

CHAPTER III METHODOLOGY

3.1 Materials

1. Natural rubber (60 wt% dry rubber content) was purchased from Rubber Research Institute of Thailand.
2. Dodecylbenzenesulfonic acid sodium salt (DBSA); anionic surfactant was obtained from Fluka, CAS No. 25155-30-0, Linear Formula $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, Molecular Weight 348.48
3. Hexadecylpyridinium chloride monohydrate (CPC) (99% purity); cationic surfactant was purchased from Sigma, CAS No. 6004-24-6, Empirical Formula (Hill Notation) $\text{C}_{21}\text{H}_{38}\text{ClN} \cdot \text{H}_2\text{O}$, Molecular Weight 358.00
4. Polyoxyethylene nonylphenol (Synperonic[®] NP30); nonionic surfactant was obtained from Aldrich, CAS No. 9016-45-9, Molecular Weight 680.00
5. 3-(4-Heptyl)phenyl-3-hydroxypropyl)dimethylammoniopropanesulfonate (C7BzO) (98% purity); zwitterionic surfactant was purchased from Sigma, Molecular Weight 399.00
6. 3-(Trimethoxysilyl)propylmethacrylate monomer (MPS) (98% purity) was obtained from Aldrich, CAS No. 2530-85-0
7. Potassium persulfate (KPS) (97% purity); initiator was purchased from Aldrich, CAS No. 7727-21-1, Linear Formula $\text{K}_2\text{S}_2\text{O}_8$, Molecular Weight 270.32
8. Sodium hydroxide (NaOH) was obtained from MERCK CAS No. 131073-2, Molecular weight 40.00
9. Hydrochloric acid (HCl) (37 wt%) was purchased from Carlo Erba Reagent Company.

All materials were used without further purification.

3.2 Equipments

1. Centrifuge: Kubota 5922
2. Shaking bath: Memmert
3. pH meter: Eutech instruments pH 510
4. Microcentrifuge: Sartorius GIBTHAI Co., Ltd.
5. Vacuum oven: Isotemp vacuum oven Model 2854
6. UV visible spectrophotometer: Shimadzu UV 1800
7. Particle size analyzer: Malvern Mastersizer X Ver.2.18
8. Fourier transform infrared spectrometer: FT-IR, Thermo Nicolet Nexus 670
9. Thermogravimetric analysis: TG-DTA, Perkin Elmer, Pyris diamond
10. Scanning electron microscope: FE-SEM, Hitachi S4800
11. Transmission electron microscope: TEM, Hitachi H-7650

3.3 Methodology

3.3.1 Purification of the NR Latex

Natural rubber latex particles were purified by centrifugation (at 20°C, 10000 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 suitable pH that depending on type of surfactant.

3.3.2 Particle Size Measurement

The size of NR latex 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 Surfactant Adsorption Isotherm

3.3.3.1 Surfactant Adsorption Isotherm for cationic surfactant (hexadecylpyridinium chloride monohydrate, CPC)

Solutions of various initial surfactant concentrations were prepared in water at pH 8. The concentrations of surfactant were prepared from 1 to 30 mM. Then, 19 ml of each of the surfactant solutions was added into a vial screw cap test tube containing NR solution 5, 10 and 20 w/v% (1, 2 and 4 g dry rubber content) and was adjusted to pH 8 and make volume to 20 ml. The tubes were agitated in a shaking bath at 30°C for a period of equilibrium surfactant adsorption (4 hrs). The NR particles were separated from the mixture by filtering the mixture through a cellulose acetate membrane. The concentrations of filtrates or equilibrium surfactant concentrations (equilibrium concentration) were determined by using the UV visible spectroscopy measurement technique. The plot of equilibrium concentration versus the amount of adsorbed surfactant was made yield the surfactant adsorption isotherm.

3.3.3.2 Surfactant Adsorption Isotherm for anionic surfactant (dodecylbenzenesulfonic acid sodium salt, DBSA)

Solutions of various initial surfactant concentrations were prepared in water at pH 3. The concentrations of surfactant were prepared from 1 to 30 mM. Then, 19 ml of each of the surfactant solutions was added into a vial screw cap test tube containing NR solution 5, 10 and 20 w/v% (1, 2 and 4 g dry rubber content) and was adjusted to pH 3 and make volume to 20 ml. The tubes were agitated in a shaking bath at 30°C for a period of equilibrium surfactant adsorption (4 hrs). The NR particles were separated from the mixture by filtering the mixture through a cellulose acetate membrane. The concentrations of filtrates or equilibrium surfactant concentrations (equilibrium concentration) were determined by using the

UV visible spectroscopy measurement technique. The plot of equilibrium concentration versus the amount of adsorbed surfactant was made yield the surfactant adsorption isotherm.

3.3.3.3 Surfactant Adsorption Isotherm for zwitterionic surfactant (3-(4-heptyl)phenyl-3-hydroxypropyl) dimethylammoniopropanesulfonate, C7BzO)

Solutions of various initial surfactant concentrations were prepared in water at pH 3 and 8. The concentrations of surfactant were prepared from 1 to 30 mM. Then, 9 ml of each of the surfactant solutions was added into a vial screw cap test tube containing NR solution 5, 10 and 20 w/v% (0.5, 1 and 2 g dry rubber content) and was adjusted to pH 3 and 8 then make volume to 10 ml. The tubes were agitated in a shaking bath at 30°C for a period of equilibrium surfactant adsorption (4 hrs). The NR particles were separated from the mixture by filtering the mixture through a cellulose acetate membrane. The concentrations of filtrates or equilibrium surfactant concentrations (equilibrium concentration) were determined by using the UV visible spectroscopy measurement technique. The plot of equilibrium concentration versus the amount of adsorbed surfactant was made yield the surfactant adsorption isotherm.

3.3.3.4 Surfactant Adsorption Isotherm for nonionic surfactant (polyoxyethylene nonylphenol, NP30)

Solutions of various initial surfactant concentrations were prepared in water at pH 3, 3.9 and 8. The concentrations of surfactant were prepared from 1 to 30 mM. Then, 19 ml of each of the surfactant solutions was added into a vial screw cap test tube containing NR solution 5, 10 and 20 w/v% (1, 2 and 4 g dry rubber content) and was adjusted to pH 3, 3.9 and 8 then make volume to 20 ml. The tubes were agitated in a shaking bath at 30°C for a period of equilibrium surfactant adsorption (4 hrs). The NR particles were separated from the mixture by filtering the mixture through a cellulose acetate membrane. The concentrations of filtrates or equilibrium surfactant concentrations (equilibrium concentration) were determined by using the UV visible spectroscopy measurement technique. The plot of

equilibrium concentration versus the amount of adsorbed surfactant was made yield the surfactant adsorption isotherm.

3.3.4 Polymerization of MPS onto Latex Particle using cationic surfactant

Admicellar polymerization of PMPS on natural rubber was carried out at various MPS concentrations (50, 100 and 200 mM). The process started with adsorption of CPC surfactant bilayer on NR particles by agitating the mixture of NR and surfactant at 30°C in the shaking bath for 4 hrs. After that, MPS monomer at various concentrations was added into the system. The mixture was continuously agitated in the shaking bath for 2 hrs. Then KPS (with ratio of MPS and initiator at 1:0.01) was added into the system to start the polymerization reaction. Polymerization reaction of MPS was set at 70°C in the shaking bath for 3 hrs. 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 and separated from the mixture by centrifuging at 3000 rpm. Finally, the products were dried in the vacuum oven at 70°C for 16 hrs.

3.3.5 Polymerization of MPS onto Latex Particle using anionic surfactant

Admicellar polymerization of PMPS on natural rubber was carried out at various MPS concentrations (50, 100 and 200 mM). The process started with adsorption of DBSA surfactant bilayer on NR particles by agitating the mixture of NR and surfactant at 30°C in the shaking bath for 4 hrs. After that, MPS monomer at various concentrations was added into the system. The mixture was continuously agitated in the shaking bath for 2 hrs. Then KPS (with ratio of MPS and initiator at 1:0.01) was added into the system to start the polymerization reaction. Polymerization reaction of MPS was set at 70°C in the shaking bath for 3 hrs. 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 and separated from the mixture by centrifuging at 3000 rpm. Finally, the products were dried in the vacuum oven at 70°C for 16 hrs.

3.3.6 Modified Natural Rubber Characterization

3.3.6.1 Particle size measurement

The size of admicelled PMPS-NR 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.

3.3.6.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra used to determine the information of PMPS film coated on surface of natural rubber. The absorption spectra were obtained from a Thermo Nicolet Nexus 670 Spectrophotometer with a resolution of 4 cm^{-1} in the frequency ranged from 4000 to 650 cm^{-1} . The absorbance were detected by using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D^* of $1 \times 10^9\text{ cmHz}^{1/2}\text{w}^{-1}$ with a repetition of 64 scans.

3.3.6.3 Thermal Properties

Thermal analysis of the products were carried out under nitrogen atmosphere at flow rate of 100 ml/min by using TG-DTA to observe thermal stability and degradation temperatures of the products. Samples were put into the Pt pan and heated from 30 - 600°C at a heating rate of $10^\circ\text{C}/\text{minute}$.

3.3.6.4 Surface Morphology

3.3.6.4.1 Field emission scanning electron microscope (FE-SEM) and Energy-dispersive X-ray spectroscopy (EDX)

FE-SEM and EDX were used to study phase morphologies of the products after admicellar polymerization. The samples were

prepared by dipping the dry specimens into liquid nitrogen and breaking in liquid N₂ at temperature about -70°C. The cross section area was coated with Pt under vacuum and observed by FE-SEM. All FE-SEM results were obtained for the magnification of 750 and 1500 times at 15kV.

3.3.6.4.2 Transmission electron microscope (TEM)

TEM observations were made on a TEM zero H-7650 (Hitachi High-Technologies Co., Japan) operating at an accelerating voltage of 100 kV. The collected samples were dispersed in distilled water under sonication for 5 min. After that, one drop of dilute suspension of the samples were deposited on a copper grid and left for drying overnight.