CHAPTER III
EXPERIMENTAL

3.1 Materials

1. Natural rubber (60% dry rubber content): Rubber Research Institute of Thailand
2. Hexadecyltrimethylammonium bromide (CTAB) (98% purity), cationic surfactant: Acros Organics
3. Styrene monomer (99% purity): Aldrich
4. 2,2'-Azobis (2-methylpropionamidine) dihydrochloride or V50 (97% purity), initiator: Aldrich
5. Sodium hydroxide or NaOH: Carrlo Eba Reagent Company
6. Sulphur: Rubber Research Institute of Thailand
7. *N*-cyclohexyl-2-benzothiazolesulfenamide or CBS: Rubber Research Institute of Thailand
8. Zinc oxide or ZnO: Rubber Research Institute of Thailand
9. Stearic acid: Rubber Research Institute of Thailand
10. Toluene: Lab-scan
11. Acetone: Lab-scan
12. Hydrophilic fumed silica (Aerosil 200, BET = 200 m^2/g, particle size = 12 nm): Degussa AG

All materials except NR were used without further purification.

3.2 Equipment

1. Centrifuge: Z 383 K, HERMLE
2. Vacuum oven: Medcenter Ernrichtugen GmbH, MMM group
3. Polymerization Reactor: Büchiglasuster BEP280 (see Figure 3.1)
    - Reactor (1000 mL of volume) equipped with adjustable agitator, buffer and blade.

4. Fourier transform infrared spectrometer (FTIR): Nexus 670 spectrometer-Nicolet (transmission mode)
5. Thermogravimetric analysis: Perkin Elmer, model Pyris diamond TG-DTA
6. Brabender Plasti-corder PL2100:
    - Dynamometer unit = DC gear motor and oscillating in bearing
    - Power = 6.5 kW (8.8 hp), torque = max. 400 Nm.
    - Capacity of mixing chamber = 50 cc.
7. Compression moulding machine: Wabash, model V50H-18-CX (50 compress tons, 5 motor hp)
8. Universal testing machine: Lloyd, model LRX
9. Refrigerator: Goldstar, model GR-492WV
10. Oscillating disk rheometer (ODR): Rheotech, model 121105
11. Shore A Durometer: Zwick/3100
12. Pneumatic Punch
13. Density kit: Sartorius BP 120 D
14. Capillary Rheometer: Ceast, model Rheologic 5000 Twin bore
    - Load cell = 40 kN
    - Circular die dimensions are;
        i. 1 mm diameter and 0.5, 5, 20 mm length
        ii. 2 mm diameter and 15 length
    - Slit die dimensions are 1 mm thick, 10 mm width and 124 mm length

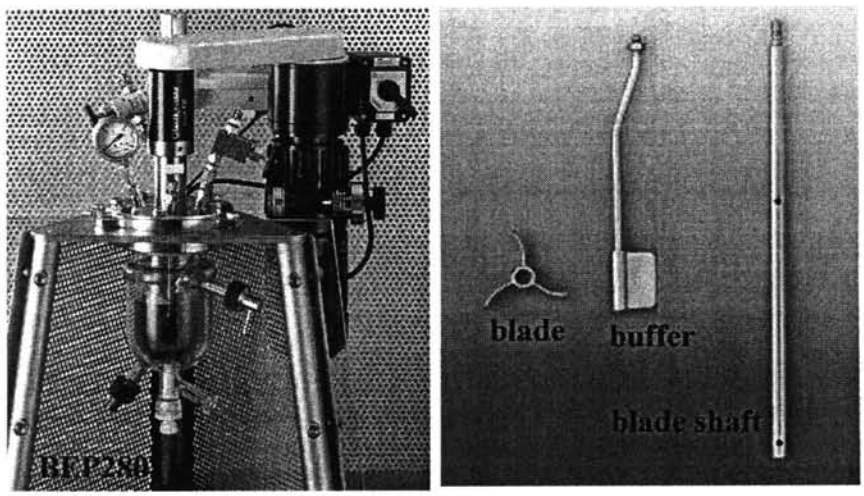

Figure 3.1 Polymerization reactor (Büchiglasuster BEP280) and accessories.

3.3 Methodology

3.3.1 Preparation of Admicelled PS-NR

3.3.1.1 *Latex purification*

Natural rubber latex particles were purified by centrifugation at the speed of 10,000 rpm (20°C) for 20 min and re-dispersed in distilled water with pH of 8 (pH is adjusted with NaOH) for 2 times to remove dissolved impurities and to reduce the particle size distribution. The resulted particles were considered to be clean. After washing, the particles were re-suspended in water with pH of 8 for supporting CTAB surfactant.

3.3.1.2 *Admicellar Polymerization*

The natural rubber latex 50 g was dispersed in distilled water with pH of 8 and re-suspended in the CTAB surfactant of 2800 μM under basic condition. The total volume of solution was made until 1,000 ml by adding water with pH of 8 and then poured into the polymerization reactor. The reaction of admicellar polymerization was started by stirring (500 rpm) at 30°C for 12 h to reach the equilibrium of surfactant adsorption. After this period, the styrene monomer with required concentration (50, 100, 200 and 300 mM) was added into polymerization reactor and kept the monomer adsolubilization reaching to equilibrium in 4 h at

30°C. After that, the V50 initiator with ratio of styrene and initiator at 1:0.04 was added into polymerization reactor to initiate the polymerization of styrene at 70°C for 4 h. At the end of polymerization reaction, the reaction was stopped by immersing the solution in the ice bath for 30 min. The natural rubber emulsions were washed by distilled water to remove the outer layer of CTAB surfactant by centrifugation at the speed of 10,000 rpm (20°C) for 20 min. After finishing the admicellar polymerization, the modified natural rubber was dried in vacuum oven at 70°C for 3 days and then the admicelled PS-NR was obtained.

3.3.2 Characterizations of Admicelled PS-NR

3.3.2.1 *Fourier Transformed Infrared Spectroscopy*

FTIR spectra was used to determine the formation of polystyrene films coated on surface of natural rubber. The absorption spectra were obtained from a Nexus 670 spectrometer (Nicolet) with 64 scans at a resolution of 4 cm^{-1} and a frequency range of 4000 to 400 cm^{-1}. To get the sharp peaks in FTIR spectra, the films of all samples for FTIR measurement were prepared by heated compression moulding machine at clamping pressure of 15 tons-force (150°C) for 15 min.

3.3.2.2 *Thermogravimetric Analysis*

Thermal analysis of the product was carried out under nitrogen atmosphere at flow rate of 100 ml/min by using TG-DTA (Perkin Elmer, model Pyris dimond TG-DTA) to observe thermal stability and degradation temperatures of admicelled PS-NR. Samples were put into the Pt pan and heated from 30-600°C at a heating rate of 10°C/minute.

3.3.3 Testing of Admiclled PS-NR

The admicelled PS-NR with styrene monomer concentrations of 50, 100, 200 and 300 mM were also prepared as 4 different products listed in Table 3.1 by Brabender Plasticorder PL2100 with average mixing time for 12 min at 60°C (30 rpm).

Table 3.1 Chemical ingredients used in admicelled PS-NR

Chemical Ingredients	Quantities (phr)			
	Pure Admicelled PS-NR	Cured samples	NR blended samples	Silica filled samples
Admicelled PS-NR	100	100	50	100
Natural rubber	-	-	50	-
ZnO	-	5	-	-
Stearic acid	-	2	-	-
CBS	-	0.8	-	-
Sulfur	-	3	-	-
Silica	-	-	-	30

3.3.3.1 *Measurement of Rheological Property*

The capillary rheometer was used to investigate the rheological behavior of admicelled PS-NR with different styrene concentrations. The measurement was separated according to different die profile.

- Circular die test

There are two different die dimensions used in measurement of apparent shear stress, apparent shear viscosity and die swell, which are;

1. Dimensions of 1 mm diameter and 0.5, 5 and 20 mm length (L/D = 0.5, 5 and 20) were used for pure admicelled PS-NR with 50 and 100 mM-styrene. The measurement was carried out at 130, 140, 150, 160 and 170°C over wide range of shear rates at 10-1,000 s^{-1}. A Rabinowitsch correction is executed automatically by the system but no Bagley correction performed.

2. Dimensions of 2 mm diameter and 15 mm length (L/D = 7.5) were used for NR blended admicelled PS-NR and silica filled admicelled PS-NR. The measurement was carried out at 150°C over wide range of shear rates at 10-1,000 s^{-1}. A Rabinowitsch correction is executed automatically by the system but no Bagley correction performed.

- Slit die test (1 mm thick, 10 mm wide and 124 mm long)

The real shear stress and real viscosity were determined using the shear rates of 10, 30, 60, 100, 200, 300 and 600s^{-1} at 150°C.

3.3.3.2 *Measurement of Physical Property*

3.3.3.2.1 Tensile testing

The Lloyd universal testing machine (LRX) was used to measure the tensile strength, elongation at break and young's modulus of samples. The specimens were prepared as standard dumbbell tensile test prescribed by ASTM D-412. Testing was done at room temperature with crosshead speed of 500 mm/min. The five specimens of same product were tested and alternatively calculated the median. The test specimen was also carried out in oven at 100°C for 48 h to test the thermal aging prescribed by ASTM D 573-04, the test pieces after aging were stored for 16 h before measuring the tensile properties.

3.3.3.2.2 Hardness

The test specimens were measured for the hardness by Shore A durometer prescribed by ASTM D-2240. The five determinations of hardness at different positions on the 5 layers of tensile specimen were alternatively calculated the median.

3.3.3.2.3 Cure Characteristics

The determination of cure characteristics (e.g. cure rate, cure time, scorch time and min/max torque) were measured using Rheotech 121105 with applied 3° arc strain and carried out at 150°C in accordance with test method D-2084.

3.3.3.2.4 Torque measurement

The admicelled PS-NR was measured for the torque using Brabender Plasticorder PL2100 at rotor speed of 30 rpm (60°C) with average mixing time for 12 min.

3.3.3.2.5 Ozone resistance

Measurement of ozone resistance was prescribed by ISO 1431. The cured specimen with dimensions of 2 mm thickness, 2 cm width and 8 cm length was stretched at 20% elongation and keep in the dark room for 48 h and then exposed to ozone atmosphere (O_3) with concentration of 50 pphm (part per hundred million), 40°C for 72 h. After exposing wit O_3, the cracking on specimen was observed.

3.3.3.2.6 Crosslink Density

The toluene solvent was used to swell the cured samples for determination of their crosslink density using Flory-Rehner equation which was prescribed by ASTM D-6814-02.

$$v_e = \rho_d / M_c = - [\ln(1-V_r) + V_r + \chi_1 V_r^2]/[V_1(V_r^{1/3}-V_r/2)]$$

where:

v_e = crosslink density (mol/cm^3)

V_r = volume fraction of polymer in a swollen network in equilibrium with pure solvent and is calculated as:

$$V_r = [W_d/\rho_d]/[(W_d/\rho_d) + (W_s/\rho_s)]$$

where:

W_d = weight of dry rubber

W_s = weight of solvent adsorbed by sample

ρ_s = density of toluene = 0.867 g/cc

ρ_d = density of dry rubber using Density kit

χ_1 = NR-toluene interaction parameter = 0.391*

V_1 = molecular volume of toluene = 106.3 cm^3/mol

M_c = average molecular weight between network crosslinks (g/mol)

* χ_1 = 0.391 obtained from ASTM D 6814-02