

CHAPTER III
EXPERIMENTAL

3.1 Equipment and Materials

3.1.1 Equipment

Table 3.1 Instruments and models used in this work

INSTRUMENT	MODEL
Total Organic Carbon Analyzer	TOC-V CSH, Shimadzu
UV-Visible Spectrophotometer	UV-2550, Shimadzu
Zeta potential	ZETA-METER 3.0 ⁺ Unit
GC headspace	Perkin Elmer
BET N ₂ surface area	Autosorb-1, Quantachrome
Particle Size Analyzer	Particle Size Analyzer Mastersizer X Ver. 2.15, MALVERN
Gel Permeation Chromatography	Water Gel Permeation Chromatography model 150-CV
Tensiometer	KRUSS model DSA 10
Thermogravimetric Analysis	Dupont Instrument model 2950
Atomic Force Microscopy	Digital Instruments Nanoscope III a

3.1.2 Materials

Arquad[®]T-50, HFP (Tallowtrimethyammonium chloride), a cationic surfactant, was obtained from Akzo Nobel. Teric[®]X-10, a nonionic surfactant, was provided from Eastasiatic Co., Ltd. Styrene (99+%) and isoprene (98+%) were supplied by Fluka. Sodium hydroxide pellets (99%)

were purchased from Fluka (Milwaukee, WI). Azobisisobutyronitrile (AIBN) with 98% purity, a water-insoluble initiator, was obtained from Aldrich Chemicals Company, Inc. (Milwaukee, WI). Tetrahydrofuran (THF) with AR grade was purchased from Lab-Scan Analytical Sciences (BKK, Thailand). Anhydrous ethyl alcohol was purchased from ITALMAR Co., Ltd. (BKK, Thailand). Hydrated amorphous silica, Hi-Sil[®]255, was obtained from Siam Silica Co., Ltd. All materials were used without further purification.

3.2 Methodology

3.2.1 Adsorption Isotherm

Samples of silica weighing 0.5 g were placed in 24 ml vials with 20 ml surfactant solution, which had been adjusted to pH 8. They were then allowed to equilibrate in a shaking waterbath at 1500 rpm, which controlled temperature at 30°C for 24 hr. The cationic/nonionic surfactant mixtures were varied at molar ratios of 3:1, 1:1, and 1:3. The supernatant was centrifuged and filtered using a syringe filter of 0.2 µm pore size. The supernatant was then analyzed for the amount of surfactant in the bulk phase by UV-Vis spectrophotometry and TOC. The surfactant adsorption was calculated by the concentration difference method, and the adsorption isotherm was plotted. From the adsorption isotherm, the critical micelle concentration (CMC) and maximum adsorption on Hi-Sil[®]255 could be determined. For the remaining admicellar polymerization runs, a feed concentration that equilibrates below the CMC (~80% of the CMC) was chosen in order to prevent micelle formation.

3.2.2 Adsolubilization Isotherm

Batch adsolubilization studies were carried out using styrene and isoprene. The organic solute and 2 g of silica were placed in 80 ml of surfactant solution at pH 8. They were stirred and allowed to equilibrate in a sealed container overnight. After equilibration, the supernatant was centrifuged and the bulk styrene and isoprene concentrations measured by headspace GC. Once the equilibrium concentrations were determined, the adsolubilization of styrene and isoprene into the mixed surfactant bilayer on silica was calculated through a simple mass balance. The

adsolubilization isotherms were plotted as adsolubilized organic solute ($\mu\text{mol/g}$) versus equilibrium organic concentration in the bulk phase (μM). This procedure was used for mixed surfactant systems (Arquad[®]T-50 with Teric[®]X-10) with three different surfactant adsorbed level ($200 \mu\text{mol/g}$, $350 \mu\text{mol/g}$ and $500 \mu\text{mol/g}$) on silica surface. A schematic diagram of the adsolubilization experimental plan is shown in Figure 3.1.

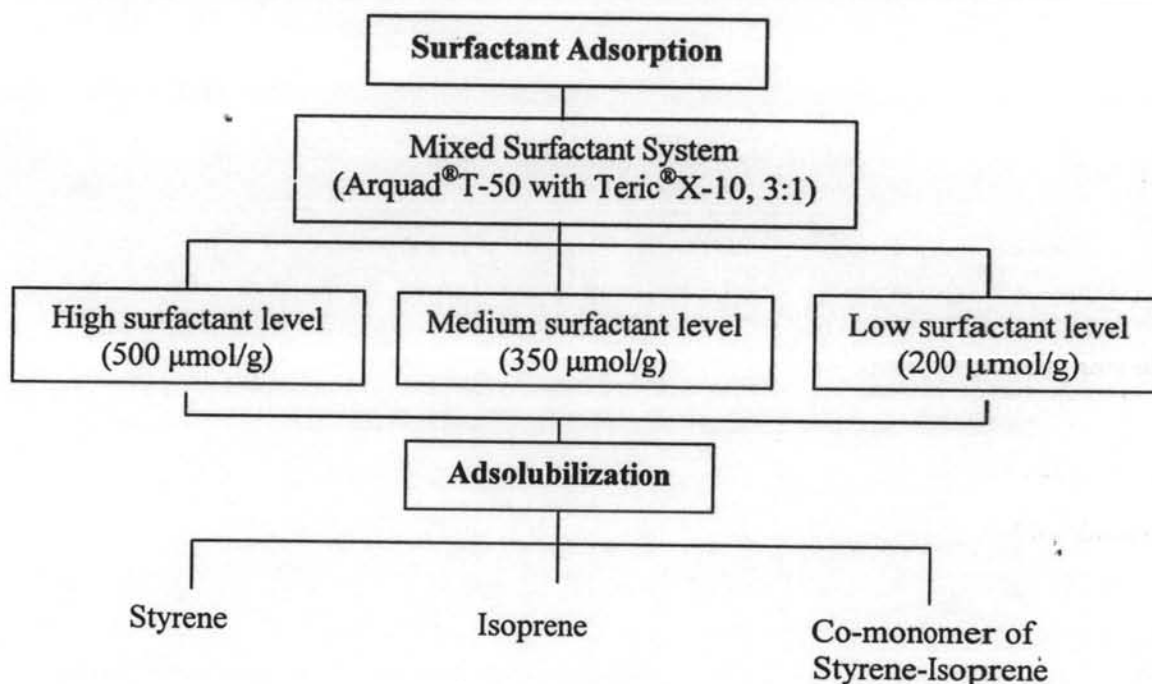


Figure 3.1 Schematic diagram of the adsolubilization.

3.2.3 Surface Modification Procedure

The continuous system mainly consists of a stirred feed tank, a polymerization reactor and a product tank. The feed tank made of stainless steel is approximately 17 l with a lid and baffles. The reactor vessel is a one-liter-borosilicate glass bottle with a screw cap. The product tank is a stainless steel bucket. Mixtures in the reactor and feed tanks were well-mixed with a magnetic bar and mechanical stirrer, respectively. Reaction temperature was maintained using a circulative heater, water bath, with $70 \pm 2^\circ\text{C}$. Fluid flow rate was controlled using a

Masterflex Digital console drive peristaltic pump with easy-load model 7518-60 head. The reactor system is shown in Figure 3.2.

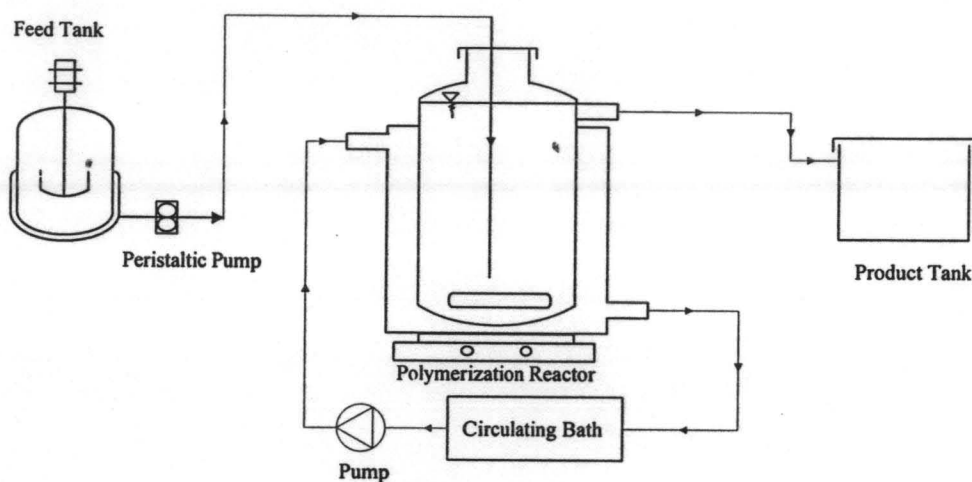


Figure 3.2 Continuous admicellar polymerization system.

The preparation of ultra-thin polymer films on silica was conducted by admicellar polymerization. Three levels of mixed surfactant adsorption and four levels of co-monomer adsolubilization (at various mole ratios of adsorbed surfactant: adsolubilized co-monomer; 4:1, 8:1, 16:1 and 32:1) were studied. The admicellar polymerization process was carried out following these steps;

1) Surfactants were added to 12.5 l of deionized water, which was adjusted to pH 8 by using sodium hydroxide solution, and stirred until dissolved. The mole ratio of AIBN and co-monomer was kept constant at 1:15.

2) AIBN and co-monomer were dissolved in 99.99 % ethanol at ratio of AIBN:ethanol, 0.5 g to 30 ml ethanol, solutions were mixed together with surfactant solution. Then, adding 1 kg of silica to the feed tank.

3) The mixture, with mechanical stirring 500 rpm, was left at 30°C for 24 hr for equilibration.

4) The polymerization was carried out by heating the 1000 ml reaction flask at 70°C with 30 min resident time then the slurry was cooled down in the product tank by the ice bath to terminate the polymerization reaction.

5) The modified silica was washed by distilled water until no foaming observed. Finally, the modified silica was dried at 110°C for 24 hr and sieved by a 120-mesh sieve.

3.2.4 Polymer Extraction

The modified silica was stirred overnight and then refluxed in THF at 65°C for 4 hr using the ratio of modified 7 g silica: 150 ml THF. The slurry was filtered and rinsed with hot THF (60°C) again. The filtrate was evaporated to reduce the volume. The polymer was precipitated by adding the concentration filtrate into methanol. The extracted polymer was filtered and dried in a vacuum oven at 40°C for 24 hr.

3.2.5 Characterization

3.2.5.1 *Electrostatic Potential Charge and Hydrophobicity*

A zeta potential meter was used to measure the electrostatic potential of unmodified silica, modified silica and extracted polymer. The silica does not dissolve in water but should be suspended. The silica particles moved from the anode toward the cathode or cathode to anode depending on the charge of the silica surface under a potential of 300 V. Hydrophobicity of the modified and unmodified silica was measured by a tensiometer. Silica was compressed to a thin plate. Then, a contact angle between water and silica surface was measured.

3.2.5.2 *Thermogravimetric Analysis*

Modified silica, extracted silica, pure silica, Arquad[®]T-50, Teric[®]X-10, silica after surfactant adsorbed and extracted polymer were analyzed by a TGA 5.1 Dupont Instrument model 2950. All samples were carried out from 30°C to 700°C at a heating rate of 10°C/min under nitrogen atmosphere.

3.2.5.3 *Gel Permeation Chromatography*

All extracted polymer samples were characterized by a 150-CV Water Gel Permeation Chromatography model. Tetrahydrofuran was used as a mobile phase at a flow rate 1.0 ml/min. Polymer solutions were auto

injected with a volume of 100 μl at temperature 30°C. The column set used was PLgel 10 μl mixed B 2 columns (Church Stretton, UK). Polystyrene standards were used for calibration.

3.2.5.4 *Surface Area and Particles size*

Surface area and particles size of modified and unmodified silica were observed by the BET autosorp technique and a particle size analyzer, respectively. For the BET autosorp technique, the silica was out gassed overnight at 200°C.

3.2.5.5 *Atomic Force Microscopy*

Samples were examined by a multimode atomic force microscope with Nanoscope IIIa software from Digital Instruments, Inc. Topographic and phase images were captured simultaneously using tapping mode AFM. A J-type scanner with the maximum scan size of 125 μm was used. Silicon tips with a resonant frequency of approximately 266.7 kHz and length of 125 μm were obtained from Digital Instruments, Inc. The microscope was enclosed within a Plexiglas® box (14" x 14" x 30"). All tapping mode images were captured at room temperature and in air with a relative humidity less than 25%.

3.2.6 Rubber Compounding

The rubber compound to be tested was formulated according to Table 3.2. The compound was a primary rubber formulation designed specifically for physical properties testing (Thammathadanukul *et al.*, 1996). A two-stage mixing procedure was employed to prepare all compounds. In the first stage, the rubber, filler and other ingredients (except vulcanizing agent) were mixed in a Dispersion Kneader Machine. The vulcanizing agent was added to the master batch in the second mixing step using a two-roll mill. All compounds were cured at 150°C to a time corresponding to T_{90} as determined on the moving die rheometer.

Table 3.2 Rubber compound formula

INGREDIENT	PARTS PER HUNDRED RUBBER (PHR)
Natural Rubber (STR 5L)	100
Silica	40
Zinc Oxide	5
Stearic Acid	2
Paraffinic Oil	5
Antioxidant (Wing stay-L)	1
Benzothiazyl Disulfide (MBTS)	1.8
Diphenyl Guanidine (DPG)	0.25
Sulphur	2

Table 3.3 Rubber compound test methods

PROPERTY	METHOD	INSTRUMENT
Cure Time (Maximum Torque, dNm; T90, minutes)	ASTM D 2084-93	Monsanto MDR 2000
Tensile (Max.Stress, Mpa; Elongation to Break %; Modulus, Mpa)	ASTM D 412-92	Instron Model 1011
Tear Strength, (N/mm)	ASTM D 2262-83	Lloyd Instruments LS 500
Abrasion Loss, (ml/kilocycles)	ISO 4649	Akron Abrasion Tester
Compression Set, %	ASTM D 395-89	Compression Set tester MILANO/ITALIA
Resilience, %	ISO 4662	Wallace Dunlop Tripsometer
Hardness, Shore A	ASTM D 2240	Lever Loader Model 716
Flex Cracking Resistance	ISO 132	DeMattia Flex Cracking Resistance

Standard test procedures as prescribed by ISO or ASTM were used for the determination of compound and vulcanized properties. The procedures are listed in Table 3.3.