

## 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<sup>3</sup>/10 min (at 275°C, load 5 kg). Density is 1.01 g/cm<sup>3</sup>. 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 yellow solid bulk form.

##### 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/butylenes 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 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<sup>3</sup>/10 min. (ASTM D1238).  $M_n$  and  $M_w$  are 57,618 and 218,468 g/mol respectively. The density is 1.05 g/cm<sup>3</sup>.

#### 3.1.1.6 *Maleic Anhydride (MA)*

Maleic anhydride (laboratory grade) that used as a reactive functional group was purchased from Acros. This material was used in form of small white opaque flakes. The molecular weight is 98 g/mol.

### 3.1.2 Reagent

#### 3.1.2.1 *Dicumyl Perioxide (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.

## 3.2 Equipment

### 3.2.1 Brabender Plasticorder

The polymer was mixed in a Brabender Plasticorder (internal mixer) model PL 2100 using a mixing head type W50 that has 60 ml mixing chamber (filled 80% of chamber capacity) with standard rotor type. Temperature and torque profile were recorded during mixing. All the tests using Nylon12 were made at 180°C, 70 round per minute (rpm). Blending conditions for PS/NR/MA 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 moldings 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 Differential Scanning Calorimeter (DSC)

Glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ) and crystalline energy of the blends were detected by Perkin Elmer DSC7 differential scanning calorimeter from -20°C to 200°C with the heating rate of 10°C/min under nitrogen purge.

### 3.2.5 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 surface, the samples were cryogenically broken after dipping in liquid nitrogen for 1 hour and then the rubber phase was removed by etching with 90%wt toluene/10%wt isopropyl alcohol mixture for reactive compatibilizer for at least 5 days at room temperature.

### 3.2.6 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.

### 3.2.7 Izod Impact Testing Machine

Impact property of the blends was studied by an Pendulum Impact Tester (Zwick model 5113). All specimens were tested according ASTM D256 with the pendulum 21.6 J. The specimens were prepared by compression molded into a 3 mm thick sheet. Then, they were cut into rectangular shape.

### 3.2.8 Dynamic Mechanical Thermal Analysis (DMTA)

Rheological properties were observed by Rheometric Scientific DMTA in three point bending mode (strain control, tension deform mode). The specimens were prepared as same as impact testing. Rheological properties were observed by varying temperature, frequency, or strain values to study the relation between temperature, frequency, and strain with the morphology and particle size of blends.

### 3.3 Methodology

#### 3.3.1 Mastication of NR

The NR is masticated on a Two-roll mill (Lab Tech, LMR 110) for 10 min at room temperature.

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

The PS/NR/MA blend that is used as a compatibilizer (the third phase) in a NR/Nylon12 blend is prepared in the Brabender Plasticorder. Firstly, the chamber is heated up to 150°C and rotors are rotated at 50 rpm. Secondly, PS is fed into the chamber to melt for 3 min. Then, DCP is added and mixed for 3 min followed by MA and mixed further for 3 min. Then, masticated NR is fed into the chamber and mixed further for another 4 min. Finally, the chamber is opened and the PS/NR/MA blend is taken out of the chamber. Temperature and torque profiles are recorded along blending steps. All blends were set to occupy 80% of chamber volume.

#### 3.3.3 PS/NR/MA Characterization

##### *3.3.3.1 Determination of melt flow index of PS/NR/MA reactive compatibilizer*

Melt flow index of PS/NR/MA reactive compatibilizer was determined by melt flow index tester (200°C, 5 kg). The reactive compatibilizer was flowed pass melt flow index tester and determined mass flow rate every 10 minutes.

##### *3.3.3.2 Determination of percent grafted maleic anhydride of PS/NR/MA reactive compatibilizer*

Percent grafted maleic anhydride of PS/NR/MA reactive compatibilizer was determined by Carbon 12 NMR. The area of the peak is the percent grafted maleic anhydride.

### 3.3.3.3 Thermal characterization of PS/NR/MA reactive compatibilizer

For PS/NR/MA blends, they were scanned by DSC from -20°C to 200°C with the heating rate of 10°C/min under nitrogen purge. The midpoint of the slope change of the heat capacity plot was determined as the glass transition temperature ( $T_g$ ).

### 3.3.3.4 Determination of gel content

After blending, %wt gel of the blends was measured. Firstly, sample was dissolved in toluene (2%wt) and stirred for 2 days to get complete dissolution. Then, the blend solution was filtered by weight filter paper (Whatman No. 1) 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 weight and %wt gel was calculated.

### 3.3.4 Preparation of [Nylon12/NR]/Compatibilizers Blends

The Brabender Plasticorder also carries out blending preparation of NR/Nylon/Compatibilizers. Firstly, chamber temperature and rotor speed are set at 180°C and 70 rpm respectively. Then, Nylon12 is fed into the chamber and molten for 3 min, then, masticated NR and compatibilizer are added and mixed for another 4 min. Lastly, rotors are stopped and the blend is taken out of the chamber. Temperature and torque profiles are recorded along with each blending step. All blends are 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 contents 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		

**Table 3.1 (Cont.)** Variations in types and contents of compatibilizer in [Nylon12/NR]/Compatibilizer blends.

Name of blend compositions	Nylon12 (parts)	NR (parts)	Compatibilizer	
			Type	Amt (parts)
[Nylon12/NR]/[PS/NR/MA] 1	80	20	[PS/NR/MA Blend]	1
[Nylon12/NR]/[PS/NR/MA] 2				2
[Nylon12/NR]/[PS/NR/MA] 4				4
[Nylon12/NR]/[PS/NR/MA] 8				8
[Nylon12/NR]/[PS/NR/MA] 16				16

### 3.3.5 [Nylon12/NR]/[PS/NR/MA] Characterization

#### 3.3.5.1 Morphology characterization

Blend morphologies were predicted by using a spreading coefficient from Harkin's equation and studied by SEM to find drop size, core size, shell size, and interfacial thickness. The sample prepared from compression molding machine (using 75g 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 of [Nylon12/NR]/[PS/NR/MA] reactive compatibilizer

For [Nylon12/NR]/[PS/NR/MA] blends, they were scanned by DSC from -20°C to 200°C with the heating rate of 10°C/min under nitrogen purge. The mid point of the slope change of the heat capacity plot was determined as the glass transition temperature ( $T_g$ ).



#### 3.3.5.4 *Determination of crystalline energy of Nylon12/NR/[PS/NR/MA] Blend*

Crystalline energy was observed by differential scanning calorimeter (DSC) from -20°C to 200°C for two steps. Crystalline energy from polymer processing step was observed at first heating step (first crystalline energy) and theory crystalline energy was observed at second heating step (second crystalline energy).

### 3.3.6 [Nylon12/NR]/Compatibilizer Characterization

#### 3.3.6.1 *Impact testing*

For the study of impact properties, the samples were prepared at the same condition as morphology characterization. The impact strength of blends was done by Izod impact testing machine.

#### 3.3.6.2 *Dynamic mechanical characterization*

For [Nylon12/NR]/Compatibilization blends, they were observed dynamic mechanical properties by DMTA with frequency sweep and temperature sweep mode. For frequency sweep mode, blends were scan isothermally from 0.01 to 100 rad/sec.