

CHAPTER III

EXPERIMENTAL SECTION



3.1 Materials

All silicas were manufactured and donated by PPG-Siam Silica Co.,Ltd. The amorphous precipitated silica used in this study was Hi-Sil[®]255, with a specific surface area $170 \pm 15 \text{ m}^2 / \text{g}$. All materials used for surface modification by *in-situ* polymerization process were obtained commercially and used as received. Hexadecyltrimethylammonium bromide (CTAB) 95 %, 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 Company (Milwaukee, WI) 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 Experimental Procedures

3.2.1 Surface Modification Procedure

The amorphous precipitated silica was modified using a combination of styrene and isoprene as co-monomers. Five surface modified silicas, differing in the percent of this co-monomer, were prepared. Samples SI-1, SI-2, SI-3, SI-4 and SI-5 represent styrene-isoprene(SI)-modified Hi-Sil[®]255 with 5, 10, 20, 30 and 40 grams of co-monomer per kg of silica charge to the

reactor, respectively. The reactor used for the polymerization a 40 liter, stainless steel tank with a stirrer for agitation during polymeriation. The reactor was sealed after charging with the comonomer solution. Heating for polymerization was given by a thermostated water jacket around the tank. The silica surface modification procedure was performed as follows:

1. CTAB was weighed, added to deionized water and stirred until it dissolved. The pH of the solution was adjusted to 8 by addition of sodium hydroxide solution.

2. Styrene and isoprene co-monomers in a 25-75 mole ratio, and AIBN were added to the alcohol at a ratio of 30 ml of alcohol per 0.5 gram of AIBN, and stirred until the AIBN was entirely dissolved.

3. Pre-determined quantities of silica were placed in a reactor at a ratio of 100 grams of silicas per liter of feed solution.

4. The AIBN/co-monomer solution was slowly added to the surfactant solution, and then the resulting solution was brought up to the desired total volume by adding deionized water. The feed solution was then added to the reactor containing the silica.

5. The system 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 silica in the reactor was allowed to settle and the supernatant was decanted. The silica slurry was placed in a büchner funnel and allowed to counter-current wash for 5 days with daily stirring or until the wash water had no persistent foam on agitation.

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

3.2.2 Testing Procedures

The properties of the unmodified precipitated silica and all surface-modified silicas were determined by using the instruments listed in Table 3.1. Extracted polymer was analyzed by Fourier Transform Infrared (FTIR) Spectroscopy. Extractions were performed by boiling 5 grams of the modified silica in refluxing tetrahydrofuran (THF) for 4 hours. The slurry was cooled to room temperature, filtered, rinsed with hot THF, and the polymer precipitated by addition of the filtrate to water. Observation of the silica aggregates was performed by Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM). Additionally, TGA was used to demonstrate the existence of co-polymer on the silica surface after modification.

The rubber compound formula used in this study is shown in Table 3.2. The compound is a rubber formulation designed specifically for physical properties testing using natural rubber (NR), but using no polyethylene glycol.

The compounds were mixed using a two-stage mixing procedure. In the first stage, the rubber, filler and other ingredients (except vulcanizing agent) were mixed in a Banbury internal mixer with the batch size adjusted to a fill factor of 0.70. In the second mixing step, the vulcanizing agent was then added to the compound on a two-roll mill. All compounds were cured at 150 °C to $t_{90}+2$ minutes as determined by the Monsanto rheometer.

To explore the limit of silica loading, five rubber compounds differing in amount of modified silica were prepared in order to investigate the effect of silica loading level on the compound physical properties. The formula was

the same as shown in table 3.2, but the modified silica loadings were varied from 10 ,20, 30, 40 to 50 parts per hundred rubber (PHR).

To studied the effect of aging on the rubber physical properties, the rubber cure compound were aged at 100°C for 22 hours.

Physical properties of rubber compounds were analyzed by using standard test procedures as prescribed by ISO or ASTM. The test procedures and equipment employed are shown in Table 3.3

Table 3.1 Silica Properties Testing

| PROPERTY | INSTRUMENT |
|--|--------------------------------|
| BET N2 Surface Area (Multi Point), Pore Volume | Micromeritics FlowSorb II 2300 |
| Mean Agglomerate Particle Size | Malvern Mastersizer |
| Transmission Electron Microscope (TEM) | Jeol JEM-200CX |
| Scanning Electron Microscope (SEM) | JSM-5200 |
| Thermogravimetric Analyzer (TGA) | Perkin-Elmer TGA 7 |
| Fourier Transform Infrared Spectroscopy (FTIR) | Perkin-Elmer System 2000 |

Table 3.2 Rubber Compound Formula

| INGREDIENT | PARTS PER HUNDRED RUBBER (PHR) |
|-------------------------------|---------------------------------------|
| Natural Rubber (TTR51) | 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 |
| Sulfur | 3 |

Table 3.3 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, (mg/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 |