

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

All materials used for surface modification by in-situ polymerization process were obtained commercially and used as received. Clays were purchased from Kitpiboon Chemical Co,Ltd. Hexadecyltrimethylammonium bromide(CTAB), at a purity 99 %, was purchased from Rhone-Poulence Company and was employed without further purification. Styrene 95 % and isoprene 95 % were purchased from Pfaltz & Bauer(Waterbury, Connecticut). Alcohol was purchased with an analysis of 95 % ethanol and 5 % methanol; 2,2-azobis-2-methylpropionitrile(AIBN) a water- insoluble initiator, was obtained from Aldrich Chemical Co; Ltd.(Milwaukee, WI) with 99 % purity. Methanol(HPLC grade) were received from Ajex Chemicals Company with 99 % purity. Tetrahydrofuran(THF) was obtained from J.T. Baker Inc.(Phillipsburg, NJ) at 99 % purity. Sodium hydroxide(NaOH) was obtained from Eka Nobel(Sweden) at 98 % purity.

3.2 Methods

3.2.1 Adsorption Isotherm of CTAB on Clay

The quantity of adsorbed CTAB on clay was calculated by the concentration difference method. Using a mass balanced and the concentration of CTAB in the aqueous feed solution and equilibrium supernatant, the amount of adsorbed surfactant can be calculated. The initial aqueous solution

was adjusted to pH 8 using sodium hydroxide solution. The CTAB concentration was determined by using a Hewlett Packard Series 1050 high performance liquid chromatography (HPLC) with an Hypersil ODS column 125 mm*5mm and an Alltech 350 conductivity detector. Gradient elution was carried out with a switching linear program from 10 % methanol and 90 % water for 1.0 minute to 90 % methanol and 10 % water for 1.5 minutes at a flow rate 2 ml/min.

3.2.2 Surface Modification Procedures

Clay was modified using a combination of styrene and isoprene as co-monomers. Five surface modified clays, differing in the amount of this co-monomer and amount of surfactant, as shown in table 3.1 and figure 3.1, were prepared. The reactor used for the polymerization was a 40 liter stainless steel tank with a stirrer for agitation during polymerization. The reactor was sealed after charging with the co-monomer solution. Heating for polymerization was given by a thermostated water jacket around the tank. The clay surface modification procedure was performed as follows:

1. AIBN and the appropriate weight of monomer(s) were added to the alcohol at a ratio of 40 ml of alcohol per gram of AIBN, and stirred until the AIBN was entirely dissolved.
2. CTAB was weighed, added to deionized water that had its pH adjusted to 10 using sodium hydroxide, and stirred until it dissolved.
3. The weighed clay was placed in the reactor at a ratio of up to 80 grams of solids per liter of feed solution.
4. The AIBN/monomer solution was slowly added to the surfactant solution, that solution brought up to the desired total volume with deionized water, and then added to the reactor containing the clay.

5. The reactor was allowed to equilibrate with stirring for 12 hours, then heated via the water jacket to 70 °C to initiate the polymerization. The system was allowed to react for 4 hours. The reaction mixture was stirred continuously during this period.

6. After polymerization, the clay in the reactor was allowed to settle and the supernatant was decanted. The clay slurry was placed in a buchner funnel and allowed to counter-current wash 5 days with daily stirring or until the wash water had no persistent foam on agitation.

7. The clay was then filtered, dried at 70 °C in an oven with circulated air for 72 hours to remove water and unpolymerized monomer, and ground through a 120-mesh sieve to return it to a powder.

3.2.3 Testing Procedures

The properties listed in table 3.2 were determined for the untreated clay and all treated clay.

The rubber compound formula used in this study is given in table 3.3. The compound is a basic rubber compound formulation designed specially for physical properties testing(Lonj, 1985 and Barlow, 1993), modified by using natural rubber(NR), but using no polyethylene glycol.

Standard test procedures as prescribed by ISO or ASTM used for the determination of compound and vulcanisate properties are listed in table 3.4.

A two-stage mixing procedure was employed for all compounds. In the first stage the rubber, filler, and other ingredients(except accelerator and vulcanizing agent) were mixed in a Banbury internal mixer with a batch size adjusted to a fill factor of 0.70. The vulcanizing agent and accelerators were then added to the compound on a two roll-mill. All compounds were cured at 150°C to T₉₈ as determined by the Monsanto rheometer.

Table 3.1 Clay Compositions

CLAY	Amount of Surfactant(g)	Amount of Co-monomers(g)	Definition
SIC # 1	11.39	2.05	high surfactant, high monomer
SIC # 2	5.69	1.03	low surfactant, low monomer
SIC # 3	11.39	1.03	high surfactant, low monomer
SIC # 4	5.69	2.05	low surfactant, high monomer
SIC # 5	8.54	1.54	intermediate

* This table calculated based on 1 kg. of clay

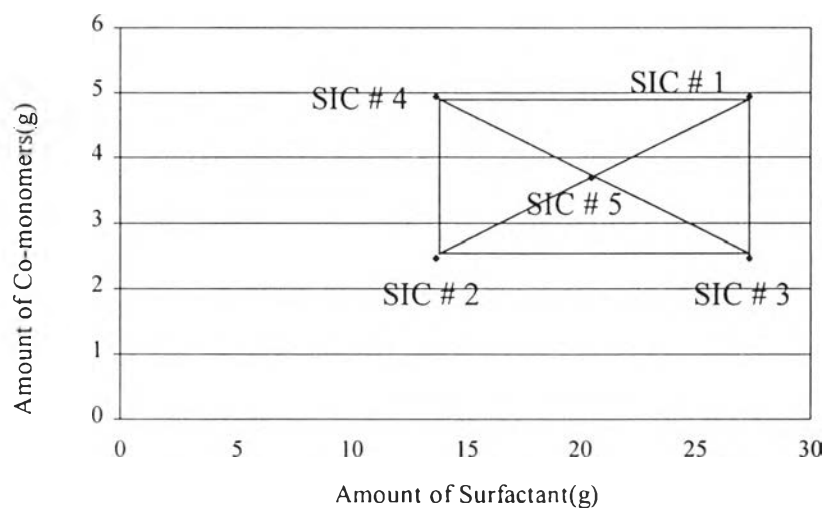


Figure 3.1 Composition of Modified Clays.

Table 3.2 Clay Properties Testing

PROPERTY	INSTRUMENT
BET N ₂ Surface Area (Multi Point), Pore Volume	Micromeritics FlowSorb II 2300
Mean Agglomerate Particle Size	Malvern Mastersizer
Percent Carbon	Dohrmannans DC-80 TOC analyzer
Scanning Electron Microscope (SEM)	JSM-5200

Table 3.3 Rubber Compound Formula

INGREDIENT	PARTS PER HUNDRED RUBBER (PHR)
Natural Rubber (TTR5L)	100
Clay	40
Zinc Oxide	5
Stearic Acid	2
Paraffinic oil	5
Antioxidant (6PPD)	1
2,2 Dibenzenothiazyl Disulfide (MBTS)	1.8
Diphenyl Guanidine (DPG)	0.25
Sulfur	3

Table 3.4 Rubber Compound Test Methods

PROPERTY	METHOD	INSTRUMENT
Cure Time, (t ₉₀ , min:sec)	ASTM D 2084-93	Monsanto MDR 2000
Tensile (Tensile Strength MPa; Elongation at 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
Flex Cracking, resistance (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