

CHAPTER III EXPERIMENTAL

3.1 Materials

Tallowtrimethylammonium chloride (ARQUAD[®]) was supported by Thai Spacialty Chemical Co., Ltd. Octyl phenol ethoxylate containing an average of ten moles of ethylene oxide per mole of octyl phenol (Teric X10) was obtained from Huntsman Co., Ltd. Isoprene (98+%) were obtained from Fluka. Azobisisobutyronitrile (AIBN), water-insoluble initiator, was purchased from Aldrich Chemicals Company with 98% purity. Tetrahydrofuran (THF) was obtained from Lab-Scan Analytical Sciences. Anhydrous ethyl alcohol was purchased from ITALMAR Co., Ltd. Montmorillonite Clay, Bentonite H (BNH) was supported by Ceramic “R” us (Bangkok, Thailand). 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 mechanical stirrer, respectively. Reactor temperatures were maintained using a circulative heater, water bath, with 70 ± 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.

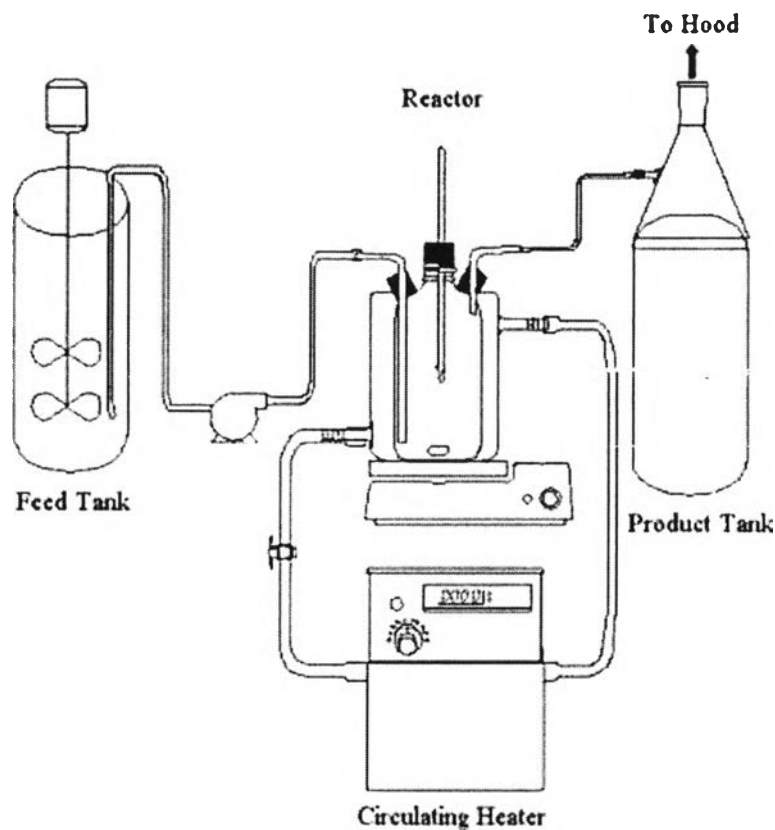


Figure 3.1 Continuous admicellar polymerization system.

3.3 Experimental Procedures

3.3.1 Adsorption Isotherm of Surfactants onto Bentonite

Adsorption experiments were conducted in 24-ml capped vials. Point two -gram samples of clay were mixed with 20 ml of ARQUAD[®] solution at different concentrations. The samples were allowed to equilibrate at 30°C for 24 hrs. and then centrifuged at 6000 rpm for 20 mins. The supernatant was taken and the concentration analyzed. The ARQUAD[®] adsorption was calculated by the concentration difference method and the adsorption isotherm was plotted.

The same procedure was carried out for mixed surfactants experiments. The mixed surfactants consist of ARQUAD[®] and Teric X10 at different molar ratios 1:3, 1:1, 3:1.

From the adsorption isotherm, the critical micelle concentration (CMC) of each surfactant can be determined as well as the feed concentration that would result in the system equilibrating just below the CMC. That is critical in preventing micelle formation and emulsion polymerization.

3.3.2 Surface Modification Procedure

The Bentonite H was modified using isoprene monomer. The amount of the monomer fed into the feed tank was calculated from the 2/1 molar ratio of surfactant and monomer. The polymerization time was 30 min. The surface modification procedure was performed as follows: (1) Weighing 125 g of clay, (2) ARQUAD[®] was weighed, added to 12.5 liter of deionized water and stirred until the surfactant completely dissolved, (3) Adding the clay to the surfactant solution in the feed tank, (4) Dissolving AIBN and isoprene 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 (5) 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. Using the constant pump 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. The modified clay was placed in a buchner funnel and washed for five days with daily stirring or until the wash water has no persistent foamed on agitation. The clay was then dried at 110°C for 24 h to remove water and unpolymerized monomer, and reground into a powder through a 180-mesh sieve to return it to a powder.

The same procedure was applied for the modification with Teric X10 and the mixed surfactants.

3.3.3 Testing Procedure

The amount of adsorbed surfactants on clay 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 ARQUAD® concentration was estimated by using a Total Organic Carbon analyzer (TOC-500A, Shimadzu), the Teric X10 concentration was estimated by using a UV VIS spectrometer (UV/VIS spectrometer Lamda 10 PERKIN ELMER).

The properties listed in Table 3.1 were determined for all modified clays. Polymer extraction was performed by boiling 7 g of the modified clay in refluxing tetrahydrofuran (THF) for 4 h. The slurry was cooled to room temperature, filtered and rinsed with hot THF. THF was evaporated out by a rotatory evaporator. Extracted polymer was analyzed by a Fourier Transform Infrared spectrophotometer (FTIR). Thermogravimetric Analyzer (TGA) was used to demonstrate the amount of polymer developed on the modified clay.

Table 3.1 Properties tested and equipment used for clay analysis

PARAMETER	TECHNIQUE/INSTRUMENT
Dispersion of surface-modified clay in rubber matrix	Wide Angle X-ray Diffractometer (WAXD) Bruker D8 ADVANCE
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. A one-stage mixing procedure was employed to prepare all compounds. The rubber, filler, vulcanizing agent and other ingredients were mixed in 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. Dispersion of surface-modified clay in the rubber compound was studied by Wide Angle X-ray Diffractometer.

Table 3.2 Rubber compound formula

MATERIAL	PARTS PER HUNDRED RUBBER (PHR)
Natural Rubber (STR XL)	100
Clay	10
Zinc Oxide	5
Stearic Acid	2
Sulfur	2.5
N-Cyclohexylbenzothiazole-2-sulfenamide (CBS)	0.6

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
Resilience, %	ISO 4662	Wallace Dunlop Tripsometer
Hardness, Shore A	ASTM D 2240	Lever Loader Model 716