CHAPTER II

EXPERIMENTAL DETAILS

2.1 Materials

2.1.1 High Density Polyethylene (HDPE)

The High Density Polyethylene (HDPE) used were H5690S, H5604F, H6205JU from Siam Chemical Trading Co., Ltd.

Table 2.1.1 Physical properties of HDPE as given by manufacterer

Physical Properties	H5690S	H5604F	H6205JU
MFI (g/10min)	0.90	0.04	5.00
Density (g/cm^3)	0.95	0.95	0.96
M_w (g/mol)	107,000	133,000	98,000
M_n (g/mol)	8,900	2,200	7,300
M_w/M_n	12.02	60.45	13.42

2.2.2 Linear Low Density Polyethylene (LLDPE)

The Linear Low Density Polyethylene (LLDPE) used were L2009 and L2020F from Siam Chemical Trading Co., Ltd.

Table2.1.2 Physical properties of LLDPE as given by manufacterer

Physical Properties	L2009F	L2020F
MFI (g/10min)	0.90	2.00
Density (g/cm^3)	0.92	0.92
M_w (g/mol)	87,000	60,700
M_n (g/mol)	4,081	2,400
M_w/M_n	21.31	25.29

2.2.3 Medium Density Polyethylene (MDPE)

The Medium Density Polyethylene (MDPE) used was M3204RU from Siam Chemical Trading Co., Ltd.

Table2.1.3 Physical properties of MDPE as given by manufacterer

Physical Properties	M3204RU
MFI (g/10min)	5.00
Density (g/cm^3)	0.93
M_w (g/mol)	33,000
M_n (g/mol)	2,700
M_w/M_n	12.22

2.2 Characterization

The characterizations were carried out to quantify physical properties of the raw materials.

2.2.1 Melt Flow Index Meter

Melt Flow Index (MFI) was determined following ASTMD 1238 (M3204RU. H5690S, H5604F and H6205JU) and ISO 1133-4 (L2009F and L2020F). The temperature was 190C with a load of 2.16kg. The services for the MFI measurements were provided from Thai Polyethylene Co., Ltd. (TPE) staff.

2.2.2 Gel Permeation Chromatography (GPC)

The molecular weight was obtained from Gel Permeation Chromatography(GPC). The services for the molecular weight measurements were provided from Thai Polyethylene Co., Ltd. (TPE) staff.

2.2.3 Density Measurement

The density was determined following ISO 1872-1(L2009F and L2020F) and ASTM D1505 (M3204RU, H5690S, H5604F and H6205JU) by a density gradient column. The services for the density measurements were provided from Thai Polyethylene Co., Ltd.(TPE) staff.

2.2.4 Zoom Stereo Microscope

The skin texture photographs were obtained from a Zoom stereo microscope. OLYMPUS B071, with a magnification range of 4-80 times. The extrudates were examined at 20x magnification.

2.3 Capillary Rheometer

2.3.1 Instrument

The flow curve measurements were performed on an Instron model 3213 capillary rheometer which was designed for use with the Instron material testing system. It comprises of an extrusion assembly equipped with a plunger driven at a constant speed. A temperature control system is contained in a separate console. It incorporates these features: a barrel length of 289 mm, a barrel diameter of 9.525 mm, a maximum load of 25kN, a precise temperature control from 40-400 C, temperature stability at the capillary of ± 0.5C. The details of capillary dies are shown in table 2.2.

Table 2.3 Capillary dies features

Die Number	Diameter (mm)	Length (mm)	l_c/d_c	Tapering
214	1.97	13.77	7.00	45°
614	0.75	25.10	33.36	45°
1855	1.25	50.10	39.92	45°
1860	1.25	50.19	40.15	45°

2.3.2 Procedure

A sample was placed in the barrel of the extrusion assembly, heated to a required temperature and then forced out through a capillary die located at the bottom of the Instron machine at a constant plunger speed. A period of 15 minutes as allowed for a load constant condition before a start of the experiment. The force and the plunger speed were converted to the shear stress and the strain rate values by simple mathematical calculations to be given below.

2.3.3 Calculations

In our calculations, we assumed that the polymer melt was imcompressible, the flow was laminar and fully developed, and there was no entrance and exit loss.

a) Determination of Wall Shear Stress (τ_w)

The force was converted into the wall shear stress by using the following equations involving the geometry of the capillary and the plunger (Dealy,1991) :

$$\tau_w = \frac{F}{4A_p(l_c/d_c)} \, , \tag{2.1}$$

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 and d_c is the diameter of capillary die. The wall shear stress is actually the apparent wall shear stress and the Bagley correction was not applied because l_c/d_c was greater than 30; the entrance and exit losses were negligible (Dealy,1991).

b) Determination of the Apparent Strain Rate (γ_a)

The plunger velocity was converted into apparent strain rate by the following equation (Dealy,1991).

$$\gamma_a = 8 \times V_p \times \frac{d_b^2}{d_c^3} \, , \tag{2.2}$$

where V_c is the capillary velocity, V_p is the plunger velocity and d_b is a barrel diameter. The plunger velocity was converted to the capillary velocity by the equation :

$$V_c = V_p \left(\frac{d_b}{d_c} \right)^2, \qquad (2.3)$$

and
$$\gamma_a = \frac{8V_c}{d_c}. \qquad (2.4)$$

c) Determination of Viscosity (η) and Power Law Index (n)

The apparent viscosity was determined from the equation (2.5) :

$$\eta = \frac{\tau_w}{\gamma_a}. \qquad (2.5)$$

We assumed a non-Newtonian melt; it obeys the power law fluid behavior

$$\tau_w = K \left(\gamma_w \right)^n, \qquad (2.6)$$

where γ_w is the wall strain rate, n is the power law index and K is a constant. Alternatively we can write equation (2.6) as

$$\tau_w = \eta \gamma_w, \qquad (2.7)$$

then it follows that

$$\eta = K \left(\gamma_w \right)^{n-1}. \qquad (2.8)$$

From the Rabinowitz correction (Ramamurthy,1986) :

$$\gamma_w = \frac{(3n+1)}{4n} \gamma_{a.s}, \qquad (2.9)$$

where $\gamma_{a.s}$ is the apparent strain rate without slip. We can write:

$$\tau_w = K\left[\left(\frac{3n+1}{4n}\right)\gamma_{a.s}\right]^n.$$ (2.10)

or $$\tau_w = K\left[\left(\frac{3n+1}{4n}\right)\left(\gamma_a - \frac{8V_s}{d_c}\right)\right]^n,$$ (2.11)

where V_s is the slip velocity. If we assumed a small slip so $8V_s/d_c$ is much smaller than γ_a then we can write

$$\tau_w \cong K\left(\frac{3n+1}{4n}\right)^n\left(\gamma_a\right)^n,$$ (2.12)

and $$\eta \cong K\left(\frac{3n+1}{4n}\right)^n\left(\gamma_a\right)^{n-1}.$$ (2.13)

Thus the power law index (n) and a constant K can be obtained from the graph of $\log\eta$ versus $\log\gamma_a$

Slope $= n-1$

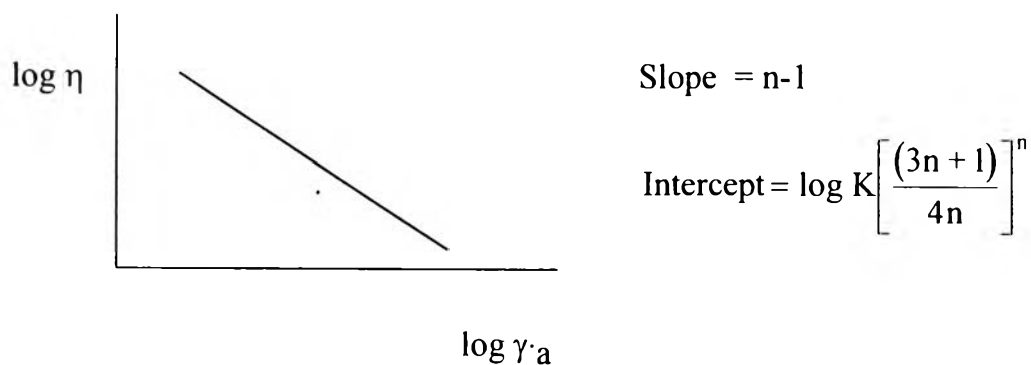Intercept $= \log K\left[\frac{(3n+1)}{4n}\right]^n$

Figure 2.1 The viscosity vs. the apparent strain rate.

d) <u>Determination of Wall Strain Rate ($\gamma \cdot_w$) and Apparent Strain Rate with out Slip ($\gamma \cdot_{a,s}$)</u>

From the power law fluid of equation (2.6) we can write:

$$\gamma_w = \left(\frac{\tau_w}{K}\right)^n , \tag{2.14}$$

Using the Rabinowitz correction, we can write:

$$\gamma_{a,s} = \frac{4n}{3n+1}\left(\frac{\tau_w}{K}\right)^{\frac{1}{n}} . \tag{2.15}$$

e) <u>Determinations of Slip Velocity</u>

The slip velocity experiment was carried out using the capillary rheometer.

Mooney Analysis:

Mooney Analysis is based the hypothesis that the apparent strain rate can be decomposed into the apparent strain rate without slip and the slip velocity term.

$$\gamma_a = \gamma_{a,s} + \frac{8V_s}{d_c} . \tag{2.16}$$

where $\gamma \cdot_{a,s}$ is the apparent strain rate corrected for the slip and V_s is the slip velocity. We assumed here that the apparent strain rate corrected for slip and the slip velocity are functions solely of the wall shear stress. A plot of $\gamma \cdot_a$ versus $1/d_c$ will give a slope equal to $8V_s$ and intercept equal to $\gamma \cdot_{a,s}$.

Modified Mooney Analysis:

Modified Mooney Analysis is based on the same hypothesis as the equation (2.16). The apparent strain rate corrected for slip can be calculated directly, base on the non-Newtonian power behavior for melt. We can write

$$\tau_w = K\dot{\gamma}_w{}^n,$$

<div align="right">(2.17)</div>

where $\dot{\gamma}_w$ is true wall strain rate, n and K are an exponent and a constant which are to be determined from viscosity- strain rate experiment without slip effect if there is no slip velocity in regime I. The modified Mooney analysis is then

$$\dot{\gamma}_a = \left(\frac{4n+1}{3n+1}\right)(\tau_w)^{\frac{1}{n}} + \frac{8V_s}{d_c}.$$

<div align="right">(2.18)</div>

where we have used the Rabinowitz correction.

Oscillating Regime Slip:

From the plot of load versus plunger travel, the load fluctuates in a certain range of strain rate. The load becomes double valued at a given plunger speed in the oscillating flow regime. The difference between the maximum and minimum loads from each fluctuation is determined as

$$\Delta\tau_w = \tau_{max} - \tau_{min},$$

<div align="right">(2.19)</div>

where τ_{max} is a stress at the upper load in a cycle and τ_{min} is the lower load of the cycle. We assume that there is no change in the apparent viscosity of the polymer melt as the load fluctuates. Only the change in the shear stress between the upper and lower values occurs. The change of the apparent strain rate ($\Delta\dot{\gamma}_a$) can be determined as

$$\Delta \gamma_a = \frac{\Delta \tau_w}{\eta m},$$
(2.20)

where $\Delta \tau_w$ is the difference in the wall shear stress between the upper and the lower points of load fluctuation. The slip velocity (V_S) for each oscillation cycle is calculated from

$$V_s = \Delta \gamma_a \times \frac{d_c}{8}.$$
(2.21)

f) Determination of Extrapolation Length

The extrapolation length was introduced by Brochard and de Gennes (1992) where they assumed that there is a thin slip layer of polymer melt near a solid wall. The non zero velocity profile can be extrapolated to a zero value inside a wall at a distance called the extrapolation length "b".
It is formally defined as

$$b = \frac{V_s}{\gamma_{a.s}}.$$
(2.22)

2.4 Parallel Plate Rheometer Studies

2.4.1 Instrument

Avanced Rheometric Expansion System (ARES) is a mechanical spectrometer that is capable of subjecting a sample to either a dynamic (sinusodial) or steady (linear) shear strain (deformation). It measures the resultant torque exerted by the sample in response to applied the shear strain. Shear strain is applied by a motor; 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. The first measurement mode was Dynamic Strain Sweep which applies a range of sinusoidal strains, each at a constant frequency to determine the limits of linear viscoelasticity. The temperature was set at 230C, the frequency was set at 1.0 rad/s and the strain was varied from $0.01-100s^{-1}$. The point per decade was set at 7 and the gap size was 1.6mm. The second measurement mode was Dynamic Frequency/Temperature Sweep. This allows application of a sinusodial strain over a range of frequencies while temperature is stepped between selectable temperature limits. The temperature was varied between 230-150 °C, the frequency was varied from 0.01-100 rad/s and soak time of 3 minutes before each measurement. The point per decade was set at 7 and the gap size was 1.6mm. This instrument gives the value of storage modulus (G') and loss modulus (G'') as a function of frequency(ω).

2.4.3 Data Analysis

a) Time - Temperature Superposition Master Curve

The effects of time and temperature are equivalent for viscoelastic materials within certain time and temperature domains. As a result, master curve can be generated that can be used to predict a material's performance outside the range of accessibility of a given instrument.

A master curve is prepared by a shift factor a_T for each test temperature relative to the reference temperature. The shift factor is a measure of how material's frequency respond changes with temperature changes, relating the material's behavior at a given test temperature to its behavior at a reference temperature. We obtained the shift factor from empirical measurements. by assuming the reference temperature of 230C and determined

the horizontal shift factor (a_T). We took the constant values to calculate the shift factor (log a_T) which was used to generate the time and temperature master curve and measuring the vertical shift factor(b_T) (Ferry, 1976) :

$$b_T = \frac{T_0}{T}.$$ (2.23)

b) Determination of viscosity.

The viscosity obtained from the parallel plates rheometer was determined from:

$$\eta' = \frac{G''}{\omega}.$$ (2.24)

where G'' is the loss modulus and w is frequency or angular velocity.

c) Cox-Merz Rule

A correspondence between the complex viscosity and the steady shear viscosity has been observed under some circumstances. This relation is know as the the Cox-Merz rule (1958) :

$$\eta^* = \sqrt{(\eta')^2 + (\eta'')^2},$$ (2.26)

where η^* is the complex viscosity. The viscosities were determined from (2.27) and (2.28)

$$\eta' = \frac{G''}{\omega}.$$ (2.27)

and

$$\eta'' = \frac{G'}{\omega}.$$ (2.28)