CHAPTER III

EXPERIMENTAL WORK

3.1 Materials

3.1.1 High Density Polyethylene (HDPE)

In this study, crystallined high density polyethylene, under the tradename of HIZEX-2208J was used. It was manufactured by Bangkok Polyethylene Co., Ltd. The structure of HDPE is shown in Figure 3.1.
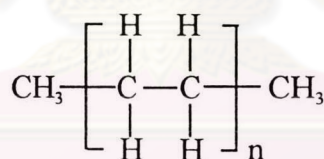
$$CH_3 \left[\begin{array}{cc} H & H \\ | & | \\ C - C \\ | & | \\ H & H \end{array} \right]_n CH_3$$

Figure 3.1: The chemical structure of high density polyethylene (HDPE).

3.1.2 Fillers

Two type of fillers are used, the organic filler and the inorganic ones. The organic filler was obtained from Thai Carbon Black Co., Ltd. It has a density of 1.80 g/cm^3. The average particle size is 29 nm. Mineral or inorganic fillers used in the present study are calcium carbonate and talc. Both fillers were obtain from Surinthip Omya Co., Ltd. The $CaCO_3$ has a density of 2.7 g/cm^3 and the average particle size

of 2.5 μm. The talc has an identical density with the $CaCO_3$, i.e. 2.7g/m^3 but the average particle size is doubled, i.e. 5 μm.

3.1.3 Coupling Agents

The fillers were treated by titanate coupling agents provided by Kenrich Petrochemical, Co., Ltd. The inorganic fillers were surface treated with Neoalkoxy tridodecyl-benzenesulfonyl titanate [Titanium IV neoalkoxy, tris(dodecylphenyl) sulfonato]. The organic filler was surface treated with Neoalkoxy tri(dodectylpyrophosphato) titanate [Titanium IV neoalkanolato tris(dioctylpyrophosphato, tris(dioctyl) pyro-phosphato]. The chemical structure of titanate coupling agents are shown in Figure 3.2.

(a) Neoalkoxy tridodecyl-benzenesulfonyl titanate [Titanium IV neoalkoxy, tris (dodecylphenyl) sulfonato].

(b) Neoalkoxy tri (dodectylpyrophosphato) titanate [Titanium IV neoalkanolato tris (dioctylpyrophosphato tris(dioctyl) pyro- phosphato].

Figure 3.2: The chemical structure of titanate coupling agents for inorganic and organic fillers in the present study.

3.2 Fillers Surface Treatments

The fillers were dried in an air circulating oven at 110°C for at least 24 hours. The slurry method for application of titanate coupling agent was suitable for the present in surface treatment of the filler particles. Titanate coupling agent was dissolved in a small quantity of methyl ethyl ketone (MEK) solvent. It was then poured into a mixing chamber and more solvent was gradually added. In the MEK solutions of titanate coupling agent, the concentration of the Neoalkoxy tridodecyl-benzenesulfonyl titanate [Titanium IV neoalkoxy, tris (dodecylphenyl) sulfonato] was 0.5%, 0.75%, 1.0%, and 1.5% respectively on basis weight of $CaCO_3$ and 0.5% on basis weight of talc while the Neoalkoxy tri (dodectylpyrophosphato) titanate [Titanium IV neoalkanolato tris (dioctylpyrophosphato tris(dioctyl) pyro-phosphato] was 1% on the basis weight of carbon black. The filler was added after continously stirring the solution for 1 hour. To eliminate the solvent, the slurry was dried in the oven at 70°C for about 48 hours.

3.3 Compounding

HDPE and the fillers were compounded using a twin-screw extruder (Brabender) shown in Figure 3.3 HDPE pellets and the filler powder such as $CaCO_3$ powder were fed simultaneously into the separate feeder of the extruder. The HDPE and the fillers were fed simultaneously into the extruder by using a separate feeder. The HDPE pellet was fed by a vibration feeder and the powder filler was fed by a screw feeder. To

prevent overloading the extruder drive at very high filler content the filler, the filler mass flow rate was gradually increased until the desired rate was reached. The barrel temperatures are set at 180°C, 190°C, 190°C respectively from the feeding zone to the die zone. The screw speed is 50 rpm. An exit rod die with two 3.5 mm-nozzols was used. The compositions of the filled-HDPE are shown in Table 3.1 and Table 3.2.
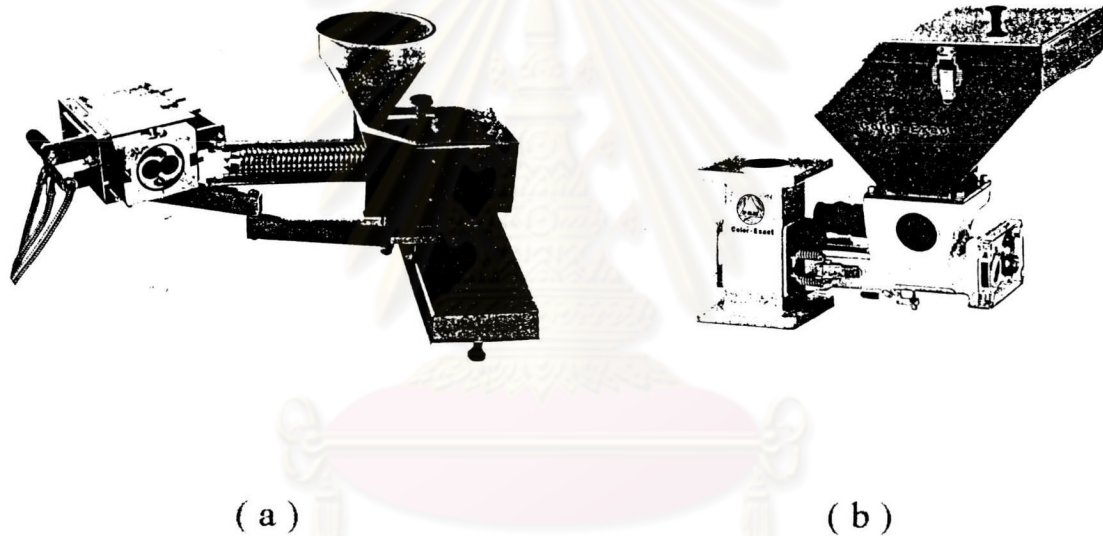

(a)   (b)

Figure 3.3: The twin-screw extruder the feeding machanism with (a) the barrel and screw extruder and (b) screw feeder.

Table 3.1: The composition of $CaCO_3$ filled-HDPE.

$CaCO_3$ (Phr)[a]	Coupling Agent (%)			
	0.5	0.75	1.0	1.5
10	✓	✓	✓	✓
20	✓	✓	✓	✓
30	✓	✓	✓	✓
40	✓	✓	✓	✓
50	✓	✓	✓	✓

[a]Parts by weight per hundred parts by weight of resin.

In some compositions, more than one type of fillers are used. Pre-mixing of the fillers must be performed prior to feeding to the extruder. This is carried out by using a V-shape blender and pre-mix for 30 min. After extrusion, the extrudate strand was quenched in the water bath, drawn and pelletized. The pellet was dried in an oven at 110°C for 1 hour in order to for remove excess moisture.

The filled-HDPE systems were prepared according to the design based on Factorial Design Theory. There are 5 varible factors, each varied at 2 levels as shown in Table 3.2.

Table 3.2: The 2^5 Factorial Design for filled- HDPE systems.

Fillers/Filler	Low level (phr)	High level (phr)
A (CaCO$_3$, treated)	0	30
B (CaCO$_3$, untreated)	0	15
C (talc, treated)	0	15
D (talc, untreated surface)	0	15
E (carbon black, treated)	0	5

3.4 Molding and Shaping

Samples for mechanical measurements were prepared by compression molding the filled HDPE pellets in the form of plates. The thickness of the plates are 2, 3 and 4 mm. The compression molding machine is shown in Figure 3.4. The condition of molding is set at a temperature of 190°C under a pressure of 5 MPa for 10 min. For cooling, the molded plate is cooled by water cooling at a rate of -10°C/min until the temperature was brought down to 55°C. After air cool to room temperature, the plates with 2 mm in thickness were punched to form specimens of dumbbell shape for tensile test. Rectangular bars for Izod impact and heat deflection temperature test were prepared and cut into the respective sample size requirements of each test by using the plates with 3 mm in thickness. The cutting of specimens for compression test was done by using a high precision diamond saw.
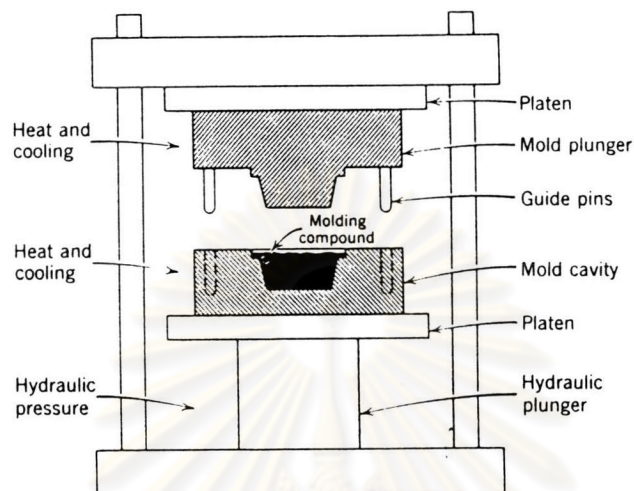
Figure 3.4: The compression molding machine and mold.

3.5 Mixing

Mixing was carried out by using an internal mixer (Brabender W50E) as shown in Figure 3.5. The HDPE pellets and the $CaCO_3$, talc and carbon black powder were weighed proportionally and dry blended prior to mixing in the internal mixer. The mixer temperature was set at 190°C. The rotor speed is 50 rpm. The period of mixing is kept constant at 10 min.

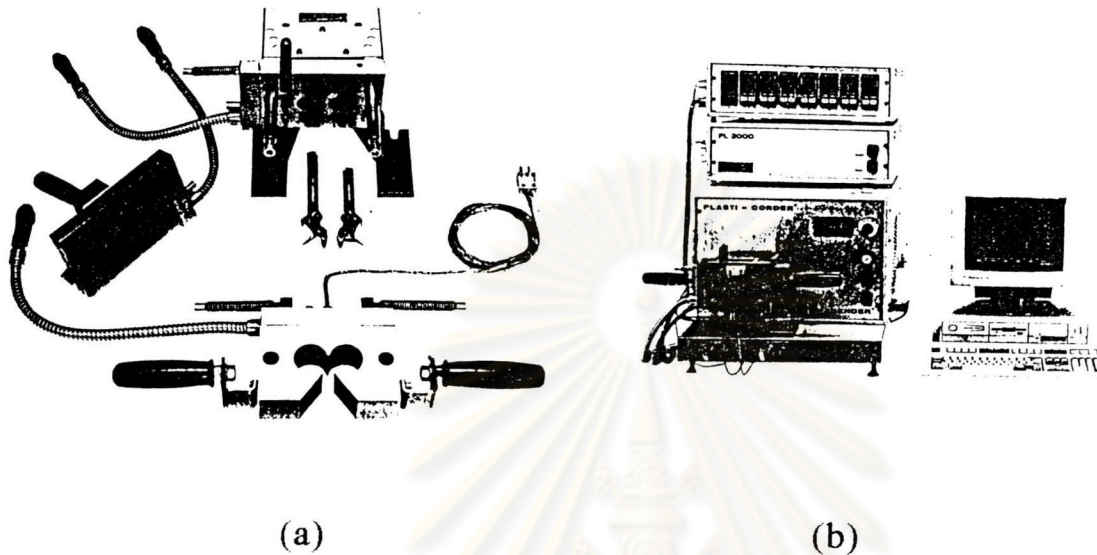(a)   (b)

Figure 3.5: The mixing machine and driving control unit consists of (a)
heater, rotor and drive elements of mixer and (b) mixer,
control system for the extruder.

3.6 Mechanical Testing

3.6.1 Tensile Test

The tensile test is applied to measure the force response when the
filled and unfilled HDPE samples were pulled at a constant strain rate.
The test provides a means to characterize the machanical properties of the
filled and unfilled HDPE in terms of the elastic modulus, elastic strength
and elongation at yield and at failure.   The tensile properties were
measured according to the ASTM D-638 test procedure by using a
mechanical testing machine   (Instron model 4501).   The dumbbell

specimen of type IV was used. The specimen dimension for tensile test is shown in Figure 3.6. The gauge length was 25 mm. The crosshead speed was set constant at 5 mm/min. The initial crosshead seperation was 64 mm. The test was carried out at standard testing condition of 23 °C and 50% relative humidity. Ten specimens were tested for each composition. Only average values were reported.

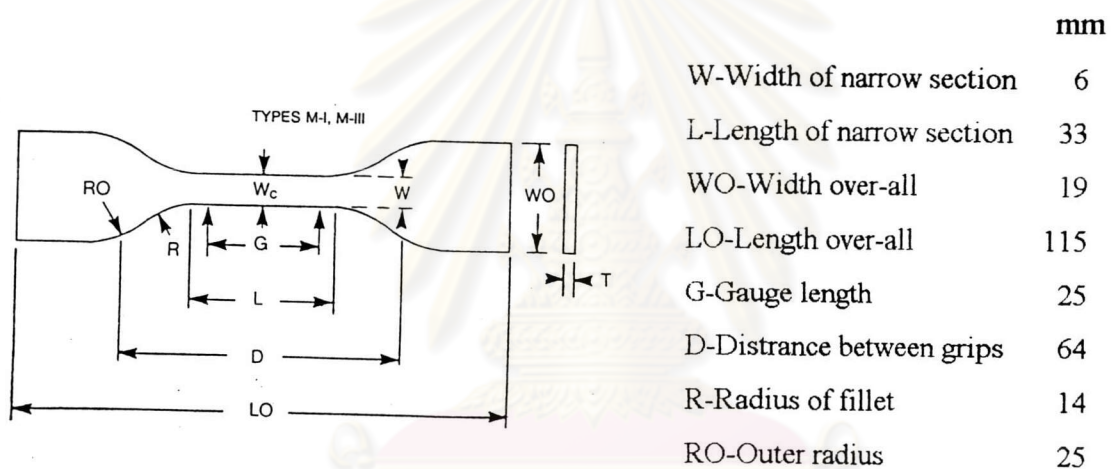|	mm
W-Width of narrow section	6
L-Length of narrow section	33
WO-Width over-all	19
LO-Length over-all	115
G-Gauge length	25
D-Distrance between grips	64
R-Radius of fillet	14
RO-Outer radius	25

Figure 3.6: The dimensions of tensile test specimen of type IV according ASTM D-638.

3.6.2 Compression Test

The compression testing of polymers is not as widely used as the tensile or the flexural tests although it is a test that yields useful information. Quite often, plastics products are subjected to compressive load for a long period of time. Their deformation is hence induced or caused by the compressive stress. Test specimens in square shape of 12 x12 mm with a thickness of 3.6 mm were compressed between two

parallel plates. The compression testing was measured by using a mechanical testing machine (LLOYD model 2000R). The crosshead speed was set constant at 5 mm/min. The test was conducted at a standard condition of 23°C. Ten specimens were tested for each composition. Only average values were reported.

3.6.3 Hardness Test

Hardness is closely related to strength, stiffness, scratch resistance, wear resistance and brittleness. The hardness test are based on the conditions and procedure set in the ASTM D-2240 (Shore or Durometer hardness) was carried out using a Durometer Instrument. There are three types of pin-shaped indentors which gave measurements in A, B, C, D, DO, O, OO scales as illustrated in Figure 3.7. The A scale is often used for measuring softer materials such as elastomers. It covers the range from 20A to 95A. The D scale is often used for harder materials such as soft plastics; it generally covers the range from 40D to 90D (40D~95A). The D scale is used for the test of filled and unfilled HDPE systems in the present study. The test specimens are 3 mm in thickness. The hardness measurement is performed at various locations on each sample surface which was flat and parallel with its bottom surface. The test was carried out at standard testing condition of 23°C and 50 % relative humidity. Ten specimens were tested for each composition. Only average values were reported.

NOTE 2—Durometer scale comparison chart only. This is not and cannot be used as a conversion reference.
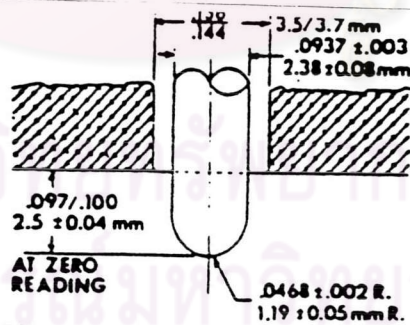
Type A		10 20 30 40 50 60 70 80 90 100		
Type B		10 20 30 40 50 60 70 80 90 100		
Type C		10 20 30 40 50 60 70 80 90 100		
Type D		10 20 30 40 50 60 60 70 80 90 100		
Type DO		10 20 30 40 50 60 70 80 90 100		
Type O	10 20 30 40 50 60 70 80 90 100			
Type OO	10 20 30 40 50 60 70 80 90 100			
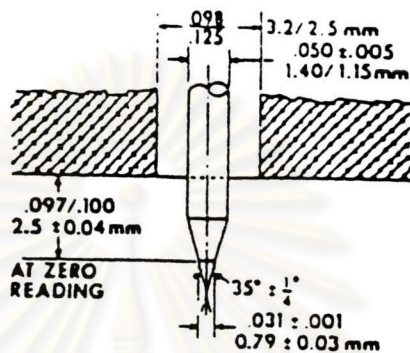
(a) Indentor for Type A and C Durometers
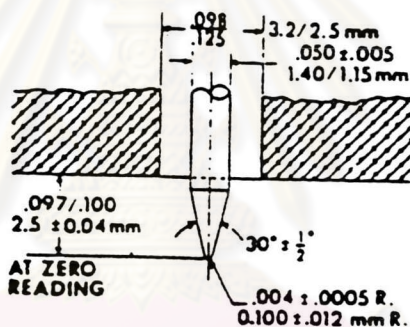
(b) Indentor for Type B and D Durometers

(c) Indentor for Type DO, O, and OO Durometers

NOTE—Spring Force Combinations:

Force, $N = 0.550 + 0.075\ H_x$

where H_x = hardness reading on Type A, B and O durometers.

Force, $N = 0.4445\ H_y$

where H_y = hardness reading on Type C, D and DO durometers.

Force, $N = 0.203 + 0.00908\ H_{oo}$

where H_{oo} = hardness reading on Type OO durometers.

Figure 3.7: Durometer sacle, Indenter and Spring Force Combinations.

3.6.4 Izod Impact Test

Izod impact test was applied to measure the energy to break a notched specimen upon application of a sudden load by using a pendulum. Notching was made by using a revolving multitooth cutter disc. Both the feed speed and the cutter speed were constant thoughtout the notching operation. In general, a combination of a high cutter speed and a slow feed rates will result in greater thermal demage than a slow cutter speed and a fast feed rate. Using a high feed rates or a high cutter speed ratio can induce crack in the specimen. Impact specimens were notched (45°) by using Toyoseiki notched cutting apparatus. The notched specimens were tested according to the ASTM D-256 procedure on the Izod Toyoseiki Tokyo tester. The Izod tester, notched specimen and specimen support are shown in Figure 3.8. The test was carried out at standard testing condition of 23°C and 50 % relative humidity. Ten specimens were tested for each composition. Only average values were reported.
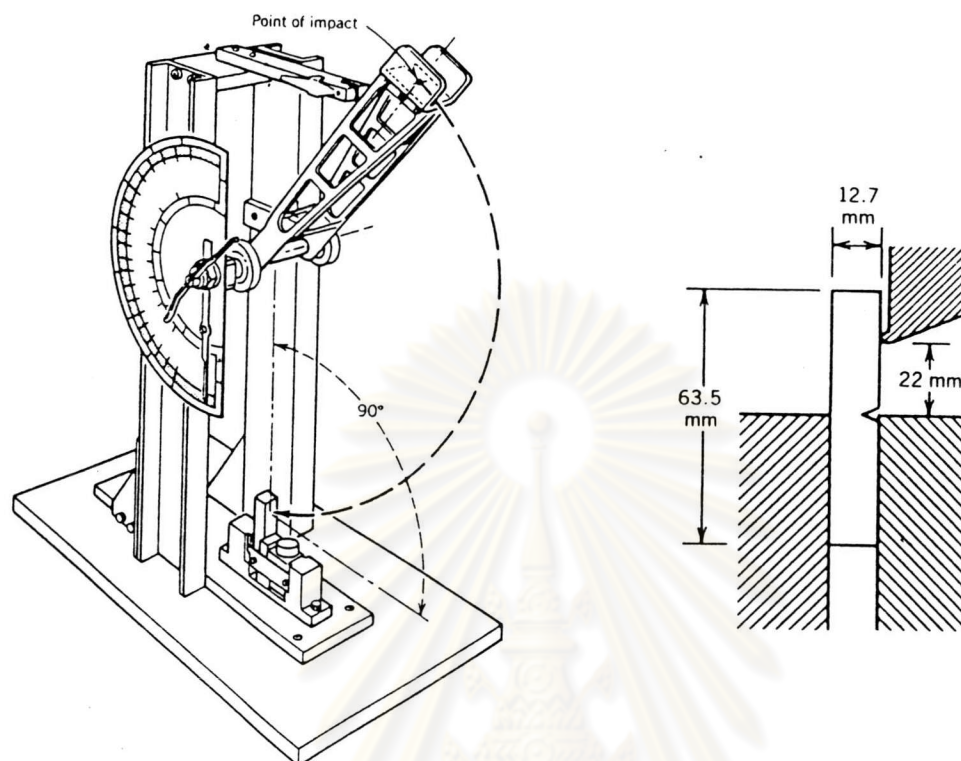
(a) The Izod impact machine.   (b) Izod test specimendimensions and sample support

Figure 3.8: The Izod impact machine and specimen support arrangement.

3.6.5 Falling Weight Test

The falling weight test enables the impact resistance to be measured. This is indicated by the energy to break or crack plastics at a high and variable weight. The plate of compression molded specimens with 2 mm in thickness was tested according to the procedure set in the ASTM D-3029. The test was done by using an Energy Absorbtion tester (model D-4092). The falling weight machine is shown in Figure 3.9. The test was performed at room temperature of 25°C. The energy absorbed

versus the sample deformation and the dart velocity were obtain for each sample. Five specimens were tested for each composition. Only average values were reported.
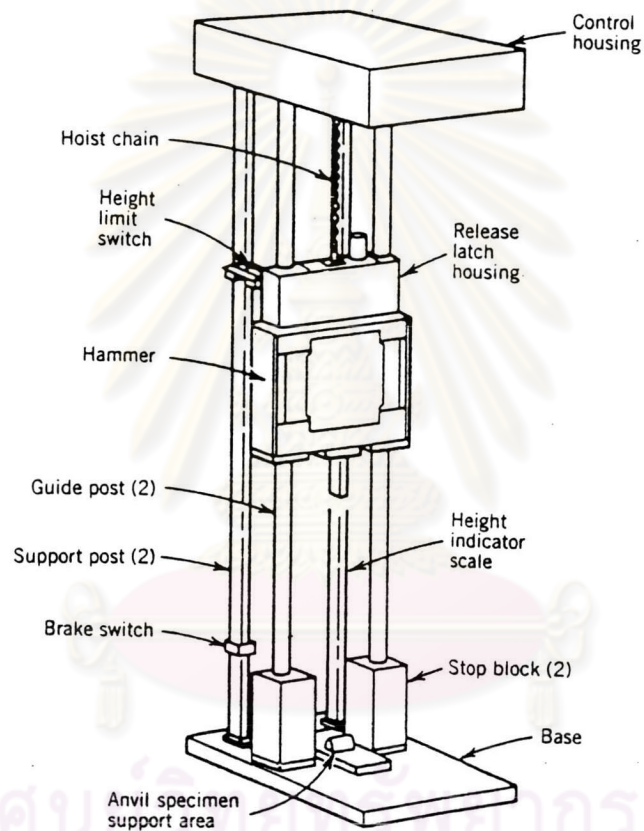

Figure 3.9: The falling weight testing machine.

3.7 Sample Characterization

3.7.1 Differential Scanning Calorimeter (DSC)

The melting point and the percent crystallinity of the filled HDPE were tested according ASTM D-2117. The equipment used was the Differential Scanning Calorimeter 2110 Dupont Instrument tester. The DSC heater and sample cells are shown in Figure 3.10. Each filled and unfilled HDPE was weighed to be as close to 10 mg as possible. It was then placed in the DSC aluminium pan. The sample was heated from 40 °C to 220°C at a heating rate of 10°C/min. A DSC scan of the specific energy against the temperature was obtained. The melting point and the degree of crystallinity of composites were calculated based upon the fact that 100 % crystallinity HDPE requires an energy of 293 J/g.
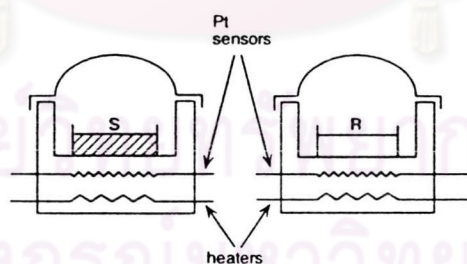

Figure 3.10: The DSC sample cell: the sample (S) and the reference (R) pans.

3.7.2 Dynamic Mechanical Thermal Analysis (DMTA)

The technique of DMTA was the used to determine the glass transition temperature (T_g) of polymers via their state of chains motion. In this method, the sample is deformed cyclically under the sinusodial stress amplitude (usually as a function of the sine wave), while the temperature was raised. The results indicated the sinusodial stress-strain relationship. Many modes of vibration are possible. The specimen can be loaded under tension, torsion, compression, bending and shear, but the most popular mode of loading is the bending mode (e.g. single or double cantilever) as show in Figure 3.11. The usual range of frequencies for DMTA test are 0.1 to 110 Hz. In the present study, a frequency of 1 Hz is selected.

The T_g of each HDPE formulation was measured by using dynamic mechanical thermal analyser (model DMTA *Mk III*; Polymer Laboratory). The single cantilever mode was used. The specimen was a regtangular bar of 5 mm in width, 25 mm in length and 2 mm in thickness. The test was made at a frequency of 1 Hz. The heating rate was 3°C/min. The specimen was tested from -150°C to 100°C. The T_g of the HDPE is seen at the peak of tan δ.
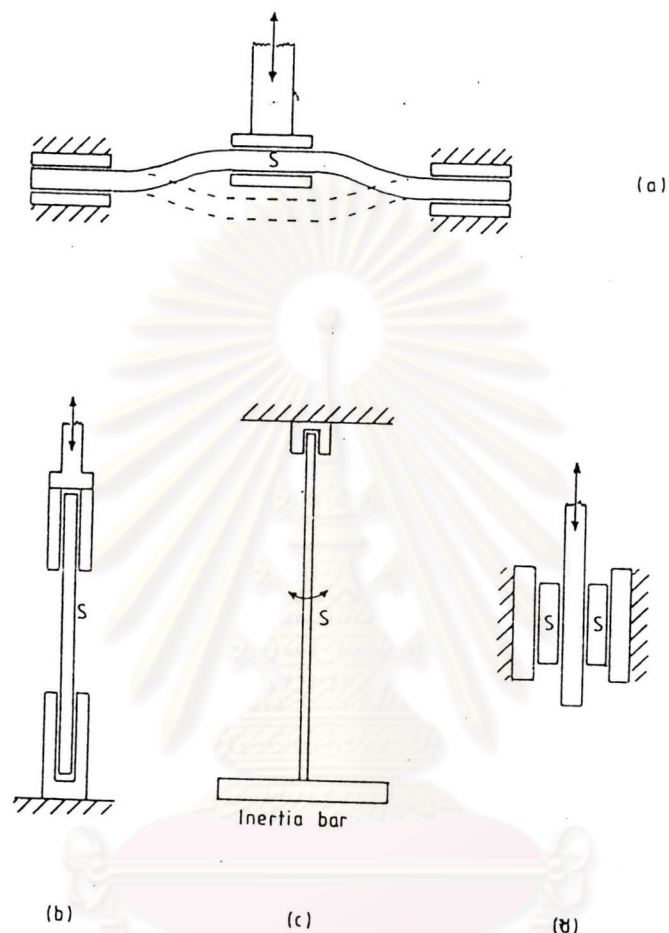
Figure 3.11: The modes of the DMTA (a) single or double cantilever: (b) tension or compression mode: (c) torsion mode and (d) shear mode.

In this experiment, the tensile stress can be defined a function of time (t) and it may be expressed as:

$$\sigma = \sigma° \sin(\omega t) \qquad (3.1)$$

where $\sigma°$ = amplitude of applied stress

      w = angular ferquency of oscillation = $2\pi f$

The strain response from the applied stress is also a sinusoidal function which may be written as:

$$\varepsilon = \varepsilon° \sin(\omega t - \delta) \qquad (3.2)$$

where $\varepsilon°$ = amplitude of the strain response

      δ = phase angle (lagging)

The lagging phase angle between the stress and the strain is illustrated in Figure 3.12.
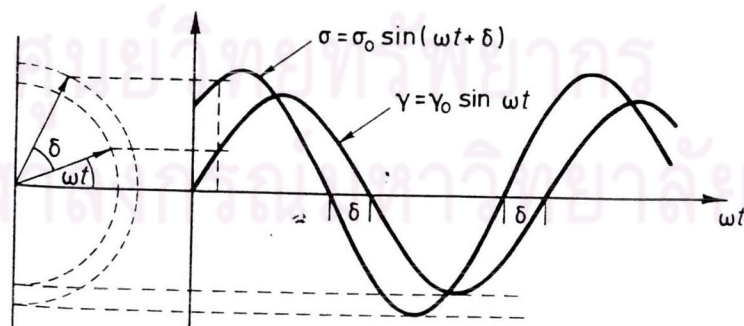

Figure 3.12: The representation of viscoelastic behaviour in polymers; the sinusodial stress (σ), with the strain response (ε) and lagging phase angle (δ).

In an ideal elastic solid, the stress follows *Hooke's law*, i.e.

where $\sigma = E\varepsilon$

σ = stress

E = Young's modulus

ε = strain

The strain is always in phase with the stress (or $\delta = 0$). Equation (3.2) can be written as:

$$\varepsilon = \varepsilon^\circ \sin(\omega t) \qquad (3.3)$$

In an ideal viscous flow, the stress follows *Newton's law of viscousity*, as shown in Equation (3.4). The stress is aways the 90° ($\delta = \pi/2$) leading phase of the strain.

$$\sigma = \eta\left(\frac{d\varepsilon}{dt}\right) \qquad (3.4)$$

Integrate Eq. (3.4) by *dt*; $\varepsilon = \int \frac{\sigma}{\eta} dt = \int \frac{\sigma^\circ}{\eta} \sin(\omega t)$ $\qquad (3.5)$

$$= -\sigma^\circ/(\eta\omega) \cos(\omega t) = -\varepsilon^\circ \cos(\omega t)$$

$$= -\varepsilon^\circ \sin(\pi/2 - \omega t) = \varepsilon^\circ \sin(\omega t - \pi/2)$$

At temperature below T_g, polymers behave as Hooken solids and there is very small deformation. At the vicinity of the T_g, their behavior is viscoelastic. The δ is time and temperature dependence; its values a between $0°$ for total elastic and $90°$ for total viscous.

The dynamic mechanical response of viscoelastic polymers under applied cyclical stress, can be described by a complex stress ($\sigma *$) as shown below.

$$\sigma * = \sigma ° \exp(i\omega t) \tag{3.6}$$

Where $i = \sqrt{-1}$

Equation (3.2) can be written as:

$$\varepsilon* = \varepsilon° \exp[i(\omega t - \delta)] \tag{3.7}$$

From Hook's law, the complex modulus ($E*$) can be defined as the ratio of the complex stress to the complex strain.

$$E* = \frac{\sigma^*}{\varepsilon^*} = \left(\frac{\sigma^o}{\varepsilon^o}\right) \exp(i\delta) \tag{3.8}$$

The complex modulus can be solved into two components, E' and E''. With the substitution of *Euler's identity* [$\exp(i\delta) = \cos\delta + i\sin\delta$] into Equation. (3.8), one will get Equation (3.9).

$$E* = \left(\frac{\sigma^o}{\varepsilon^o}\right)\cos(\delta) \; + \; \left(\frac{\sigma^o}{\varepsilon^o}\right)\sin(\delta) \qquad (3.9)$$

Equation (3.9) may be written in general form as following:-

$$E* = E' + iE'' \qquad (3.10)$$

$$\tan(\delta) = E''/E' = \sin(\delta)/\cos(\delta) \qquad (3.11)$$

E' is called the *storage modulus* which measures the recoverable strain energy in the deformation. E'' is called the *loss modulus* and it is related to the hysteresial energy dissipation. The ratio of the loss and to the storage moduli is the *loss tangent* (tan δ). The relationship of DMTA parameters at each local temperature point is best summarised in Figure 3.13.
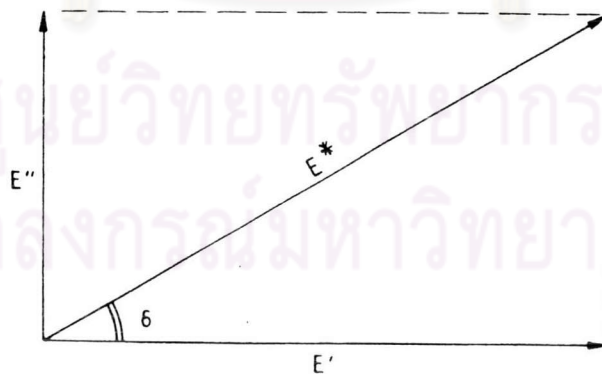

Figure 3.13: The DMTA parameter test.

3.7.3 Heat Deflection Temperature (HDT)

The heat deflection temperature is also called the heat distortion temperature. The method of test is set in the ASTM D648. The test specimen is mounted on supports which are 10.16 cm (4 inch.) apart and loaded by a beam as shown in Figure 3.14. A bending stress of either 66 psi (455 Pa) or 246 psi (1,820 Pa) is applied at the center of the span. The test is conducted in a bath of oil, with the temperature increased at a constant rate of 2°C per minute. The HDT is the temperature at which the sample attains a deflection of 0.254 mm (0.010 in).
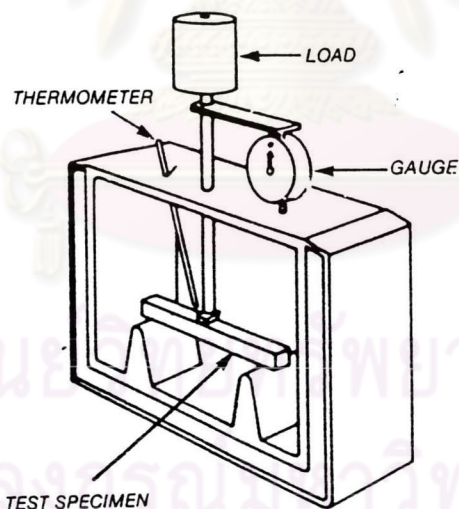

Figure 3.14: The instrument of heat deflection temperature test.

3.7.4 Density Test

The polymers density depends on whether a majority of the chains are linear or branched, the averaged molecular weight and the past thermal history. Polymers have a density range from 0.88-2.3 g/cm^3. The density measurement of plastics can be performed by using the density gradient technique. This is based on the technique set in the ASTM D-1505. The liquid used in the density column should be a nonsolvent for the polymers such as an aqueous or an alcohol mixture. Suitable liquid systems for the preparation of a density gradient column are listed in Table 3.3.

Table 3.3: Liquid systems for density gradient technique.

Liquid system	Density Range (g/cm^3)
Methanol-benzyl alcohol	0.80-0.92
Isopropanol-water	0.79-1.00
Isopropanol-diethylene glycol	0.79-1.11
Ethanol-carbon tetrachloride	0.79-1.59
Toluene-carbon tetrachloride	0.87-1.59
Water-sodium bromide	1.00-1.41
Water-calcium nitrate	1.00-1.61
Carbon tetrachloride-trimethylene dibromide	1.60-1.99
Trimethylene dibromide-ethylene bromide	1.99-2.18
Ethylene bromide-bromoform	2.18-2.89

Toluene and carbon tetrachloride are selected for the density gradient study of the HDPE composites in the present work. Several mixtures of liquids can be prepared at many compositions as a function of gradient density from 0.87-1.59 g/cm^3. The position along the height of the tube against the liquid density was calibrated to form a calibration curve for the determination of the sample density.

3.7.5 Scanning Electron Microscope (SEM)

In scanning electron microscopy, electron can be reflected from the surface of the object which are often used for display. The incident electrons from the electron source acted as a beam, which is then scanned over the entire area of fracture surfaces. The morphology of fractured composites was studied by using a scanning electron microscope (JOEL JSM 840A). The fracture surfaces were sputter-coated with 300 A° gold. The accelerating voltage for the SEM was 10 KV.

3.7.6 Polarized Light Microscopy

This method is especially good for studying spherulites because of the difference in the birefingence between the crystal lamellae and the amorphous regions or the different orientation of the lamellae as radiate out from the centre in all directions. The spherulites morphology were studied using a polarized light microscope (Nikon Optiphot-2) as is schemetically represented in Figure 3.15. The light source passes the polarizer to filtrate the single angle plane of light. The analyser rotated to

the crossed position of the polarizer which has been placed between the specimen and the eyepiece.
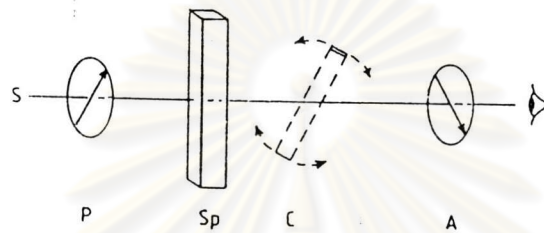

Figure 3.15: The polarized microscope; S light source: P polarizer: Sp specimen: C compensator and A analyser.

Very thin samples with thickness range of 5-40 μm are used. The sample is cut from the compression moulded plate into a very thin section. The method of cutting is made by using a knife as shown in Figure 3.16. The thin film was placed on a glass microscope slide and a cover slip for viewing microscopically using an optical microscope.
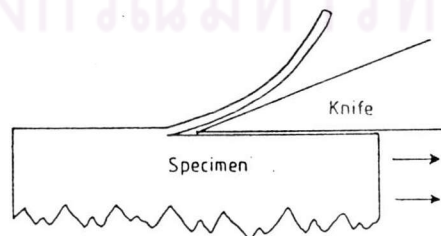

Figure 3.16: The cutting of a thin film from a moulded plate.