



CHAPTER III EXPERIMENTAL

3.1 Materials

Hexadecyltrimethylammonium bromide (CTAB) (98%), Triton X-100 (100%), styrene (99+%) and isoprene (98+%) were obtained from Fluka (Buchs, Switzerland). Azobisisobutyronitrile (AIBN) with 98% purity, water-insoluble initiator, was purchased from Aldrich Chemicals Company (Milwaukee, WI, USA). Sodium hydroxide pellets with 99% purity were obtained from BDH Laboratory Supplies (Philisburg, USA). Tetrahydrofuran (THF) was obtained from Lab-Scan Analytical Sciences (Bangkok, Thailand). Anhydrous ethyl alcohol was purchased from ITALMAR Co., Ltd (Bangkok, Thailand). Amorphous precipitated silica, Hi-Sil[®]255, was obtained from PPG-Siam Silica Co., Ltd (Bangkok, Thailand).

3.2 Experiment Set-up

In this study, a continuous in situ polymerization system consists primarily of a stirred feed tank, a polymerization reactor and a product tank. The feed tank made of stainless steel was approximately 17 liters with a lid and baffles. The reactor vessel was a one-liter-borosilicate glass bottle with a screw cap. The product tank was a stainless steel bucket. Mixtures in the reactor and feed tank were well mixed with a magnetic bar and a mechanical stirrer, respectively. Reactor temperatures were maintained at 70 ± 2 °C using a circulating heater and a water bath. Fluid flow rates were controlled using a Masterflex Digital console drive peristaltic pump with an easy-load model 7518-60 head. The experimental set-up of reactor system is shown in Figure 3.1.

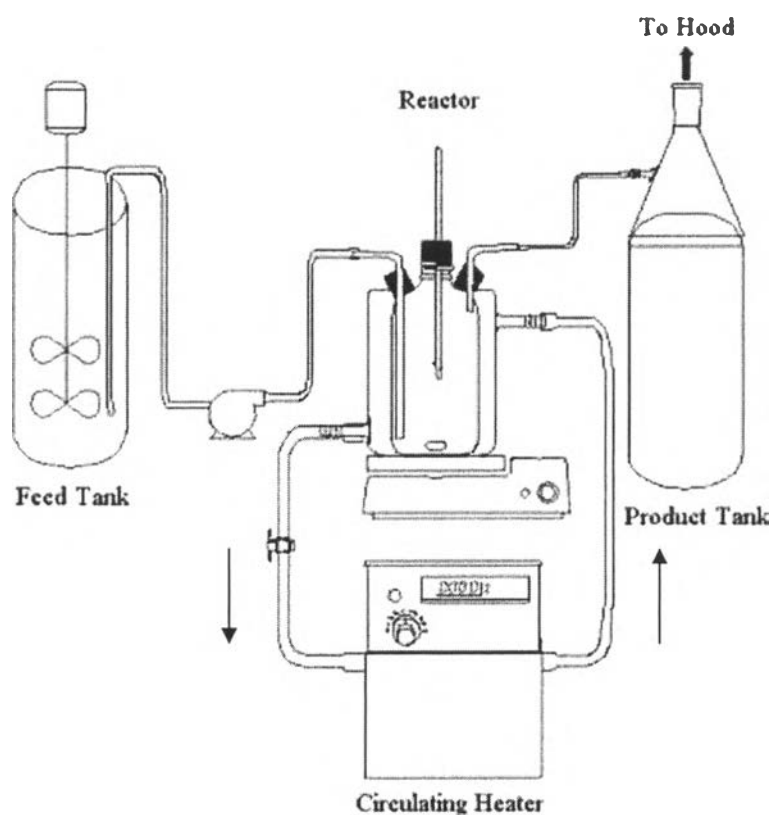


Figure 3.1 Continuous admicellar polymerization system.

3.3 Experimental Procedures

3.3.1 Adsorption Isotherm of Surfactants onto Silica Hi-Sil[®] 255

Adsorption experiments were conducted in a series of 24-ml capped vials. Two -gram samples of silica were mixed with 20 ml of pH 8 CTAB solutions at different concentrations. The resultant mixtures were allowed to equilibrate at 30°C for 24 h. and then centrifuged at 2000 rpm for 10 min. The supernatant was taken for CTAB concentration analysis. The CTAB adsorption was calculated by the concentration difference method and the adsorption isotherm was plotted. Also the complete monolayer was also confirmed by a Zeta meter. (ZETA METER3.0+, ZETA METER)

The same procedure was used for Triton X-100 and mixed surfactant adsorption experiments. The mixed surfactants consisted of CTAB and Triton X-100 at different molar ratios, 1:3, 1:1, 3:1.

From the adsorption isotherm results, for each surfactant system (pure CTAB, pure Triton X-100 and mixtures of CTAB and Triton X-100) total surfactant concentrations were determined for both monolayer and bilayer coverage which were used the polymerization experiments.

3.3.2 Surface Modification Procedure

The amorphous precipitated silica was modified using combinations of styrene and isoprene co-monomers at a 1:3 molar ratio. The amount of the co-monomers fed into the feed tank was 5 g per kg of silica and the polymerization time was 30 min according to our previous results (Nontasorn, 2002). The feed solution was prepared as follows: (1) Weighing one kg of silica, (2) CTAB was weighed, added to 12.5 liter of deionized water and stirred until the surfactant completely dissolved, (3) Adjusting the pH of the surfactant solution to 8 by adding of sodium hydroxide solution, (4) Adding the silica to the surfactant solution in the feed tank, (5) Dissolving AIBN and 1:3 molar ratio of styrene and isoprene co-monomer into 99.7% ethanol at the ratio of 30 ml per 0.5 g of AIBN and then slowly adding this mixture to the feed tank, and (6) Allowing the system to equilibrate with constant stirring for 24 h, forming the feed stock.

The reactor was heated to 70°C in a water bath heated by a circulating heater to initiate the polymerization. The polymerization reaction was allowed to proceed at a constant residence time of 30 min by controlling the feed flow rate using a peristaltic pump. The reaction effluent, collected in the product tank, was allowed to settle and the supernatant was decanted. The modified silica was washed by counter current washing for five days with daily stirring or until the wash water no longer foamed on agitation. The silica was then dried at 110°C for 24 h and reground by passing through a 120-mesh sieve.

The same procedure was applied for the modification with Triton X-100 and the mixed surfactants.

3.3.3 Testing Procedures

The amount of adsorbed surfactants on Hi-Sil[®]255 was calculated by the concentration difference method using a mass balance of the concentration of surfactant in the aqueous feed solution and the equilibrium supernatant. The CTAB concentration was estimated by using a Total Organic Carbon analyzer (TOC-500A, Shimadzu), the Triton X-100 concentration was estimated by using a UV VIS spectrometer (UV/VIS spectrometer Lamda 10, PERKIN ELMER) and the complete monolayer coverage was confirmed by a Zeta meter (ZETA METER3.0+, ZETA METER).

The properties listed in Table 3.1 were determined for all modified silicas. The silica aggregates observation was performed by a Scanning Electron Microscope (SEM) (JSM-5200, Jeol). Thermogravimetric Analyzer (TGA) (TGA 7, Perkin Elmer) was used to confirm the polymer formation on the modified silica samples. Moreover, nitrogen BET surface areas and mean agglomerate particle sizes of all modified silicas were also investigated.

Table 3.1 Properties tested and equipment used for silica characterization

PARAMETER	TECHNIQUE/INSTRUMENT
Specific surface area	BET N ₂ Surface Area Analyzer Autosorb-1 Quantachrome
Particle size	MALVERN Mastersizer X Ver. 2.15
Surface morphology	Scanning Electron Microscope (SEM) JEOL JSM-5200
Polymer formation	Thermogravimetric Analyzer (TGA) Du Pont Instrument TGA 2950

The rubber compound formula is given in Table 3.2. The compound is a primary rubber formulation modified by eliminating poly(ethylene glycol), which is used to complex with the silanol groups on the surface of the silica to prevent them

from reacting with the activator, and designed specifically for physical properties testing (Thammathadanukul *et al.*, 1996).

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 (6PPD)	1
Benzothiazyl disulfide (MBTS)	1.8
Diphenyl guanidine (DPG)	0.25
Sulphur	2

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 close internal mixer. 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 the optimum cure time (t_{90}) the moving die rheometer.

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.

Table 3.3 Rubber compound test methods

PROPERTY	METHOD	INSTRUMENT
Cure Time (Maximum Torque, dNm; T90, min)	ASTM D 2084-93	RheoTech/TechPRO
Tensile (Maximum 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

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