

CHAPTER III EXPERIMENTAL



3.1 Materials

3.1.1 Linear Low Density Polyethylene (LLDPE)

In this study, linear low density polyethylene (LLDPE) of film extrusion grade (DOWLEX 2045.11G and DOWLEX 2035) was used as the polymer matrix. It was obtained from Dow Chemical company and was used as received. Some physical properties are listed in Table 3.1.

Table 3.1 Physical properties of LLDPE films.

Grade	Properties	Value
DOWLEX 2045.11G	MFI (g/10 min)	1.0
	Density (g/cm ³)	0.922
DOWLEX 2035	MFI (g/10 min)	6.0
	Density (g/cm ³)	0.919

3.1.2 Natural Rubber (NR)

The natural rubber (NR), used as dispersed phase, was purchased from Rayong Bangkok Rubber Co., Ltd. It is SRT5L grade. Some specifications are listed in Table 3.2.

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

Specification	Specification limit
Dirt retained in 44 μm aperture (max, %wt.)	0.04
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 Acros company with density 1.48 g/cm^3 and melting point 57 $^\circ\text{C}$ was used. This material was used as a reactive agent to functionalize LLDPE so that it can perform as compatibilizer in the blending of LLDPE/NR. The reason for using this material as compatibilizer was the succinic anhydride can attach to the chain ends of PE and the double bond of NR thus providing a compatible blend of LLDPE/NR.

3.1.4 Epoxidized Natural Rubber (ENR-50)

Epoxidize natural rubber (ENR-50) was supplied from laboratory by Dr.Nandh Thavarungkul from King Mongkut's University of Technology. In this studied ENR-50 was used as a coagent of blending with LLDPE and natural rubber as coagent by reacting with Ma on LLDPE chains grafted in order to enhance adhesion to NR.

3.2 Experimental

3.2.1 Preparation of Natural Rubber (NR)

Natural rubber was masticated by two-roll mill at room temperature. The mastication time of natural rubber was designated as 10 min. NR was milled at a roller speed of 30 rpm. The gap between the rolls was adjustable with in a range of 5-10 mm and the rubber was kneaded by multiple passes through the gap before removal from the mill.

3.2.2 Preparation of LLDPE/NR Blends

A certain amount of LLDPE of each composition (90/10 and 80/20) was melted by using the Brabender Mixer W50 for 2 min at 170 °C. Then the NR was added into the melted LLDPE and the blend was further mixed for 10 min. The blend was then shredded into small pieces by a shredder machine and was placed in the Collin twin-screw extruder to complete a mixing. Temperature setting from zone 1 to the die was 150, 155, 160, 175, 185 and 195 °C, respectively with a screw speed of 80 rpm. The extrudate was cooled in water at 25 °C and pelletized by a granulator.

3.2.3 Preparation of LLDPE/NR/MA/ENR Blends

A certain amount of LLDPE of each composition was melted by using the Brabender Mixer W50 for 2 min. Maleic anhydride was added into the melted LLDPE at 2 min, ENR was added at 3 min and the blend was further mixed for 3 min. The temperature of the Brabender was 170 °C. Then the NR was added into the grafted LLDPE with MA at 6 min and further mixed for 4 min. The blend was shredded into small pieces by a shredder machine and then placed in the Collin twin-screw extruder to complete the mixing. Temperature setting from zone 1 to the die was 150, 155, 160, 175, 185 and 195 °C, respectively with a screw speed of 80 rpm. The extrudate was cooled in water at 25 °C and pelletized by granulator.

3.2.4 Chill Roll Cast film Extrusion

The LLDPE, LLDPE/NR blends and LLDPE/NR/MA/ENR 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 X 250 mm) in size. Draw ratio was varied from 7, 10 to 15. Temperature setting for chill roll cast film from zone 1 to the die was 150, 155, 160, 175, 185 and 195 °C respectively. Screw speeds of chill roll cast film was 40 rpm and the extrusion rate was 24 cm/min. The speed of the chill roll was adjusted according to the following table.

Table 3.3 Speed of chill roll for draw ratios of 7, 10 and 15.

Draw ratio	7	10	15
Chill roll speed (cm/min)	168	240	360

3.2.5 Testing and Characterization

3.2.5.1 *Melt Flow Index (MFI)*

LLDPE blends in pellet form were tested by a melt flow index tester at the temperature of 190 °C with a 2.16 kg load cell. according to ASTM 1238.

3.2.5.2 *X-Ray Diffractometer (XRD)*

X-ray diffraction is a very convenient method for the study of crystallinity of polymer. The results of the measurements are displayed in the form of intensity vs. θ curves.

3.2.5.3 Gas Permeability Tester

The Brugger gas permeability tester type GDP/E was used to detect the permeability of oxygen gas through the blend films. The blend films were cut into a circular shape with a diameter of 110 mm and about 70-200 μm in thickness. The flow rate of oxygen was controlled at 100 cm^3/min at room temperature. The oxygen permeability (\underline{P}) was calculated by the following equation:

$$\underline{P} = G \times \text{film thickness}$$

$$G = \frac{1.49 \times 10^7}{TN}$$

Where \underline{P} = oxygen permeability ($\text{cm}^3 \mu\text{m}/\text{m}^2 \cdot \text{sec} \cdot \text{bar}$),

G = gas transmission rate ($\text{cm}^3/\text{m}^2 \cdot \text{sec} \cdot \text{bar}$),

T = temperature (K)

N = reciprocal of the slope from the plot of the change of the vacuum pressure versus time.

3.2.5.4 UV-VIS Spectrometer

UV-VIS Spectrometer, Perkin Elmer lamda 10, in range of 200-800 nm was used for measuring the transmittance of radiation in the visible range.

3.2.5.5 Thermal Analysis

Thermal properties were analyzed by differential scanning calorimeter (DSC), Perkin Elmer DSC-7, with N_2 cooling unit. Heating and cooling curves of selected films were obtained at 10 $^\circ\text{C}/\text{min}$. Structural changes are usually associated with changes in heat absorption or emissions. Scanning calorimetry can measure changes at constant heating or cooling rates. The differences in heat loss or gain between the sample and the reference cell are measured in a differential scanning calorimeter.

The thermal behavior of the LLDPE/NR blends samples was determined on a NETZSCH DSC-200. Sample of 5-7 mg was sealed in a clamped

aluminum sample pan. The sample was heated from 30 °C to 150 °C and cooled down to 30 °C to determine the melting temperature (T_m), and crystallization temperature (T_c).

3.2.5.6 Birefringence

The birefringence measurement was carried out using an opticalpolarizing microscope, Leica model DMRX, Xe 75 lamp polarizer. The measurements were made by placing a sample at 45 degree 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.

3.2.5.7 Infrared Dichroism

Infrared spectra were recorded using Bruker Equinox 55 FT-IR spectrometer with a resolution of 16 scans. Background readings for both 0 and 90 degree IR polarization were obtained using wire grid polarizer in front of the empty holder and measurements were done with the 0 and 90 degree polarization. To determine the orientation of amorphous and crystalline phases of LLDPE, the dichroic ratio for band at 1464 cm^{-1} was assigned. Dichroism was detected at different draw ratios.

3.2.5.8 Tensile Testing

Yield strength of LLDPE/NR cast film was measured using a Lloyd universal-testing machine. The test was conducted according to ASTM D882. Strips of uniform width and thickness cut from the film samples were used as test specimens. The specimens used were 125 mm long and 5 mm thick.