

CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Chemicals

ARQUAD[®] T-50 HFP (Tallowtrimethylammonium chloride), cationic surfactant, was obtained from Akzo Nobel (Stenungsund, Sweden). Teric[®] X-10, nonionic surfactant, was provided from Eastasiatic Co., Ltd (Bangkok, Thailand). Styrene (99+ %) and isoprene (98+ %) were supplied by 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 CARLO ERBA reagent (Milan, Italy). Anhydrous ethyl alcohol was purchased from CARLO ERBA reagent (Milan, Italy). Hydrated amorphous silica, Hi-Sil[®]255 was obtained from Siam Silica Co., Ltd (Bangkok, Thailand)

3.1.2 Equipment

Continuous Admicellar Polymerization Reactor (Chaisirimahamorakot, 2001)

Tensiometer (DSA 10 MK2 Krüss)

Total Organic Carbon Analyzer (TOC-V CSH, Shimadzu)

UV-Visible Spectrophotometer (UV-2550, Shimadzu)

Zeta Potential Meter (ZETA-METER 3.0⁺Unit)

BET N₂ surface area (Autosorb-1, Quantachrome)

Particle Size Analyzer (Mastersizer X Ver. 2.15, MALVERN)

Thermogravimetric Analyzer (TG-DTA Pyris Duamond, Perkin-Elmer)

3.2 Experimental

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 liters 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 ± 2 °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 3.1.

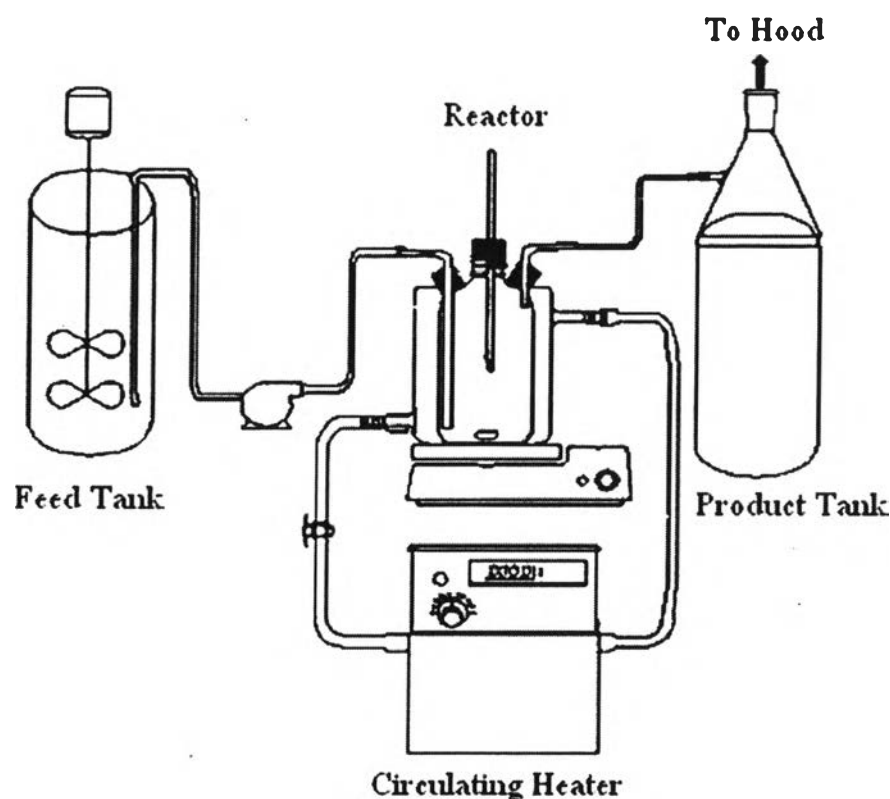


Figure 3.1 Continuous admicellar polymerization system.

3.2.1 Adsorption of Surfactants

3.2.1.1 *Adsorption of Surfactant onto the Liquid/Gas Interface*

Surface tension of studied surfactant solutions, cationic, nonionic, and their mixtures, with various concentrations were analyzed by the pendant drop method using a tensiometer (DSA 10 MK2 Krüss). The data was

plotted between the surface tension and logarithm of concentration to determine the CMCs.

3.2.1.2 *Adsorption Isotherm of Surfactant onto Silica Hi-Sil[®] 255*

Adsorption experiments were conducted in screw-capped 24-ml vials. A 0.5 gram sample of silica was mixed with 20 ml of pH 8 surfactant solution at varying known concentrations. Two types of surfactant were used, cationic and nonionic, both singly and in mixtures at various molar ratios (3:1, 1:1, and 1:3 of cationic:nonionic). The samples were allowed to equilibrate at 30°C for 24 hours and then centrifuged at 1500 rpm for 15 minutes. The supernatant was removed for quantitative analysis. 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) on Hi-Sil[®] 255 and maximum adsorption could also be determined. The feed concentration for admicellar polymerization was then chosen so that the equilibrium concentration would be below the CMC in order to prevent micelle formation and thus, emulsion polymerization.

3.2.2 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 grams per kilogram of silica. The surfactant concentration was selected from the adsorption isotherm. The concentrations were used in approximating monolayer coverage. The two polymerization times were studied at 15 and 30 minutes.

The silica surface modification procedure consisted of: (1) weighing one kg of silica, (2) adding surfactant to 12.5 liters of deionized water and stirring until the surfactant completely dissolved, (3) adjusting surfactant solution to pH 8 with sodium hydroxide solution, (4) adding the silica to the surfactant solution in the feed tank, (5) dissolving 1.65 grams 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 gram of AIBN and then adding this mixture to the feed tank, and (6) allowing the system to equilibrate with constant stirring for 24 hours, forming the feed stock.

The reactor was heated to 70°C in a water bath heated by a circulating heater. By adjusting the pump flow rate, the reaction was allowed to proceed for various resident times. 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 hours and reground into a powder through a 120-mesh sieve.

The same procedure was applied for the modification with nonionic surfactant and the mixed surfactant systems.

3.2.3 Testing Procedure

The amount of adsorbed surfactants on Hi-Sil[®] 255 was calculated by the concentration difference method using a mass balance and the concentration of surfactants in the aqueous feed solution and the equilibrium supernatant. The surfactant concentration was estimated by using a Total Organic Carbon analyzer (TOC-V CSH, Shimadzu), and UV-Visible Spectrophotometer (UV-2550, Shimadzu) and the complete monolayer coverage was analyzed by a Zeta potential meter. The critical micelle concentrations (CMCs) of the surfactant mixtures were determined from breaks in plots of surface tension, measuring by Tensiometer (DSA 10 MK2, Krüss), versus logarithm of concentration.

Table 3.1 shows parameter analyzed along with techniques for the analysis. A Thermo gravimetric Analyzer (TGA) was used to verified copolymer developed on the surface of modified silica. Moreover, nitrogen BET surface area and agglomerate size were also investigated.

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).

Table 3.1 Properties tested and equipment used for silica analysis

PARAMETER	TECHNIQUE / INSTRUMENT
Surfactant concentration	Total Organic Carbon Analyzer TOC-V CSH, Shimadzu
Surfactant concentration	UV-Visible Spectrophotometer UV-2550, Shimadzu
Surface Tension	Drop Shape Analysis System DSA 10 MK2, Krüss
Zeta potential	ZETA-METER 3.0 ⁺ Unit
Specific surface area	BET N ₂ surface area Autosorb-1, Quantachrome
Particle size	Particle Size Analyzer Mastersizer X Ver. 2.15, MALVERN
Polymer formed	Thermogravimetric-Differential Thermal Analyzer TG-DTA Pyris Duamond, Perkin-Elmer

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
Polyethylene glycol (PEG)	2
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 Dispersion Kneader Machine. The vulcanizing agent was added to the master batch in the second mixing step using a two-roll mill. All compounds are cured at 150°C to a time corresponding to T_{90} as determined on the moving die rheometer.

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

Table 3.3 Rubber compound test methods

PROPERTY	METHOD	INSTRUMENT
Cure Time (Maximum Torque, dNm; T ₉₀ , 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