CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Polymers

3.1.1.1 *Polyamide12 (PA12, Nylon12)*

The PA12 is commercially available under the product name Grilamid L25 natural 6112. It was supplied by EMS-Chemie (ASIA) Ltd. The polymer is in opaque-white pellet-bead form. The melt volume-flow rate is 20 cm^3/10min (at 275°C, load 5 Kg). Density is 1.01 g/cm^3. Melting point is 178°C.

3.1.1.2 *Natural Rubber (NR)*

The NR grade STR 5L was purchased from Rayong Bangkok Rubber Co., Ltd. in solid bulk form. Number average molecular weight (M_n) and weight average molecular weight (M_w) are 106,270 and 518,984 g/mol, respectively. The density is 0.9 g/cm^3.

3.1.1.3 *Styrene-Ethylene-Butylene-Styrene Block Copolymer (SEBS)*

The triblock copolymer, SEBS, was supplied by Shell Chemical Co.,Ltd. This copolymer has styrene end blocks and hydrogenated butadiene mid block reassembling an ethylene/butylene copolymer. Three types of SEBS: Kraton G1652, Kraton G1650, and Kraton G1657 were used.

Kraton G1652 contains about 30%wt styrene and the molecular weight is 79,000 g/mol.

Kraton G1650 is a higher molecular weight version of Kraton G1652 with very similar physical properties except higher solution and melt viscosities. It contains 30%wt styrene as Kraton G1652. The molecular weight is 104,600 g/mol.

Kraton G1657 contains 13%wt styrene. The molecular weight is 142,400 g/mol.

3.1.1.4 *Styrene-Ethylene-Butylene-Styrene Block Copolymer Grafted by Maleic Anhydride (SEBS-g-MA)*

The SEBS functionalized with 2%wt maleic anhydride onto the hydrocarbon chains of the mid block, which designate as SEBS-g-MA, is Kraton FG1901x where molecular weight and styrene contents are the same as those of Kraton G1652 (Horiuchi *et al.,* 1997). It has 29%wt styrene (Oshinski et al., 1992, 1996) and 1.8%wt maleic anhydride. The Kraton FG1901x was also supplied from Shell Chemical Co., Ltd.

3.1.1.5 *Polystyrene (PS)*

Polystyrene is a general purpose grade with the commercial name STYRON™ 656D. It was supplied by Dow Chemical Co., Ltd. The polymer was in opaque-white pellet-bead form; melt volume-flow rate = 8 cm^3/10min. (ASTM D1238 Cond G. M_n and M_w are 57,618 and 218,468 g/mol respectively. The density is 1.05 g /cm^3.

3.1.2 Reagent

3.1.2.1 *Dicumyl Peroxide (DCP)*

The DCP (commercial grade) used as an initiator was purchased from Fluka. This material was used in form of small white opaque flakes with melting point 39-41°C.

3.1.3 Solvent

3.1.3.1 *Toluene*

Toluene was purchased from Lab-scan Co., Ltd. The solvent was in clear liquid form with boiling point 110.6 °C and was used as a solvent for NR and PS.

3.1.3.2 *Methyl Ethyl Ketone(MEK)*

Methyl Ethyl Ketone was purchased from Lab-scan Co., Ltd. The solvent was in clear liquid form with boiling point 79.6°C and was used as a solvent for PS.

3.1.3.3 *Isopropanol(IPA)*

IPA is commercial grade from Lab-scan Co., Ltd. was used as a solvent for SEBS-g-MA.

All materials were used as received.

3.2 Equipment

3.2.1 Brabender Plasticorder

The polymers were mixed in a Brabender Plasticorder (internal mixer) model PL 2000 using mixing head type W50 that have 60ml mixing chamber (filled 80% of chamber capacity) with standard rotor type. Temperature and torque profiles were recorded during mixing. All the tests using Nylon12 were made at 180 °C, 70 round per minute (rpm). Blending conditions for PS-NR mixing were performed at 150 °C and 50 rpm.

3.2.2 Two-roll Mill

A Lab tech LRM 110 Two-roll mill was used for masticating NR at room temperature.

3.2.3 Compression Press

The blended samples were pressed by Wabash V50H compression press. The steps used in the process for this study were started by heating a mold at 190°C without pressure for 5 min. Then, the mold was pressed at 190°C by 10 tons force for 10 min. And then, the molding were cooled under pressure to room temperature with cooling rate about 20°C/min. The mold used was a picture-frame type made from stainless steel coated with chromium. Thickness of the mould cavity was about 3 mm.

3.2.4 Gel Permeation Chromatography (GPC)

GPC chromatograms were performed by Waters GPC 600E attached with RI (Waters 410) and UV detector (Waters 486). Three columns, Styragel HR0.5, HR4E, and HR5E were connected in series and used THF (HPLC grade) as the eluent. The flow rate was maintained at 1 ml/min throughout the experiment. It was used for the determination of PS and NR molecular weights.

3.2.5 Fourier Transform Infrared Spectrometer (FT-IR)

FT-IR spectra were carried out on Bruker FRA 106/S spectrometer using deuterated triglycinesulfate detector (DTGS) at the resolution of 2 cm^{-1} (32 scan per sample).

3.2.6 Differential Scanning Calorimeter (DSC)

Glass transition temperature (T_g), melting temperature (T_m), crystalline temperature (T_c), and crystallization energy of the blends was

detected by Netzch DSC 2000 differential scanning calorimeter from 25°C to 200°C with the heating rate of 10 °C/min under nitrogen purge for T_g and T_m. T_c of nylon12 in the blends was also detected by DSC from 200°C to 30°C with the cooling rate of 5°C/min.

3.2.7 Scanning Electron Microscope (SEM)

A JEOL JSM 5200-2AE (MP52001) scanning electron microscope (SEM) with magnification 10,000 times was used at 25 kV to investigate the morphology of the blend surfaces after coating by gold, a conductive material. For the preparation of the blend surfaces, the samples were cryogenically broken after dipping in liquid nitrogen for 15 min and then the rubber phase was removed by etching with toluene and 90%wt toluene/10%wt isopropyl alcohol mixture for non-reactive and reactive compatibilizer respectively for at least 5 days at room temperature.

3.2.8 Transmission Electron Microscope (TEM)

TEM analysis Joel model JEM-200CX with 120kV was employed to identify the microstructure and morphology of the blends. The specimens were stained by osmium tetraoxide (OsO_4) by submerging in 1% of OsO_4 in aqueous solution for 24 hr. Then, they were embedded in spur resin by molding at 70°C for 8 hr. The samples were, later, cut into very thin section about 90 nm thick using an ultra-thin microtome. Finally, the specimens were placed on copper grid and investigated by TEM.

3.2.9 Instron Universal Testing Machine

Tensile properties of the blends were carried out by an Instron universal testing machine model 4206. All specimens were tested according to ASTM D638-91 at the gauge length of 50 mm, the load cell of 100 kN and the crosshead speed of 10 mm/min. The specimens were prepared by

compression molded into a 3 mm thick sheet. Then, they were cut into bone shape.

3.3 Methodology

3.3.1 Mastication of NR

The NR was masticated on a two-roll mill (Lab Tech, LMR 110) for 10 min at room temperature. The molecular weight of the masticated NR was found to be $\bar{M}_n$ and M_w are 106,270 and 518,984 g/mol respectively.

3.3.2 Preparation of PS/NR [60/40 %wt] Reactive Blends

The PS/NR blend that was used as a compatibilizer (the third phase) in a Nylon12/NR blend was prepared in the Brabender Plasticorder (PL-2000). Firstly, the chamber was heated up to 150°C and rotors were rotated at 50 rpm. Secondly, PS was fed in the chamber to melt for 3 min. Then, DCP was added and mixed for 3 min, Then, NR was fed into the chamber and mixed further for another 4 min. Finally, the chamber was opened and the PS-NR blend was taken out of the chamber. Temperature and torque profiles were recorded along blending steps. In order to find an optimum content of DCP in this blend, DCP amount was varied: 0.5, 1, 1.5, 2 part per hundred (phr) in [PS/NR], [60/40] blends. All blends were set to occupy 80% of chamber volume.

3.3.3 Preparation of [Nylon12/NR]/Compatibilizer Blends

Blending preparation was also carried out by the Brabender plasticorder (PL-2000). Firstly, chamber temperature and rotor speed were set at 180°C and 70 rpm respectively. Then, 80 %wt of Nylon12 was fed into the chamber and molten for 3 min, then, 20 %wt of NR and compatibilizer were added and mixed for another 5 min. Lastly, rotors were stopped and the blend

was taken out of the chamber. Temperature and torque profiles were recorded along with each blending step. All blends were also set to occupy 80% of the chamber volume. Next, the blends were formed into a sheet by Wabash V50H compression press machine. Variation of types and content of compatibilizer were shown in Table 3.1

Table 3.1 Variations in types and content of compatibilizer in [Nylon12/ NR]/Compatibilizer blends.

Name of blend compositions	Nylon12 (parts)	NR (parts)	Compatibilizer	
			Type	amt (parts)
[Nylon12/NR]/1652 1	80	20	Kraton G1652	1
[Nylon12/NR]/1652 2				2
[Nylon12/NR]/1652 4				4
[Nylon12/NR]/1652 8				8
[Nylon12/NR]/1652 16				16
[Nylon12/NR]/1650 1			Kraton G1650	1
[Nylon12/NR]/1650 2				2
[Nylon12/NR]/1650 4				4
[Nylon12/NR]/1650 8				8
[Nylon12/NR]/1650 16				16
[Nylon12/NR]/1657 1			Kraton G1657	1
[Nylon12/NR]/1657 2				2
[Nylon12/NR]/1657 4				4
[Nylon12/NR]/1657 8				8
[Nylon12/NR]/1657 16				16
[Nylon12/NR]/1901 1			Kraton FG1901x	1
[Nylon12/NR]/1901 2				2
[Nylon12/NR]/1901 4				4
[Nylon12/NR]/1901 8				8
[Nylon12/NR]/1901 16				16
[Nylon12/NR]/[PS/NR] 1			[PS/NR Blend]	1
[Nylon12/NR]/[PS/NR] 2				2
[Nylon12/NR]/[PS/NR] 4				4
[Nylon12/NR]/[PS/NR] 8				8
[Nylon12/NR]/[PS/NR] 16				16

3.3.4 PS/NR blends Characterization

3.3.4.1 Determination of Gel Content

After blending, %wt gel of the blends were measured. Firstly, sample was dissolved in toluene (2%wt) and stirred for a week to get complete dissolution. Then, the blend solution was filtered by weighted filter paper (Whatman No. 4) under vacuum. Then, the wet filter papers containing gel were dried at 110°C for at least 5 hours to ensure steady dry weight. Finally, the filter paper with gel was weighted and %wt gel was calculated by

$$\%Gel = \frac{Filter\ paper\ with\ gel\ weight - Filter\ paper\ weight}{Blend\ weight} x\,100 \qquad (3.1)$$

3.3.4.2 Determination of PS part

The blends after filtering the gel out were measured for PS part. Firstly, a sample was dissolved in methyl ethyl ketone (solvent for PS but non solvent for NR) and stirred for at least 3 days to get complete dissolution. A blend solution was then filtered by a filter paper (Whatman No. 4) under vacuum. Then, PS part (soluble part) was evaporated in petridish and dried at 80°C for at least 5 hours to ensure steady dry weight. Finally, petridish with PS part was weighed and observed by FT-IR spectroscopy. %wt PS part was calculated by

$$\%PS\ part = \frac{Petridish\ with\ PS\ weight - Petridish\ weight}{Blend\ weight} x\,100 \qquad (3.2)$$

The separation procedure for %Gel and %PS determination. was shown in Figure 3.1.

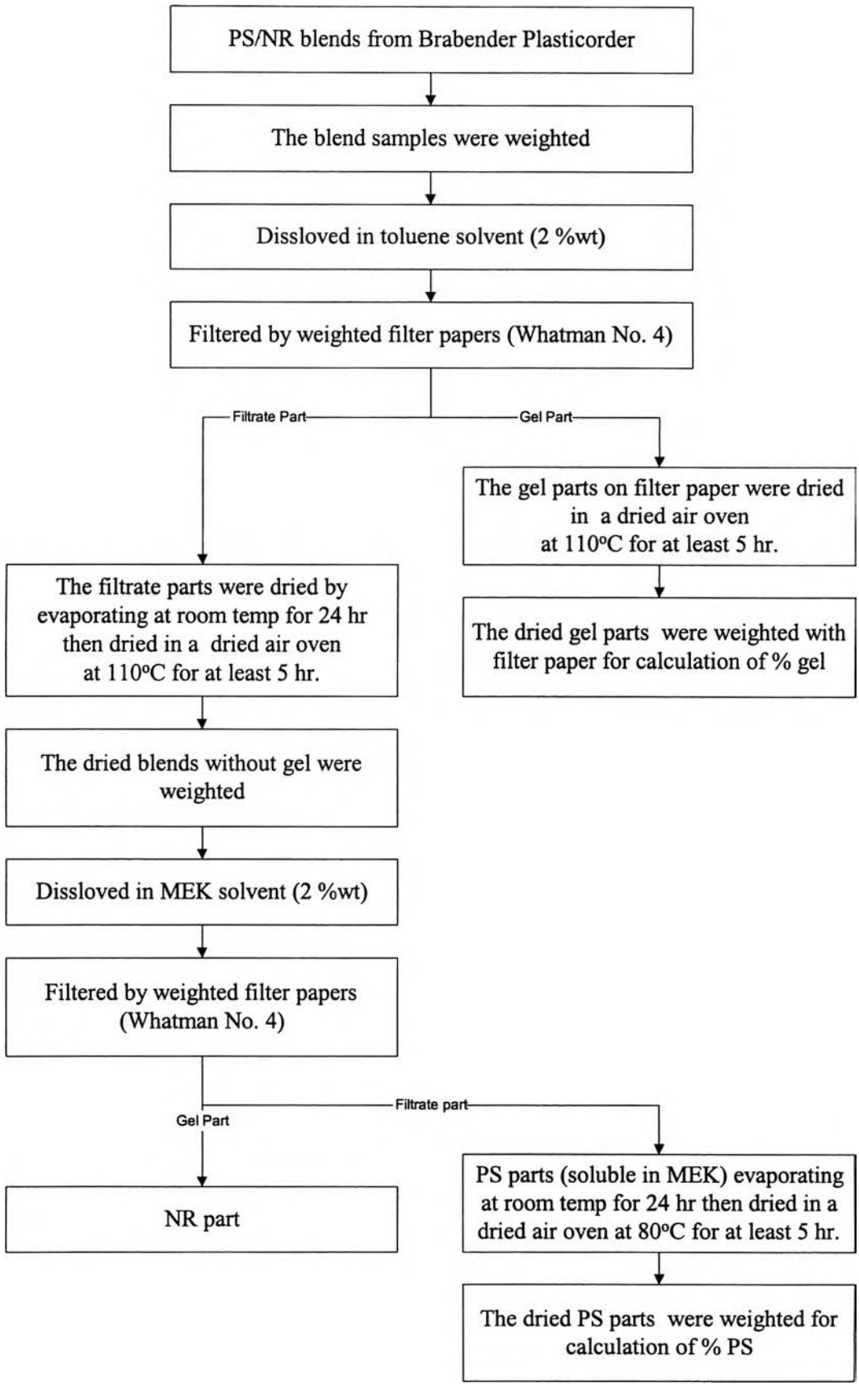

Figure 3.1 The separation procedure for %Gel and %PS determination.

3.3.4.3 Thermal Characterization

For [PS/NR]/DCP blends, they were scanned by DSC from 30°C to 120°C with the heating rate of 10 °C/min under nitrogen purge. The mid point of the slope change of the heat capacity plot in the second scan was determined as the glass transition temperature (T_g).

3.3.5 [Nylon12/NR]/Compatibilizer Characterization

3.3.5.1 Morphology Characterization

Blend morphologies were predicted by using a spreading coefficient. From Harkin's equation and studied by SEM, and TEM in order to find drop size, core size, shell size, and interfacial thickness. The samples prepared from compression molding machine (using 75 g of sample compressed at 190°C and 10 ton pressure for 12 min) were taken to study the morphology.

3.3.5.2 Mechanical Characterization

For the study of mechanical properties, the samples were prepared at the same condition as morphology characterization. The tensile strength and tensile modulus of blends were done by Instron universal testing machine.

3.3.5.3 Thermal Characterization

The [Nylon12/NR] blend were scanned by DSC from 25°C to 200°C with the heating rate of 10 °C/min under nitrogen purge for T_g and T_m. T_c of nylon12 in the blends was also detected by DSC from 200°C to 30°C with the cooling rate of 5°C/min.

3.3.5.4 Crystallinity Characterization

The [Nylon12/NR] blends were scanned by DSC from 200°C to 30°C with the cooling rate of 5°C/min under nitrogen purge. %Crystallinity was calculated from the area under crystalline peak of nylon12 after equalized weight of Nylon12 in all blends to be the same as pure nylon12. %Relative crystallinity was calculated by

$$\%\text{Relative Crystallinity} = \frac{\text{Equalized area under crystalline peak of Nylon12 in the blend}}{\text{Area under crystalline peak of pure Nylon12}} \times 100 \qquad (3.3)$$