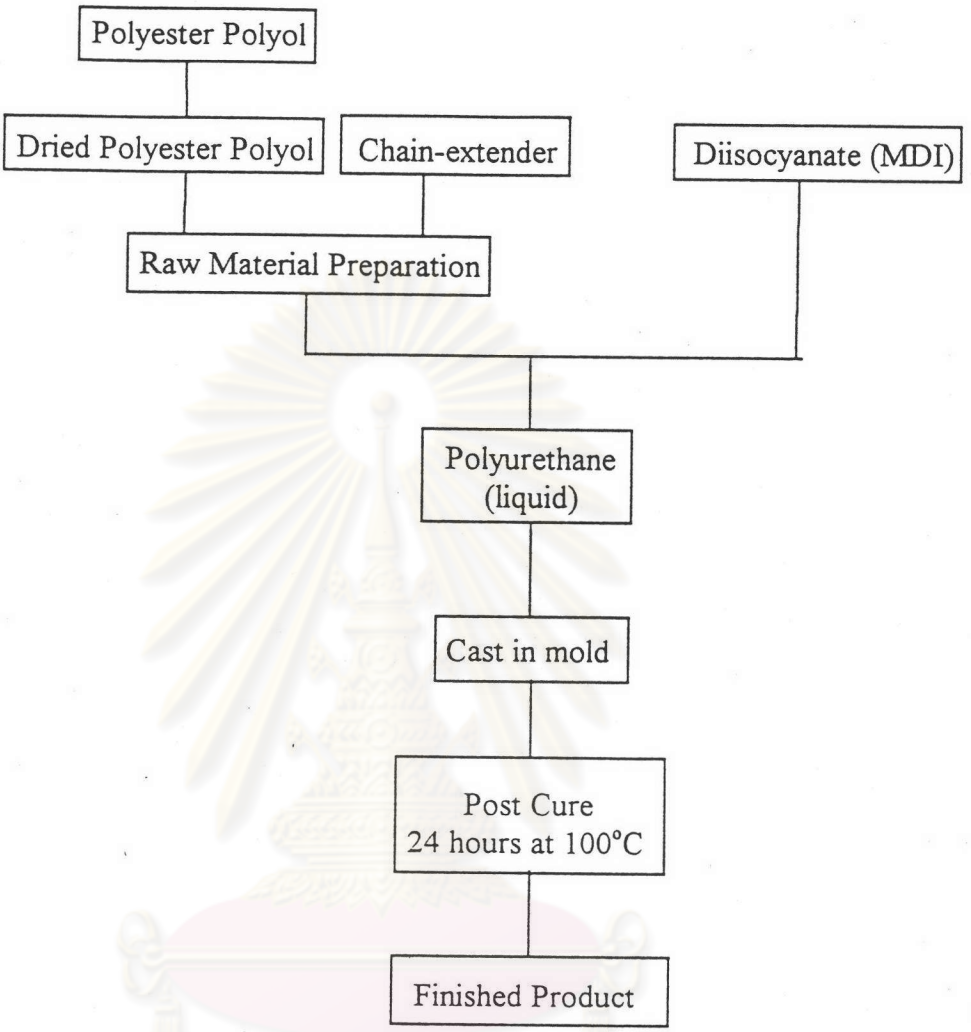

Figure 4.7 Manufacturing one shot production for unfilled polyurethane

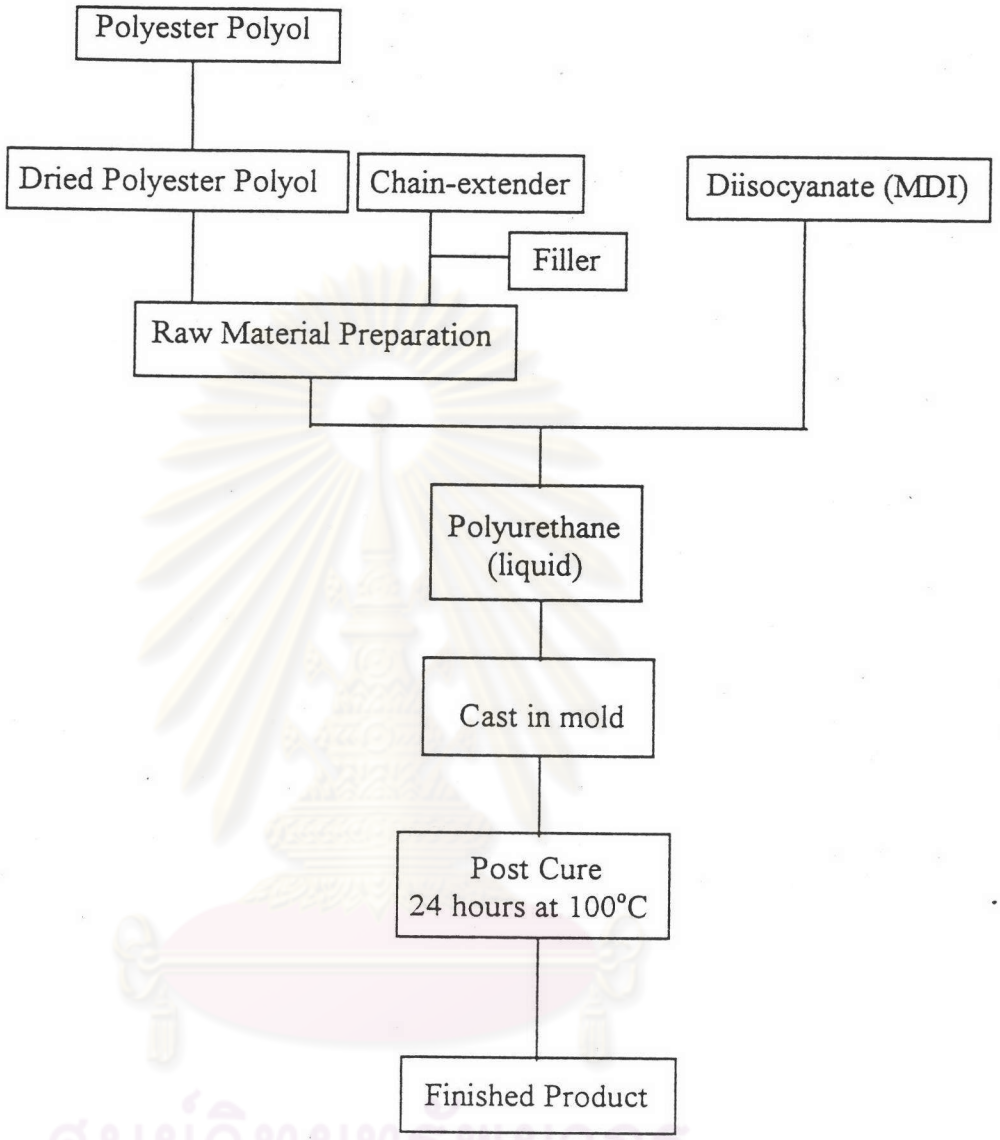

Figure 4.8 Manufacturing one shot production for filled polyurethane

4.3.3 Product Study Program

Guise et.al.(1980) and Korodi et.al.(1983) reported that chemical compositions had influenced on mechanical properties. The strategy to obtain polyurethane product of the most suitable composition is summeried in Figure 4.9.

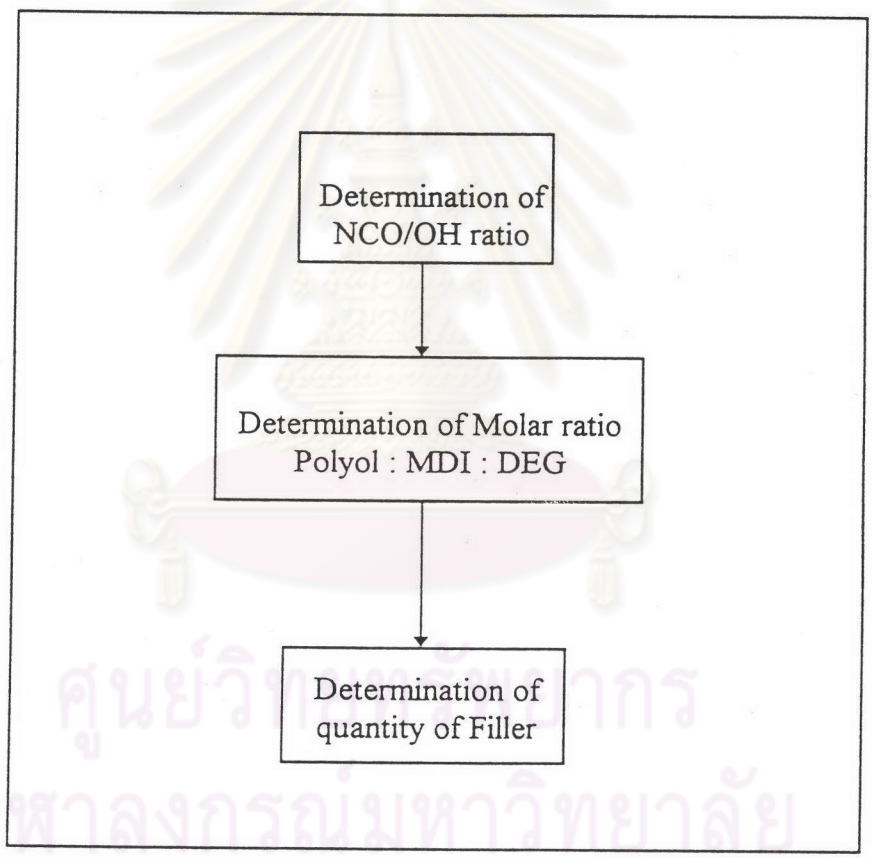

Figure 4.9 Strategy for Formulation of Product

4.3.4 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 1.14. The detail of the ratio which is used to make the polyurethane products is given in Table 4.4.

4.3.5 Determination of Molar ratio

In this prt of study, the NCO/OH ratio was fixed at 1.02 and 1.11. For each NCO/OH ratio, samples of polyurethane were produced for various molar ratio. The molar ratio of polyester polyol:MDI:DEG was varied from 1:2:1 to 1:6:5 (J. Fox and H. Janik, 1989).

The details of the NCO/OH ratio of 1.02 and 1.11 are given in the Table 4.5 and Table 4.6, respectively.

4.3.6 Determination of Quantity of brick powder

In this part of study, the molar ratio of polyester polyol:MDI:DEG was fixed at 1:4:3 and a fixed NCO/OH ratio of 1.02 and 1.11 while the weight percentage of brick used was varied.

The details of this part are presentd in the Table 4.7 and Table 4.8, respectively.

Table 4.4 NCO/OH ratio of the investigated polyurethane

gradient	Quantity of material (pbw)								
	NCO/OH ratio								
	0.90	0.93	0.96	0.99	1.02	1.05	1.08	1.11	1.14
Polyol	100	100	100	100	100	100	100	100	100
MDI	47.92	49.51	51.11	52.17	54.30	55.90	57.50	59.10	60.69
DEG	15.89	15.89	15.89	15.89	15.89	15.89	15.89	15.89	15.89

Table 4.5 Molar ratio of the investigated polyurethane at NCO/OH ratio 1.02

Molar ratio	Quantity of Polyol : MDI : DEG (pbw)
1 : 2 : 1	100 : 27.15 : 5.30
1 : 3 : 2	100 : 40.73 : 10.59
1 : 4 : 3	100 : 54.30 : 15.89
1 : 5 : 4	100 : 67.88 : 21.19
1 : 6 : 5	100 : 81.45 : 26.48

Table 4.6 Molar ratio of the investigated polyurethane at NCO/OH ratio 1.11

Molar ratio	Quantity of Polyol : MDI : DEG (pbw)
1 : 2 : 1	100 : 29.55 : 5.30
1 : 3 : 2	100 : 44.33 : 10.59
1 : 4 : 3	100 : 59.10 : 15.89
1 : 5 : 4	100 : 73.88 : 21.19
1 : 6 : 5	100 : 88.65 : 26.48

Table 4.7 Various weight percentage of brick for filled polyurethane at NCO/OH ratio 1.02

% Brick Powder	Quantity of polyol : MDI : DEG : brick (pbw)
0	100 : 54.30 : 15.89 : 0
5	95 : 51.59 : 15.10 : 8.51
10	90 : 48.87 : 14.30 : 17.02
15	85 : 46.16 : 13.51 : 25.53
20	80 : 43.44 : 12.71 : 34.04
25	75 : 40.73 : 11.92 : 42.55

Table 4.8 Various weight percentage of brick for filled polyurethane at NCO/OH ratio 1.11

% Brick Powder	Quantity of polyol : MDI : DEG : brick (pbw)
0	100 : 59.10 : 15.89 : 0
5	95 : 56.15 : 15.10 : 8.75
10	90 : 53.19 : 14.30 : 17.50
15	85 : 50.24 : 13.51 : 26.25
20	80 : 47.28 : 12.71 : 34.99
25	75 : 44.33 : 11.92 : 43.75

4.4 Continuous Experimental

The previously obtained suitable composition of NCO/OH ratio of 1.02, molar ratio of polyester polyol:MDI:DEG of 1:4:3 was used in this part.

In the container or storage tank labeled "Part A", the polyester polyols, chain-extender, filler and catalyst were stored as a liquid mix. The other storage tank or container labeled "Part B" simply contained a liquid polymeric MDI. Liquid in container A and container B are fed directly into the static mixer by gear pump in correct volumetric flowrate. Volumetric flowrate of liquid mix "Part A" is approximate 1,200 cm^3/min. and volumetric flowrate of diisocyanate is approximate 550 cm^3/min..The product which flows out from static mixer are kept every 1 minute. Then the product sample were taken to test mechanical properties.

4.5 Mechanical Properties Analysis

All samples produced in sections 4.3.4-4.3.6 were subjected to tensile testing and hardness testing to determine the polyurethane product of the most suitable constituents.

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

Polyurethane, containing hydrophilic groups such as aminogroups and polyoxyethylene segments, have reduced secondary intermolecular bonding when the amount of water vapour percent 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 condition:

- 23°C ± 2°C
- 50% ± 5% relatively humidity (R.H.)

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

4.5.1 Tensile Testing (ASTM D638)

The cross head speed of tensile testing at 500 mm./min. was used. The median of five specimen was taken as the characteristic of the material tested. The tensile strength and percentage of elongation at break was calculated and by Tensometer T10. The unit of tensile strength was shown in form MPa (N/mm^2).

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

Thickness was measured by a thickness micrometer. Three measurements of thickness were taken and the median value was used for calculated.

4.5.2 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.