CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 High Density Polyethylene (HDPE)

The polymers used in this study are commercial grades and are chosen based on their melt flow index value. In particular, high density polyethylene (HDPE) based on a melt index of 0.06 or less gives excellent results. Even those resins having zero melt index are now extruded into high quality sheet which is suitable for pick up truck liners. Thus, in this study HDPE, under the trade name of MARLEX and a grade number HXM 50100 was selected. It is manufactured by the Chevron Phillips Petroleum Company, Singapore.

3.1.2 Metallocene Linear Low Density Polyethylene (MLLDPE)

The MLLDPEs used in this study are commercial grades and are chosen based on both similar melt flow index values and similar density values. First, MLLDPE based on the enhanced polyethylene is a copolymer produced via INSITE Technology from Dow Plastics, (Thailand), with the grade name Elite 5100. Second, MLLDPE based on the hexane copolymer produced using Exxon Chemical's EXXPOL metallocene catalyst is a single-site catalyst technology from ExxonMobil Chemical, (USA), by the grade name Exceed 350 D60. Third, MLLDPE based on the Phillips catalyst is a single-site catalyst technology from Chevronphillips Petroleum Company, (Singapore), with the grade name Mpact D139. However, the difference between the Phillips catalyst and Exxpol metallocene catalyst is that the first can form homogeneous short chain branching distributions, whereas the latter follows the long chain branching distributions. Therefore, the three types of MLLDPE, Exceed 350 D60 from ExxonMobil, Mpact D139 from Chevron Phillips and Elite 5100 from Dow Plastic were used, which were produced by using metallocene catalyst respectively. The basic properties of the three resins are shown in Table 3.1.

Table 3.1 The basic properties of metallocene linear low density polyethylene.

Properties	Mpact D139	Exceed 350 D60	Elite 5100
Melt flow index, g/10 min	1.0	1.0	0.85
Density, g/cm^3	0.918	0.917	0.920

3.2 Blending and Sample Preparation

3.2.1 Blending

The blending in this study was dry blend of HDPE and MLLDPE performed according to the formulation shown in Table 3.2, using the tumble blender. Mixing time for a period was 10 minutes, the blend was melt blended in proportion to the weight ratios at 90/10, 80/20, 70/30, and 60/40. The pellets for injection molding were prepared by single screw extruder on a Bandera extrusion machine. A single screw extruder had a screw diameter 45 mm and L/D ratio is 32 : 1. The temperature profiles were 190, 200, 210, and 220 ^{o}C for feed zone, the compression zone and the metering and die end respectively, as shown in Figure 3.1. The screw speed was held at 25 rpm and extruded materials were pelletized after passing through cold water at 30 ^{o}C. Subsequently molded into specimens.

Table 3.2 Formulations of HDPE/MLLDPE blends (%) by weight.

HDPE	MLLDPE		
	Mpact D139	**Exceed 350 D60**	**Elite5100**
100	0	0	0
90	10	10	10
80	20	20	20
70	30	30	30
60	40	40	40

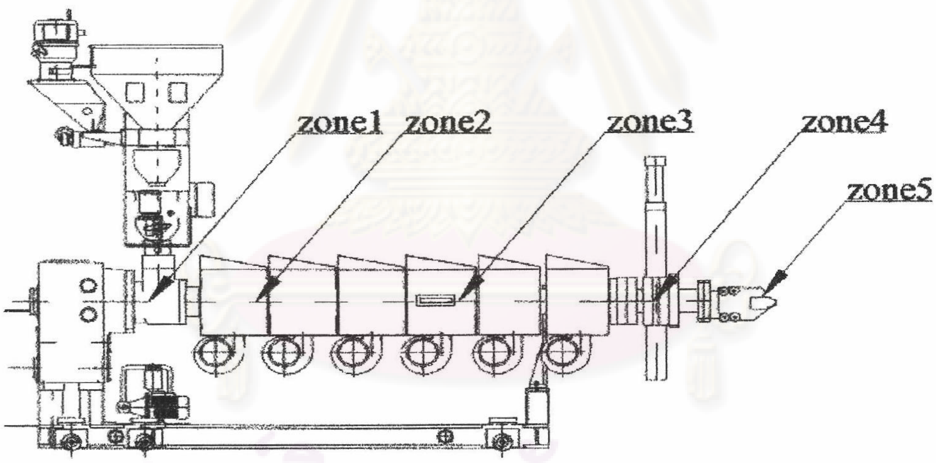

Figure 3.1 Schematic diagram of single screw extruder.

Zone 1	:	Temperature of feed zone	=	190 °C
Zone 2	:	Temperature of compression zone	=	200 °C
Zone 3	:	Temperature of metering zone	=	210 °C
Zone 4	:	Temperature of screen changer	=	220 °C
Zone 5	:	Temperature of Die	=	220 °C

3.2.2 Moulding and Specimen Preparation

Test specimens for mechanical testing were prepared by injection molding on a Toshiba IS 100 injection molding machine at 300 kg/cm^2 injection pressure, with 3 and 5 seconds of injection and cooling times, respectively, followed by cooling at ambient temperature. The temperature profiles were 190, 200, 210, and 220 $^{\circ}$C for the feed zone, the compression zone and the metering and nozzle end, respectively, as shown in Figure 3.2. All the specimens were conditioned according to ASTM D638. Tests were conducted at 25 ± 2 $^{\circ}$C. The sample geometries conformed to ASTM D790 for flexural modulus and ASTM D256 for impact tests.

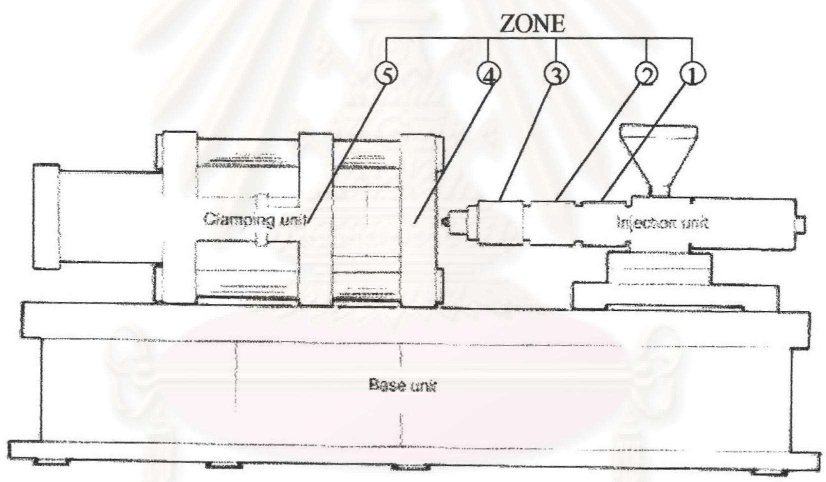

Figure 3.2 Schematic diagram of injection molding machine.

Zone 1	:	Temperature of feed zone	=	190 $^{\circ}$C
Zone 2	:	Temperature of compression zone	=	200 $^{\circ}$C
Zone 3	:	Temperature of metering zone	=	210 $^{\circ}$C
Zone 4	:	Temperature of nozzle	=	220 $^{\circ}$C
Zone 5	:	Temperature of mould	=	25 $^{\circ}$C

3.2.3 Sheet Extrusion Test

The sheet extrusion test was processed by sheet extrusion on a Bandera TR90 sheet extrusion machine as shown in Figure 3.3. Resin was fed into an extruder consisting of a heated barrel with an internal rotating screw, pumps the melted resin into a flat sheet die. Sheet exits the die in a semi-viscous state and travels through a series of three rolls to cool and pulling by a haul off unit. Then sheet was cut to a specified length and width. However, in accordance with this sheet extrusion processability study, we had to controlled the temperature of extruder constant. The temperature profiles were 180, 185, 190, 195, 215, and 195 ^{o}C for the feed zone one (1), feed zone two (2), compression zone one (3), metering zone one (4), compression zone two (5), metering zone two (6) whereas, the screen changer and gear pump temperature required 215 ^{o}C which was higher than the static mixer zone and die end, respectively. In addition, the screw speed was held at 90 rpm as shown in Table 3.3.

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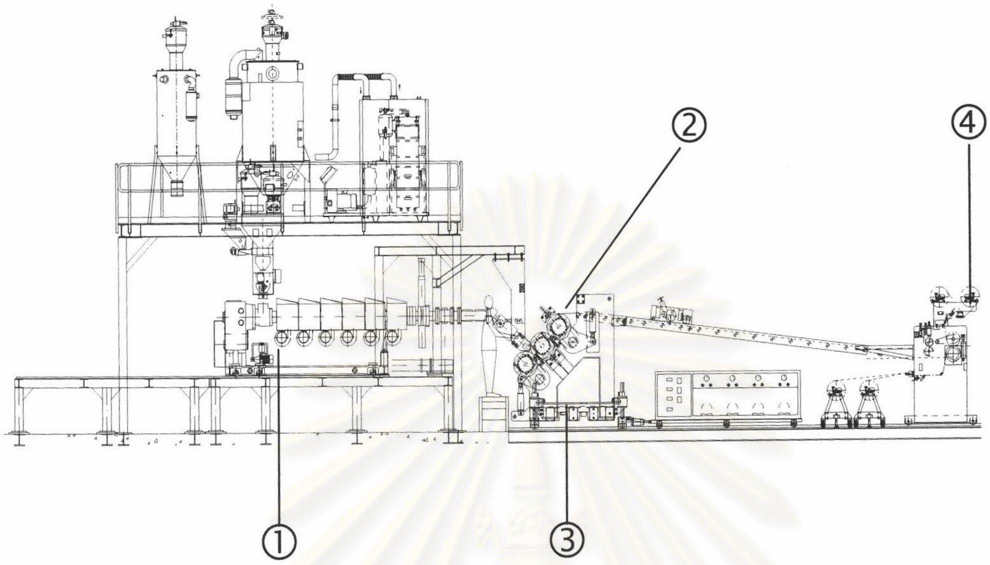

Figure 3.3 Schematic diagram of sheet extrusion processing.

Component ① : Extruder

Component ② : Flat die

Component ③ : Calender roll stack

Component ④ : Take off system

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Table 3.3 Extrusion conditions.

Extrusion conditions	HDPE	HDPE/MLLDPE	HDPE/MLLDPE
HDPE/MLLDPE blends, wt%	100	80 / 20	70 / 30
Extruder temperature	°C	°C	°C
Extruder Zone 1	180	180	180
Extruder Zone 2	185	185	185
Extruder Zone 3	190	190	190
Extruder Zone 4	195	195	195
Extruder Zone 5	195	195	195
Extruder Zone 6	195	195	195
Extruder Zone F	215	215	215
Screen Changer	215	215	215
Zone Gear Pump	215	215	215
Zone Static Mixer	195	195	195
Zone Die	195	195	195
Roll Temperature	°C	°C	°C
Top / Mid / Bottom	99/71/60	95/68/55	92 / 65 / 55
Extruder Pressure	(kg/cm^2)	(kg/cm^2)	(kg/cm^2)
Melt Pressure	63	76	79
Inlet Pump	18	20.5	22
Outlet Pump	58	69	72
Screw Speed	rpm	rpm	rpm
Main Extruder	90	90	90
Motor Current	Amp	Amp	Amp
Main Extruder	190	200	205
Out put	(kg/hr)	(kg/hr)	(kg/hr)
Main Extruder	210	220	230

3.3 Mechanical Testing of Sample

All mechanical testing was conducted with between 7 and 10 specimens to delete the minimum and maximum values for standard deviation calculations. All statistical calculations were performed in 5 specimens as shown in Tables A1-A5.

3.3.1 Tensile Strength and Elongation Testing

The tensile strength and elongation properties were measured according to ASTM D638 using the Lloyd model 10 K. The dumb-bell specimen of type I was used as shown in Figure 3.4, the dimensions of the dumb-bell specimen of type I, the crosshead speed was set constant at 5 mm/min.

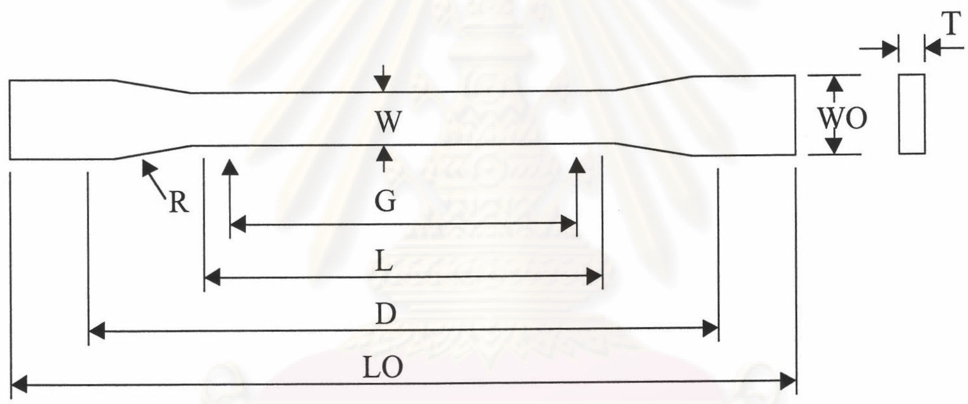

Figure 3.4 The dimensions of dumb-bell specimen of ASTM D638, type I.

W :	Width of narrow section	13
L :	Length of narrow section	57
WO :	Width overall	19
LO :	Length overall	165
G :	Gauge length	50
D :	Distance between grips	115
R :	Radius of fillet	76
T :	Thickness	3.2

All dimension in millimeters (mm)

3.3.2 Flexural Modulus Testing

Flexural Modulus testing was performed according to ASTM D790 using the Lloyd model 10K as shown in Figure 3.5. The sample was placed on the supports , the crosshead speed was set for constant rate at 2.0 mm/min.

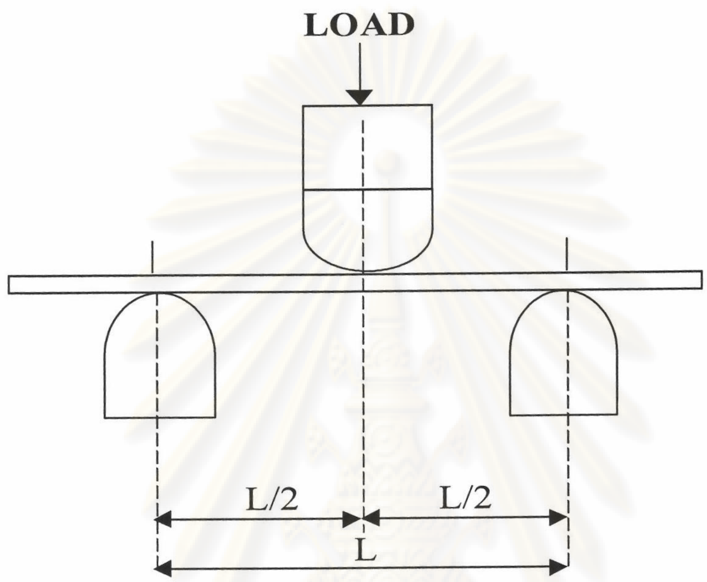

Figure 3.5 Schematic diagram of the flexural modulus testing

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3.3.3 Impact Strength Testing

Impact testing was performed according to ASTM D256 using the Zwick impact tester as shown in Figure 3.6. The sample was placed on the tester, the pendulum was released to hit the sample with its head and the energy that caused the sample to fracture was measured.

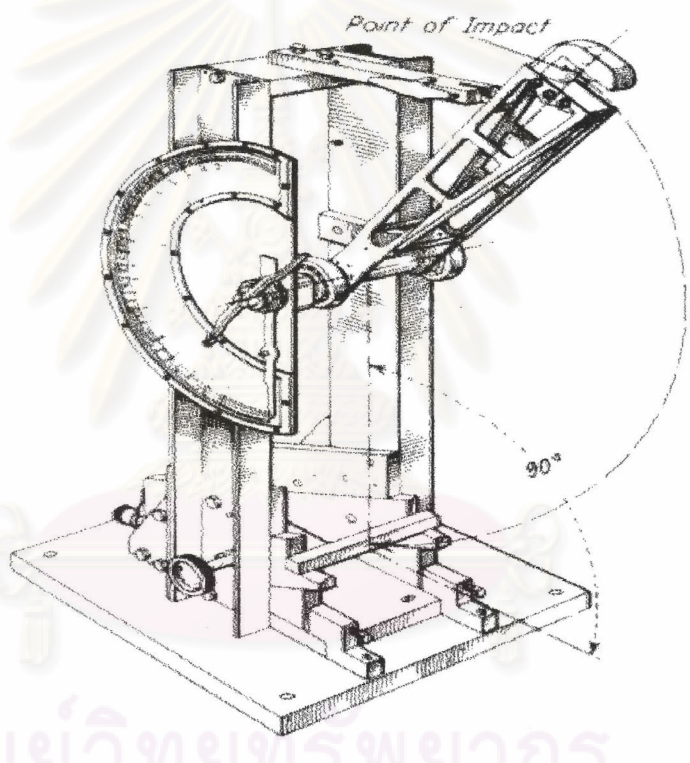

Figure 3.6 Schematic diagram of the impact tester.

3.3.4 Heat Distortion Testing

Heat distortion testing was performed according to ASTM D648 using the Davenport deflection temperature tester as shown in Figure 3.7. The sample was placed on the metal supports for the specimen which are 100 mm apart, allowing the load to be applied on top of the specimen vertically and midway between the supports and provided with a means of raising the temperature at a uniform rate.

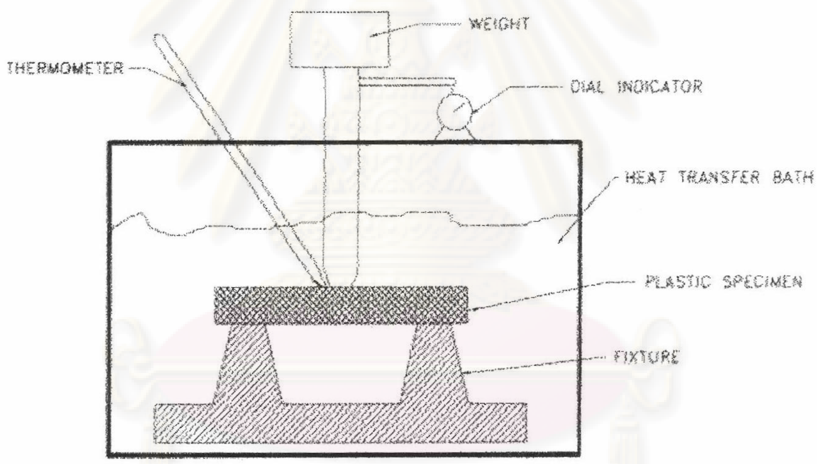

Figure 3.7 Schematic diagram of heat distortion tester.

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3.4 Physical Properties of HDPE/MLLDPE blends

3.4.1 Melt Flow Index (MFI) Analysis

The melt flow index was measured according to ASTM D1238 using the Keyeness model 7049. The weight in gram of molten resin through an orifice for 10 min. under a weight of 2.16 kg and 21.6 kg at a temperature of 190°C.

3.4.2 Density Measurement

The density measurement of resin was measured by using the Davenport, a two column density apparatus. The density gradient technique was according to ASTM D1505. The media for density gradient columns were toluene and carbon tetrachloride. The heights of the sample and the float were measured, both values calculated the density of the samples.

3.4.3 Differential Scanning Calorimetry (DSC)

The melting temperature of the HDPE/MLLDPE blends were tested according to ASTM D2117 in which the crystallization and melting behavior were studied by differential scanning calorimetry (DSC) using the Mettler Toledo model FP900. A nitrogen flux of 70 cc/s was sent through the samples during the heating and cooling experiments. Sample ranging in size from 5 to 6 mg was sealed in an aluminium pan and covered for analysis. A reference standard was used to calibrate the temperature scale and enthalpy of melting. First, the sample was melted by raising the temperature to 200 °C, kept for 10 min to ensure complete melting and to remove the thermal history. The sample was then cooled to 50 °C. The melting endotherm after crystallization was recorded by heating the sample directly to 200 °C at the heating rate of 10 °C/min. The sample cell was then submerged in the liquid nitrogen for the rapid crystallization, thus a DSC scan of the specific energy against the temperature was obtained, whereas melt temperature was calculated based on the reference temperature is defined 100% crystallization. Finally, the melting endotherm of the quenched sample was obtained with the above procedure.

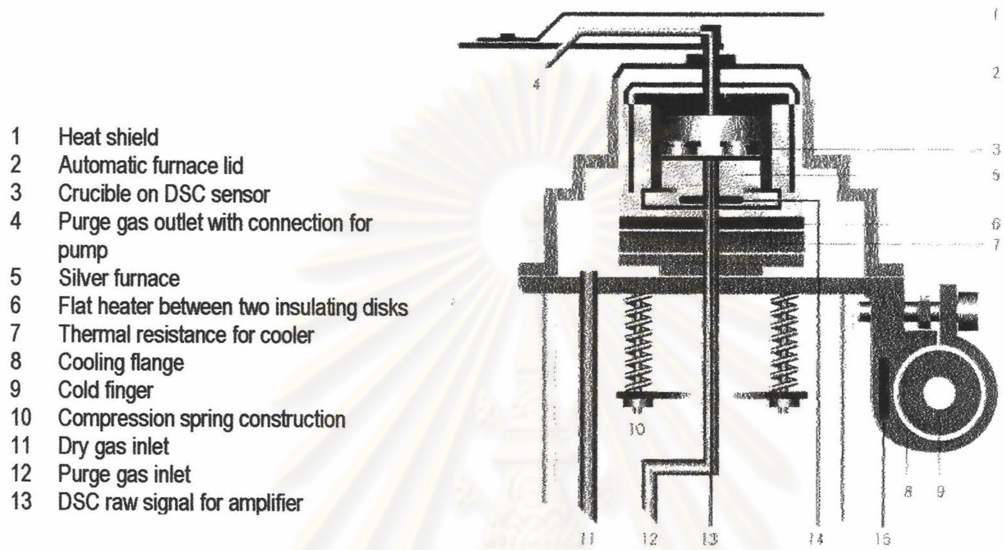


Figure 3.8 Schematic diagram of the Mettler (DSC).

3.4.4 Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic mechanical measurements were carried out in a DMA 7 e unit from Perkin Elmer instruments operating in the single cantilever mode. The specimen thickness and width were a rectangular sheet of 3.0 mm in width, 15 mm in length and 2 mm in thickness. The glass transition temperature of the HDPE/MLLDPE (Elite 5100 blends) at three different ratios 80/20, 70/30, and 60/40 were obtained at a frequency of 1 Hz. The temperature was raised from - 140 ^{o}C to melting point at heating rate of 10 ^{o}C/min. The storage and loss moduli were determined by the transducers monitoring the stress and strain, respectively.

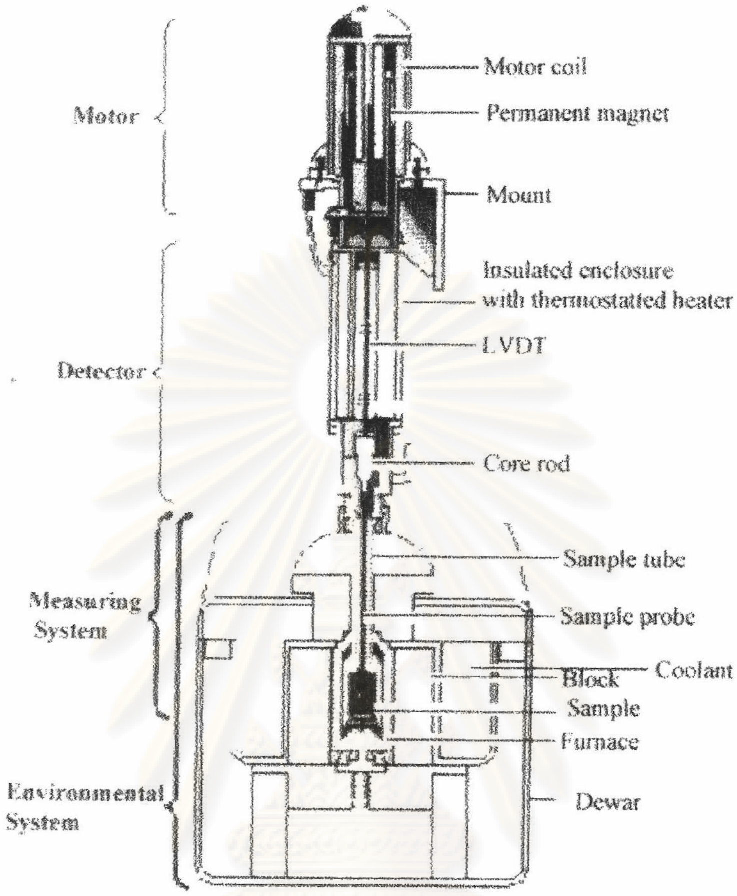
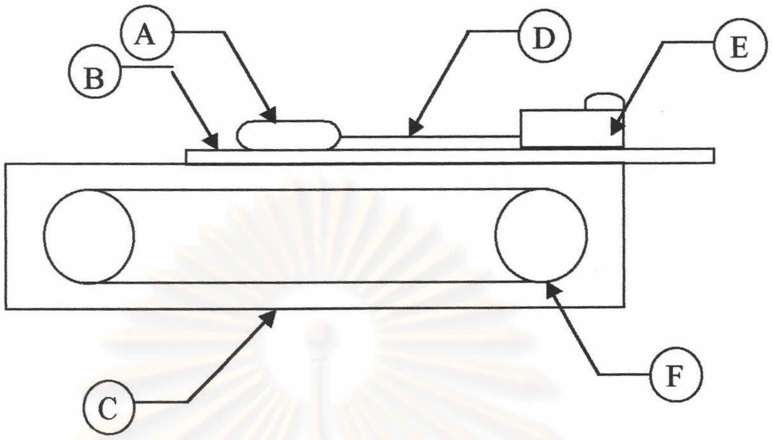


Figure 3.9 Schematic diagram of the Perkin-Elmer DMA 7 e.

3.5 Friction Testing

Friction testing was performed according to ASTM D1894 using the IDM instrument coefficient of friction tester model COF/3 as shown in Figure 3.10. The sheet specimen to be attached to the plane was cut 250 mm in the machine direction and 130 mm in the transverse direction. A sheet specimen covered sled hook was cut 63.5 mm and attached to the sled face with double side tape, keeping the machine direction of the specimen parallel to the length of the sled. The motor was started then the static friction force was recorded.



A : Sled

B : Plane

C : Supporting base

D : Nylon monofilament

E : Spring gauge

F : Constant speed chain drive

Figure 3.10 Schematic diagram of the friction tester.

3.6 Sheet Orientation Test

The sheet orientation testing equipment required the hot air oven with temperature and time controller. The sheet specimens were cut into 50 x 250 mm. size. The specimen was placed on the tray with talcum powder and heated into the oven at 210°C for 30 minutes. The sheet width in the machine direction of each specimen was measured as shown in Figure 3.11. The orientation of the sheet can be calculated by using the equation 3.1.

$$\% \text{ Orientation} = \frac{100 \times (\text{initial dimension} - \text{final dimension})}{\text{initial dimension}} \quad \text{.............. Eq 3.1}$$

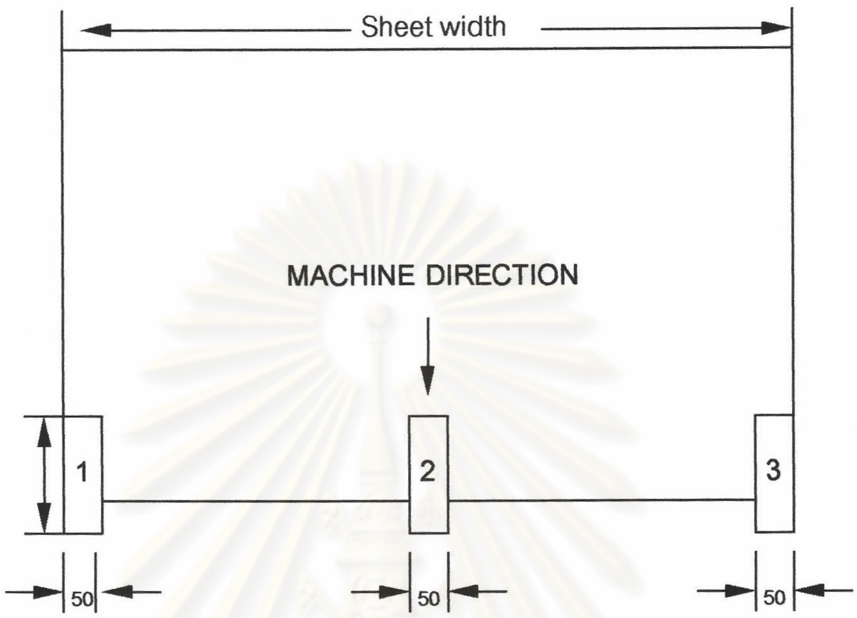


Figure 3.11 Orientation across the sheet width in machine direction.

3.7 Thermoforming Processability Test

The thermoforming test was processed as shown in Figure 3.12. The plastic sheet is clamped and heated. It is then drawn over the raised mold, a seal was created between the sheet and the mold, vacuum was applied beneath the sheet and then the sheet down against the mold's surface for final cooling. The temperature profile and forming condition were tested according to the sheet sample preparation which was HDPE/MLLDPE blends at 80/20 and 70/30 % content, compared with conventional HDPE as shown in Table 3.4. With a thermoforming processability conducted the samples of between 5 to 7 sheets were taken to determine the maximum and minimum values for standard deviation. All statistical calculations were performed in the 5 specimens.

Table 3.4 Thermoforming conditions.

Thermoforming conditions	HDPE	HDPE/MLLDPE	HDPE/MLLDPE
HDPE/MLLDPE blends, wt%	100	80/20	70/30
Thermoforming temperature	°C	°C	°C
Mold temperature	85	85	85
Sheet temperature	180	210	225
Oven temperature	295	285	230
Thermoforming time	Seconds	Seconds	Seconds
Heating time	180	170	170
Forming time	90	90	90
Cooling time	90	60	60
Total cycle time	360	320	320
Sagging distance (mm)	45	50	50

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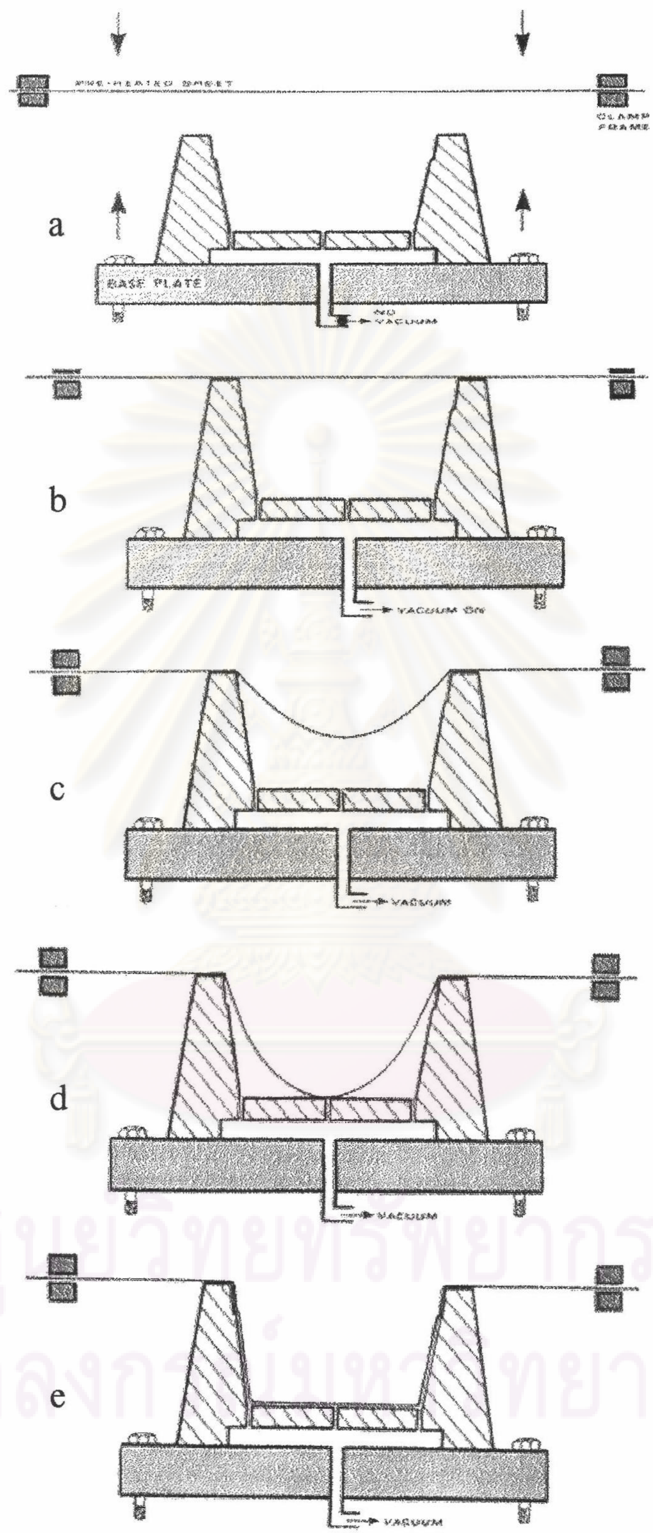

Figure 3.12 Schematic diagram of female mold vacuum thermoforming process.

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3.7.1 Sagging of Heated Sheet Test

The sagging distance was measured by a photoelectric eye as shown in Figure 3.13. The sheet was sagged during heating as shown in Figure 3.12 (d).

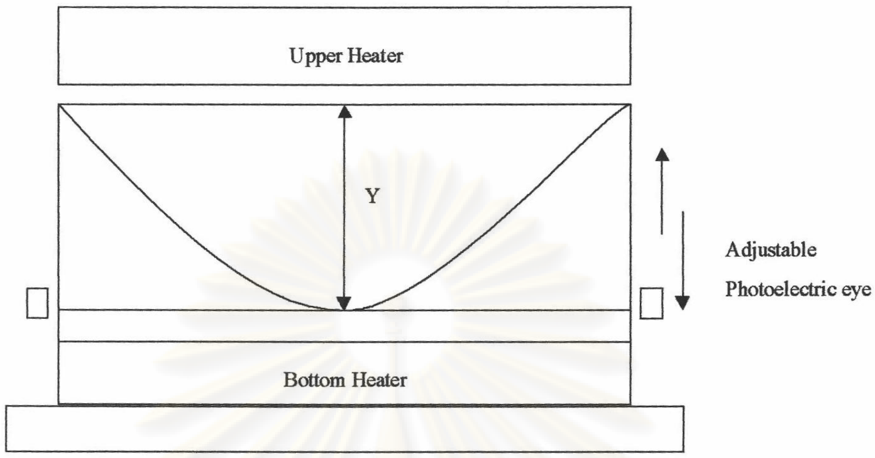

Figure 3.13 Schematic diagram of how photoelectric eye detects sagging distance.

3.7.2 Pick Up Truck Formed Part Shrinkage Test

Part shrinkage was performed on the pick up truck liner formed part as shown in Figure 3.14 the formed parts were exposed at the ambient temperature for at least 24 hours. Subsequently, the length of the formed part were changed and measured, which expressed in percentage of shrinkage (1.5%-2.5%) or shrinkage rate (0.150-0.250 mm/mm). The formed part shrinkage was calculated by using the equations 3.2 and 3.3.

$$\%\ \text{Shrinkage} = \frac{100\ (L_1 - L_2)}{L_1} \qquad \text{Eq 3.2}$$

$$\text{Shrinkage rate (mm/mm)} = \frac{L_1 - L_2}{L_1} \qquad \text{Eq 3.3}$$

L_1 = Length of pick up truck mold

L_2 = Length of pick up truck formed part

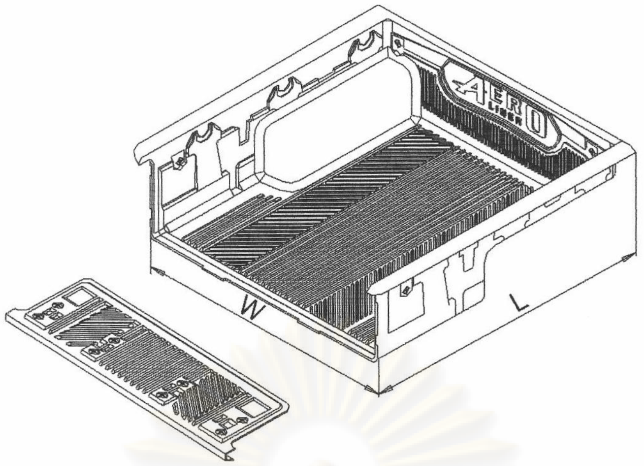

Figure 3.14 Schematic diagram of pick up truck liner formed part.

3.8 Reproducibility Test

To comply with industry applications, consequently, the reproducibility testing mechanical properties testing such as tensile and impact strength was chosen. The blending HDPE/MLLDPE (Elite blend) at 70/30 ratio by weight was mixed by using the same procedure in section 3.2.

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