

CHAPTER III

EXPERIMENT

3.1 Materials

1. Silicon Wafers (International Wafer Service, 100 orientation, P/B doped, resistivity ~ 20-40 ohm-cm, thickness ~ 450-575 μm)
2. Natural Rubber STR5L (Rubber based industry research and development center, Thailand)
3. Hi-Sil 255-S (F-10-02), PPG-Siam Co., LTD (Thailand)

3.2 Chemicals

1. Ethanol : Merck
2. Hexane : Merck
3. Toluene : Carlo
4. Sulfuric acid : Merck
5. Hydrogen peroxide (30%) : Merck
6. Anhydrous toluene : Aldrich
7. Ethyldiisopropylamine : Fluka
8. Vinyl dimethylchlorosilane : Gelest
9. Trivinylchlorosilane : Gelest
10. Squalene : Fluka
11. Squalane : Fluka
12. Bromine Conc. : Fluka

13. Chloroform : Carlo
14. Bis(triethoxy silyl propyl tetrasulfide) : JJ-Degussa Co., Ltd.
15. *p*-toluenesulfonic acid : Fluka
16. *t*-butyl peroxide : Aldrich
17. 2,2'-Azobisisobutyronitrile(AIBN) : Aldrich
18. Sodium dichromate : Merck
19. Sodium hydrogen carbonate dihydrate : Merck
20. Zinc oxide (ZnO) : Fluka
21. Tetramethyl thiuram disulphide(TMTD) : Sunny World (1989) Co., Ltd.
22. Stearic acid : Fluka
23. Sulphur : DYNA Trade Co., Ltd.
24. Montaclare : Fluka
25. Mercaptobenzothiazole disulfide(MBTS): Sunny World (1989) Co., Ltd.
26. Ultrapure distilled water : Mill-Q Lab system
27. Hexadecane : Aldrich

3.3 Instruments and Apparatus

1. Gas tight syringe : Hamilton, Nevada, USA.
2. Two-roll mill : Model R11-3FF (3338) Tokyo, Japan
3. Rheometer : Monsanto MDR2000, USA
4. Tensile testing machine : Instron Corporation Series IX

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- Automated Materials Testing
System 6.05 Model 1011, USA.
5. Mooney viscometer : Visc. Tech., USA.
 6. Hardness testing machine : Durometer Hardness system
(shore A) Model 716, USA.
 7. Compress air sample cutter : Model SDAP-100-N
Intro Enterprise Co., Ltd., USA
 8. Compression molding hydrolic : Model V75h-18-BPX, Serial
9593 Wabash, Indiana, USA.
 9. Lab shear adhesive tester : LLOYD Instruments, USA
 10. Mastersizer-S : Version 2.19 Malvern
Instruments Co., Ltd. UK
 11. Autosorb-1 and Ultrapycnometer 1000 : Quantachrome, USA
 12. Scanning electron microscopy (SEM) : Model JSM-5800L
 13. X-ray photoelectron spectroscopy (XPS) : Perkin-Elmer-Physical
Electronics 5100 spectrometer
 14. Ellipsometry : Model L115C, Waferskan™
Chicago, IL

3.4 Experimental Section

3.4.1 Model Studies

3.4.1.1 Surface Treatment of Silicon Substrates

Silicon wafers were cut to $1.5 \times 1.5 \text{ cm}^2$ pieces. The samples were held in a custom designed (slotted hollow glass cylinder) holder and put in a freshly prepared mixture of 7 parts of concentrated sulfuric acid containing dissolved sodium dichromate (3-5 wt %) and 3 parts of 30% hydrogen peroxide. Silicon plates were submerged in the solution overnight, rinsed with $10 \times 50 \text{ mL}$ of water and dried in an oven at 120°C for 2h.

3.4.1.2 Reaction of Silicon Wafers with Vinyl-containing Silanes

Reactions were carried out immediately after surface treatment of silicon plates described above. Dried silicon plates were covered with anhydrous toluene (20 mL) in a Schlenk flask containing diisopropylethylamine (DIEA) (0.34 mL, 1 mmol). Vinyltrimethylchlorosilane (VTMCS) (0.28 mL, 1 mmol) or trivinylchlorosilane (TVS) (0.31 mL, 1 mmol) were added *via* syringe. Reactions were carried out at room temperature under nitrogen atmosphere. After a desired period of time, the plates were removed and rinsed with solvents by a following sequence : toluene ($2 \times 20 \text{ mL}$), ethanol ($3 \times 20 \text{ mL}$), 1:1 ethanol/water ($2 \times 20 \text{ mL}$), water ($2 \times 20 \text{ mL}$), ethanol ($2 \times 20 \text{ mL}$), water ($2 \times 20 \text{ mL}$). The plates were dried under reduced pressure ($< 50 \text{ mtorr}$) at ambient temperature overnight prior to surface characterization.

3.4.1.3 Bromination of Vinyl-containing Silicon Surfaces

The vinyl-containing silicon plates were soaked in a Schlenk flask containing 5% (v/v) bromine in chloroform at room temperature. After 4h of reaction time, the silicon plates were isolated and rinsed with solvents by the same sequence used after silanization.

3.4.1.4 Reactions of Vinyl-containing Silicon Surfaces with Squalane or Squalene using Catalysts

The vinyl-containing silicon plates were held in a custom designed holder and suspended in a Schlenk flask containing squalane (SqA) or squalene (SqE) and a initiators; α, α' -azo(bis-isobutyronitrile)(AIBN), *t*-butyl peroxide or *p*-toluenesulfonic acid (*p*-TsOH). Reactions proceeded in stirred solutions with nitrogen bubbled inside the solution throughout at 40°C, 70°C or 150°C. After the desired reaction time, the plates were rinsed with toluene, sonicated (5min) and soxhlet extracted (2h) in hexane, then rinsed with ethanol, 0.5% NaHCO₃(aq) (only when *p*-TsOH was used) and water respectively. The silicon plates were dried under reduced pressure (< 50 mtorr) overnight prior to surface characterization.

3.4.1.5 Reactions of Vinyl-containing Silicon Surfaces with Squalane or Squalene in the Presence of Curing Agents

The vinyl-containing silicon plates were held in a custom designed holder and suspended in a Schlenk flask containing squalane (SqA) or squalene (SqE) and curing agents; sulfur, zinc oxide (ZnO), stearic acid, tetramethyl thiuram disulphide(TMTD) and mercaptobenzothiazole disulfide (MBTS). Reactions proceeded in stirred solutions throughout at 150°C. After the desired reaction time,

the plates were rinsed with toluene, sonicated (5min) and soxhlet extracted (2h) in hexane, then rinsed with ethanol, and water respectively. The silicon plates were dried under reduced pressure (< 50 mtorr) at overnight prior to surface characterization.

3.4.1.6 Surface Characterization

Contact angle measurement : Deionized water was dropped onto the film surface by a Gilmont Syringe with a 24-gauge flat-tipped needle. Milli-Q water and hexadecane were used as the probe fluids. Images of water droplets on the film surface were taken with a digital camera (Sony, Model F707). The contact angles were measured with Adobe Photoshop 6.0 Software. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively.

X-ray photoelectron spectroscopy (XPS): X-ray photoelectron spectra were obtained using a Perkin-Elmer-Physical Electronics 5100 spectrometer with Al $K\alpha$ excitation (15 kV, 400W). Spectra were recorded at two different take-off angles, 15° and 75° between the plane of the sample surface and the entrance lens of the detector optics. Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: C_{1s},0.210; O_{1s},0.560; Si_{2p},0.210; Si_{2p},0.540; Br_{3d},0.830.

Ellipsometry : Ellipsometric data were obtained using Model L115C, WaferskanTM Ellipsometry Gaertner Scientific Corporation, Chicago, IL. Ellipsometer analyzed

the effect of reflection on the polarization of the laser light striking the surface of materials. Ellipsometric measurements involve illuminating the sample surface with monochromatic light of a known wavelength and polarization and then analyzing the polarization of the reflected light into photodetector.

Specification of Ellipsometer

Laser Light Source	: 632.8 nm. Helium-Neon (Red)
Incidence Angles	: 50° and 70°
Sample Size	: 150 mm of diameter
	: 10 mm of thickness
Film Thickness	: 0-60,000 Å

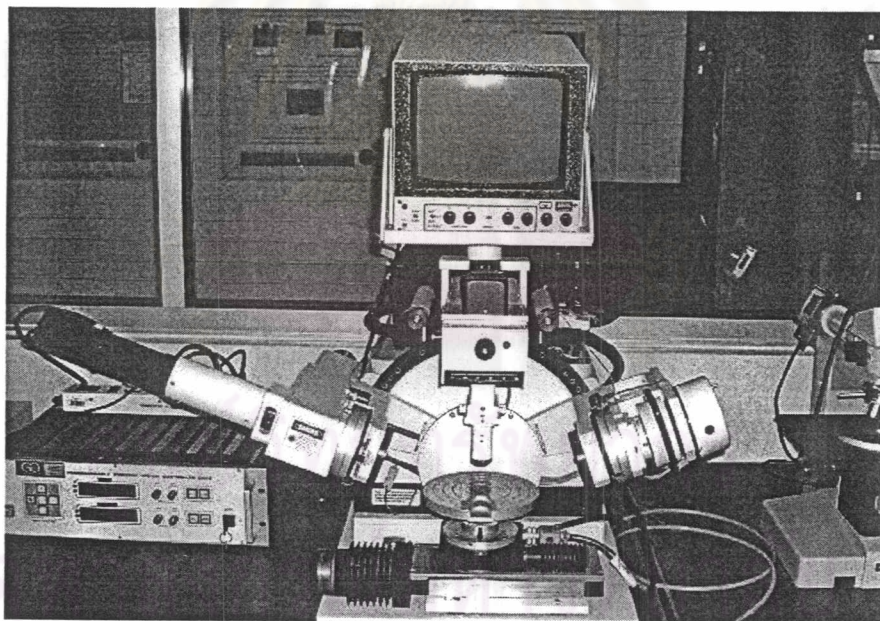


Figure 3.1 Instrument set up of Ellipsometer.

3.4.2 Characterization of Silica Particles

The surface area of fillers was determined by the Brunauer-Emmett-Teller (BET) method on the Autosorb-1. The density and mean agglomerate particle size were measured by Ultrapycnometer 1000 and Mastersizer-S, respectively.

3.4.3 Determination of Curing Behavior and Mechanical Properties

The vulcanized rubber sheets were prepared by compression molding before mechanical testing. The formulation of compound rubber is shown in Table 3.1.

Table 3.1 Formulation of silica-filled natural rubber composites

Ingredient	Quantity of mix (phr)
Natural rubber (STR 5L)	100.0
Silica or treated silica	0-30.0
ZnO	3.0
Stearic acid	2.0
TMTD	0.3
MBTS	1.0
Sulfur	2.0
Montaclere	1.0
Si-69 ^a	3.0

a : bis(triethoxysilyl propyl tetrasulphide) (Si-69) was added in some formulations

Determination of curing behavior and mechanical properties of vulcanized natural rubber filled with vinyl-containing silica were investigated by following the ASTM test methods as follows:

3.4.3.1 Mixing Standard Compounds and Preparing Standard Vulcanized Sheets (ASTM D3182-89)

The standard mill has rolls between 150-155 mm in diameter. The mill equipped with retaining guides, with a distance between the guides at the nip of 150-280 mm. The speed of the slow roll is 24 rpm and the ratio between slow and fast roll shall be 1:4. Mix compounds with rubber banded on the slow roll. Carefully collect materials falling through the nip from tray and return to the mix. Weigh the batch, remove the test specimens for Mooney viscosity or cure time. Condition the test specimens for 1-24 h at 25°C and humidity not greater than 55%. Place the test specimens on a flat, dry, clean metal surface and cut pieces shorter in width and length than the corresponding dimensions of the mold cavity. The press shall be capable of exerting a pressure of not less than 3.5 MPa, at 150°C on the total cross-section area of the mold during the entire period of vulcanization. Condition vulcanizates of compounds at 25°C for at least 16 h and for not more than 96 h before preparing and testing.

3.4.3.2 Oscillating Disk Cure Meter (ASTM D2084-93)

A test specimen of vulcanization rubber compound is inserted into the cure meter test cavity and after a closure action is contained in a sealed cavity under positive pressure. The rubber totally surrounds a biconical disk after the dies are

closed. The disk is oscillated through a small rotation amplitude and this action exerts a shear strain on the test specimen. The force required to oscillate or rotate the disk to maximum amplitude is continuously recorded as a function of time, with the force being proportional to the shear modulus of the test specimen at the test temperature (160°C). The test specimen cut a circular form a sample shall be 30 mm. in diameter and 11.5 mm. in thickness.

3.4.3.3 Mooney Viscometer (ASTM D1646-94)

An instrument consisting of a motor-driven rotating disk within a cylindrical die cavity formed by two dies maintained at specified conditions of temperature and closure force. The mooney viscometer measures the effect of temperature and time on the viscosity of rubber. The disk shall be rotated relative to the dies at a rotational rate of 2.0 r/min. Temperature for viscosity determination shall be 100°C. Results of a typical test would be reported as follows: “50-UML 1+4(100°C)”

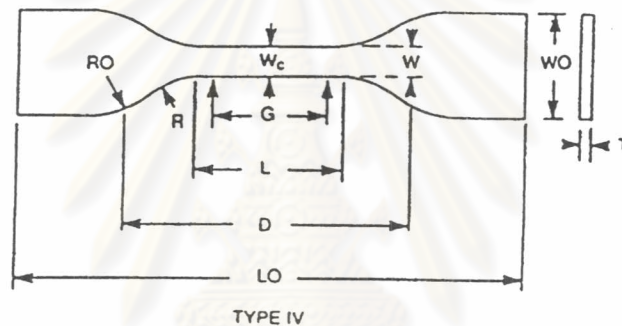
50-	Viscosity number
U	Unmassed specimen
M	Mooney
S	Larger rator (S = small rotor)
1	Time (min) before starting the motor
4	Time (min) after starting the motor

3.4.3.4 Tensile Stress- Strain Properties (ASTM D412)

The properties of vulcanized rubber, which were determined are the tensile strength, the elongation at break and the stress at a given elongation (modulus). The

vulcanized rubber was stamped with a compress air sample cutter (Model SDAP-100-N) using a dumbbell (Type IV). The stress-strain curve of samples was measured using the following condition.

Temperature	25 °C
Humidity	60 %
Sample Rate	10.00 pts/sec
Crosshead speed	500 mm/min



W : 6 mm	WO : 19 mm	G : 25 mm	R : 14 mm	T : 4 mm or under
L : 33 mm	LO : 115 mm	D : 65 mm	RO : 25 mm	

Figure 3.2 Schematic diagram of tensile test specimen (Type IV).

3.4.3.5 Tear Properties (ASTM D624-91)

The vulcanized rubber was stamped with a compress air sample cutter (Model SDAP-100-N) using a “Die C”. The specimens for tear resistance tests shall be cut out with one of the steel dies conforming to the dimensions shown in Figure 3.3, the cutting edges of which shall be kept sharp and free of all nicks to avoid leaving ragged edges on the specimens. It is important that the apex of 90° angle due

be sharpened to provide a sharp corner. The samples was measured using the following condition.

Temperature	25 °C
Humidity	50 %
Sample thickness	1.3-3.2 mm.
Crosshead speed	50 mm/min

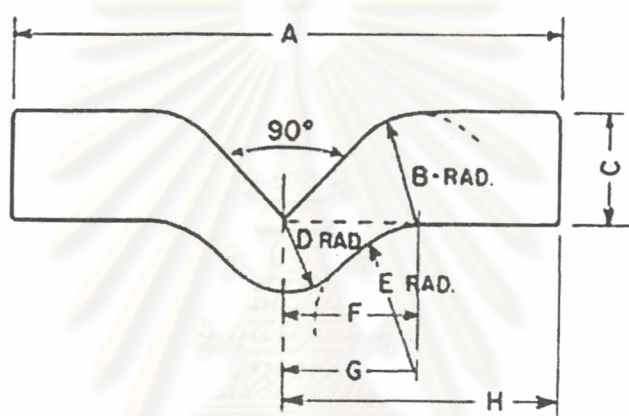


Figure 3.3 Schematic diagram of tear test specimen (Die C).

3.4.3.6 Hardness Properties (ASTM D 2240)

The Durometer Hardness System Model 716 was used for measuring the hardness of vulcanized rubber sheets. The specimen was of at least 6 mm. in thickness unless it was known that the results were equivalent to the 6 mm. values. The specimen was composed of plied pieces to the necessary thickness. The surfaces of the specimen were flat and parallel over sufficient area to permit the pressure foot to contact the specimen. The lateral dimensions of the specimen were measured at least 12 mm from any edge. The condition in this testing are shown as follows:

Temperature	25° C
Relative humidity	50 %
Number of pieces plied	3 pieces

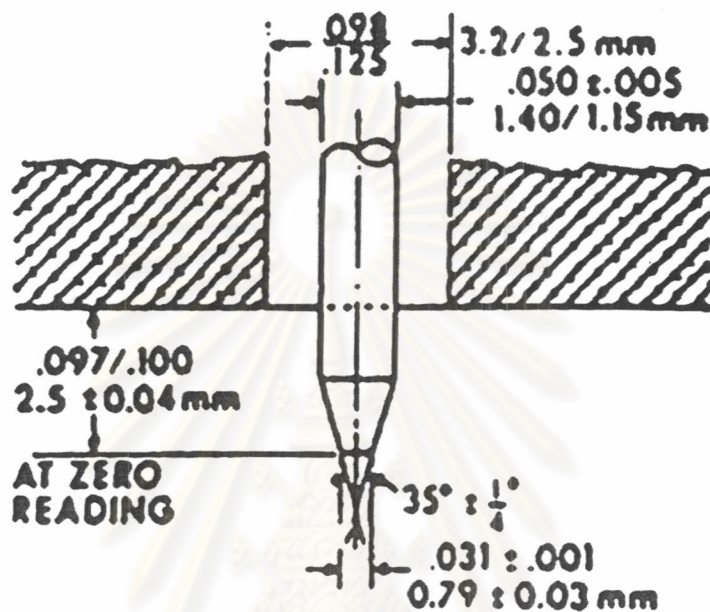


Figure 3.4 Schematic diagram of hardness (Shore A).

3.4.4 Determination of Silica Distribution using SEM

Examination of the fracture surface was carried out on Scanning electron microscopy (SEM), Model JSM-5800L. The objective was to get an insight into the fracture mode in an attempt to draw a picture of the matrix and filler surfaces and filler dispersion. All the surfaces specimens were sputter coated with a thin layer of gold to avoid electrostatic charging and poor image resolution during examination after embrittling in liquid nitrogen.