

## CHAPTER III EXPERIMENTAL

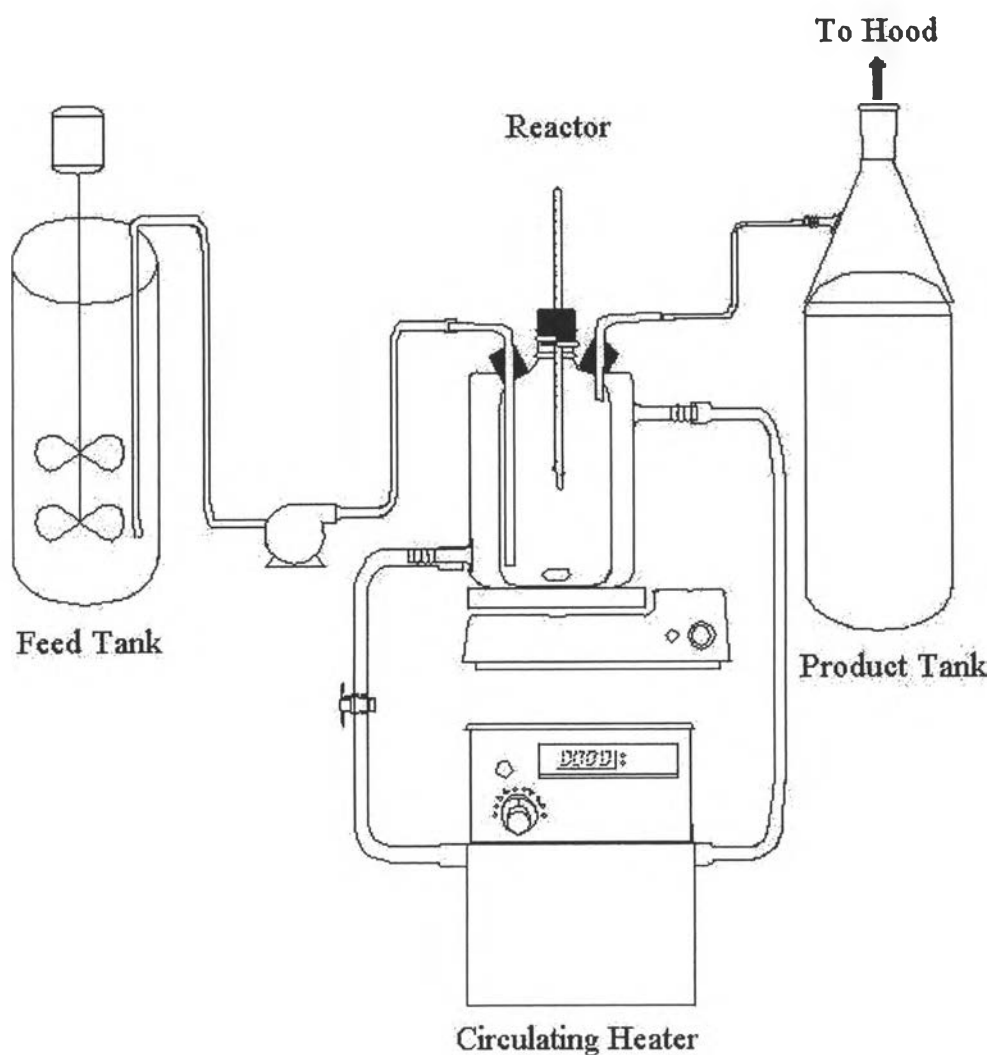


### 3.1 Materials

The amorphous precipitated silica used in this study was Hi-Sil<sup>®</sup>255 with the specific area of  $170 \pm 15 \text{ m}^2/\text{g}$ . Hexadecyltrimethylammonium bromide (CTAB) 98%, styrene 99% and isoprene 98% were purchased from Fluka (Buchs, Switzerland). 2,2'-Azobisisobutyronitrile (AIBN), a water insoluble initiator, was obtained from Aldrich Chemicals Company with 98% purity (Milwaukee, WI, USA). Sodium hydroxide pellets with 99% purity were obtained from J.T. Baker Inc. (Philipsburg, USA). Tetrahydrofuran (THF) was obtained from Lab-Scan Analytical Sciences (Bangkok, Thailand). Ethanol absolute anhydrous was obtained from J.T. Baker Inc. (Edo. De Mex, Mexico). All materials were used without further purification.

### 3.2 Experimental Setup

The continuous system mainly consisted of a stirred feed tank, a polymerization reactor and a product tank. The feed tank made of stainless steel had approximately 17 l 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. The mixtures in the reactor and feed tank were well mixed by using a magnetic bar and a mechanical stirrer, respectively. Reactor temperature was maintained at  $70 \pm 2 \text{ }^\circ\text{C}$  using a circulating heater and a water bath. The flow rate of the feed solution was controlled using a peristaltic pump (Masterflex Digital console drive with easy-load model 7518-60 head). The reactor system is shown in Figure 3.1.



**Figure 3.1** The continuous admicellar polymerization system

### 3.3 Experimental Procedures

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

Adsorption experiments were conducted in capped 24 ml vials. Two-gram samples of silica were mixed with 20 ml of CTAB solution at different concentrations and at a constant pH of 8. The samples were allowed to equilibrate at 30°C for 24 h and then centrifuged at 2000 rpm for 10 min. The supernatant was taken and analyzed for CTAB concentration. The CTAB adsorption was calculated by the concentration difference method and 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. The value of CMC obtained was used to choose the CTAB concentration for the polymerization experiment. The appropriate CTAB concentration had to be below the CMC value in order to prevent micelle formation.

### 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 amounts of the co-monomers fed into the feed tank were 5, 20 and 30 g per kg silica. The polymerization times were 30, 45 and 60 min, which are denoted by L, M and H, respectively.

The silica surface modification procedure consisted of: (1) adding 200 g CTAB to 12.5 l of deionized water and stirring until the surfactant completely dissolved, (2) adjusting the pH of the surfactant solution to 8 using dilute sodium hydroxide solution, (3) adding 1 kg silica to the surfactant solution in the feed tank, (4) dissolving 1.65 g of 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 AIBN and then adding this mixture to the feed tank, and (5) allowing the system to equilibrate with constant stirring for 24 h to obtain the feed stock.

The reactor temperature was controlled constant at 70°C using a water bath heated by a circulating heater. By adjusting the pump flow rate, the reaction was allowed to proceed for various retention times. The reaction effluent collected in the product tank, was allowed to settle and the settled solids were then decanted. The modified silicas produced were washed by counter current washing with deionized water for five days with daily stirring or until the wash water no longer foamed on agitation. The silicas were then dried at 110°C for 24 h. The dried silicas were reground and passed through a 120 mesh sieve.

### 3.3.3 Analytical Methods and Measurements

The CTAB adsorption isotherm on HI-Sil<sup>®</sup>255 was used to determine for the initial CTAB concentration giving the equilibrium bulk concentration below

CMC (920  $\mu\text{M}$ ) which was used for the surface modification procedure as mentioned before. The quantity of adsorbed CTAB on Hi-Sil<sup>®</sup>255 was calculated by the concentration difference method. The CTAB concentration was determined by using a Total Organic Carbon Analyzer (TOC-5000 A, Shimadzu).

The properties listed in Table 3.1 were determined for the control and all modified silicas. Polymer extraction was performed by refluxing 7 g of the modified silica with tetrahydrofuran (THF) for 4 h. The slurry was cooled to room temperature, filtered, and rinsed with hot THF. The extracted polymer was precipitated by adding the filtrate to water. The extracted polymer was characterized by a Fourier Transform Infrared Spectrophotometer (FTIR) (Perkin Elmer 1760X). The silica aggregates were also imaged by using a Scanning Electron Microscope (SEM) (JEOL JSM-5200). Thermogravimetric Analyzer (TGA) (Dupont Instrument TGA 2950) was used to determine the amount of co-polymer developed on the modified silica surface. Additionally, nitrogen BET surface area and mean agglomerate particle size were also measured using Autosorb-1 Quantachrome and Malvern Mastersizer X Ver. 2.15, respectively.

**Table 3.1** Parameters to be measured for modified silicas in this study

<b>Parameter</b>	<b>Technique / Instrument</b>
CTAB concentration	Total Organic Carbon Analyzer (TOC.5000A, Shimadzu)
Specific surface area	BET N <sub>2</sub> surface area (Autosorb-1 Quantachrome)
Particle size	MALVERN Mastersizer X Ver. 2.15
Surface morphology	Scanning Electron Microscope (SEM) (JEOL JSM-5200)
Functional groups	Fourier Transform Infrared Spectroscopy (FTIR) (PERKIN ELMER 1760X)
Amount of polymer formed	Thermogravimetric Analysis (TGA) (DU PONT Instrument TGA 2950)

The rubber compound formula used for evaluation is given in Table 3.2. The compound is a basic rubber formulation designed specifically for physical properties testing (Thammathadanukul *et al.*, 1996). The rubber was modified by eliminating polyethylene glycol, which is sometimes used to form complexes with the silanol groups on the surface to prevent them from reacting with the accelerator.

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 formation

<b>Ingredient</b>	<b>Part 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 the compound and vulcanizate properties. The aging condition was maintained at 100°C, and 22 h. The testing parameters and methods of all rubber compound prepared with different modified silicas are listed in Table 3.3.

**Table 3.3** Rubber compound test methods

<b>Property</b>	<b>Method</b>	<b>Instrument</b>
Cure Time, (min)	ASTM D 2084-93	Monsanto MDR 2000
Tensile Properties (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, (vol. loss/kilocycles)	ISO 4649	Akron Abrasion Tester
Flex Cracking, (kilocycles)	ISO 132	DeMattia Flex Cracking
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
Heat Build Up, °C	ASTMD 623 (Method A)	Ferry Industry Inc S/N 181094