CHAPTER II
EXPERIMENTAL SECTION

2.1 Materials

High density polyethylene's used in this study were H5690S and H5603B, supplied by Thai Polyethylene Co., Ltd. The materials were in pellet form.

2.2 Characterization

2.2.1 Rheological Properties

2.2.1.1 Melt and Solid Rheometer

The rheological measurements were performed on a melt and solid rheometer using cone-and-plate geometry (Rheometric Scientific, model ARES). The advantages of the cone-and-plate geometry for use with melts are small sample of material is needed, the shear rate is approximately uniform throughout the sample, and there is ready access to all surfaces to facilitate sample loading and cleaning.

The 25-mm upper fixture was a stainless steel cone with cone angle of 0.1 radian, while the lower 8-mm fixtures were aluminum disposable plates. Disposable aluminum plates were used as lower fixtures so that samples adhering to this fixture could be accumulated and stored for later microscopy. The gap was fixed at 0.0508 mm. The maximum and minimum torques that the transducer able to measuring are 200 and 0.2 gm.cm, respectively and the temperatures ranging from -150 to $600^{\circ}C$.
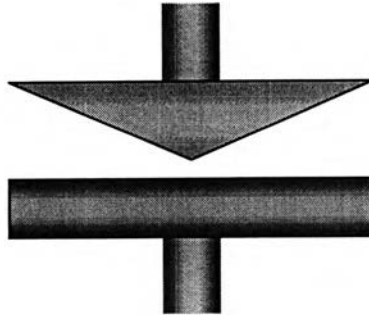
Figure 2.1 Cone-and-plate rheometer fixtures.

The measurable quantities and fixed parameters for cone-and-plate flow are the fixture radius, R, the cone angle, β, the rotational speed, ω (rad/s), the torque, τ, and the normal force, F. The following equations can be used to calculate quantities of rheological importance.

$$\dot{\gamma} = \frac{\omega}{\beta} \qquad \qquad \ldots(6)$$

$$\sigma = \frac{3\tau}{2\pi R^3} \qquad \qquad \ldots(7)$$

$$N_1 = \frac{2F}{\pi R^2} \qquad \qquad \ldots(8)$$

2.2.1.2 Conditions in Oscillatory Measurement

It is instructive to discuss the response of viscoelastic materials to an oscillatory shear. In oscillatory shear, a complex shear modulus G^* is given by:

$$\sigma(t) = G^*(\omega)\,\gamma(t) \qquad \qquad \ldots(9)$$

where $\qquad G^* = G' + iG''$

where G' and G'' are referred to the storage modulus and loss modulus, respectively.

As an alternative to the complex shear modulus, complex viscosity η^* can be defined as the ratio of the shear stress to the rate of shear:

$$\sigma(t) = \eta^* \, \dot{\gamma}(t) \qquad \qquad \ldots(10)$$

where
$$\eta^* = \eta' - i\eta''$$

where η' is the loss viscosity. The parameter η'', the storage viscosity, is related to the dynamic rigidity through $G' = \eta'' \, \omega$.

1) Dynamic Strain Sweep Default Test

Normally, the rheological properties of a viscoelastic material are independent of strain up to a critical strain level γ_c. Beyond this critical strain level, the material behavior is nonlinear and the moduli decline. So, the first step for characterization of viscoelastic behavior is the measurement of the strain amplitude dependence of the storage and loss moduli (G', G"). Dynamic strain sweep applies a range of sinusoidal strains, each at a constant frequency. The strains used in these experiments are in the range from 1-500%, the temperature from 140-200°C, and frequency of 1 rad/s.

2) Dynamic Frequency Sweep Default Test

Data can be generated for short and long time intervals outside the range of measurement by studying the frequency dependence of the storage and loss moduli over a wide range of temperature, and employing time-temperature superposition by horizontal shift the data for any temperature T onto the same curve as data for the reference temperature T_O. The horizontal shift factor a_T can be determined by measuring the temperature dependence of the viscosity.

$$a_T = \frac{\eta_o(T)}{\eta_o(T_o)} \qquad \qquad \ldots(11)$$

The relationship for $\eta_o(T)$ is the Arrhenius equation:

$$\frac{\eta_o(T)}{\eta_o(T_o)} = exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \qquad \ldots(12)$$

where E_a is an "activation energy for flow." This equation is often found to be valid as long as the temperature is at least 100K above T_g. The experiments were taken at the temperatures of 140, 160, 180, and 200ºC, frequencies ranging from 0.1-100 rad/s, and strain ranging from 5-50 %.

3) Dynamic Time Sweep Default Test

A material's mechanical stability can be sensitively assessed in a time sweep by simply measuring the moduli at a constant frequency, strain, and temperature in a selected atmosphere over an extended period of time. The experiments were taken at the temperatures of 160, 180, and 200ºC for a period of 2 hours and the time per measurement is 200 seconds. The strains used in these experiments were in the range from 15-300%.

2.2.1.3 Conditions in Steady State Measurement

Steady shear is a simple shear flow that has been carried out at a constant shear rate for a sufficient length of time that the stresses have reached steady values. In this case, the stresses are functions only of the shear rate. For a Newtonian fluid, the shear stress is proportional to shear rate,

$$\sigma = \eta\dot{\gamma}$$

and $N_1 = N_2 = 0$. The shear stress is not, in general, proportional to the shear rate, and the first and second normal stress differences are not equal to zero.

1) Steady Rate Sweep Default Test

Rate sweep applies steady shear deformation at user-commanded shear rates. Zero shear viscosity can be determined from a constant value η_o at low shear rates as shown in Figure 2.2.
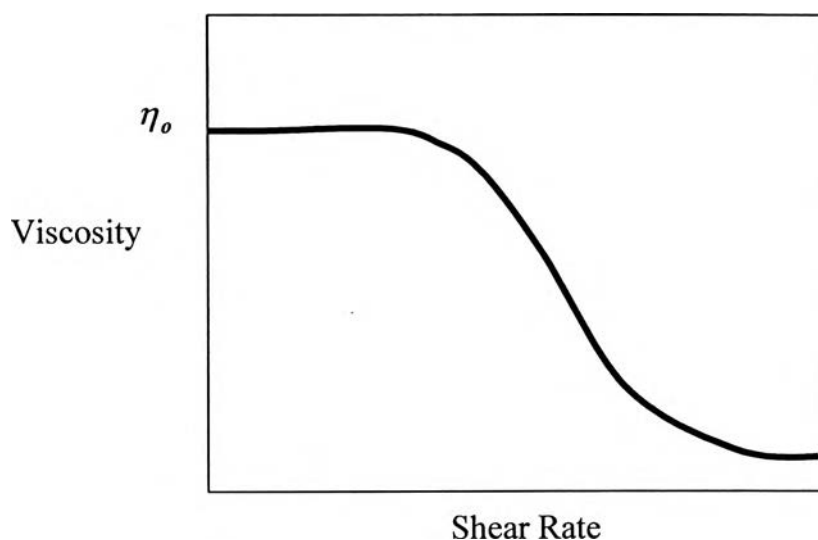

Figure 2.2 Viscosity versus shear rate curve for a shear thinning material.

The experiments were taken at the temperatures of 140, 160, 180, and 200°C and shear rates ranging from 0.01-100 s^{-1}.

2.2.2 Melt Flow Index Determination

The measurement was performed on the Zwick4105 melt indexer using a 'plug-in' temperature module. The melt flow index (MFI) was calculated as the weight of material extruded in 10 minutes. A free-flowing material has a higher MFI because a lot of the material is easy to extrude in 10 minutes while a stiff-flowing material emerges slowly from the die, hence a lower MFI. The temperature used in this experiment was set equal to 190°C with a loading of 10 kg.

2.2.3 Molecular Weight Determination

2.2.3.1 Gel Permeation Chromatography (GPC)

GPC (Waters 150-C Plus) is a form of liquid chromatography in which the molecules are separated according to their molecular size. The solution of H5690S and H5603B were prepared by dissolving 0.01g of each sample in solvent o-dichlorobenzene and stored in oil bath at 140°C until the pellet was absolutely dissolved. The procedure involved creating a calibration curve of standard high density polyethylene and injecting a dilute solution of H5690S and H5603B into a continuous flow of o-dichlorobenzene passing through a column containing tightly packed microporous gel particles at 140°C.

2.2.3.2 Melt and Solid Rheometer

Molecular weight distribution of the polymers which are slightly soluble in common solvents at ambient temperatures can be determined by rheological methods. The quantitative relationship that relates the observed mechanical properties of a polydisperse melt and the polymer structure is called a mixing rule. The double reptation mixing rule, used in the rheometer (Rheometric Scientific, model ARES) has the following mathematical structure:

$$G(t) = G_N \left[\int_0^\infty F^{\frac{1}{2}} (M,t)W(M)\,dM \right]^2 \qquad ...(13)$$

$G(t)$ is the relaxation modulus, $F^{1/2}(M,t)$ is the monodisperse relaxation function which represents the time dependent fractional stress relaxation of a monodisperse polymer following a small step strain, and $W(M)$ is the weight based molecular weight distribution. To calculate a molecular weight distribution for a given material it will be necessary to supply material

dependent data to the application. The plateau modulus G_N and the form of the monodisperse relaxation function $F^{1/2}(M,t)$ must be supplied.

The procedure is started from a known sample was loaded into cone-and-plate rheometer 8 mm and then the parameters were supplied at the reference temperature. Storage and loss modulus were measured at the frequencies ranging from 0.01-100 rad/s in order to cover both terminal and entanglement plateau zones. Molecular weight distribution was calculated by Orchestrator program. Table 2.1 shows the material parameters for molecular weight calculation.

Table 2.1 Material parameters of molecular weight calculation for high density polyethylene.

Parameters	HDPE
$T_{ref}(^oC)$	160
K_λ	3.58×10^{-20}
X	3.42
$G_N(dyn/cm^2)$	1.4×10^7
M_e	1900
M_c	2500
$E_A(kJ)$	27.3

K_λ is the front factor, x is the relaxation time, G_N is the plateau modulus, M_e is the molecular weight between entanglement points, M_c is the critical molecular weight for entanglement, and E_A is the activation energy.

2.2.4 The Percentage of Crystallinity

Differential Scanning Calorimetry (DSC) is specifically designed to measure the thermal properties of the material under examination. In this method 4-8 mg of a sample and a reference sample in film forms were

provided with independent heaters. The temperature of each cell was measured continuously and compared with the instantaneous value of the programmed temperature. The sample was heated from 50°C to 150°C at the heating rate of 20°C/min. and hold for 2 min at 150°C and then cooled from 150°C to 50°C at the cooling rate of 20°C/min.

The percentage of crystallinity can be calculated from

$$\% \, Crystallinity \;\; = \;\; \frac{\Delta H_f}{\Delta H_f^o} \times 100 \qquad\qquad ...(14)$$

where ΔH_f = the enthalpy of fusion of a semicrystalline polymer sample

ΔH_f^o = the enthalpy of fusion of a completely crystalline sample of the same polymer.

2.2.5 Fractured Surface Studies

2.2.5.1 Scanning Electron Microscopy (SEM)

The SEM (Joel model 5200, magnification: 35-200,000) provides unique information about the surfaces of materials and is outstanding for topographic examination. After removal from the rheometer, the sheared samples were heated at about 100°C for 1 hour to removed moisture and stored in desiccator before microscopic examinations. The examinations were separated into 2 parts: outer surface (the interface between polymer melt and aluminium plate) and inner surface (the surface of the sample after has been cracked under liquid nitrogen condition). The examinations for each part were also divided into 3 categories: below, critical, and above critical condition for the onset of fracture in order to compared the surface roughness. The samples were stick on stubs and coated with gold by ion sputtering device (JFC-1 100E) for 4 minutes. The examinations were taken through this microscope with magnification of 2,000.