

CHAPTER III EXPERIMENTAL

3.1 Materials

Natural Rubber (60% dry rubber content) was obtained from Rubber Research Institute of Thailand. Hexadecyltrimethylammonium bromide (CTAB, 98%) and styrene monomer (99%) were purchased from Fluka. 2,2' Azo-bis(2-methylpropionamidine) (V50, 97%), a water insoluble initiator, was provided from Aldrich. Sodium bromide (99.5%) was obtained from Unilab. Tetrahydrofuran (THF/99.8%) was purchased from LAB-SCAN. Ethanol absolute anhydrous (99.9%) was obtained from J.T. Baker. All materials were used without further purification.

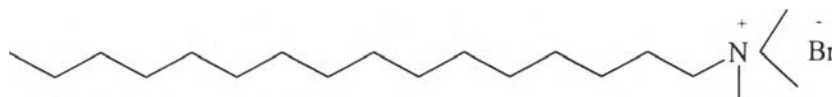


Figure 3.1 Cetyltrimethylammonium bromide.

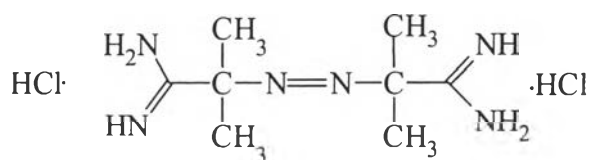


Figure 3.2 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V50).

3.2 Equipment

- Particle size analyzer: MALVERN Mastersizer X Ver.2.15
- Centrifuge: Z 383 K, HERMLE
- Shaking bath: MEMMERT
- Vacuum oven: Medcenter Emrichtugen GmbH, MMM group

- Optical microscope: ELICA DMRXP
- Scanning electron microscope: JEOL JSM -5200
- Thermogravimetric analysis: Perkin Elmer, model Pyris diamond TG-DTA
- Fourier transform spectrometer: BRUKER EQUINOX55/S
- UV visible spectroscopy: PERKIN ELMER LAMDA 10
- Drop shape analysis: KRUSS DSA 1v 1.80
- Hydraulic pressure: GRASEBY SPECAC
- Electrophoretic mobility: Zeta meter 3.0+
- Refrigerator
- Nylon membrane: Spectra[®]/Por[®] Pore Size 0.2 μm
- Screw-cap test tube
- Compression molding

3.3 Experimental Procedures

3.3.1 Purification of the NR Latex

NR latex particles were purified by centrifugation (at 20°C, 8,000 rpm, 20 min) and were redispersed in distilled water 2 times to remove dissolved impurities and to reduce the particle size distribution. The resulting particles were considered to be clean. After washing, the particles were resuspended in water at pH 8.

3.3.2 Particle Size Measurement

The size of NR latex after purification was measured using a particle size analyzer according to instructions provided with the instrument and using a 45 mm lens. The results were measured by the principle of beam obscuration (beam length 2.4 mm). The instrument yielded the average particle size, the standard size distribution and the specific surface area. The specific surface area was calculated from the particle diameter with the assumption of spherical particles of constant volume.

3.3.3 Electrophoretic Mobility Measurement

The surface charge of latex particles is important to determine the surfactant adsorption. The solution pH is a parameter that influences the surface charge of particles. From this reason, electrophoretic mobility was used to determine the surface charge of the latex particles at various solution acidities. The pH of the natural rubber solution was adjusted by 0.01 and 0.1 M standard solution of hydrochloric solution (HCl) and sodium hydroxide (NaOH). The electrophoretic mobility of the latex particles was observed at room temperature with Zeta Meter 3.0+

3.3.4 Equilibration Time for Surfactant Adsorption

The hexadecyltrimethylammonium bromide (CTAB) solutions were prepared in water pH 8. Then, 20 mL was pipetted into a vial screw cap test tube (6 dam) containing 1 mL of 1 % NR solution. The mixture consisted of 0.01g rubber particles and 2,000 μ M CTAB in a total volume of 21 mL. Tubes were agitated in a shaking bath at 30 °C and samples were taken out periodically to find the time for equilibrium. The NR particles were separated from the mixture by filtering the mixture through a nylon membrane. The concentration of filtrate or equilibrium CTAB concentration (equilibrium concentration) was determined by measuring the surface tension. The linear region of the relationship between surface tension and CTAB concentration was used as the calibration curve. The CTAB solution of unknown concentration was diluted into the linear region and the equilibrium concentration calculated. The difference between the final concentration and equilibrium concentration is called adsorbed CTAB. The plot of time and the adsorbed surfactant was prepared to get the time for equilibrium adsorption where there is no donor charge in adsorbed surfactant.

3.3.5 Surfactant Adsorption Isotherm

Solutions of various initial CTAB concentrations were prepared in water pH 8. The concentration of CTAB prepared must be calculated for suitable final CTAB concentration (final concentration). Then, 20 mL of each of the CTAB solutions was added into a vial screw cap test tube (6 dram) containing 1 mL of 1 % NR solution (0.01 g DRC). The tubes were agitated in a shaking bath at 30 °C for a period of equilibrium surfactant adsorption (15 hrs). The NR particles were separated from the mixture by filtering the mixture through a nylon membrane. The concentrations of filtrates or equilibrium CTAB concentration (equilibrium concentration) were determined by using the surface tension measurement technique as above. The plot of equilibrium concentration versus the amount of adsorbed surfactant was made to yield the surfactant adsorption isotherm.

3.3.6 Styrene Adsolubilization Measurement

Hexadecyltrimethylammonium bromide solution concentration 2,100 μM was prepared in water pH 8. Then, 10 mL was pipetted into a vial screw cap test tube (6 dram) containing 1 mL of 1 % NR solution and 9 mL of water. The mixture was agitated in a shaking bath at 30°C for an equilibration period of 15h to form surfactant bilayer. The pure styrene monomer was pipetted into each tube. These mixtures consisted of 0.01g rubber particles, 1,000 μM CTAB and styrene monomer at various concentrations (final styrene concentrations) in a total volume of 21 mL. The tubes were agitated in a shaking bath at 30 °C again for 2 hrs for adsolubilization of styrene into surfactant bilayer. The NR particles were separated from the mixture by filtering the mixture through a nylon membrane. Concentrations of styrene monomer in the filtrates or equilibrium styrene concentrations were determined using UV visible spectroscopy at wavelength 247 nm. The difference between the final styrene concentration and equilibrium styrene concentration is called adsolubilized styrene concentrations (adsolubilized concentrations). The plot of equilibrium styrene concentration and absorbed styrene concentration was made as the graph of styrene adsolubilization.

3.3.7 Polymerization of Polystyrene onto Latex Particle

Admicellar polymerization of polystyrene on natural rubber was carried out at various styrene concentrations. The conditions of polymerization of polystyrene on NR particles are shown below.

CTAB concentration = 1,000 μM

Styrene:V50 molar ratio = 2:1

Dry rubber content of natural rubber = 1 g.

Table 3.1 Concentrations of styrene monomer and V50 used in the experiments.

Monomer(styrene) (μM)	Initiator(V50) (μM)
5	2.5
10	5
20	10
30	15
40	20
50	25
100	50

The polymerization experiment followed the same procedure as in monomer adsolubilization experiment. The process started with adsorption of CTAB bilayer on NR particles by agitating the mixture of NR and CTAB at 30°C in the shaking bath for 15 h. After that, styrene monomer at various concentrations as shown in Table 3.1 was added into the system. The mixture was continuously agitated in the shaking bath for 2 h for monomer adsolubilization. Then V50 was added into the system (the amount as shown in Table 3.1) to start the polymerization reaction. Polymerization reaction of styrene was set at 70°C in the shaking bath for 2 h. At the end of the polymerization time, the reaction was stopped by immersing the reaction vials in an ice bath for 10 minutes. The NR particles were washed with water to remove the upper layer of surfactant by filtering through a dialysis tube (Cellulose membrane, what molecular weight cutoff: 12,000) and separated from the mixture by

centrifuging at 3000 rpm. Finally, the products were dried in the vacuum oven at 70°C for 16 hours.

3.3.8 Testing and Characterization

Fourier Transform Spectrometer

FTIR spectra was used to study the chemical composition of the product with 32 scans at a resolution of 4 cm^{-1} . The samples were detected in the frequency range 4000-400 cm^{-1} using a deuterated triglycinesulfate (DTGS) as a detector with a specific directivity, D^* , of $1 \times 10^9 \text{cm} \cdot \text{Hz}^{1/2} \cdot \text{W}^{-1}$. Because FTIR has very high sensitivity, the products were compressed by compression molding before characterization to form a very thin film of sample and to get sharp peaks in the FTIR spectra. The condition of compression molding (Wabash model V50H-18-CX) was preheating at 150 °C for 3 minutes and compressing at 150 °C, pressure 10 tons for 3 minutes, then cooling the sample to 40°C under pressure.

Thermogravimetric Analysis

To study the thermal property of the product, TG-DGA (Perkin Elmer, model Pyris diamond TG-DTA) was used to observe thermal stability and degradation temperature of the product. Samples were put into the Pt pan and heated from 30-600°C at a heating rate of 10°C/minute under nitrogen atmosphere with 100 mL/min flow rate.