CHAPTER IV

EXPERIMENTS

The study of unsaturated polyester synthesized from post consumer PET bottle was experimentally devided into three parts.

1. Depolymerization of PET
2. Preparation of unsaturated polyesters
3. Determining of mechanical properties

The details of experiments were explained in the following sections.

4.1 CHEMICALS

1. PET [poly(ethylene terephthalate)] used in this study was obtained from post consumer "Sprinkle"drinking water bottles. Viscosity-average molecular weight of PET is 1.09 X 10^4 g/gmol (method for determined viscosity-average molecular weight was illustrated in Appendix A) The PET bottles were cut into small pieces which have average size of 5 x 5 mm.

2. Ethylene glycol [$CH_2OH{\cdot}CH_2OH$] (abbreviated as EG) was supplied by Ajax Chemicals, Australia, and used without further purification.

3. Propylene glycol [$CH_3CHOH{\cdot}CH_2OH$](abbreviated as PG) was supplied by E.Merck, Federal Republic of Germany, and used without further purification

4. Zinc acetate [$(CH_3COO)_2\ Zn{\cdot}2H_2O$] was supplied by Ajax Chemicals, Australia.

5. Maleic acid [$C_4H_4O_4$] was supplied by Fluka Chemical AG., Switzerland.

6. Acetic anhydride [$C_4H_6O_3$] was supplied by Riedel-De Haen AG.

7. Pyridine [C_5H_5N] was supplied by Ajax Chemicals, Australia.

8. Potassium Hydroxide [KOH] was supplied by Ajax Chemicals, Australia.

9. Acetone [CH_3COCH_3] was supplied by E.Merck, Federal Republic of Germany.

10. Ethanol 95% [CH_3CH_2OH] used in this experiment was of commercial grade.

11. Styrene [C_8H_8] used in this experiment was of commercial grade.

12. Hydroquinone [$C_6H_4O_2$] was supplied by E.Merck, Federal Republic of Germany.

4.2 APPARATUS

1. Depolymerization Reactor:- a 500 cm^3 round bottomed glass flask with three-necks.

2. Heating Mantle:- able to heat up to maximum temperature of 450°C.

3. Reactor for synthesis of unsaturated polyester:-a 500 cm^3 round bottomed glass flask with five-necks.

4. Reflux condenser

5. Distillation condenser

6. Thermometer:- temperature range from 0 to 200 °C.

7. Mechanical stirrer

8. 250 cm^3 round bottomed flask

4.3 EXPERIMENTAL PROCEDURES

4.3.1 Depolymerization of PET

Post consumer PET bottles were depolymerized at different molar ratios of PET to EG - PG mixture by employing 0.5% w/w zinc acetate, based on weight of PET, as catalyst. The solution and small pieces of post consumer PET were charged to a round bottomed three-necked flask which was fitted with reflux condenser and thermometer. The reaction was carried out at 190-200 °C at various reaction times.

At the end of each reaction times, contents of the reactor were separated into two parts. The first was analyzed for hydroxyl value before removal of free glycol, and was used for synthesis of unsaturated-polyester. The latter was extracted with water and filtered. The filtrate containing water, free glycol , and some soluble oligomers was concentrated by evaporation and then chilled in order to precipitate out the water-soluble oligomers. Then it was filtered again. The second filtrate contained water and free glycol. The cakes remaining after twice filtrations were dried and weighted together. Then it was analyzed for hydroxyl value after removal of free glycol. Flow diagram of this procedure was showed in Figure 4-1.

The hydroxyl value of samplings and the glycol-free products were analyzed according to ASTM D2849 Method A [12]. This method is briefly described as follows. About 0.5-1.0 g .of sample was accurately weighted and then added into 10 ml acetylating solution containing 88:12(v/v) pyridine and acetic anhydride, which is in a 250 ml round- bottomed flask. After that, the flask was fitted with a vertical reflux condenser and heated in a boiling water bath for 2 hrs. The mixture was then cooled to room temperature and hydrolyzed by 100 ml of chilled distilled water in another flask. The resulting solution was titrated against 0.5 N KOH standard solution using phenolphthalein as a indicator. A blank run, without the sample, was also performed in the same fashion. The hydroxyl value is then calculated based on the following formular [12].

$$\text{Hydroxyl value} = [\,(B-A)\,N \times 56.1\,] / W \qquad (4\text{-}1)$$

where:

A = KOH required for titration of the sample, (ml)

B = KOH required for titration of the blank,(ml)

N = normality of the KOH, (N)

W = grams of sample used (g)

EG/PG and PET ratios were varied from 1 to 4 by mole. The reaction temperature was controlled in the range of 190-200 °C. Each ratio was varied by depolymerization time from 1, 2, 4, 6 to 8 hrs. The detail of each batch was illustrated in Table 4-1 and Table 4-2.

Table 4-1 Molar ratio of (EG+PG)/PET and depolymerization time of PET

Molar ratio of (EG+PG)/PET (-)	Depolymerization time (hrs)	Run (-)	Mole of		
			PET (mol)	EG (mol)	PG (mol)
1	1	gly 1,1	0.40	0.20	0.20
	2	gly 2,1	0.40	0.20	0.20
	4	gly 4,1	0.40	0.20	0.20
	6	gly 6,1	0.40	0.20	0.20
	8	gly 8,1	0.40	0.20	0.20
2	1	gly 1,2	0.40	0.40	0.40
	2	gly 2,2	0.40	0.40	0.40
	4	gly 4,2	0.40	0.40	0.40
	6	gly 6,2	0.40	0.40	0.40
	8	gly 8,2	0.40	0.40	0.40
3	1	gly 1,3	0.33	0.495	0.495
	2	gly 2,3	0.33	0.495	0.495
	4	gly 4,3	0.33	0.495	0.495
	6	gly 6,3	0.33	0.495	0.495
	8	gly 8,3	0.33	0.495	0.495
4	1	gly 1,4	0.25	0.50	0.50
	2	gly 2,4	0.25	0.50	0.50
	4	gly 4,4	0.25	0.50	0.50
	6	gly 6,4	0.25	0.50	0.50
	8	gly 8,4	0.25	0.50	0.50

Table 4-2 Weights of PET, EG, PG, and catalyst used in the reactions at various time

Molar ratio of (EG+PG)/PET (-)	Depolymerization time (hrs)	Run (-)	Weight (g.)			
			PET	EG	PG	Zinc acetate
1	1	gly 1,1	76.80	12.40	15.20	0.384
	2	gly 2,1	76.80	12.40	15.20	0.384
	4	gly 4,1	76.80	12.40	15.20	0.384
	6	gly 6,1	76.80	12.40	15.20	0.384
	8	gly 8,1	76.80	12.40	15.20	0.384
2	1	gly 1,2	76.80	24.80	30.40	0.384
	2	gly 2,2	76.80	24.80	30.40	0.384
	4	gly 4,2	76.80	24.80	30.40	0.384
	6	gly 6,2	76.80	24.80	30.40	0.384
	8	gly 8,2	76.80	24.80	30.40	0.384
3	1	gly 1,3	63.36	30.69	37.62	0.317
	2	gly 2,3	63.36	30.69	37.62	0.317
	4	gly 4,3	63.36	30.69	37.62	0.317
	6	gly 6,3	63.36	30.69	37.62	0.317
	8	gly 8,3	63.36	30.69	37.62	0.317
4	1	gly 1,4	48.00	31.00	38.00	0.240
	2	gly 2,4	48.00	31.00	38.00	0.240
	4	gly 4,4	48.00	31.00	38.00	0.240
	6	gly 6,4	48.00	31.00	38.00	0.240
	8	gly 8,4	48.00	31.00	38.00	0.240

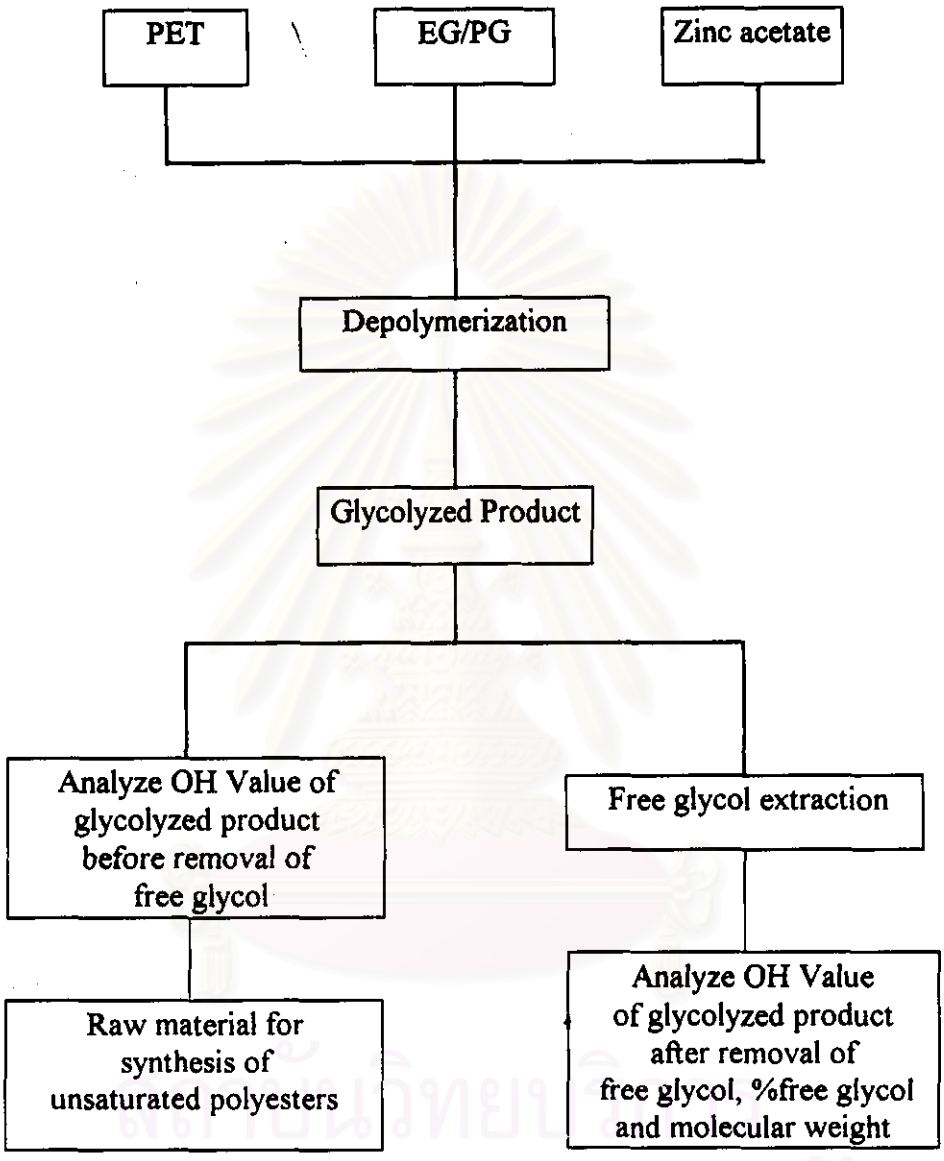


Figure 4-1 A flow diagram of depolymerization of PET

4.3.2 Preparation of unsatured polyesters

(a) *Polymerization*

The unsaturated polyester resins were prepared by reaction of the glycolyzed products (without separation of free glycol) with maleic acid at 1.1:1 hydroxyl to carboxyl ratio. The hydroxyl value of the glycolyzed product without separation of free glycol was used to determine the amount of maleic acid. The detail of each batch were illustrated in Table 4-3.

The polyesterification was carried out in a round- bottomed flask having a distillation condenser, a thermometer, and a stirring assembly. The reactants were heated from room temperature to 180 °C, 1-1.5 hrs. The temperature was then held at 180 °C for 3 hrs and finally increased to 200 °C and maintained at that point while acid value was off-line monitored during the reaction.

The acid value of sampling was analyzed according to ASTM D4662 [13]. This method is briefly described as follows. The weighted sampling was introduced to a 250 ml erlenmeyer flask with 20 ml acetone and 0.5 ml phenolphthalein indicator solution, then mix well until the sample was completely dissolved (heat only if necessary, and do not boil). The resulting solution was immediately titrated with 0.1 N standard alcoholic KOH at temperature below 30 °C by using a 10 ml burret to add the KOH solution and using phenolphthalein as the indicator. A blank run, without the sample, was also performed in the same fashion. The acid value is the calculated in milligrams of KOH/gram of sample[13], as follows :

$$\text{Acid value} = [\,(A - B)N \times 56.1\,] / W \qquad (4\text{-}2)$$

where:

A = KOH solution required for titration of the sample, (ml)

B = KOH solution required for titration of the blank, (ml)

N = Normality of the KOH solution, (N)

W = sample used, (g)

When the acid value dropped to about 50 ± 2 mgKOH/g, added the hydroquinone about 0.2% of the final weight of unsaturated polyester. Then this batch was cooled down to 90 °C and added monomeric styrene about 35% of the final weight of unsaturated polyester and cooled as rapidly as possible.

(b) *Casting*

The resulting unsaturated polyesters were casted by mixed with 0.5 part per hundred resin (phr) methyl ethyl ketone peroxide. The curing condition was 1 hr at 100 °C, and finally 2 hrs at 80 °C.

Two testes were carried out according to the following specifications: impact testing (ASTM D256) and hardness testing(ASTM D2240)

Figure 4-2 showed the flow diagram of this procedure.

Table 4-3 Weight of glycolyzed product and maleic acid were used for synthesized unsaturated polyester.

molar ratio of (EG+PG)/PET	code of unsat-polyester	amount of glycolyzed product		amount of maleic acid	
		mole	weight (g)	mole	weight (g)
1	UPGLY 1,1	0.6084	111.40	0.5531	64.20
	UPGLY 2,1	0.6555	113.50	0.5959	69.17
	UPGLY 4,1	0.7159	111.70	0.6508	75.55
	UPGLY 6,1	0.7059	108.20	0.6417	74.49
	UPGLY 8,1	0.7028	107.00	0.6389	74.16
2	UPGLY 1,2	0.6807	102.84	0.6188	71.83
	UPGLY 2,2	0.9010	129.43	0.8191	95.08
	UPGLY 4,2	0.7735	110.40	0.6420	74.52
	UPGLY 6,2	0.7585	105.10	0.6895	80.04
	UPGLY 8,2	0.8383	116.90	0.7621	88.46
3	UPGLY 1,3	0.7624	104.70	0.6930	80.45
	UPGLY 2,3	0.7277	99.00	0.6615	76.79
	UPGLY 4,3	0.9103	122.95	0.8275	96.06
	UPGLY 6,3	0.8638	115.10	0.7852	91.15
	UPGLY 8,3	0.7788	100.50	0.7080	82.18
4	UPGLY 1,4	0.705	98.00	0.6368	73.92
	UPGLY 2,4	0.7350	97.99	0.664	77.59
	UPGLY 4,4	0.7625	101.45	0.6932	80.47
	UPGLY 6,4	0.7800	102.76	0.7091	82.31
	UPGLY 8,4	0.8025	101.58	0.7296	84.69

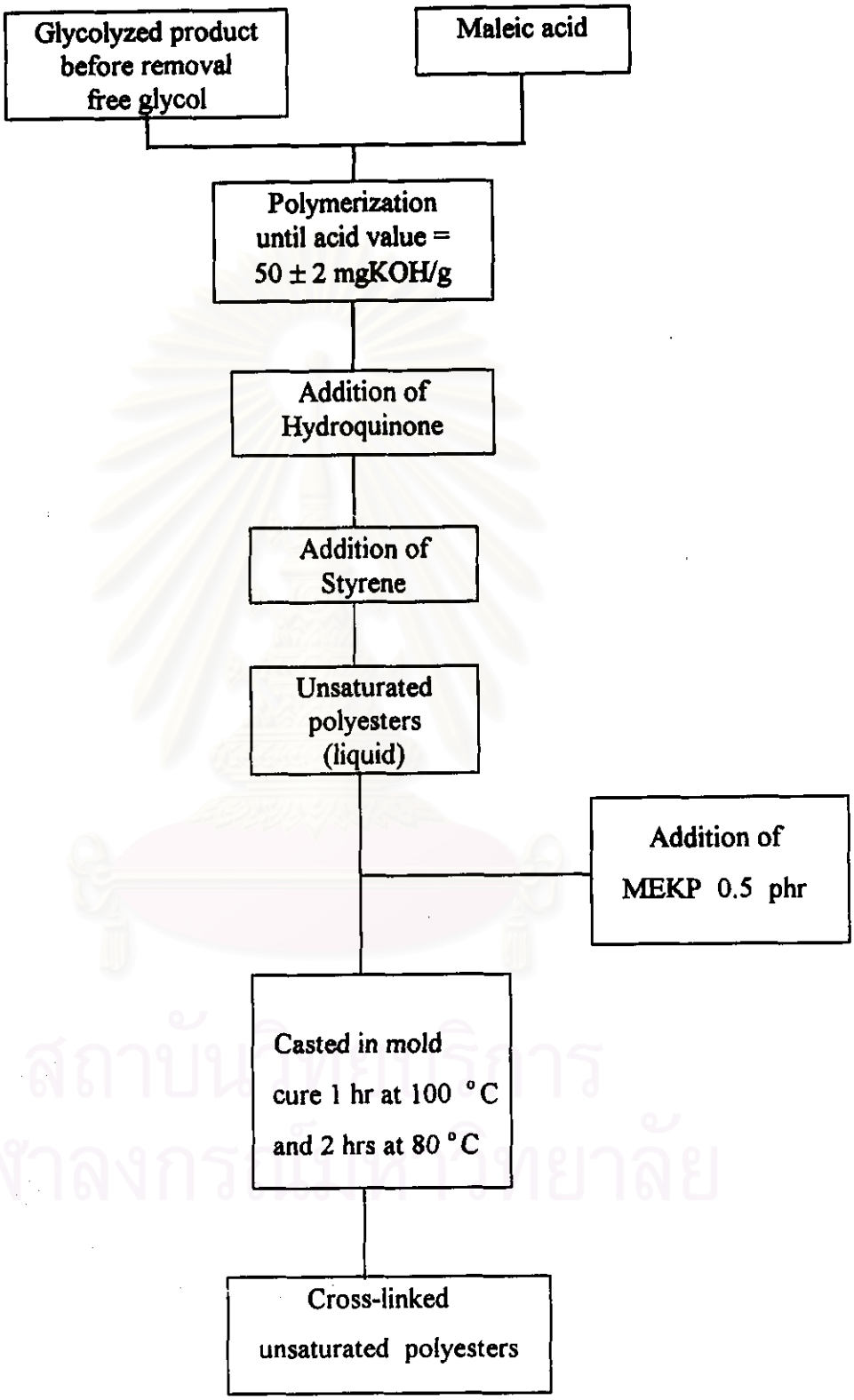


Figure 4-2 A flow diagram of synthesizing unsaturated polyester

4.3.3 Determination of mechanical properties

All samples produced in section 4.3.2 were subjected to impact testing and hardness testing to determine the effect of molar ratio of (EG + PG)/PET and depolymerization time on casted unsaturated polyesters.

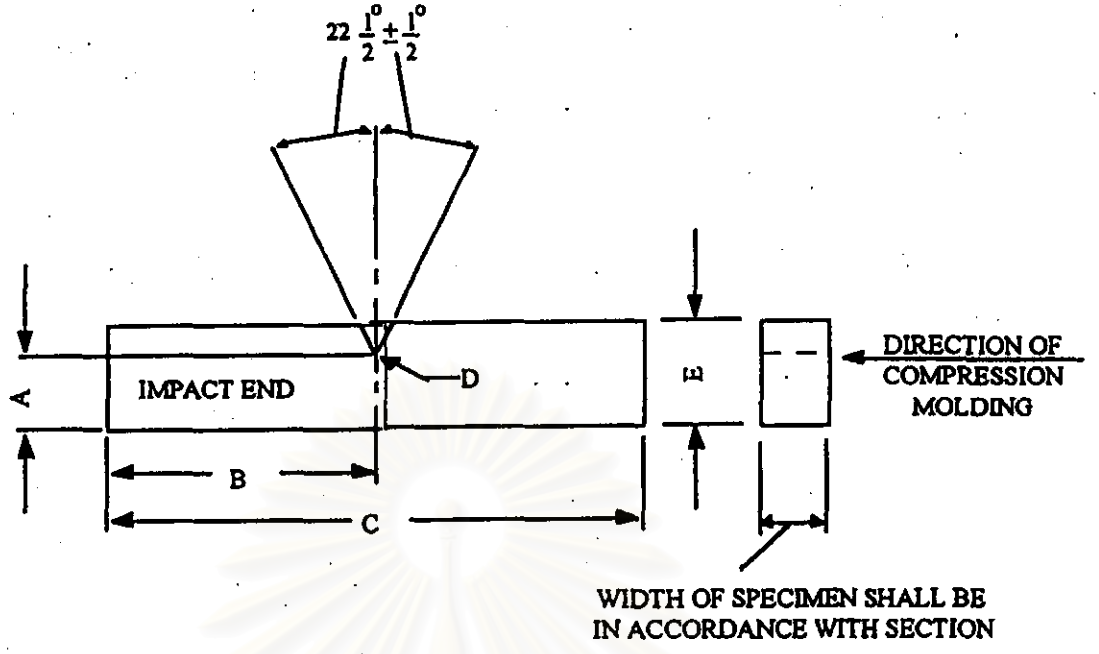
(a) *Impact testing (ASTM D256)* [14]

impact testing for this experiment was of Izod type. The Izod impact testing indicated the energy required to break notched plastics or the resistance to breakage under standard condition. A vertically notched sample was impacted with a pendulum release from a fixed position . The notch in the sample always faces the direction of the impact. In the Izod method, a test specimen is rigidly supported at one end and it is struck by a hammer. Either notched or unnotched samples may be used in the Izod impact test.

The specimens of unsaturated polyesters were prepared by casting in a mold. The curing condition was at 100 °C, 1 hr and at 80 °C, 2 hrs.

The notched specimens were tested according to the procedure described in ASTM D256 and the dimensions of Izod type test specimen was shown in Figure 4-2. The mean value of five measurements for each formulation was calculated. In the test, impact values are usually expressed in term of the energy needed to break the test specimen which was reported in kilogram-centimeter per centimeter.

The Izod Impact testing equipment is schematically shown in Figure 4-3. It consists of a massive base on which it is mounted a vise for holding the specimen and to which it is connected through a rigid frame and anti-friction bearings. One of a number of pendulum-type hammer has an initial energy suitable for use with the particular specimen to be tested on the base. Furthermore, there are a pendulum holding, releasing mechanism, a pointer and dial mechanism for indicating the excess energy remaining in the pendulum after breaking the specimen.



	mm.	in.
A	10.16 ± 0.05	0.400 ± 0.002
B	32.00 max	1.260 max
	31.50 min	1.240 min
C	63.50 max	2.500 max
	60.30 min	2.375 min
D	0.25R ± 0.05	0.010R ± 0.002
E	12.70 ± 0.15	0.500 ± 0.006

Figure 4-3 The Izod test specimen shape and dimension [14]

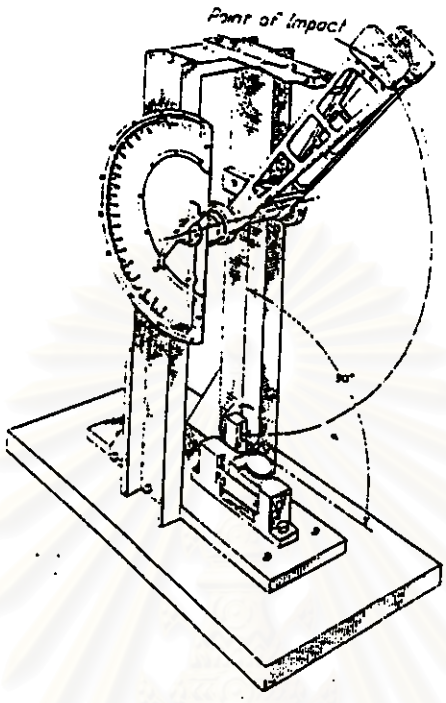


Figure 4-4 The Izod impact machine [14]

(b) *Hardness testing (ASTM D2240)* [15]

Hardness is defined as the resistance of a material to deformation, particularly the permanent deformation, indentation or scratching. The hardness testing method was carried out by using a Durometer testing Instrument.

The durometer is a well-known and widely used instrument for measuring hardness of virtually all types of plastics, rubbers, and various rubber-like materials. The durometer measures hardness by means of indentation much like hardness testing of metals. However, the indenters used in durometers are spring loaded instead of being forced by weights. Several types of durometers have been developed that accommodate the full range of hardness, and specially developed instruments are available for testing O-rings and extremely thin materials. The various types available are listed in Table 4-4. However, the D scale was used for the present study.

Most durometer are available in either the quadrant or the round styles (Figure 4-5 and 4.6).

The test specimens are 6 mm in thickness. The hardness measurement was performed at six position on each specimen surface. The average values were reported.

Table 4-4 Specifications of durometers [16]

Durometer type	Main spring	Indenter	For use on:
A (conforms to ASTM D 2240)	822 g	Frustum cone	Soft vulcanized rubber and all elastomeric materials, natural rubber, GR-S, GR-1, neoprene, nitrile rubbers, Thiokol, flexible polyester cast resins, polyacrylic esters, wax, felt, leather, etc.
B	822 g	Sharp 30° included angle	Moderately hard rubber such as typewriter rollers, platens, etc.
C	20 lb	Frustum cone	Medium hard rubber and plastics
D (conforms to ASTM D 2240)	10 lb	Sharp 30° included angle	Hard rubber and the harder grades of plastics such as rigid thermoplastic sheet, Plexiglas, polystyrene, vinyl sheet, cellulose acetate and thermosetting laminates such as formica, paper-filled calendar rolls, calendar bowls, etc.
DO	10 lb	3/32-in. sphere	Very dense textile windings, slasher beams, etc.
O	822 g	3/32-in. sphere	Soft printers rollers, Artgum, medium-density textile windings of rayon, orlon, nylon, etc.
OO	4 oz	3/32-in. sphere	Sponge rubber and plastics, low-density textile windings; not for use on foamed latex
000 (available with round dial only)	4 oz	1/2-in. diam. spherical	Ultrasoft sponge rubber and plastic
T	822 g	3/32-in. sphere	Medium-density textile windings on spools and bobbins with a maximum diameter of 100 mm (4 in.), types T and T-2 have a concave bottom plate to facilitate centering on cylindrical specimens

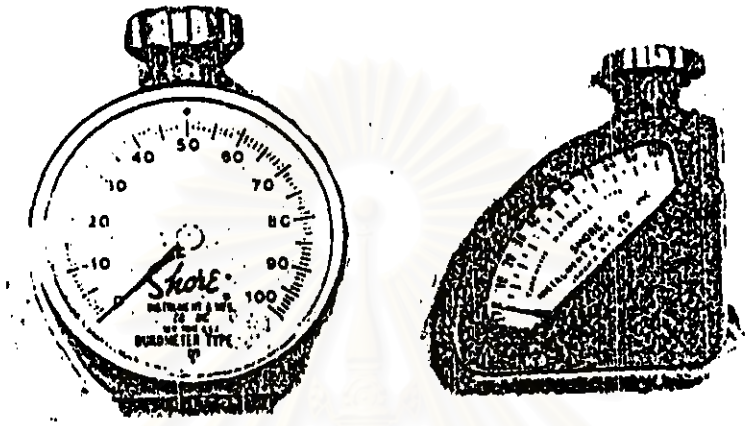


Figure 4.5 Round- and quadrant-style durometers [16]

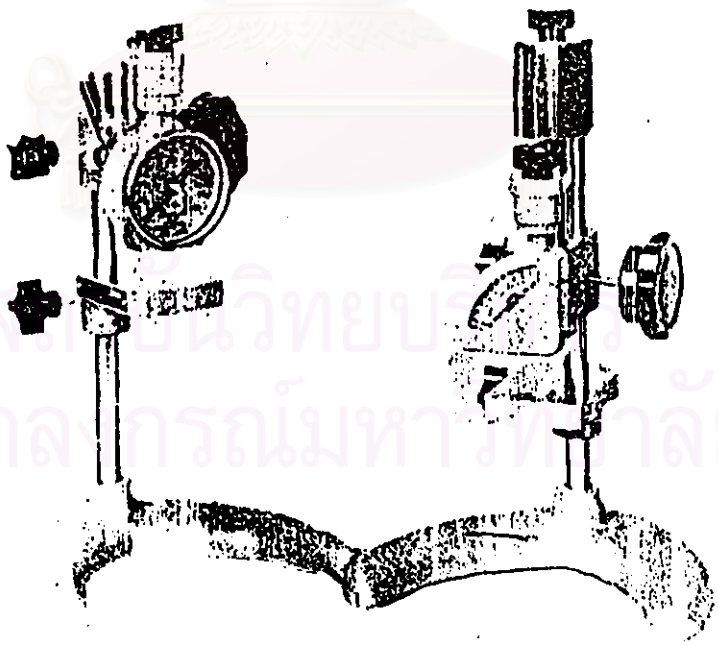


Figure 4-6 Durometers mounted in operating stands [16]