

CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

2.1.1 High Density Polyethylene (HDPE)

The HDPE used in this work was blown-film grade A3355, supplied by Thai Petrochemical Industry Public Co., Ltd. The material was in pellet form with MFI 0.06 (2.16 kg/ 190°C).

2.1.2 Starch

Starch was supplied by Siam Modified Starch Co., Ltd. Two types of starch were used in this work :

- Tapioca starch
- Rice starch

2.1.3 Calcium Oxide (CaO)

CaO was purchased from BDH Laboratory Supplies.

2.1.4 Natural Rubber (TTR5L)

This rubber was obtained from Victor & Prosper Limited Partnership Co. Ltd.

2.1.5 Zinc Stearate (C₃₆H₇₀O₄Zn)

This chemical was purchased from Imperial Industrial Chemical (Thailand) Co., Ltd.

2.2 Instruments

2.2.1 Two-roll Mill

A Lab Tech LRM 110 two-roll mill was used to mill HDPE and natural rubber compounds. The temperature of the front roll and the back roll were 160°C and 150°C, respectively. The blends were milled for 8 min. The materials were removed from the mill and granulated.

2.2.2 Twin-screw Kneader

The materials were mixed in a Collin co-rotating twin-screw kneader ZK-25 (25 x 30D). After passing through the extruder the extrudate was air cooled before being cut into pellet form in a pelletizer.

2.2.3 Compression Molding Machine

The granules of the samples were pressed on a Wabash V50H compression press. The steps used in the process for this study were 180°C without pressure for 5 min, 180°C with 5 tons force for 5 min, and 180°C with 20 tons force for 5 min. Moldings were cooled under pressure to room temperature. The mold used was a picture-frame type made from stainless steel coated with chromium. Thickness of the mold cavity was about 0.8 mm.

2.2.4 Capillary Rheometer

The capillary rheometer used was an Instron model 3213 with a 25 kN load cell operated with constant piston speed. Test temperatures used were 160, 180, and 200°C. The capillary was a tapered type having a length of 2.5507 mm and a diameter of 0.7645 mm, giving a length to diameter ratio of 33.4. The diameter of the barrel was 9.525 mm.

2.2.5 Dynamic Mechanical Spectrometer

Viscoelastic and elastic behaviors of the samples were determined by a Rheometric Scientific RHIOS instrument using the mode of “ frequency sweep default test ” and “ step rate default test ”, respectively. All tests were done in a rectangular torsion fixture at 30°C.

2.2.6 Scanning Electron Microscope (SEM)

SEM digitized micrographs were obtained from a JEOL 5200-2AE (MP 15152001) scanning electron microscope with magnification range of 35-200,000 times. Micrographs of the fractured surfaces were made using a voltage of 15-25 kV and 350-1,000X magnification.

2.3 Procedure

2.3.1 Sample Preparation

2.3.1.1 *Masterbatch Preparation.*

- Starch Masterbatch

Starch was dried in a hot air oven at 100°C for 2 hours and then stored in a desiccator before use. HDPE was compounded with 50 wt % of starch and 4 wt % of CaO in a twin-screw extruder. The compounded material was then pelletized and stored in sealed containers.

- Zinc Stearate Masterbatch

10 wt % of zinc stearate was blended with HDPE in a twin-screw extruder. The product was pelletized and stored in sealed containers prior to use.

- Rubber Masterbatch

HDPE was compounded with 25 wt % of natural rubber on a two-roll mill for 8 min. The temperature of the front roll and the back roll were 160°C and 150°C, respectively. The product was comminuted in a granulator.

Table 2.1 Conditions for compounding materials in the twin screw extruder

Condition		Sample		
		Starch Masterbatch	Zinc Stearate Masterbatch	Starch-based HDPE Blend
Feed Rate (arbitrary units)		200	200	300
Temperature (°C)	Zone 1	145	110	145
	Zone 2	155	120	155
	Zone 3	160	145	160
	Zone 4	160	160	160
	Zone 5	160	160	160
	Zone 6	160	160	160
Screw Speed (rpm)		55	40	55

2.3.1.2 Compounding. HDPE was compounded with 8 wt % of the rubber masterbatch, 10 wt % of the zinc stearate masterbatch and 0-40 wt % of the starch masterbatch in a twin-screw extruder. The blends were pelletized and stored in sealed containers prior to use.

2.3.1.3 Molding. The blended materials were compression-molded to form 0.8 mm thick plaques in a press at 180°C for 15 min.

2.3.2 Rheological Measurements

2.3.2.1 *Viscous Behavior.* A capillary rheometer (Instron model 3213) was used to study the flow behavior of the blends under steady-state conditions. This test was performed in accordance to ASTM D3835-90.

- Methodology

Initially, the required temperature and plunger speed schedule were set. The material was poured into the barrel through a funnel and packed down with a plunger until the first extrudate appeared at the capillary exit. The sample was allowed to reach the set temperature (after 5-10 min) then forced through the capillary by the plunger at pre-selected velocities. The next velocity in the measurement schedule began when the load versus extension curve reached a slope close to zero. The load, together with the corresponding plunger speed, were used to calculate the shear stress and the shear strain for the specimen under test.

- Calculation

It was assumed that the melt was incompressible, the flow was laminar and fully developed, and there was no slippage at the wall.

The load on the plunger and the plunger speed were converted into apparent shear stress and shear rate at the wall respectively by using the following equations involving the geometry of the capillary and the barrel.

$$\tau_w = \frac{FD_c}{4A_p L_c} \quad (2.1)$$

where

$$\begin{aligned} \tau_w &= \text{apparent shear stress at the wall} \\ F &= \text{the force acting on the plunger} \\ A_p &= \text{cross sectional area of the plunger} \\ D_c &= \text{diameter of the capillary die} \end{aligned}$$

L_c = length of the capillary die

$$\dot{\gamma}_w = \frac{2V_p D_p^2}{15D_c^3} \quad (2.2)$$

where

$\dot{\gamma}_w$ = apparent shear rate at the wall

V_p = plunger speed

D_b = barrel diameter

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} \quad (2.3)$$

where

η_a = apparent viscosity

The true shear rate was determined by using the Rabinowitsch correction,

$$\dot{\gamma}_{tr} = \frac{3n+1}{4n} \dot{\gamma}_w \quad (2.4)$$

where

$\dot{\gamma}_{tr}$ = true shear rate

n = Power law index

Thus, “n” was the slope of the plot of $\log \tau_w$ versus $\log \dot{\gamma}_w$, computed by the application of regression analysis.

In this study, the Bagley correction was not applied because the L/D ratio was 33.3, which was sufficiently long to neglect end effects. So the true viscosity was determined from

$$\eta_{tr} = \frac{\tau_w}{\dot{\gamma}_{tr}} \quad (2.5)$$

2.3.2.2 *Elastic Behavior.* Compression molded sheets were cut into rectangular strips of dimension 8 mm x 36 mm x 0.8 mm. The shear stress-strain curve of the blends were determined by a Rheometric Scientific RHIOS instrument using the mode of “ step rate default test ”. The samples were subjected to 0.001% strain, ranging in time from 0 to 8 sec at 30°C.

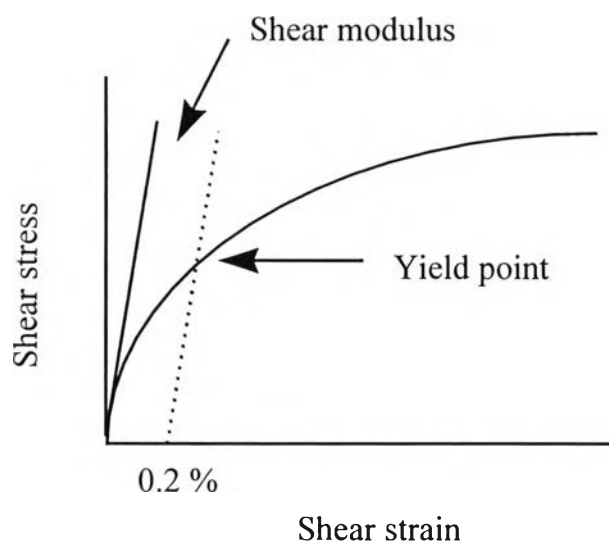


Figure 2.1 Shear stress-strain curve of a solid.

Figure 2.1 shows shear stress-strain curve of a solid. The values of shear modulus, shear yield stress, and shear yield strain are obtained from this curve. The initial slope of the curve is equal to shear modulus value. The shear stress and shear yield strain are the corresponding stress and strain values at the yield point, respectively. Yield point is defined as the point at which a line beginning at 0.2 % shear strain and having a slope equal to the initial slope of the curve, crossed the curve.

2.3.2.3 *Viscoelastic Behavior.* Molded sheets were cut into rectangular strips of dimension 8 mm x 36 mm x 0.8 mm. A Rheometric Scientific RHIOS instrument was used to evaluate the viscoelastic behavior of the blends by using the mode of “ frequency sweep default test ” The samples were subjected to a sinusoidal strain in the torsion mode. The blends were subjected to 0.05% strain between frequencies of 0.1 and 100 rad s⁻¹ at 30°C.

2.3.3 Microstructure Characterization

The fractured samples obtained after impact testing were cut about 2 mm below the fractured surface and stuck to aluminium stubs. The samples were then coated with gold by vapour deposition and observed under a scanning electron microscope (JEOL 5200-2AE).