CHAPTER III
EXPERIMENTAL SECTION

3.1) Materials

Linear low-density polyethylene used for the experiment was blown-film grade L1810F, supplied by Thai Polyethylene Co., Ltd. Natural rubber was STR 5L grade, purchased from Rayong Bangkok Rubber Co., Ltd. Maleic anhydride used as compatibilizer was purchased from Fluca Co., Ltd. Calcium carbonate was supplied by Lime Quality Co., Ltd. The characteristics of the materials used are given in Table 1.

3.2) Instruments

3.2.1 Two-Roll Mill

A Lab Tech LRM 110 two-roll mill was used for masticating natural rubber (NR) at room temperature and grafting maleic anhydride (MA) to linear low-density polyethylene (LLDPE) and natural rubber at 170°C.

3.2.2 Twin-Screw Kneader

The materials were mixed in a Collin co-rotating twin-screw kneader ZK-25. After processing through the extruder, the extrudate was cooled by water and cut into pellet by a pelletizer.

3.2.3 Melt Flow Index Tester

The melt flow index were determined by using ZWICK model 4105 Extrusion Plastomer with recommended temperature of 190°C and a load of 10 kgs for polyethylene. The procedure was followed ASTM 1238.

Table 1.Characteristics of the raw materials.

Physical Properties	LLDPE	NR	MA
MFI (g/10 min)	1	-	-
M_w	84460	86536	-
MWD	24.26	5.5	-
Density(gcm^{-3})	0.918	0.900	0.934

3.2.4 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 170°C without pressure for 3 min, 170°C with 5 tons force for 2 min, and 170°C with 15 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 3.2 mm.

3.2.5 Capillary Rheometer

The capillary rheometer used was an Instron model 4303 with a 25 kN load cell operated with constant piston speed. Test temperatures used were 140, 160 and 180°C. The die was a 45° tapered type no.614 having a length of 25.51 mm. and a diameter of 0.7645 mm. Its length to diameter ratio was 33.4. The diameter of the barrel was 9.525 mm. And barrel length was 289 mm.

3.2.6 Dynamic Mechanical Spectrometer

The dynamic measurements were carried out on a Rheometric Scientific RHIOS instrument using a cone-and-plate geometry in the temperature range 140–180°C. Torsion rectangular geometry was used for measure the elastic behavior of the samples below 30°C. Depending on the temperature and frequency, the strain amplitude was taken between 25 and

50% to obtain a high enough value of the torque. It was always verified that the behavior of the sample was in the range of linear viscoelasticity.

3.2.7 Scanning Electron Microscope (SEM)

SEM digitized micrographs were obtained from a JEOL 5200-2AE (MP52001) scanning electron microscope with magnification range of 35-200,000 times. The samples fractured under liquid nitrogen were coated with gold to make them electrically conductive. Fractured samples were also subjected to selective extraction in toluene for at least 2 days to remove the NR phase and then examined in the SEM. Micrographs of the fractured surfaces were made using a voltage of 5 kV and 2000X magnification.

3.3) Procedures

3.3.1 Sample Preparation

Binary blends of NR and LLDPE with and without MA were prepared by melt mixing techniques. The polymer blending process involved three steps. First the natural rubber was masticated for 10 minutes on a temperature controlled two-roll mill at room temperature then MA was added. The mixing was continued for 5 minutes before sheeting off the rubber blend. The second step was the preparation of MA-g-LLDPE. The LLDPE was melted on the two-roll mill at 170°C and then MA was added and blended for another 5 minutes. After that the sheet of MA-g-NR was added into the blends. The mixing was continued for another 3 minutes. The milled blend was then cut into pieces and pelletized again in the pelletizer. The third step was blending in the twin screw extruder. The extruder was operated at temperature setting from zone 1 to die of 150, 155, 160, 175, 185 and 195°C respectively and a screw speed of 130 rpm. The extrudates were quenched in a water bath and

pellettized. For mechanical testing, the blended materials were compressed at 170°C and cut into rectangular strips of dimension 12.9 X 36 X 2.9 mm.

3.3.2 Rheological Measurements

3.3.2.1 Capillary Rheometer Studies

The flow behavior of the blends under steady-state conditions was studied by using an Instron model 4303 capillary rheometer. 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. A precise temperature can be controlled in the range of 40-400°C and temperature stability of ± 0.5°C. The capillary used was a tapered type having a length of 25.507 mm and a diameter of 0.7645 mm. The diameter of the barrel is 9.525 mm. Test temperatures used were 140, 160, and 180°C. The velocity schedule used is following the Table 2.

Steady viscosity measurement

Firstly, the required temperature and plunger speed schedule were set on the computer program and then the material was poured into the barrel and packed down with a plunger. The sample was heated to a required temperature about 5-10 min and then forced out through a capillary die located at the bottom of the Instron machine at a constant plunger speed. The next velocity in the measurement schedule began when the load versus extension curve reached a slope close to zero. The computer recorded the resultant forces. These forces, together with the corresponding plunger speeds, were used to calculate the shear stress and shear rate for the specimen under test by simple mathematical calculations involving the geometry of the extruder.

Table 2. The velocity profile schedule used in capillary rheometer.

Velocity number	Velocity (mm/min)	Term Slope (kN/mm)	Time Limit (sec)	Graph Maximum Load* (kN)	Graph Maximum Extention (mm)
1	1	-300	210	500	3.5
2	3	-300	200	500	10
3	5	-300	150	500	12.5
4	7	-300	100	500	11.67
5	15	-300	55	500	13.75
6	20	-300	50	500	16.67
7	30	-300	25	500	12.5
8	40	-300	18	500	12
9	60	-300	12	500	12
10	150	-300	5	500	12.5
11	200	-300	4	500	13.33

In our calculations, we assumed that the polymer melt was incompressible, the flow was laminar and fully developed and there was no slippage at the wall. The force and the crosshead speed were converted into shear stress and shear rate at the wall respectively using the following equations involving the geometry of the capillary and the plunger.

$$\tau_w = \frac{F}{4A_p\left(\frac{l_c}{d_c}\right)} \tag{3.1}$$

where

τ_w = apparent shear stress at the wall

F = the force acting on the plunger

A_p = cross sectional area of the plunger (mm^2)

l_c = length of the capillary die (mm)

d_c = diameter of the capillary die (mm)

$$\dot{\gamma}_w = \frac{32Q}{\pi d_c^3} \tag{3.2}$$

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

Q = the volume flow rate (mm³/s)

In order to obtain better results, the Rabinowitsch correction was applied to the above equations. The shear rate at the wall for a power-law model fluid is given by

$$\dot{\gamma}_{tr} = \left(\frac{3n+1}{4n}\right)\frac{32Q}{\pi d_c^3} \tag{3.3}$$

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

n = power law index is defined by;

$$n = \frac{d(\log \tau_w)}{d\left(\log \dot{\gamma}_w\right)}$$

and n is determined by regression analysis of the value of slope from the plot of $\log \tau_w$ and $\log \dot{\gamma}_w$ obtained from the experimental data.

Similarly, true shear stress at the wall is calculated by applying Bagley correction according to the following expression;

$$\tau_w = \frac{\Delta P}{2[(L/R)+e]} \tag{3.4}$$

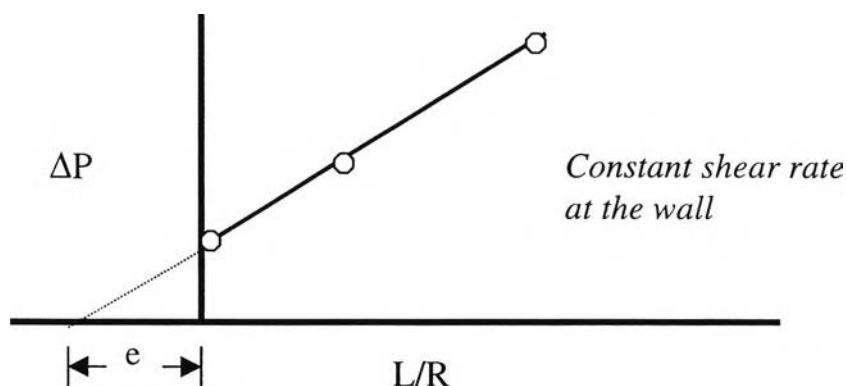where the Bagley correction factor term "e" is evaluated from the flow data recorded with at least three different dies of L/R.

Figure 3.1 Variation of entrance-exit pressure drop ΔP with L/R ratio of capillary at constant shear rate.

In this study, the end correction was not applied. So the viscosity was determined from

$$\eta = \frac{\tau_w}{\dot{\gamma}_{tr}} \qquad (3.5)$$

For Newtonian fluid the viscosity is independent of the shear rate, but the viscosity of non-Newtonian fluid change with shear rate. Figure 3.2. presents schematic plot of shear stress versus shear rate for Newtonian and non-Newtonian fluids. Polymer solution and melt are usually non-Newtonian, their viscosity's decrease when the shear rate increase. This phenomenon is called shear thinning or pseudoplasticity. Less common is shear thickening or dilatancy in which the viscosity increases with increasing shear rate.

3.3.2.2 Cone-and-plate Rheometer studies

The cone- and-plate rheometer is widely used for measurements of shear flow rheological properties of a polymer melt. This instrument is a mechanical spectrometer that is capable of subjecting a sample to either a dynamic (sinusoidal) or steady (linear) shear strain (deformation), then

measuring the resultant torque expended by the sample in response to the shear strain. Shear strain is applied by the motor, torque is measured by the transducer.

Viscoelastic measurement

A Rheometric Scientific RHIOS instrument was used to evaluate the viscoelastic behavior of the blends by using the mode of "Dynamic frequency sweep default test". The sample were subjected to a sinusoidal strain in cone-and-plate (cone diameter = 25 mm and angle = 0.1 rad) geometry. The blends were subjected to 25-50% strain between frequencies of 0.1 and 100 rad/sec at temperature of 140, 160, and 180°C. In this work, the complex viscosity (η^*), storage modulus (G') and loss modulus (G") were measured as a function of frequency (ω).

Shear stress

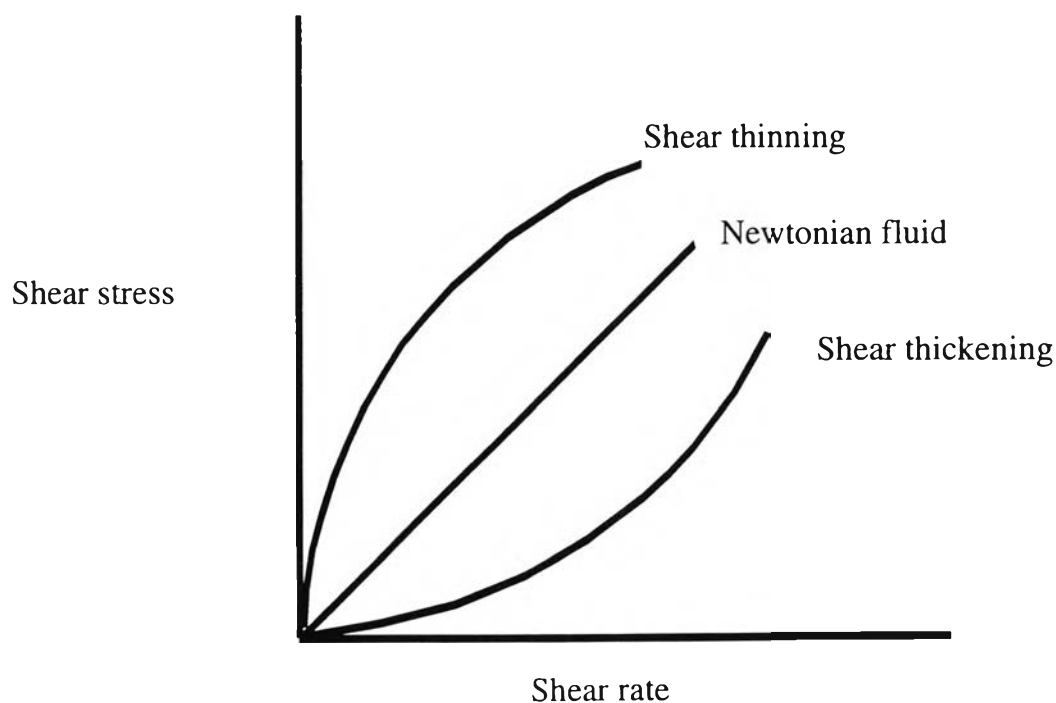Shear thinning

Newtonian fluid

Shear thickening

Shear rate

Figure 3.2. Schematic plot of shear stress versus shear rate for Newtonian and non-Newtonian fluids.

3.3.2.3 <u>Torsion Rectangular Rheometer Studies</u>

The torsion rectangular rheometer is used for study the dynamic mechanical properties of materials.

In a dynamic mechanical test, an oscillatory strain is applied to a sample and the resulting stress developed in the sample is measured. For solids, the resulting stress is proportional to the strain amplitude, and the stress and strain signals are in phase. If the sample is a fluid and it behaves ideally, then the stress is proportional to the strain rate. In this case, the stress signal was out of phase with the strain signal; i. e. leading the strain signal by $90°$. So the stress signal generated by a viscoelastic material can be separated into two components: an elastic stress which is in phase with the strain, and a viscous stress which is in phase with the strain rate ($90°$ out of phase with the strain). The elastic and viscous stresses are related to material properties through the ratio of stress to strain, modulus. Thus the ratio of elastic stress to strain is the storage modulus (G') and the ratio of the viscous stress to strain is the loss modulus (G"). The complex modulus (G*), a measure of a material overall resistance to deformation, can be calculated from:

$$G^* \quad = \quad G' \ + \ iG'' \tag{3.6}$$

where i is the imaginary unit

The ratio of the loss modulus to the storage modulus is the tangent of the phase angle shift " δ " between the stress and the strain thus:

$$\tan\delta \quad = \quad \frac{G''}{G'} \tag{3.7}$$

This measures the damping ability of the material. Tanδ, a damping term, is a measure of the ratio of energy dissipated as heat to the maximum energy stored in the materials during one cycle of oscillation. The dynamic

mechanical behavior of an ideal polymer is shown in Figure 3.3. The maximum point in G" and tanδ are sometimes used as the definition of T_α or glass transition temperature of material in which the portion of the molecule excited comprises from 10 to 50 atoms or more.
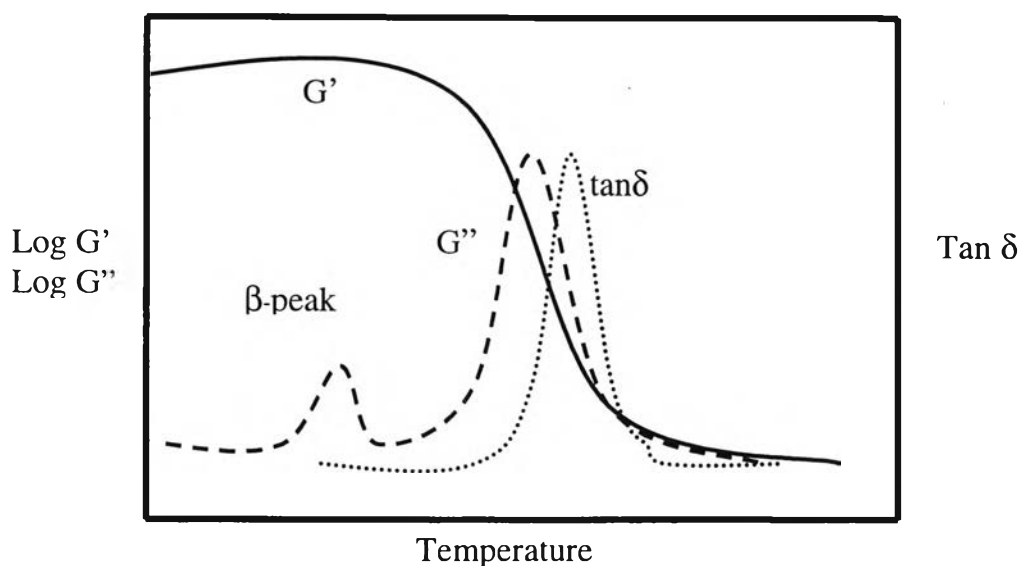

Figure 3.3. The dynamic mechanical behavior of an ideal polymer.

Glass transition temperature (T_g) measurement

The glass transition temperature (T_g) of pure LLDPE, NR and their blends were determined by using torsion rectangular geometry of a Rheometric Scientific RHIOS instrument in the mode of "temperature step default test". The rectangular samples were scanned isochronally at 3°C/min between −100°C and 30°C at frequency of 1 rad/sec and 0.06% strain.

3.3.3 Time-Temperature Superposition

Rheological properties are usually highly temperature dependent. This means that to obtain a complete picture of the behavior, even if the behavior is linear, experimental must be carried out at several temperatures. It is often found that data, for example G'(ω), G"(ω), taken at several temperatures can

be brought together on a single master curve by means of "time-temperature superposition". This greatly simplifies the description of the effect of temperature. Furthermore, it makes possible the display on a single curve of material behavior covering a much broader range of time or frequency than can ever be measured at a single temperature. Materials whose behavior can be displayed in this way are said to be "thermorheologically simple".

A master curve is prepared by first calculating a shift factor for each test temperature relative to some reference temperature. The shift factor is a measure of how a material's frequency response changes with temperature changes relating the material's behavior at a given test temperature to its behavior at a reference temperature. Several methods are used to calculate the shift factor such as Arrhenius equation;

$$a_T \quad = \quad \exp\left\{ \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0} \right) \right\} \tag{3.8}$$

where E_a ="activation energy for flow" and T_0 = reference temperature. This equation is often found to be valid as long as the temperature is at least 100 K above T_g. Closer to the glass transition temperature, The WLF equation has been found useful.

$$\text{Log } (a_T) \quad = \quad \frac{-C_1^\circ (T - T_o)}{\left[C_2^\circ + (T - T_o) \right]} \tag{3.9}$$

Time-temperature superposition procedures can be derived for any type of strain history. If the ratio $(T_0 \rho_0 / T\rho)$ varies little with temperature, superposition can often be accomplished by plotting;

$$G'(\omega) \text{ versus } \omega a_T$$

$$G''(\omega) \text{ versus } \omega a_T$$