# CHAPTER III

# EXPERIMENTAL

## 3.1 Materials

In this work, high density polyethylene (HDPE), low density polyethylene (LDPE), and polystyrene (PS) were chosen based on their differing molecular weights and polydispersity. The HDPE used were H5604F, H5840B, and H5690S (without additive) from Thai Polyethylene Co., Ltd.. The LDPE used were LD2130FA (without additive) from Thai Polyethylene Co., Ltd. and D2022, and S1018 from Thai Petrochemical Industry Public Co., Ltd.. PS was from sigma-aldrich. The physical properties of these materials are shown in Table 3.1 as quoted from the company

**Table 3.1** Physical properties of HDPE, LDPE, and PS used as quoted by manufacturer

| Materials | | $M_w$ (g/mol) | $M_n$ (g/mol) | $M_w/M_n$ | Density (g/cm$^3$) |
|---|---|---|---|---|---|
| HDPE | H5604F (no additive) | $2.7 \times 10^5$ | $3.5 \times 10^3$ | 77.4 | 0.956 |
| | H5840B (no additive) | $1.3 \times 10^5$ | $6.7 \times 10^3$ | 19 | 0.958 |
| | H5690S (no additive) | $2.4 \times 10^5$ | $5.8 \times 10^4$ | 4.1 | 0.956 |
| LDPE | LD2130FA (no additive) | - | - | - | 0.921 |
| | D2022 | - | - | - | 0.921 |
| | S1018 | - | - | - | 0.916 |
| PS | PS | $2.3 \times 10^5$ | $1.7 \times 10^5$ | 1.4 | 1.04 |

## 3.2 Characterization

### 3.2.1 Melt Flow Index Meter

Melt flow index measurement was carried out on a Zwick melt flow indexer (model 4105) following an ASTM D1238. The temperature was set at 190 °C with a load of 2.16 kg. 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 melt flow indices measured are tabulated below in Table 3.2

**Table 3.2** Melt flow index of HDPE, LDPE, and PS

| Materials | MFI (g/10min) | Quoted (g/10min) |
|---|---|---|
| H5604F (no additive) | 0.063 | 0.04 |
| H5840B (no additive) | 0.630 | 0.40 |
| H5690S (no additive) | 0.863 | 0.90 |
| LD2130FA (no additive) | 1.105 | 0.30 |
| D2022 | 1.413 | 0.25 |
| S1018 | 18.59 | 20.0 |
| PS | 8.34 | 7.50 |

### 3.2.2 Differential Scanning Calorimeter

Differential scanning calorimetry (DSC) was carried out on a NETZSCH (model DSC 200) differential scanning calorimetry. The technique determines a thermogram of polymer. Samples of 5-10 mg were prepared and put into aluminum sample pans. The temperature was programmed at a

heating rate of 10 $^0$C/min from 35$^0$C to 200 $^0$C. The chamber was purged with dry nitrogen at a flow rate 25 ml/min. The melting point ($T_m$) was determined from the thermogram by using the peak area method. Table 3.3 lists the melting temperatures found for our materials used.

**Table 3.3** Melting temperature of HDPE and LDPE

| Materials | $T_m(^oC)$ |
|---|---|
| H5604F (no additive) | 133.2 |
| H5840B (no additive) | 134.2 |
| H5690S (no additive) | 137.2 |
| LD2130FA (no additive) | 121.4 |
| D2022 | 117.6 |
| S1018 | 107.0 |

3.2.3   Gel Permeation Chromatography (GPC)

The molecular weight distribution (MWD) of polystyrene was determined by using gel permeation chromatography (GPC, Waters 600E) at room temperature (30$^o$C). The polystyrene standard solution was prepared by dissolving 0.3 g of standard polystyrene in 100 g of tetrahydrofuran. The standard solution was injected into a continuous flow of tetrahydrofuran passing through the series of column (Styragel HR 0.5, Styragel HR 4E, and Styragel HR 5E) which containing tightly packed microporous gel particles. The results from the standard polystyrene solution were used to determine the calibration curve by using Maxima 820 program. The polystyrene solution was prepared by dissolving 0.3 g of polystyrene in 100 g of tetrahydrofuran (THF). Then the solution was injected into a continuous flow of

tetrahydrofuran passing through a set of three columns at 30°C to measure the molecular weight distribution (MWD).

### 3.2.4 Melt and Solid Rheometer

Rheological measurements were carried out on a melt rheometer using a cone and plate geometry (Rheometric Scientific, model ARES). Cone and plate rheometer is widely used in rheometry for highly viscous polymer melts and concentrated polymer solutions. Figure 3.1 shows a scheme of the cone and plate rheometer. The advantages of the cone and plate geometry for using with melts are that small sample of material is needed, the shear rate is approximately uniform throughout the sample, and there is already access to all surfaces to facilitate sample loading and cleaning. The upper 25 mm fixture is a stainless steel cone with cone angle of 0.1 radian, while the lower 25 mm fixture is an aluminum disposable plate. The gap between cone and plate was fixed at 0.0508 mm. The transducer can measure torque in the range of 0.2 - 200 gm-cm for transducer no.1 and 2 - 2000 gm-cm for transducer no.2, respectively. The temperatures ranging from –150°C to 600°C. The rheometer can be used into 3 modes: steady state mode, dynamic mode and transient mode. The strain can be varied from 0.005% to 500% within a frequency range of 0.001-100 rad/s for the dynamic testing mode whereas it can apply shear rate from 0.1 to 100 $s^{-1}$ in steady state mode. Melt Rheometer provided us the required rheological data: storage modulus (G') and loss modulus (G").
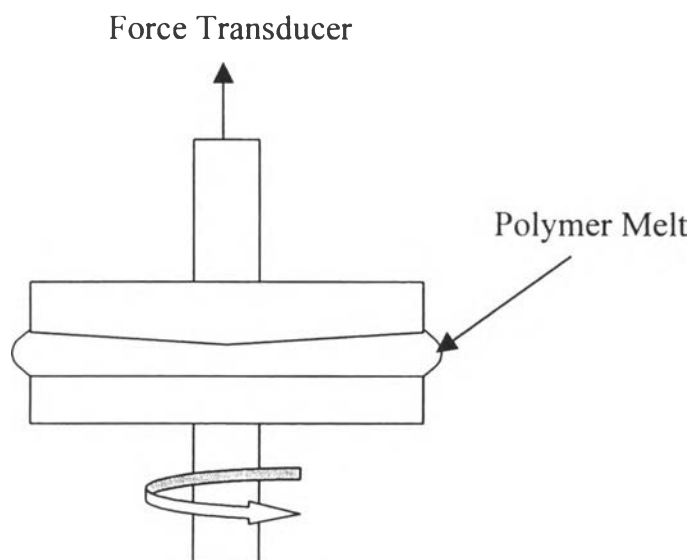
Force Transducer

Polymer Melt

**Figure 3.1** Schematic of cone and plate rheometer.

a) Sample Preparation

A compression molding (Wabash, model V50W-18-CX) was used to prepare samples by a melt mixing process. It consists of two heated plates: the upper plate is stationary whereas the lower plate is movable. The temperature of both plates was controlled by using air and water system. The pressure required to press the samples were between 10 tons.

b) Procedure

The temperature was set at a particular value ($T>T_m$). Then the gap was zeroed at the temperature to be operated. The sheeted samples were loaded between a cone and plate and subsequently set to the standard gap before starting the experiment. 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 mathematical formulars below.

c) Steady State Mode

The measurable quantities and fixed parameters for cone and plate flow are the fixture radius, $R$, the cone angle, $\beta$, the rotational

speed, $\omega$ (rad/s), the torque, $\tau$, and the normal force, $F$. the following equations can be used to calculate quantities of rheological importance.

$$\dot{\gamma} = \frac{\omega}{\beta} \tag{3.1}$$

$$\sigma = \frac{3\tau}{2\pi R^3} \tag{3.2}$$

$$N_1 = \frac{2F}{\pi R^2} \tag{3.3}$$

### 3.2.4.4 Oscillatory Mode Measurement

In oscillatory shear, a storage modulus (G') and loss modulus (G") are given by:

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{3.4}$$

$$\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) \tag{3.5}$$

where   $\gamma_0$ = strain amplitude

$\omega$ = angular frequency (rad/s)

Boltzmann's superposition principle gives:

$$
\begin{aligned}
\sigma(t) &= \int_{-\infty}^{t} dt' G(t-t')\gamma_0 \omega \cos \omega t \\
&= \gamma_0 \omega \left[ \int_0^{\infty} G(s) \sin \omega s \, ds \right] \sin \omega t + \\
&\quad \gamma_0 \omega \left[ \int_0^{\infty} G(s) \cos \omega s \, ds \right] \cos \omega t \\
&= \gamma_0 \omega \left[ G'(\omega) \sin \omega t + G''(\omega) \cos \omega t \right]
\end{aligned}
\tag{3.6}
$$

where  G' = storage modulus

G" = loss modulus

## 3.3 Experimental Procedure

### 3.3.1  Sample Preparation

For long time stability in the molten state and protection against oxygen, a stabilizer 1% IRGANOX1010 was added in HDPE (H5604F, H5840B, and H5690S) and LDPE (LD2130FA). Then compress polymer sample by using a compression molding to a disc form with 25 mm. in diameter and 1 mm. thick.

### 3.3.2  Rheological Measurement

The storage modulus (G') and loss modulus (G") were determined by using the melt rheometer. The sample was placed on the cone and plate rheometer in dynamic frequency sweep mode.

The cone and plate configuration (0.1 radian gap angle) was applied and tested at $160^{o}C$ for PS and at $190^{o}C$ for HDPE and LDPE. The dynamic strain sweep test was used to find the linear viscoelastic regime at frequency equal to 100 rad/s. After that the dynamic frequency sweep test was used to measure the storage modulus and loss modulus.

### 3.3.3  Molecular Weight Distribution Measurement

The molecular weight distribution of PS was determined by using gel permeation chromatography at room temperature ($30^{o}C$). For HDPE and LDPE, molecular weight distribution was determined by using gel permeation chromatography at high temperature ($140^{o}C$). The molecular weight distribution (MWD) measurements of HDPE and LDPE were provided from Thai Polyethylene Co., Ltd. (TPE) staff.

**Table 3.4** Molecular Weight Distribution of HDPE, LDPE, and PS

| Material | $M_w$ (g/mol) | $M_n$ (g/mol) | $M_w/M_n$ |
|---|---|---|---|
| H5604F | $4.9 \times 10^5$ | $6.4 \times 10^2$ | 77.3 |
| H5840B | $4.7 \times 10^4$ | $1.1 \times 10^3$ | 40.5 |
| H5690S | $4.5 \times 10^4$ | $2.0 \times 10^3$ | 22 |
| S1018 | $7.2 \times 10^4$ | $6.4 \times 10^2$ | 111 |
| LD2130FA | $5.4 \times 10^4$ | $1.5 \times 10^3$ | 37.2 |
| D2022 | $1.1 \times 10^5$ | $5.7 \times 10^3$ | 18.5 |
| PS | $2.3 \times 10^5$ | $3.4 \times 10^4$ | 6.7 |

## 3.4 Computations

### 3.4.1 Raw Data Manipulation

The data from GPC were discretized by using linear interpolation before using in the calculations of G' and G''.

a) From molecular weight distribution of gel permeation chromatography:

Molecular weight (N) and volume fraction (v)

b) Discrete data:

$$\text{deltamw} = \frac{\text{mw max} - \text{mw min}}{\text{ndiv}} \qquad (3.7)$$

where   deltamw = molecular weight increment

mwmax = maximum molecular weight

mwmin = minimum molecular weight

ndiv = number of discrete molecular weight

c) Calculate new molecular weight data (mw) :

$$mw(n) = mw\,min + \left[(n-1) * deltamw\right] \qquad (3.8)$$

d) Calculate new volume fraction (nv):

if $(N(m) < mw(n) < N(m+1))$ then

$$nv(n) = v(m) + \left[\frac{mw(n) - N(m)}{N(m+1) - N(m)}\right] * \left[v(m+1) - v(m)\right] \qquad (3.9)$$

e) Normalize new volume fraction:

$$nv(n) = \frac{nv(n)}{\sum\limits_{i=1}^{ndiv} nv(i)} \qquad (3.10)$$

### 3.4.2 Calculation of Storage Modulus and Loss Modulus Using Double Reptation Theory

From molecular weight distribution, after discreting the GPC raw data, the distribution was used to predict the storage modulus (G') and loss modulus (G") by using the double reptation model and then the calculated values of G' and G'' were compared with the experimental data.

a) From double reptation theory the stress-relaxation modulus, $G_{total}(t)$, can be calculated from equation

$$G_{total}(t) = G_N^o m_d(t) \qquad (3.11)$$

b) From molecular weight distribution:

Constitutive equation of double reptation theory is

$$m_d(t) = \sum_A \sum_B w_A w_B p_A(t) p_B(t) = \left[\sum_i w_i p_i(t)\right]^2 \qquad (3.12)$$

where $\quad m_d(t)$ $\quad=$ fraction of unrelaxaed stress at time t

$\quad\quad\quad\quad w_i$ $\quad=$ volume fraction of chain i

$\quad\quad\quad\quad p_i$ $\quad=$ the tube survival probability of chain i at time t

c) The tube survival probability of chain i at time t can be calculated from:

$$p_i(t) = \exp\left[-t\Big/\tau_{rep,i}\right] \quad\quad (3.13)$$

where $\tau_{rep}$ is the characteristic relaxation time of chain i

$$\tau_{rep,i} = KM_{w,i}^{3.4} \quad\quad (3.14)$$

where K is the empirical parameter

d) Once we get $G_{total}(t)$ we can calculate storage modulus (G') and loss modulus (G") by

$$G'(\omega) = \omega \int_0^\infty G_{total}(t)\sin(\omega t)dt \quad\quad (3.15)$$

and

$$G''(\omega) = \omega \int_0^\infty G_{total}(t)\cos(\omega t)dt \quad\quad (3.16)$$