

CHAPTER III



EXPERIMENTAL

3.1 Chemicals

The high ammonia NR latex containing ca. 60% DRC was obtained from Rubber Research Institute (Bangkok, Thailand). The solid NR (STR-5L) was purchased from Thai Hua Chumpon rubber Co., LTD. (Samutsakorn, Thailand). The nitrile rubber (NBR) of Krynac[®]3345F grade (33±1% ACN) obtained from Bayer Elastomers S.A. (France). The properties of NBR and NR are shown in Appendix A. Styrene (ST) monomer was supplied by Acros Organics (Geel, Belgium). Acrylonitrile (ACN) monomer and 2,2' azoisobutyronitrile (AIBN) were purchased from Aldrich (Singapore). Cumene hydroperoxide (CHPO), tetraethylene pentamine (TEPA) and potassium persulfate (K₂S₂O₈) were obtained from Fluka (Steinem, Switzerland). Benzoyl peroxide (BPO) was products of Panreac Sintesis (Barcelona, Spain). Anhydrous sodium sulfate (Na₂SO₄), sodium dodecylsulfate (SDS), isopropanol, toluene, formic acid, potassium hydroxide, light petroleum ether and dimethy formamide were obtained form Fisher Scientific (Leicestershire, UK). Zinc oxide, stearic acid, sulphur, trimethyl thiurum disulphide (TMTD) and n-cyclohexyl-2-benzothiazyl-sulphenamide (CBS) were supplied by Pan Asia Industrial Co., Ltd (Bangkok, Thailand). The commercial grade nitrogen gas with 95% purity was manufactured by TIG (Chachoengsao, Thailand).

3.2 Reactor for Synthesis of Graft Copolymer

The high pressure batch reactor (3.5 liters) was purchased from the Parr Instrumental Company. This reactor consisted of a stainless steel 316 cylindrical bomb with split ring closures and bomb heater. It could be operated under pressure of range 0-153 bar at 0-450 °C. The reaction temperature was automatically controlled by temperature controller obtained from SW company. The range of the stirring speed could be adjusted in the range of 0-1000 rpm.

3.3 Purification of Monomers

The purification method for ST and ACN monomers was described in the previous literature (Sintoorahat, Prasassarakich and Wongwisetisirikul, 2000). The ST monomer (b.p. 145.2°C/760 mm Hg) was washed with 1.0 % NaOH solution to remove hydroquinone used as an inhibitor for self-polymerization of ST. Then, it was washed with anhydrous Na₂SO₄. The dried ST monomer was distilled under reduced pressure (50-60°C/20 mmHg). Finally, the obtained pure ST monomer was stored in a refrigerator.

For ACN monomer (b.p. 78°C/760 mm Hg) a trace of *tert*-butyl catechol as an inhibitor containing in ACN monomer was removed by the procedure as described above. The dried ACN was then distilled under reduced pressure at 20 mm Hg (40 °C) and also kept in a refrigerator.

3.4 Typical Preparation of Graft Natural Rubber (GNR)

3.4.1 Emulsion Method

The NR latex (60 g, 60% DRC) mixed with 200 cm³ of 0.1 wt% KOH, 10 phr of isopropanal (stabilizer) and 0.5 phr of SDS (emulsifier) was transferred into the high pressure reactor with constant stirring speed of 200 rpm. The mixture was deoxygenated by passing nitrogen gas for ca. 30 min at room temperature. Then, 3 wt% ST was continuously added with stirring for 30 min to allow the swell of latex particles. The 100 phr of ST/ACN monomers mixture (3/1 by wt) was slowly dropped into the rubber solution. The reaction was initiated by using K₂S₂O₈ or redox initiator (CHPO/TEPA). For using K₂S₂O₈, this initiator was gradually added into the reaction mixture before heating to desired reaction temperature (60-80°C). For the redox initiator, 10 wt% aq solution of TEPA was added as an activator agent. The CHPO initiator (1.0-3.0 phr) was then slowly dropped into the reaction mixture. The ratio of CHPO/TEPA was kept constant at 1/1 by wt. When the reaction temperature reached to the target value, the reaction was carried out under N₂ atmosphere at 1-6 bar for 6 h with constant agitation rate. Then, the graft NR was precipitated in 10 wt% formic acid and dried in a vacuum oven at 40°C.

3.4.2 Solution Method

The 20 g of solid NR (STR 5L) was dissolved in toluene (1,000 cm³) and then transferred into the high pressure reactor. The rubber solution was deoxygenated by passing nitrogen gas for approximately 30 min at room temperature with agitation speed at 500 rpm. The 3 wt% ST monomer was then continuously added with stirring for 30 min to swell latex particles. Subsequently, 100 parts per hundred of rubber (phr) of ST/ACN monomer mixture at 3/1 by wt and the desired amount of initiators (BPO or AIBN) in the range of 5-20 phr were gradually dropped into the rubber solution. The rubber solution was then heated up to 60-90°C under 1-6 bar of N₂ pressure. The reaction was then allowed to proceed for 6 h under continuous agitation to complete the polymerization. When the reaction was terminated, the resulting product was precipitated in excess ethanol and dried in a vacuum oven at 40°C.

3.5 Determination of Grafting Properties

The obtained GNR consisted of three parts: graft copolymer (NR-*g*-(ST-*co*-ACN)), free NR (ungraft NR) and free copolymer. The free NR and free copolymer were removed by using soxhlet extraction with petroleum ether and dimethyl formamide, respectively. The dried final residue was the graft copolymer of (ST-*co*-ACN) onto NR. The different weight between initial and extracted samples obtained from soxhlet extraction was used to determine the contents of graft copolymer, free NR and free copolymer. All calculations are presented as eq. 3.1-3.5.

$$\text{Total conversion (\%)} = \frac{\text{Weight of gross polymer products} - \text{weight of NR}}{\text{Weight of monomer charged}} \times 100 \quad (3.1)$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Weight of monomer grafted}}{\text{Weight of monomer polymerized}} \times 100 \quad (3.2)$$

$$\text{Free NR (\%)} = \frac{\text{Weight of free NR}}{\text{Weight of gross polymer products}} \times 100 \quad (3.3)$$

$$\text{Free copolymer (\%)} = \frac{\text{Weight of free copolymer}}{\text{Weight of gross polymer products}} \times 100 \quad (3.4)$$

$$\text{Graft copolymer (\%)} = \frac{\text{Weight of graft copolymer}}{\text{Weight of gross polymer products}} \times 100 \quad (3.5)$$

3.6 Characterization of Graft Copolymer

After soxhlet extraction, the structure and composition of graft copolymer, NR-*g*-(ST-*co*-ACN), were evaluated.

3.6.1. Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR spectra of the graft copolymer obtained after soxhlet extraction was compared to NR structure by using a Perkin Elmer 2000 model: Thermo 470 FT-IR in the range of 4000–400 cm^{-1} . The sample was dissolved in chloroform and then casted onto a NaCl disk.

3.6.2. Nuclear Magnetic Resonance Spectroscopy (NMR)

The rubber samples were swollen in CDCl_3 . The structure of graft copolymer was analyzed by using ^1H -NMR and ^{13}C -NMR spectroscopy (DPX-400). The results from NMR spectra were used to determine the content of specific functional groups: styrene, isoprene and acrylonitrile in the structure of graft copolymer.

3.6.3. CHN Analyzer

Elemental Analyzer, model of Perkin Elmer, was used to measure the contents of carbon, hydrogen and nitrogen in the NR-g-(ST-co-ACN) samples.

3.7 Preparation of NR/NBR Blends Compatibilized by GNR

The NR/NBR blends at 50/50 wt% were compatibilized by mixing with various content of GNR (5-20 phr) obtained from solution graft copolymerization initiated by BPO. The GNR in these blends contained various % graft copolymer from 53-85%. These blends were prepared by using a two-roll mixing mill at room temperature. NR was masticated for 2 min and then NBR was subsequently added. After the homogenization of the rubber blend (ca. 5 min), the GNR and chemicals for vulcanization were added. The processing time after each component addition was ca. 2 min. The vulcanizing agents used for blending was given as shown in Table 3.1. Thin rubber sheets from the two-roll mill were then pressed by a compression-molding machine at 150 °C with a pressure of 150 kg cm⁻² and optimum cure time detected by Oscillating Disk Rheometer (ODR, Techpro Model 121105) at the same compression temperature.

3.8 Mechanical and Physical Testing of NR/NBR Vulcanizates

3.8.1 Tensile Properties (ASTM D 412)

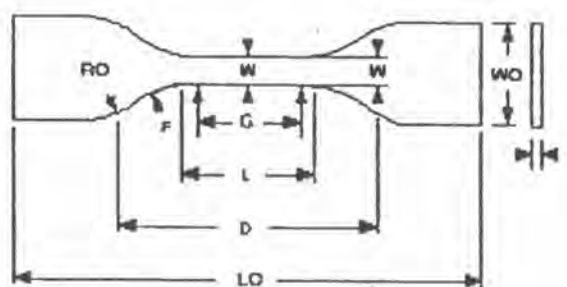
The NR/NBR vulcanizates were cut as dumbbell-shaped pieces (Type IV) as illustrated in Figure 3.1. The thickness of the test specimens was 2.0 mm. The tensile properties of NR/NBR vulcanizates were performed on a universal testing machine (LLOYD LR 10 K) with a cross-head speed of 500 mm/min.

3.8.2 Hardness

The method for hardness testing followed ASTM D 2240. The hardness of specimens were measured using a Durometer Hardness System Model 716 shore A.

Table 3.1 Formulation for vulcanization system.

Ingredients	phr
NR	50
NBR	50
ZnO	5.0
Stearic acid	1.5
Sulphure	2.5
TMTD	1.0
CBS	0.6



W : 6 mm WO : 19 mm G : 25 mm R : 14 mm T : 4 mm
L : 33 mm LO : 115mm D : 65 mm RO : 25mm

Figure 3.1 Diagram of tensile test specimen (type IV).

3.8.3 Measurement of Swelling Behaviour

Oil resistance of the NR/NBR vulcanizates was determined by swelling method. Oil used in this test was IRM 903 oil (ASTM #3 oil). The NR/NBR vulcanizates were slivered approximately $2 \times 2 \text{ cm}^2$ in size and weighted before immersion before in oil (ca. 60 cm^3) at room temperature for 70 h. The specimens were then removed, quickly dipped in acetone at room temperature and lightly wiped by tissue paper to remove the excess oil from their surface and weighted to redetermine. The %change in mass was calculated by using eq. 3.6.

$$\%Swelling = \frac{(M_2 - M_1)}{M_1} \times 100 \quad (3.6)$$

where :

M_2 is mass of specimen after immersion, g

M_1 is mass of specimen before immersion, g

3.8.4 Determination of volume fraction

The crosslinking efficiency of the specimens was evaluated in terms of crosslink density using an equilibrium solvent swelling test method. The specimens (10x10x2 mm) with accurately weighted were immersed in toluene and allowed to swell in closed vessels for 7 days. Then, the surface of the swollen samples was quickly wiped and weighed (w_1). After drying at 40°C for 48 h, the dried rubber samples were weighed (w_2) to determine the amount of absorbed toluene inside the sample. The volume fraction of polymer in the swollen specimens (v) was calculated using eq.3.7.

$$v = \frac{w_2(\delta_r)^{-1}}{w_2(\delta_r)^{-1} + (w_1 - w_2)(\delta_s)^{-1}} \quad (3.7)$$

where δ_r and δ_s are the density of rubber and solvent (0.87g/cm³) (Sperling, 2006), respectively.

3.8.5 Scanning Electron Microscopy (SEM)

The morphology of tensile fracture surface of the NR/NBR vulcanizates obtained from the tensile properties test was investigated using a JEOL model JSM-6400 scanning electron microscopy at 15 kV. The specimens were mounted on a SEM stub using a double-side tape and the fracture surface of specimens was coated with gold.

3.8.6 Determination of the Morphology of GNR latex

The morphology of the GNR latex was examined using a transmission electron microscope (TEM) (JEM- 2100) and the accelerating voltage was in the

range of 160-200 kV. The GNR latex was diluted for 400 times with distilled water to a concentration of 0.05 wt%. In 1 cm³ of this solution, 2% aq. OsO₄ solution was added and allowed to stain the NR phase in the graft product for overnight. The latex was then placed on a grid and dried before evaluation.

3.8.7 Determination of Dynamic Mechanical Properties of Vulcanizates

Dynamic mechanical analysis (DMA) of NR/NBR vulcanizates in a rectangular shape (3x10x2 mm) was investigated using a dynamic mechanical analyzer (Mettler Toledo DMA/SDTA 816°). The range of testing temperature was -130 to 100°C with 5°C min⁻¹ of heating rate under nitrogen atmosphere. The tension mode was applied with a constant frequency and amplitude at 1 Hz and 1 μm, respectively. The storage modulus (E'), loss modulus (E'') and the mechanical loss factor ($\tan \delta = E''/E'$) were reported.