

CHAPTER III
EXPERIMENTAL PART

3.1 Materials

3.1.1 Linear Low Density Polyethylene (LLDPE)

In this study, linear low density polyethylene (LLDPE) of film extrusion grade (L1810FI) was used as the polymer matrix. Some physical properties were listed in Table 3.1.

Table 3.1 Physical properties of LLDPE films.

Properties	Value
MFI (g/10min.)	1.0
Density (g/cm ³)	0.918
Tensile strength (kg/cm ²)	MD:105, TD*:110
Tensile strength at break (kg/cm ²)	MD:410, TD*:320
Ultimate elongation (%)	MD:620, TD*:840
Tear resistance (g/25 micron)	MD:145, TD*:370
Falling dart impact strength (mJ/mm ²)	150*

Note: * film thickness = 38 micron, BUR = 2, DR = 1, MD = machine direction and TD = transverse direction

3.1.2 Natural Rubber (NR)

The natural rubber (NR) was used as dispersed phase from Rayong Bangkok Rubber was used NR grade STR 5L. Some specifications were listed in Table 3.2.

Table 3.2 Specification for standard Thai rubber (STR 5L).

Specification	Specification limit
Dirt	0.04
Retained in 44 μ aperture (max, % wt.)	
Ash (max. % wt.)	0.40
Nitrogen (max. %wt.)	0.60
Volatile matter (max. %wt.)	0.80
Initial plasticity (P_0) (min.)	35
Plasticity Retention Index (PRI) (min.)	60
Color Lovibond Scale (Individual value, max.)	6.0

3.1.3 Maleic Anhydride (MA)

Maleic anhydride (MA) from Fluka company with density 0.20 g/cm^3 and melting point $52.6 \text{ }^\circ\text{C}$ was used. This material was used to form *in-situ* the compatibilizer in blending of LLDPE/NR. The reason for using this material as a compatibilizer was the succinic anhydride attached to the chain ends of PE and attached to double bond of NR led to form a miscible blend of LLDPE/NR.

3.2 Experimental

3.2.1 Characterization of the Materials

3.2.1.1 Weight Average Molecular weight (M_w), Number Average Molecular weight (M_n) and Molecular Weight Distribution (MWD)

Gel permeation chromatography (GPC) was performed by Waters 150 C ALC/GPC connected with 3 columns of μ -styragel 10^4 , 10^5 , 10^6 . Dichlorobenzene at 140°C was used as solvent at a flow rate of $1 \text{ cm}^3/\text{min}$. The calibration curve preparation is shown in Appendix B.

Room temperature gel permeation chromatography (GPC) was carried out by Waters 600E to determine the molecular parameters of NR. Tetrahydrofuran was used as solvent. The operating temperature, flow rate, and injection volume were 35.2°C , $1 \text{ cm}^3/\text{min}$, and $60 \text{ }\mu\text{L}$, respectively. Characteristics of the column HT4 were calibrated using narrow standard polystyrene (see also Appendix B).

3.2.1.2 Melt Flow Index (MFI)

The materials were tested for melt flow index at temperature 190⁰C with load cell 2.16 Kg according to ASTM D 1238.

3.2.2 Preparation the Materials

3.2.2.1 Twin Screw Extruder

LLDPE and NR were preliminary grafted by maleic anhydride with 75 and 25 wt% respectively, then LLDPE-g-MA and NR-g-MA were mixed on a two-roll mill at temperature 170⁰C for 5 min. The premix was then processed in the Collin twin screw extruder.

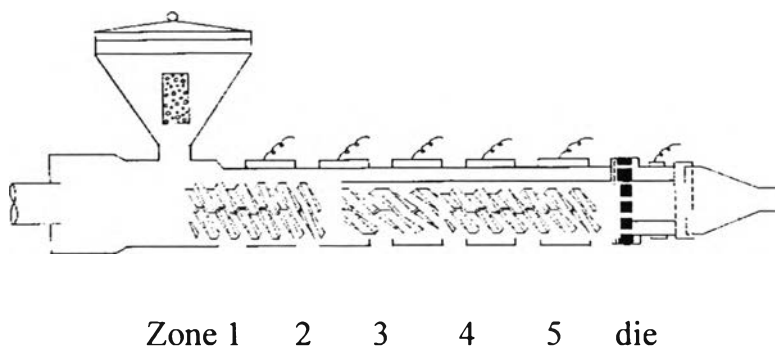


Figure 3.1 Twin screw extruder.

Temperature settings from zone 1 to die were 150, 155, 160, 175, 185, and 195 ⁰C, respectively with a screw speed of 130 rpm. The extrudate was cooled in water at 25⁰C and pelletized by granulator.

This set of temperature series was obtained by trial and error and as recommended by Collin manual.

3.2.2.2 Blown Film Extrusion

The seven compositions of LLDPE and LLDPE/NR blends were processed in Betol blown film extruder that has a single flight screw of 15 mm diameter and a L/D ratio of 40. The molten materials were extruded through a 25 mm annular die with a die gap of 0.5 mm. The freeze line was set at 100 mm. Blow up ratio was varied from 1, 3 and 5. Each blow up ratio was varied with three-draw ratio 1, 3 and 5 respectively (see Appendix A).

Temperature settings for blown film from zone 1 to die were 150, 155, 160, 175, 185, and 195 °C respectively. Screw speeds for blown film was 75 rpm.

3.2.2.3 Chill Roll Cast Film Extrusion

The LLDPE and LLDPE/NR blends were melted in a Collin chill roll cast film extruder with a diameter of 30 mm and L/D of 40. Extrusion was performed through a flat-slit, 20000 mm² (80 mm X 250 mm) in size. The extruded melt entered a tempering two-drum unit that provided reliable tempering and a strict hindering of longitudinal flow by superposition of a strong viscous drag before a subsequent extension and crystallization. Draw ratio was varied from 1, 3, and 5.5. The prepared film was wound on a standard bobbin.

Temperature settings for chill roll cast film from zone 1 to die were 150, 155, 160, 175, 185, and 195 °C respectively. Screw speeds of chill roll cast film was 100 rpm.

3.2.3 Testing the Properties of the Blends

3.2.3.1 Melt Viscosity of Blend Component

The polyethylene resins and the corresponding compounds in a pellet form were tested by following ASTM D 3835-90 using Instron capillary rheometer model 3213 at 180 °C and shear rate ranging from 30 to 1200 s⁻¹ with a 25 kN load cell (the L/D ratio of capillary die was 40). The Rabinowitsch corrections were applied to the capillary rheometer data.

3.2.3.2 Scanning Electron Microscope

The phase morphology of the blends was examined by using of a Jeol JSM 5200 at 10 kV scanning electron microscope. Capillary extrudates were cryogenically fractured in liquid nitrogen, and underwent etching to selectively remove NR by toluene extraction. Sample was gold- sputtered and examined. The magnification was 2,000X.

3.2.3.3 Thermal Properties

Thermal properties were analyzed by differential scanning calorimeter (DSC) with N₂ cooling unit. Heating and cooling curves of selected films were obtained at 10⁰C /min. The degree of crystallinity was calculated as weight fraction relative to 100% degree crystallinity of polyethylene (heat of fusion $\Delta H_{f100} = 299.1 \text{ J/g}$).

3.2.4 Mechanical Properties

3.2.4.1 Tensile Properties Testing

Tensile strength at break of LLDPE/NR blown film and chill roll cast film in both the MD and TD were measured using a Lloyd universal-testing machine. The test was conducted according to ASTM D882. Cutting strips of uniform width and thickness from the film samples were used as test specimens. The specimens used were 125-mm long, 25.4 mm wide and 30-100 μm thick. Ten specimens for five MD and five TD, were tested and the results were averaged to obtain a mean value. Test conditions were summarized in Table 3.3.

Table 3.3 Test condition for tensile testing.

Test parameter	Value
Load cell (N)	2500
Initial grip separation (mm)	25
Crosshead speed (mm/min)	500
Initial strain rate (mm/mm.min)	10

3.2.4.2 Impact Strength

Impact resistance for films were determined following ASTM D256 by Instron impact tester, model ITR-2000. The films produced from blown film

and chill roll cast film extrusions were cut to the size of 15X15 cm, speed of puncture was 4 m/s.

3.2.4.3 Tear Resistance

The force required to propagate tearing across LLDPE and LLDPE/NR film were measured using the Elmendorf 2000 tear tester with the 'C' pendulum (3200 mN full- scale load). This test was conducted according to ASTM D1922. Test specimens were cut as shown in Figure 3.2 to form a constant radius and certain testing length to compensate for oblique tearing. Two sets of specimens were cut, one set which was torn parallel to the machine direction (MD) and the other set was torn parallel to the transverse direction (TD). Ten measurements were conducted for each sample and the results were averaged to obtain a mean value.

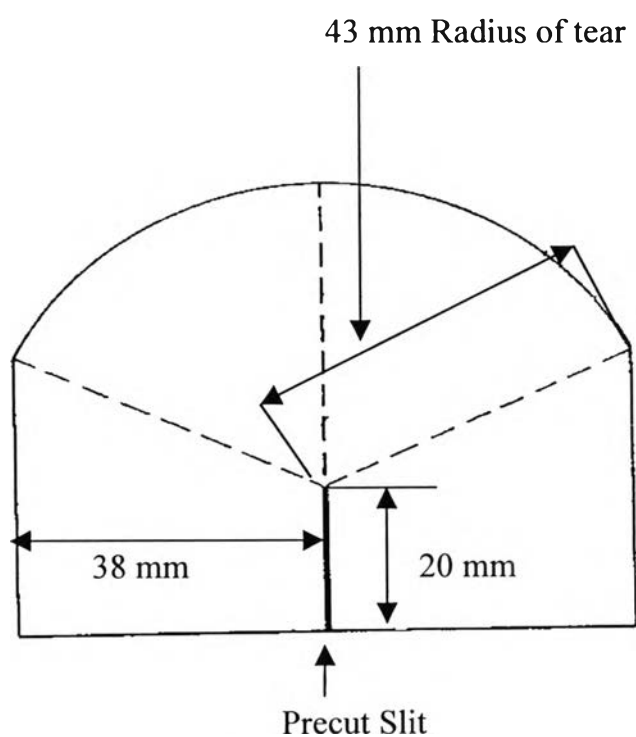


Figure 3.2 Constant-radius specimens for tear resistance test.

3.2.5 Molecular Orientation

3.2.5.1 Infrared Dichroism

Infrared spectra were recorded using FTIR spectrometer with a resolution of 16 scans collected, Bruker RFS 100 FT-IR spectrometer. Background reading for both 0 and 90 degree IR polarization were obtained using wire grid polarizer in front of the empty sample holder and measurement were done with the 0 and 90 degree polarization. To determine orientation of amorphous and crystalline phase of LLDPE, the dichroic ratio for bands at 1368 and 1464 cm^{-1} were assigned. Dichroism was detected at different draw ratio and blow up ratio.

3.2.5.2 Birefringence

The birefringence measurement was carried out using an optical polarizing microscope, Leica model DMRX, Xe 75 lamp polarizer. The measurements were made by placing a sample at 45 degrees to the cross polars. The sample machine direction was parallel or very closed to polarized direction. Birefringence was measured by retardation technique with a lamda (λ) plate and quarter ($\lambda/4$) plate.