CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

The materials used in this study were used as received:

3.1.1 Linear Low Density Polyethylene (LLDPE)

The LLDPE used in this studied was supplied by Thai Polyethylene Company Limited in blown-film grade (L1810FI). The polymer was in opaque-white pellet-bead form with a density of 0.918 g/cm^3 and melt flow index of 1 g/10 min. Its MW determined by GPC is 84,460 (Limsila,1999).

3.1.2 Natural Rubber (NR)

The NR was purchased from Rayong Bangkok Rubber Co., Ltd. The rubber grade was STR 5L with a density of 0.9 g/cm^3.

3.1.3 Maleic Anhydride (MA)

The MA was purchased from Fluka Co., Ltd. This material was in the form of white flakes with melting point 52-54°C and was used as a reactive compatibilizer.

3.1.4 Dicumyl Peroxide (DCP)

The DCP was purchased from Merck Co., Ltd. This material was in the form of small white opaque flakes with melting point 39-41°C and was used as an initiator.

3.1.5 Acetone

The acetone was purchased from Lab-scan Co., Ltd. The solvent was in clear liquid form with boiling point 56.1°C and was used as a solvent in MA extraction.

3.1.6 Chloroform

The chloroform was purchased from Lab-scan Co., Ltd. The solvent was in clear liquid form with boiling point 61.2°C and was used as a solvent in rubber extraction.

3.1.7 Xylene

The xylene was purchased from Lab-scan Co., Ltd. The solvent was in clear liquid form with boiling point 138-140°C and was used as a solvent in LLDPE extraction and also used for the determination of gel content.

3.2 Methodology

3.2.1 Preparation of Blends

3.2.1.1 Mastication of NR

The NR was masticated by using a two-roll mill (Lab Tech, LMR 110) for 10 minutes at room temperature. Molecular weight of the masticated NR was found to be 482715, see appendix A for GPC results.

3.2.1.2 Blending of LLDPE and NR (Study effect of processing condition)

Blending preparation was carried out in a Brabender Plasticoder (PL-2000). In order to find suitable process condition, two composition of LLDPE/NR/MA/DCP were used i.e. 90/10/3/0.5 and

50/50/7/0.5. Processing conditions are shown in Table 3.1-3.2. The blending preparation was done as following steps.

LLDPE was melted in Brabender for 3 min. Then DCP, MA and NR were added respectively. Each material addition consumed 1 minute interval. Blending was finished within 10 min.

The most suitable process condition for each composition was used to study effect of MA and DCP.

3.2.1.3 Preparation of Grafting NR with MA

Masticated NR was put into Brabender at room temperature and rotor speed 50 rpm for composition 90/10 and 30 rpm for composition 50/50. Then ¼ portion of MA was added and mixed for 5 min then removed from the chamber.

3.2.14 Blending of LLDPE and NR (Effect of MA and DCP)

LLDPE was melted for 3 min at temperature 150 °C at 50 rpm and 30 rpm for composition 90/10 and 50/50. The variation of MA and DCP are shown in Table 3.2. Then ¾ portion of MA, DCP, and NR-g-MA were added respectively. After the last addition, mixing was continued for 5 min and the resulting blend was removed from the chamber.

If consider the blend compositions (Table 3.2) will see the fraction of each material was assume to be exactly percentage which, in fact, they came from the calculation of input materials in the Brabender (see appendix F).

Table 3.1 Processing conditions for LLDPE/NR/MA/DCP blend compositions of 90/10/3/0.5 and 50/50/7/0.5.

LLDPE/NR/MAH/DCP	Temperature (°C)	Rotor speed (rpm)
90/10/3/0.5	140	50
	150	30
		50
		70
	160	50
50/50/7/0.5	140	50
	150	30
		50
		70
	160	50

Table 3.2 Variations in amounts of MA and DCP used with compositions of LLDPE/NR 90/10 and 50/50 blend.

Composition	LLDPE(g)	NR (g)	MA (g)	DCP (g)
90/10/1/0.5	90	10	1	0.5
90/10/3/0			3	0
90/10/3/0.5				0.5
90/10/3/1.0				1
90/10/3/1.5				1.5
90/10/5/0.5			5	0.5
90/10/7/0.5			7	0.5
50/50/1/0.5	50	50	1	0.5
50/50/3/0.5			3	0.5
50/50/5/0.5			5	0.5
50/50/7/0			7	0
50/50/7/0.5				0.5
50/50/7/1.0				1
50/50/7/1.5				1.5

Note: MA 1% wt here means 1 g MA in 100 g of LLDPE/NR blend

DCP 0.5% wt here means 0.5 g DCP in 100 g of LLDPE/NR blend

3.2.2 Solvent Extraction

3.2.2.1 Determination of Suitable Time for Solvent Extraction

A certain amount of sample was refluxed with each solvent in round bottom flask. The insoluble sample was separated every hour, and dried on a hotplate at temperature about 100 °C under a hood for 3 hours and weighed until reaching constant weight. The suitable time for each sample was obtained.

3.2.2.2 Determination of % free MA (acetone extracted part)

One gram of shredded sample was refluxed with 50 ml of acetone at 60°C for 1 hr in a 250 ml round bottom flask in order to remove non-reacted MA. The suspension was filtered through filter paper (whatman no.4). The insoluble part was washed with acetone and dried in a hood for 24 hours and used for chloroform extraction. Amount of free maleic anhydride was calculate by

$$\% \text{ Free MA} = \frac{\left[\frac{\text{Weight of MA in petri dish}}{\text{Weight of crude sample}} \times 100\right]}{\text{Amount of added MA (\%)}} \times 100 \qquad (3.1)$$

3.2.2.3 Determination of Rubber Content

Then the insoluble sample from acetone extraction was refluxed with 50 ml of chloroform at 60 °C for 1½ hr in a 250 ml round bottom flask in order to separate the unbounded NR part. The suspension was filtered through filter paper (whatman no.4). The chloroform-insoluble part was washed with chloroform and dried in a hood for 24 hr. The insoluble part was dried and used for determination of gel content. The filtrate part was poured into petri dish and let the solvent to evaporate. The amount of rubber content was calculated by

$$\% \text{ Rubber content} = \frac{\text{Weight of rubber in petri dish}}{\text{Weight of the crude sample}} \times 100 \qquad (3.2)$$

3.2.2.4 Determination of Gel Content

The insoluble sample from chloroform extraction was refluxed with 50 ml of chloroform at 60 °C for 1 hr in a 250 ml round bottom flask in order to separate the unbounded NR part. The suspension was filtered through filter paper. The chloroform-insoluble part was washed with chloroform and dried in a hood for 24 hr. Then the dried sample was refluxed with 70 ml of xylene at 120-130°C for 5 hr in a 250 ml round bottom flask in order to separate the gel part. The hot suspension was filtered through filter paper (in a hot filter) into 140 ml of acetone in order to precipitate the xylene-soluble part (Gaylord *et al.*, 1987). The xylene-insoluble part was dried in a hood for 5 days and weighed as gel content. The precipitated part was filtered through filter paper and dried as extracted LLDPE phase. The gel content can be calculated by

$$\% \text{ Gel content} = \frac{\text{Weight of gel}}{\text{Weight of crude sample}} \times 100 \qquad (3.3)$$

3.2.3 Determination of % Graft of MA by FTIR Technique

Infrared spectroscopy is the technique that detects the change of bond dipole moment due to vibration of the interatomic bonds after absorbing the energy. Each molecule shows its characteristic of particular functional groups in vibrational frequencies.

Quantitative IR analysis employs the vibration of infrared light that pass through an absorbing polymer follows the LAMBERT-BEER law:

$$E = \log_{10} I_0/I = e^* \cdot c \cdot d \qquad (3.4)$$

To avoid the effect of sample thickness, the ratio of the interested absorption peak/area to the reference absorption peak/area were used. Hence the relative absorption can be determined as

$$E/E_{ref} = c/c_{ref} \qquad (3.5)$$

The reference peak is chosen from the material characteristic peak that is always shown in FTIR spectrum.

where E = absorbance (measure of absorption)

I_0 = intensity of radiation before traversing the sample

I = intensity of radiation after traversing the sample

e^* = molar absorptivity (cm^2/mol)

c = concentration (mol/cm^3)

d = thickness of layer (cm).

3.2.3.1 Preparation of Sample Film for FTIR Characterization

A certain amount of dry sample from crude samples, and xylene-soluble samples were pressed between two plates of stainless steel coated with chromium at 170°C 15 ton forces for 4 min and cooled under pressure until temperature below 40°C.

3.2.3.2 Preparation of Rubber Part for FTIR Characterization

A certain amount of sticky solution of NR in chloroform was applied onto the KBr disc and let the chloroform evaporated. (See appendix H for FTIR peaks of pure components, crude samples, separated samples).

3.2.4 Molding of Sample for Mechanical Testing

A 37 g of each crude sample was put into picture-frame mold which has thickness about 1.2 mm and put between two plates of stainless steel coated with chromium. The molds were pressed by a Wabash V50H compression molding. The sample was preheated at 170°C for 3 min, and 170°C at 5 tons forces for 3 min, and 170°C at 15 tons forces for 3 min. Then the sample was cooled under pressure to temperature below 40°C

3.3 Instrumental

3.3.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectrometer that used in this study was Bruker FT-IR spectrometer with a deuterated triglucinesulfate detector (DTGS) with a specific detectivity (D^*) of 1 x 10^9 $cmHz^{1/2}W^{-1}$.

FTIR spectroscopic test was performed in frequency range 4000-400 cm^{-1} and 16 scans at resolution of 4 cm^{-1}. The percent grafted of MA was measured by curve fitting to determine the integral ratio of absorption peak at 1713 cm^{-1} and 1646 cm^{-1}, which was the peak of carbonyl and reference peak of LLDPE and NR.

The sample films were placed on standard FTIR sample plate with a removable magnetic cover for holding the samples.

The KBr discs were placed on standard KBr sample.

The calculation for % grafted MA by FTIR was performed as following:

a. % grafted MA in crude sample
b. % grafted MA in NR phase (chloroform soluble part)
c. % grafted MA in LLDPE phase (xylene soluble part)

3.3.2 Scanning Electron Microscope (SEM)

Scanning electron microscopy is the versatile technique that used for studying morphology of polymers. However, a limitation with polymers is that polymers are non-conductive materials. To overcome this problem, coating polymers with a conductive material such as gold and silver are applied. Although this technique is quite complicated, it is easy to operate. This technique uses electron beam (from tungsten filament) to interact with solid surface. When electron beam impacts the surface, there are 3 types of electron detected i.e. backscattered electron, secondary electron, and x-ray.

For studying morphology, the secondary electrons are detected to generate signal to create the secondary image (SEI). There are many applications of secondary electron image studying such as fiber morphology, fiber composites, fractures surface, etc.

SEM, JEOL 5200-2AE (MP152001) with a magnification range of 35-200,000 times was used for this study. The small crude samples sheet were cryogenically broken (after dipped in liquid nitrogen) to bring about cryofracture surface. The samples were etched to remove NR phase for 2 days by chloroform. The magnifications of the images were 2000 at 10 kV and 15 kV.

3.3.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is the technique that measures the change in weight of materials with increasing temperature or time. There are many applications for polymer studying such as degradation profile, polymer blend composition, additives in polymers, and so on.

Thermal property was characterized by using a Dupont thermogravimetric analyzer, TGA 2950, at room temperature to 530 °C. Heating rate was at 10°C/min under N_2 atmosphere.

3.3.4 Intron Universal Testing Machine

The mechanical properties were measured by using an Intron Universal Testing Machine, Model 4206. In this study, all of specimens were tested according to ASTM D638-91 by using load cell of 5 kN and 100 mm/min crosshead speed in 25 mm gauge length. The sample plates that got from compression molding were cut into dumbbell shape to get narrow section about 6 mm wide and 1.2 mm thick.