

## **CHAPTER III EXPERIMENTAL**

### **3.1 Materials**

Hexadecyltrimethylammonium bromide (CTAB) with a purity of 98%, styrene with a purity of 99+% and isoprene with a purity of 98+% were obtained from Fluka. Azobisisobutyronitrile (AIBN), water-insoluble initiator, was purchased from Aldrich Chemicals Company with 98% purity. Sodium hydroxide pellets with 99% purity were obtained from BDH Laboratory Supplies. Tetrahydrofuran (THF) was obtained from Lab-Scan Analytical Sciences. Ethyl alcohol anhydrous was purchased from ITALMAR Co., Ltd. Amorphous precipitated silica, Hi-Sil<sup>®</sup>255, was obtained from PPG-Siam Silica Co., Ltd.

### **3.2 Experiment Set-up**

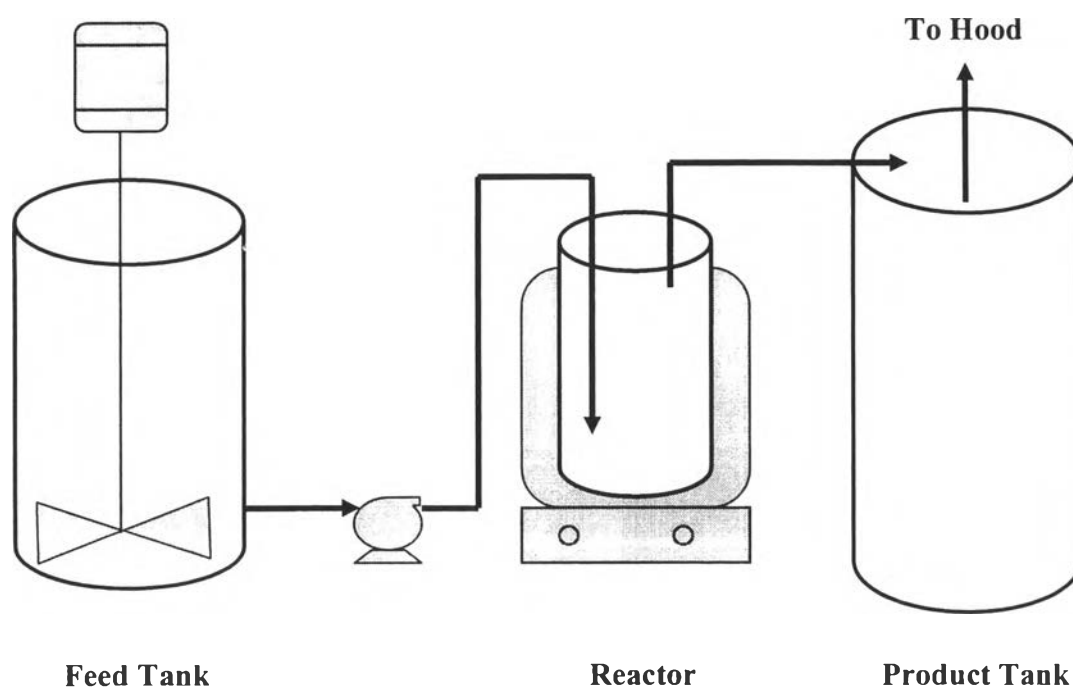
The continuous system mainly consisted of a stirred feed tank, a polymerization reactor and a product tank. The feed tank made of stainless steel was approximately 17 liters with a lid and baffles. The reactor vessel was a one-liter-borosilicate glass bottle with a screw cap. The product tank was a stainless steel bucket. Mixtures in the reactor and feed tanks were well mixed with a magnetic bar and a mechanical stirrer, respectively. Reactor temperatures were maintained using a circulative heater, water bath, with  $70 \pm 2$  °C. Fluid flow rates were controlled using a Masterflex Digital console drive peristaltic pump with easy-load model 7518-60 head. The reactor system is shown in Figure 3.1.

### **3.3 Experimental Procedures**

#### **3.3.1 Adsorption Isotherm of CTAB onto Silica Hi-Sil<sup>®</sup>255**

Adsorption experiments were conducted in 24-ml capped vials. Two gram samples of silica were mixed with 20 ml of pH 8 CTAB solution at different concentrations. The samples were allowed to equilibrate at 30°C for 24 hours and

then centrifuged at 2000 rpm for 10 minutes. The supernatant was taken to analyze CTAB concentration. The CTAB adsorption was calculated by the concentration difference method and then the adsorption isotherm was plotted. From the adsorption isotherm, the critical micelle concentration (CMC) of CTAB on Hi-Sil<sup>®</sup>255 could be determined as well as the feed concentration that would result in the system equilibrating just below the CMC, in order to prevent micelle formation which is undesirable for emulsion polymerization.



**Figure 3.1** Continuous admicellar polymerization system.

### 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. The surface modification procedure was performed 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 addition 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. A peristaltic pump was used to introduce the feed solution into the reactor at a constant flow rate and the polymerization reaction was allowed to proceed at 30 min resident times. The reaction effluent collected in the product tank was allowed to settle and the supernatant was decanted to remove all solid particles. 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 into a powder through a 120-mesh sieve.

### 3.3.3 Testing Procedures

For the adsorption isotherm experiment, the amount of adsorbed CTAB on Hi-Sil<sup>®</sup>255 was calculated by the concentration difference method using a mass balance and the concentration of CTAB in the aqueous feed solution and the equilibrium supernatant. The CTAB concentration was estimated by using a Total Organic Carbon analyzer (TOC-500A, Shimadzu).

Polymer extraction was performed by boiling 7 g of the modified silicas in refluxing tetrahydrofuran (THF) for 4 h. The slurry was cooled to room temperature, filtered and rinsed with hot THF. The polymer was precipitated by adding the filtrate to water. Extracted polymer was analyzed by a Fourier Transform Infrared spectrophotometer (FTIR). The silica aggregates observation was performed by Scanning Electron Microscope (SEM). Thermogravimetric Analyzer (TGA) and Differential Scanning Calorimeter (DSC) were used to determine the amount of copolymer developed on the modified silica. Moreover, nitrogen BET surface area and mean agglomerate particle size were also investigated. Table 3.1 summarizes techniques and instruments used for analyzing and measuring all testing parameters.

**Table 3.1** Properties tested and equipment used for silica analysis

PARAMETER	TECHNIQUE / INSTRUMENT
Specific surface area	BET N <sub>2</sub> surface area/ Quantachrome, Autosorb-1
Particle size	MALVERN Mastersizer X Ver. 2.15
Surface morphology	Scanning Electron Microscope (SEM)/ JEOL, JSM-5200
Functional groups	Fourier Transform Infrared Spectroscopy (FTIR)/ BRUKER, EQUINOX55/S
Amount of polymer formed	Thermogravimetric Analysis (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).

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<sub>90</sub> as determined on the moving die rheometer.

**Table 3.2** Rubber compound formula

<b>INGREDIENT</b>	<b>PARTS PER HUNDRED RUBBER (PHR)</b>
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

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

<b>PROPERTY</b>	<b>METHOD</b>	<b>INSTRUMENT</b>
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