

## **CHAPTER II**

### **EXPERIMENTAL SECTION**

#### **2.1 Materials**

The experiments were carried out using linear low density polyethylenes (LLDPE ; L2009F, L2020F) and a medium low density polyethylene (MDPE ; M3204RU) which were of film grade (pellet form), and HDPE (H5690S, N3260, R1760) as supplied by Thai Polyethylene Co., Ltd. Their properties are summarized in table 2.1.

#### **2.2 Characterizations**

The characterization studies were used to quantify physical properties of the raw materials. Their properties are summarized below.

**Table 2.1** Physical properties of LLDPE, MDPE and HDPE

Sample	Physical properties			
	MFI (g/10 min)	density (g/cm <sup>3</sup> )	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)
L2009F	0.9	0.920	5,132	1.03 × 10 <sup>5</sup>
L2020F	2.0	0.920	4,492	6.07 × 10 <sup>4</sup>
M3204RU	4.0	0.932	3,723	3.36 × 10 <sup>4</sup>
N3260	0.8	0.956	9,812	1.92 × 10 <sup>4</sup>
H5690S	0.9	0.956	9,780	1.84 × 10 <sup>4</sup>
R1760	3.0	0.957	8,214	1.36 × 10 <sup>4</sup>

### 2.2.1 Melt flow Index (MFI : g/10 min)

Our procedure followed ISO 1133-4 (L2009F,L2020F) and ASTM D 1238 (M3204RU). The temperature was 190 °C with a load of 2.16 kg. for polyethylene. The MFI measurements were carried out by Thai Polyethylene Co., Ltd. (TPE) staff. The results are shown in Table 2.1.

### 2.2.2 Density ( $\rho$ : g/cm<sup>3</sup>)

ISO 1872-1 (L2009F, L2020F) and ASTM D 1505 (M3204RU) procedures were followed to obtain the density by a density gradient column at the temperature of 23 °C with sodium acetate and methanol as solvents. The density measurements were carried out by Thai Polyethylene Co., Ltd. (TPE) staff. The results are shown in Table 2.1.

### 2.2.3 Weight Average Molecular Weight ( $M_w$ : g/mol)

$M_w$  was obtained from Gel Permeation Chromatography (GPC) (WATERS, model 150-C) at 130 °C with dichlorobenzene as the solvent or Size Exclusion Chromatography (SEC). The measurements were carried out by Thai Polyethylene Co., Ltd. (TPE) staff. The results are shown in Table 2.1.

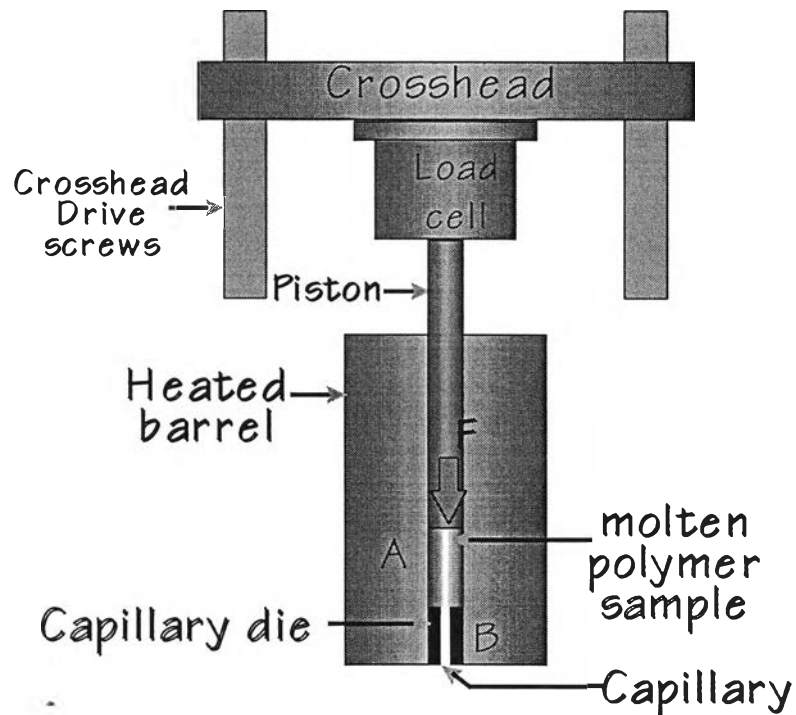
## 2.3 Capillary Rheometer

### 2.3.1 Instrument

The measurements were performed on an Instron 3213 capillary rheometer. It comprises of an extrusion assembly equipped with a plunger driven at a constant speed. It incorporates these features : a barrel length of 289 mm, a barrel diameter of 9.525 mm, a maximum load of 25 kN, a precise temperature control from 40-400 °C with a resolution of 0.1 °C, and a temperature stability of  $\pm 0.5$  °C. Three capillary dies were used in our study; each die has a 45 tapering at the inlet. The length and diameter of each die are listed below.

**Table 2.2** Characteristics of the three dies

Die No.	$d_c$ (mm)	$l_c$ (mm)	$l_c/d_c$
214	1.9675	13.775	7.01
614	0.7525	25.105	33.4
1860	1.2550	50.188	40.1



**Figure 1.1** Capillary Rheometer (Instron 3213).

### 2.3.2 Procedure

A sample (LLDPE, MDPE and HDPE) was placed in the barrel of the extrusion assembly, heated to a required temperature (190 °C) for 30 minutes and then forced out through a capillary die located at the bottom of the Instron machine at a constant plunger speed. A force corresponding to a specific plunger speed can be plotted on a chart recorder. The force and the plunger speed were converted to wall shear stress values by simple calculations involving the geometry of the extruder.

### 2.3.3 Calculations

We assumed that the polymer melt was incompressible, the flow was laminar and fully developed, and there was no entrance and exit loss.

a. Determination of Wall Shear Stress ( $\tau_w$ )

The force required to move a plunger at a constant speed,  $F$ , can be converted to the wall shear stress,  $\tau_w$ , as follows:

$$\tau_w = \frac{F}{4A_p(l_c/d_c)}, \quad (2)$$

where  $F$  is the force or load of the plunger,  $A_p$  is the cross section area of the plunger,  $l_c$  is the length of capillary die,  $d_c$  is the diameter of capillary. The wall shear stress is actually the apparent wall shear stress because it includes the capillary entrance and exit losses. For  $l_c/d_c$  greater than 30, the losses are negligible and the Bagley correction was not applied to our data.

b. Determination of the Apparent Strain Rate ( $\dot{\gamma}_a$ )

The plunger velocity was converted into the apparent strain rate by the following equation

$$\dot{\gamma}_a = 8V_p \frac{d_b^2}{d_c^3}, \quad (3)$$

where  $V_p$  is the plunger velocity,  $d_b$  is a barrel diameter and  $d_c$  is the capillary diameter. Implicitly, the apparent strain rate is determined by assuming that the volume flow rates in the plunger and in the capillary are the same, or the melt is incompressible. The plunger velocity was converted to the capillary velocity by the equation

$$V_c = V_p (d_b/d_c)^2, \quad (4)$$

and therefore

$$\gamma_a = 8 \frac{V_c}{d_c} \quad (5)$$

c. Determination of Viscosity ( $\eta$ )

The apparent viscosity was determined from :

$$\eta = \frac{\tau_w}{\gamma_a} \quad (6)$$

## 2.4 Parallel Plate Rheometer

### 2.4.1 Instrument

Advanced Rheometric Expansion System (ARES) is a mechanical spectrometer that is capable of subjecting a sample to either a dynamic (sinusoidal) or steady (linear) shear strain (deformation). It measures the resultant torque exerted by the sample in response to the input shear strain. Shear strain is controlled by the actuator ; torque is measured by transducers.

### 2.4.2 Procedure

A sample was placed in the gap between the two parallel plates which was 25 mm in diameter and the gap was about 0.6 mm so the diameter and gap ratio was about 40.

First measurement was Dynamic Strain Sweep Default Test. We can selected *DSImSwp* from the Description of test Parameters. The strain was varied between 0.1-100 rad/sec, frequency 1 rad/sec, temperature 190 °C, and selected 5 point per decade.

The next measurement mode was Dynamic Frequency/Temperature Sweep. We can selected *DF/T Swp* from the Description of test Parameters. The sweep mode was log. The frequency was from 0.1-100 rad/s The temperature was varied between 230-110 °C, and temperature increment was 10 °C for the ranges 230-120 °C and 2 °C for the ranges 118-110 °C. Soak time was 180 seconds.

This instrument gives the value of storage modulus ( $G'$ ) and loss modulus ( $G''$ ) vs. Frequency ( $\omega$ ).

### 2.4.3 Normalizations

We had to do an experiment at several temperatures and to creat the time and temperature superposition master curve for a wider range of frequency. We obtained shift factor( $a_T$ ) from empirical data, by using the temperature of 190 °C as the reference temperature ( $T_0$ ) The vertical shift factor ( $b_T$ ) used was (*Ferry 1981*)

$$b_T = \frac{T}{T_0} \quad (7)$$

In all cases. the data sets show two zones: the terminal zones and the entanglement plateau zones which is characterized by the plateau values  $G''_N$ .

Normalization of the wall shear stress was by the recoverable shear factor,  $S_R$ . defined as

$$S_R = \frac{\tau_{w,c}}{G_N''} \quad (8)$$

where  $\tau_{w,c}$  is the critical wall shear stress and  $G'$  is some characteristic value of storage modulus in the limit of large frequency. We propose to do the following normalization's:

a. Asymptotic Value was done by setting  $G'$  equal to  $G_N''$  obtained from the plateau value:

$$S_R = \frac{\tau_{w,c}}{G_N''} \quad (9)$$

$G_N''$  was obtained from the master curve of each sample at a particular reference temperature. If the plateau was not obtainable directly, we used *the fit equation*.

$$b_T G'(\omega) = G_N'' + C_1 (a_T \omega)^{-C_2} \quad (10)$$

to evaluate  $G_N''$  where  $C_1$  and  $C_2$  are constants. From equation (10) we can plot a graph between  $\log G_N'' - b_T G'(\omega)$  versus  $\log a_T \omega$  and we can evaluate  $G_N''$  of each materials by selecting  $G_N''$  that maximizing  $r^2$  the fitting coefficient where  $C_1$  was intercept and  $C_2$  was slope.



b. Local Value was done by setting  $G'$  equal to  $G'(\omega)$ :

$$S_R = \frac{\tau_{w,c}}{G'(\omega)}, \quad (11)$$

where  $\omega$  is the angular frequency and can be calculated from

$$\omega = 2\pi\gamma_a \frac{h}{R}, \quad (12)$$

$h$  is the gap spacing and  $R$  is the plate radius. Since  $G_N^o$  is the asymptotic state but it is not actual elastic force incurred in the capillary, the local value of  $G'$  seems to be a possible candidate of the elastic stress that actually occurs.

c. The modulus can be obtained from  $G \approx \eta_0/\lambda$ , where  $\eta_0$  is the zero-shear viscosity and  $\lambda$  is a characteristics relaxation where it can be calculated from (*Larson, 1992*)

$$\lambda = \lim_{\omega \rightarrow 0} \frac{G'}{G''\omega} \quad (13)$$

d. Steady state equilibrium compliance ( $J_e^o$ ) can be obtained by integration which are equivalent to summing over all the elements of an

infinite Maxwell model : for viscoelastic liquids at very low frequencies (*Ferry 1981*)

$$G' = \omega^2 \int_{\alpha}^{\infty} H\tau^2 \ln\tau = A_G \omega^2 = J_e^0 \eta_0^2 \omega^2 \quad (14)$$

$$G'' = \omega \int_{\alpha}^{\infty} H\tau \, d \ln\tau = \omega \eta_0 \quad (15)$$

giving the proportionalities to  $\omega^2$  and  $\omega$ , respectively, We obtain

$$\frac{(G'')^2}{(G')^3} = \frac{(\omega \eta_0)^2}{J_e^0 (\omega \eta_0)^3} = \frac{1}{J_e^0} \quad (16)$$

and we can use this ratio to find  $S_R$  because we assume  $G'$  is identical to  $1/J_e^0$ .

## 2.5 The Extrudates Surface and Sharkskin Studies

### 2.5.1 Zoom Stereo Microscopy

Zoom stereo microscope used was OLYMPUS B071, with a magnification range of 4 - 80 times. The extrudates were examined at 20 × magnification to examine approximate onsets of sharkskin and other flow regimes.

### 2.5.2 Optical Microscopy

Optical microscopic use was OLYMPUS PM20, with a magnification range of 12.5-1,500 times. The extrudates were examined at 100 × magnification to detect a critical point of surface defect in each regime of the flow curves.

### 2.5.3 Scanning Electron Microscopy (SEM)

SEM was used JWOL 5200 - 2AE (MP152001), with a magnification range of 35 - 200,000 times. The sharkskin extrudates were examined at  $200 \times$  magnification to measure wavelengths ( $\lambda_S$ ) and amplitude ( $\epsilon_S$ ) of the sharkskin extrudates.