

CHAPTER III EXPERIMENTAL

3.1 Materials

In this work, high density polyethylene (HDPE) was chosen with a series of the different molecular weights and polydispersities to study in the steady shearing flow behavior in capillary rheometer.

The HDPE used were H5604F, H5840B, H5818J and H5690S, reactor grade (no additives), from Thai Polyethylene Co., Ltd. The physical properties of these materials are shown in Table 3.1 as quoted from the company.

Table 3.1 Physical properties of HDPE used as quoted by the manufacturer

Physical properties	H5604F	H5840B	H5818J	H5690S
MFI (g/10 min)	0.04	0.4	18	0.9
Density (g/cm ³)	0.956	0.958	0.962	0.956
M _w (g/mole)	2.66x10 ⁵	1.33x10 ⁵	6.39x10 ⁴	2.40x10 ⁵
M _n (g/mole)	3.45x10 ³	6.76x10 ³	2.63x10 ³	5.80x10 ⁴
M _w /M _n	77	20	24	4.1

3.2 Characterization of Physical Properties

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

3.2.1 Melt Flow Index Meter

Melt Flow Index (MFI) was determined following ASTM D1238. The temperature was 190⁰C with a load of 2.16 kg. The melt flow indices are tested below in Table 3.2.

Table 3.2 Melt flow index

Materials	MFI (g/10 min)	Quoted (g/10 min)
H5604F	0.07	0.04
H5840B	0.5	0.4
H5818J	18.8	18
H5690S	1.0	0.9

All measured values are slightly greater than the quoted values due to all materials studied were of the reactor grade that did not contain any additives. The small amount of additives in commercial grade can cause different rheological properties as well as the MFI value.

3.2.2 Density Measurement

ASTM D792 test method B procedure was followed to obtain the density by using a pycnometer with a volume of 25 cm³ and used the methanol as a solvent. The density values are shown in Table 3.3.

Table 3.3 Density measurement

Materials	Density (g/cm ³)	Quoted (g/cm ³)
H5604F	0.914	0.956
H5840B	0.913	0.958
H5818J	0.920	0.962
H5690S	0.926	0.956

All materials studied were of reactor grade and their densities were measured by using a pycnometer. The densities of the commercial grade materials are generally measured by the density gradient column technique (ASTM 1505-85). The distinctive technique could be the cause of the differences in the density values found.

3.2.3 Molecular Weight Measurement

Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity (M_w/M_n) were determined by using the cone and plate rheometer (25-mm diameter) in dynamic frequency sweep mode to measure storage modulus (G') and loss modulus (G''). The measurements were carried out in the linear viscoelastic region (LVR) at 190⁰C and operated within the angular frequency range of 0.1-100 rad/s. Subsequently G' and G'' were used to obtain molecular weight distribution using the Orchestrator software with the standard parameters as shown in Table 3.4.

Table 3.4 Fixed parameters for molecular weight measurement for HDPE at the temperature of 190 °C

Parameters (unit)	Value
Relax time exponent	3.6
Plateau modulus (dyn/cm ²)	2.30x10 ⁷
Activation energy (KJ/mol-K)	27.3
Front factor	2.52x10 ⁻²¹
Entanglement molecular weight (g/mol)	1,250
Reptation molecular weight (g/mol)	2,500

The unimodal distribution was arbitrarily chosen to calculate the molecular characteristic. The molecular characteristics are indicated below in Table 3.5.

Table 3.5 Molecular weight measurement

Materials	M _n (g/mol)	M _w (g/mol)	M _z (g/mol)	Polydispersity (M _w /M _n)
H5604F	4.56x10 ⁴	1.64x10 ⁶	5.15x10 ⁷	36.1
H5840B	7.27x10 ⁴	5.39x10 ⁵	3.95x10 ⁶	7.4
H5818J	6.81x10 ⁴	2.99x10 ⁵	1.31x10 ⁶	4.4
H5690S	9.64x10 ⁴	7.23x10 ⁵	1.37x10 ⁶	7.4

3.2.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was carried out on a PERKIN ELMER (model DSC7). Samples of 5-10 mg were prepared in aluminum sample pans. The temperature was programmed at a heating rate of 10⁰C/min from 40⁰C to 200⁰C. The chamber was purged with dry nitrogen at

a flow rate 25 ml/min. The melting point (T_m) and heat of fusion (ΔH_f) were determined from the thermogram by using the peak area method. The corresponding degree of crystallinity of the samples were calculated from the ΔH_f , Endothermic peak area, by using the following equation:

$$\text{Percentage crystallinity} = (\Delta H_f / \Delta H_{fc}) * 100, \quad (3.1)$$

where ΔH_f is the heat of fusion of sample from thermogram and ΔH_{fc} is the theoretical heat of fusion of 100 percent crystallinity of the same polymer. ΔH_{fc} of HDPE (Brandrup and Immergut, 1989) is 277.1 J/g. The melting temperature and the percentage of crystallinity are shown in Table 3.6.

Table 3.6 Melting temperature and percentage of crystallinity

Materials	T_m ($^{\circ}\text{C}$)	ΔH_f (J/g)	%Crystallinity
H5604F	130.3	167.9	60.6
H5840B	130.7	170.4	61.5
H5818J	132.1	160.6	57.9
H5690S	134.7	159.1	57.4

3.3 Characterization of Rheological Properties

3.3.1 Capillary Rheometer

a) *Instrument*

The capillary rheometer is an Instron (model 3213), operated in a constant piston speed mode. 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 25 kN, a precise

temperature control from 40 to 400 °C, with temperature resolution at the capillary of ± 0.5 °C. The details of the capillary dies used are shown in Table 3.7.

Tables 3.7 Capillary die features

Die number	Diameter (mm)	Length (mm)	l_c/d_c ratio	Tapering
214	1.97	13.77	7.00	45°
614	0.75	25.10	33.63	45°
1855	1.25	50.10	39.92	45°
1860*	1.25	50.19	40.15	45°

*This is the main die to obtain each flow curve in the experiment.

b) Procedure

A sample powder was loaded in the barrel of the extrusion assembly, heated to a required temperature and subsequently forced out through a capillary die located at the bottom of the Instron machine at a constant plunger speed. A period of 10 minutes was allowed for a constant load condition before starting of the experiment. The force and the plunger speed were converted to the shear stress and the apparent shear strain rate values by using simple mathematical calculations to be described below.

c) Calculations

In our calculations, we assumed that the polymer melt was incompressible, isothermal throughout the die, the flow was laminar with fully developed velocity profile and the entrance and exit losses were negligible.

(I) Determination of Wall Shear Stress

The force was converted into the wall shear stress by using the following equations involving the capillary and the plunger (Dealy, 1991) which can be expressed as:

$$\tau_w = \frac{F}{4A_p(l_c/d_c)} \quad (3.2)$$

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 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 and Wissbrun, 1990).

(II) Determination of Apparent Shear Strain Rate

The plunger velocity was converted into apparent strain rate by the following equations (Dealy and Wissbrun, 1990)

$$\dot{\gamma}_{app} = 8 \times V_p \times \frac{d_b^2}{d_c^3} \quad (3.3)$$

where 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:

$$V_c = V_p \left[\frac{d_b}{d_c} \right]^2 \quad (3.4)$$

and

$$\dot{\gamma}_{app} = \frac{8V_c}{d_c} \quad (3.5)$$

(III) Determination of Slip Velocity and Apparent Shear Strain Rate without Slip

The slip velocity experiment was carried out by using the capillary rheometer and employing the classic method, the so-called Mooney analysis.

Mooney Analysis: Mooney Analysis hypothesizes that the apparent shear strain rate ($\dot{\gamma}_{app}$) can be decomposed into the apparent strain rate without slip ($\dot{\gamma}_{app,s}$) and the slip velocity term (Dealy and Wissbrun, 1990)

$$\dot{\gamma}_{app} = \dot{\gamma}_{app,s} + \frac{8V_s}{d_c}, \quad (3.6)$$

where $\dot{\gamma}_{app,s}$ is the apparent strain rate corrected for the slip and V_s is the slip velocity. We assume that the apparent strain rate corrected for slip and the slip velocity is function only of the wall shear stress. A plot of $\dot{\gamma}_{app}$ versus l_c/d_c will give a slope equal to $8V_s$ and intercept equal to $\dot{\gamma}_{app,s}$.

(IV) Determination of Extrapolation Length

Brochard and de Gennes (1992) introduced the extrapolation length where they assumed that there is a thin slip layer of polymer melt close to a solid wall and leads to the non-zero velocity profile which instantly causes extrapolation length “ b ”. It is formally defined as

$$b \equiv \frac{V_s}{\dot{\gamma}_{app,s}}. \quad (3.7)$$

(V) Determination of Power Law Index and Power Law Correction

For a non-Newtonian fluid the shear stress no longer varies linearly with shear rate and the viscosity as a function of $\eta(\dot{\gamma})$ must be taken to derive an expression for $\dot{\gamma}(r)$ as indicated in Figure 3.1.

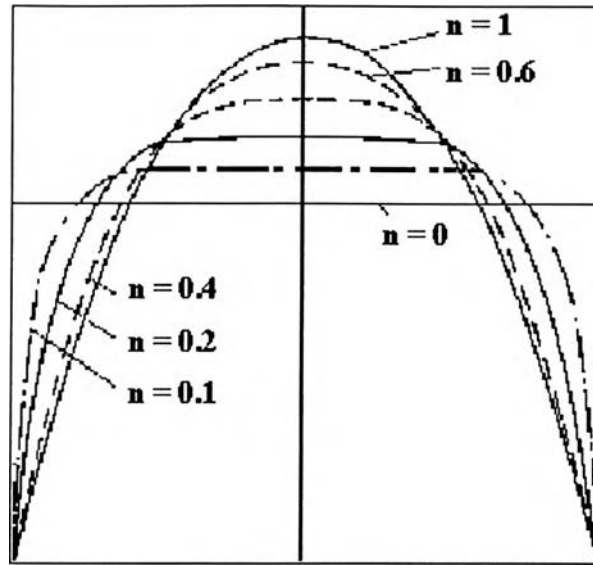


Figure 3.1 Tube flow velocity profiles calculated from the power law for several values of power law index (n).

The power law index (n) can be used to represent various velocity profiles. For basic Newtonian fluid, parabolic velocity profile can be expressed but polymer melts typically flow as a plug-like profile. Thus the shear stress will be related to shear rate according to the power law model (Dealy and Wissbrun, 1990)

$$\tau_w = K \dot{\gamma}_{app,s}^n \quad (3.8)$$

and we can obtain a relationship between the pressure gradient and the velocity gradient as:

$$\frac{r}{2} \left(-\frac{dP}{dz} \right) = K \left(-\frac{dv}{dr} \right)^n \quad (3.9)$$

Again taking the velocity at the wall to be zero (no slip) the velocity profile can be determined by integrating equation 3.9. Profile for several values of n are shown in figure 3.1 then the shear rate at the wall is given by (Dealy and Wissbrun, 1990)

$$\dot{\gamma}_w = \left(\frac{3n+1}{4n} \right) \left(\frac{4Q}{\pi R^3} \right) = \left(\frac{3n+1}{4n} \right) \dot{\gamma}_{app,s} \quad (3.10)$$

Combining equation 3.10 with equation 3.8 we obtain

$$\tau_w = K \left(\frac{3n+1}{4n} \right)^n \left(\dot{\gamma}_{app,s} \right)^n \quad (3.11)$$

Thus a log-log plot of shear stress versus shear strain rate is a straight line with a slope of n . Nevertheless, the bending on this flow curve may give rise to nonunique value of n because of the qualitative change in the velocity profile as a function of shear rate on a particular shear rate range.

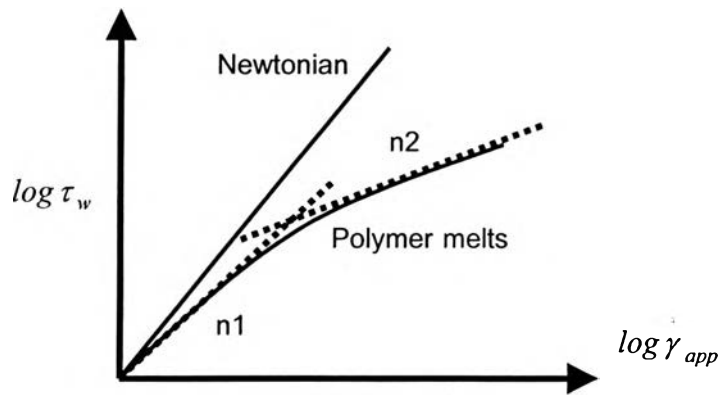


Figure 3.2 Schematic flow curve of polymer melts shows the bending and gives two power law indices n_1 and n_2 following the power law correction.

3.3.2 Cone and Plate Rheometer

Cone and plate rheometer is widely used in rheometry for highly viscous polymer melts and concentrated polymer solutions. Figure 3.3 shows a scheme of the cone and plate rheometer. The liquid under study is deformed between the cone and the plate. This fixture can provide a homogeneous strain rate and normal stress along the cone radius.

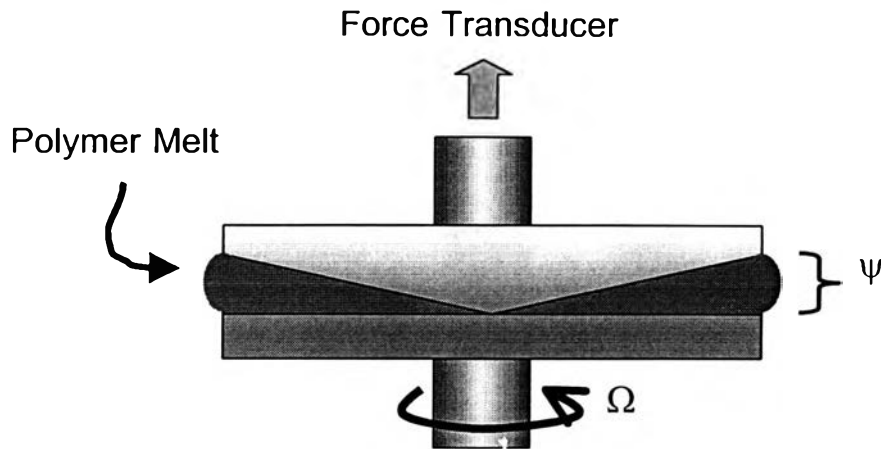


Figure 3.3 Schematic of cone and plate rheometer.

The cone angle is only several degrees or less and has been exaggerated in this sketch. In this set-up, the bottom plate is rotated with speed, Ω , and the cone is stationary. The torque on the cone and its speed can be used to determine viscosity. Pressure taps and the thrust measurement can be used to determine normal forces.

There are several modes that can be carried out by this instrument. In this experiment we used the controlled strain mode which comprises of many basic test modes, such as the below following:

- Strain (Amplitude) Sweep Test

The fixed parameter is angular frequency and temperature. The input parameter is amplitude (or strain) and the measured parameters are $\tan \delta$, storage modulus and loss modulus.

- Frequency Sweep Test

The fixed parameter is amplitude (or strain) and temperature. The input parameter is angular frequency and the measured parameters are $\tan \delta$, storage modulus and loss modulus

a) Instrument

Cone and plate rheometer was the ARES (Rheometrics Scientific). The fixture used was 25-mm diameter and cone angle was 0.1 rad. The upper 25-mm fixture is the stainless steel cone, whilst the lower 25-mm fixture is an aluminum disposable plate.

b) Procedure

The temperature was set at a particular value ($>T_m$). Then the gap was zero fixtures at that temperature operated. The sheeted samples were loaded between a cone and a plate and subsequently set to the standard gap before starting the experiment. The standard gap is equal to 0.051 mm for 0.1-radius cone angle. The force and the cone rotational speed were converted to the shear stress, the shear strain rate, storage modulus and loss modulus values by using simple mathematical calculations to be described below.

c) Calculations

The measurable quantities and fixed parameters for cone and plate flow are the fixture radius, R , the cone angle, ψ , the rotational speed, Ω (rad/s), the torque, M , and the normal force, F . The following equations can be used to calculate quantities of rheological importance (Tadmor and Gogos, 1979)

$$\dot{\gamma} = \Omega / \psi \quad (3.12)$$

$$\sigma = 3M / 2\pi R^3 \quad (3.13)$$

and
$$N_1 = 2F / \pi R^2. \quad (3.14)$$

(I) Determination of Phase Shift

Small amplitude oscillatory shear can be used to determine the linear viscoelastic properties of polymer substance. In this experiment, a thin sample of a material is subjected to a simple shearing deformation such that the shear strain as a function of time is given by

$$\gamma(t) = \gamma_0 \sin(\omega t), \quad (3.15)$$

where γ_0 is the strain amplitude and ω is the frequency. The stress is then measured as a function of time. By differentiating with respect to time, we find that

$$\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) = \dot{\gamma}_0 \cos(\omega t), \quad (3.16)$$

where $\dot{\gamma}_0$ is the shear rate amplitude. The shear stress is sinusoidal in time and has the same frequency as the strain:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta), \quad (3.17)$$

where σ_0 is the stress amplitude and δ is a phase shift, which is called the "mechanical loss angle".

(II) Determination of Storage Modulus and Loss Modulus

The stress amplitude and phase shift as functions of frequency have a direct relationship with the material functions usually used to describe viscoelastic behavior. The stress response can be written as (Dealy and Wissbrun, 1990)

$$\sigma(t) = \gamma_0 [G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)], \quad (3.18)$$

where $G'(\omega)$ is called the "storage modulus" and $G''(\omega)$ is called the "loss modulus". The storage modulus can physically indicate the elasticity whereas the loss modulus indicates the viscous character of the material.

3.4 Methodology

Two rheometers were used to study in this experiment. First, the capillary rheometer was used to obtain the final actual flow curve and to investigate the slip phenomena. The cone and plate rheometer was utilized to characterize two molecular characteristics, the crossover modulus and the crossover frequency. Three effects were mainly emphasized: (I) effect of molecular weight (II) effect of polydispersity (III) effect of temperature. The procedures of these two rheometers are described in details below:

3.4.1 Flow Curve Investigation

Rheological flow curve was obtained by using the capillary rheometer which operated with the die number 1860, the longest die ($L/R > 32$), in order to neglect the Bagley end correction, shear stress correction, (Dealy and Wissbrun, 1990). Normally the flow curve obtained is the apparent flow curve therefore Mooney analysis is used to characterize the slip velocity and after subtracting this slip term out, the apparent shear strain rate without slip is obtained and this plot is called the apparent flow curve without slip effect. Subsequently power law correction is again taken into account to obtain the actual flow curve as shown in Figure 3.4.

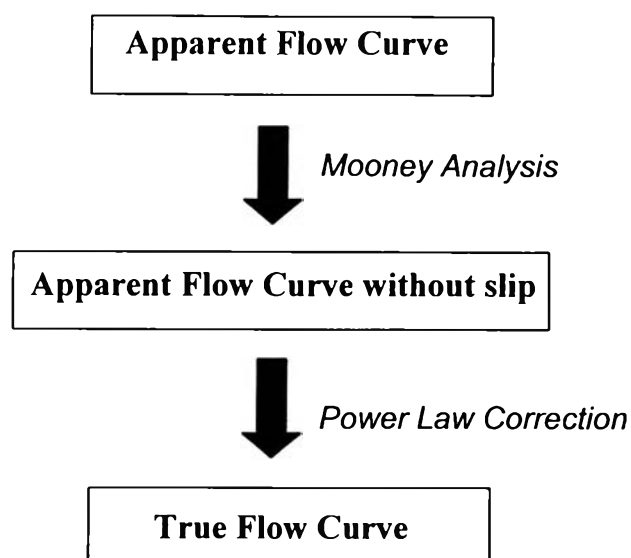


Figure 3.4 Flow chart of true flow curve, a plot of shear stress versus true shear strain rate.

a) Effect of Molecular Weight and Polydispersity

Slip velocity (V_s) and extrapolation length (b) can be determined from the Mooney analysis. The conditions of the capillary rheometer were set as indicated in Table 3.8.

Table 3.8 The conditions of capillary rheometer focused on the effect of molecular weight

Temperature ($^{\circ}\text{C}$)	180			
Shear strain rate (s^{-1})	0.1 – 1500			
Material	H5604F	H5840B	H5818J	H5690S

b) Effect of Temperature

Slip velocity (V_s) and extrapolation length (b) can be determined from the Mooney analysis. The conditions of the capillary rheometer were set as indicated in Table 3.9.

Table 3.9 The conditions of capillary rheometer focused on the effect of temperature

Materials	H5604F			H5840B		
Shear strain rate (s^{-1})	0.1 – 1500			0.1 – 1500		
Temperature ($^{\circ}C$)	160	180	200	160	180	200

3.4.2 Crossover Modulus Characterization

The crossover modulus and the crossover frequency were characterized by using the cone and plate rheometer in the dynamic frequency sweep mode and within the linear viscoelastic region (LVR). The conditions of cone and plate rheometer were set as indicated in Table 3.10.

Table 3.10 The conditions of cone and plate rheometer of dynamic frequency sweep

Materials	H5604F	H5840B	H5818J	H5690S
Temperature ($^{\circ}C$)	130-200	130-200	130-200	130-200
Frequency (rad/s)	0.1-100	0.1-100	0.1-100	0.1-100

The time-temperature-superposition (T-T-S) method was carried out to obtain a master curve at a particular reference temperature and to find out the crossover modulus and the crossover frequency.

3.4.3 Normalization of Flow Curve

The crossover modulus and the inverse crossover frequency which were determined by cone and plate technique were taken to normalize the shear stress and the true shear strain rate. Then the normalized flow curve which is a plot of two dimensionless parameters between shear stress/crossover modulus (τ_w/G_c) and Weissenberg number (Wi) was obtained.