CHAPTER III

EXPERIMENTALS

3.1 Materials

Natural rubber latex, a high ammonia (HA, 0.7%) type with 60% dry rubber content (DRC), was obtained from the Post Harvest and Processing Research and Development Office, Department of Agriculture, Thailand. Tetraethoxysilane (TEOS), vinyltriethoxysilane (VTOS), ethyltriethoxysilane (ETOS) and *iso*-butyltriethoxysilane (BTOS) were purchased from Fluka. Zinc oxide (ZnO) was obtained from Univentures Public Co., Ltd. Stearic acid was obtained from Imperial (Thailand) Co., Ltd. Mercaptobenzothiazole disulfide (MBTS) and tetramethyl thiuram disulfide (TMTD) were obtained from Reliance Technochem (Flexsys) Co., Ltd. Wingstay L (antioxidant) was obtained from Goodyear Co., Ltd. Silica (Hisil-255) was obtained from United Silica Siam (USA). Sulfur (S) was obtained from Loxley Public Co., Ltd.

3.2 Procedures

3.2.1 *In Situ* Generation of the Silica in NR Matrix

In situ silica-filled NR composite was prepared by mixing concentrated latex (0.7% NH_3) with alkoxysilanes that were composed of various molar ratios of TEOS and organotrialkoxysilanes. TEOS and organotrialkoxysilanes were added into the latex with stirring at 800 rpm by a mechanical stirrer (IKA RW20 DZM.n) for 10-15 minutes to obtain a homogeneous milky mixture. The homogeneous mixture was immediately poured into a mold and tightly closed with a wrapping film covered. The mold was heated in a 50°C oven for 5 days. At this stage, the latex-silane mixture started to harden, having soft tofu-like texture. The soft composite was then dried in the oven for another 2 days at 50 °C followed by vacuum drying at 50 °C for 4 days.

The partially dry composites was then fed through a two-roll mill operated at 50 °C for 10-15 minutes to get rid of water and ammonia retained in the samples [11, 12].

3.2.2 Silica Content in the Composites

The silica content was determined by cutting the NR-silica composite into small pieces (ca. 50 mg). They were placed in aluminum oxide cups and heated under air atmosphere, from room temperature to 850 °C in an oven (Carbolite GM 11/7). The temperature was kept at 850 °C for 15 minutes. The weight of the remaining ash was calculated for the silica content by Eq. 3.1 [11, 12].

$$\text{Silica content (phr)} = 100\ (W_1/W_2) \qquad \text{Eq. 3.1}$$

The conversion of silanes to silica was calculated using Eq. 3.2.

$$\text{Conversion (\%)} = 100\ (W_3/W_4) \qquad \text{Eq. 3.2}$$

where W_1 was the weight of silica in the sample, and W_2 was the weight of the rubber. W_3 was the amount of *in situ* generated silica in the sample, which was obtained from Eq. 3.1. W_4 was the theoretical amount of silica generated assuming a quantitative conversion of silanes to silica by

$$n\ R{-}Si(OC_2H_5)_3 + 1.5n\ H_2O \xrightarrow{\cdot OH^-} \left[R{-}SiO_{1.5}\right]_n + 3n\ C_2H_5OH$$

TEOS : R = OC_2H_5 VTOS : R = $HC{=}CH_2$

ETOS : R = CH_2CH_3 BTOS : R = $CH_2CH(CH_3)CH_3$

Scheme 3.1 Hydrolysis and condensation of alkyltriethoxysilanes to give polysilsesquioxane

3.2.3 Preparation of NR-Silica Vulcanizates

A typical formulation of rubber compound is shown in Table 3.1. The compound was mixed by a two-roll mill at a temperature of about 70 °C. The mixing proceeded until a homogeneous compound was obtained. The rubber mixes were conditioned at room temperature for about 24 h prior to a cure assessment on a

Rotorless curemeter (Monsanto MDR 2000) according to ASTM D5289. Samples of the respective compounds were tested at the vulcanization temperature (150°C). The vulcanized composite sheets with ca. 2 mm were compression moulded at 150°C with force of 1.5 MPa using a hot press according to respective cure times, t_{90}, determined with the MDR 2000. Here, NR vulcanizates without silica, with commercial silica, and with *in situ* silica are abbreviated as NR, NR-mix, and NR-*in situ*, respectively.

Table 3.1 Compound formulation.

Ingredients	NR (phr[a])	NR-mix (phr[a])	NR-*in situ* (phr[a])
NR	100.0	100.0	0
NR with *in situ* silica	0	0	100+[b]
ZnO	3.0	3.0	3.0
Stearic acid	2.0	2.0	2.0
TMTD	0.3	0.3	0.3
MBTS	1.0	1.0	1.0
Wingstay L	1.0	1.0	1.0
Sulfur	2.0	2.0	2.0
Silica (Hisil-255)	0	14.0	0

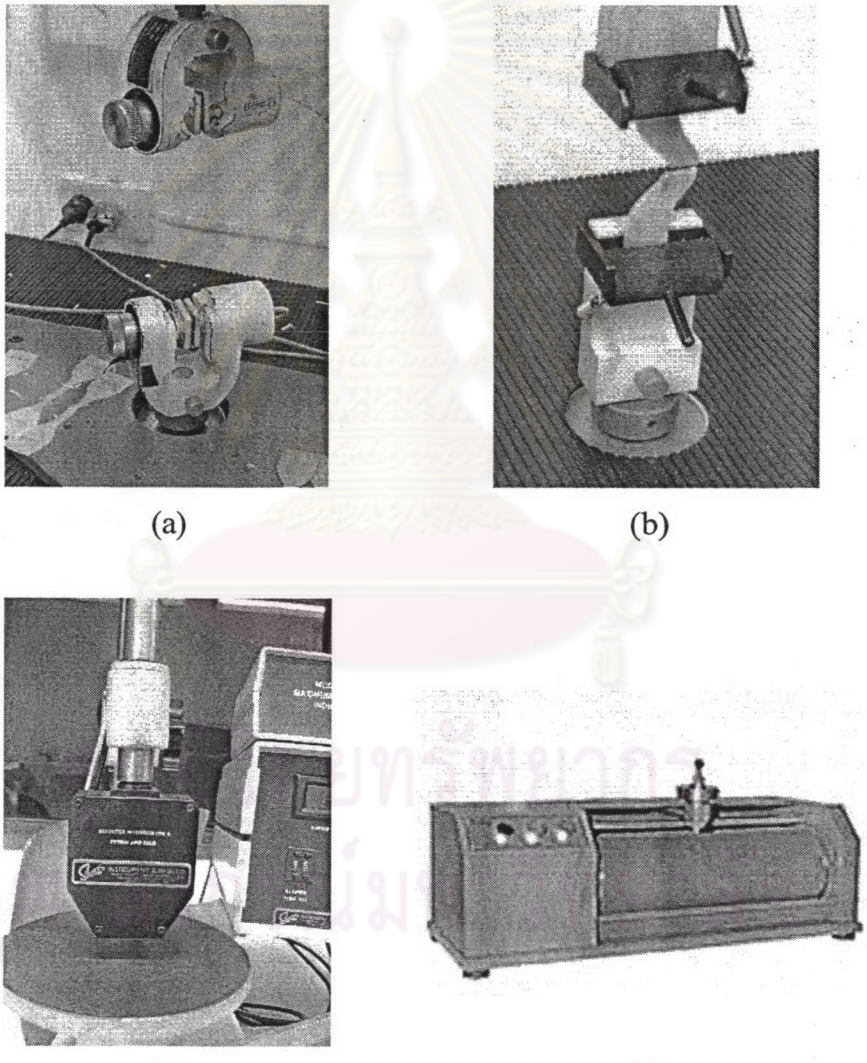
[a] phr = part per hundred rubbers by weight

[b] 100+ = weight of rubber includes *in situ* silica (silica content is shown in Table 4.2)

3.2.4 Measurement of Mechanical Properties

After the vulcanization, various mechanical property evaluations were performed. Tensile properties were measured according to ASTM D412 using Instron Corporation Series IX Automated Materials Testing System 6.05el 1011 at a crosshead speed of 500 mm/min. The values reported for each sample were based on an average of six measurements. Tear properties were measured using LLOYD Instruments LS 500 according to ASTM D624 (Die C) at a crosshead speed of 500 mm/min. The values reported for each sample were averaged from six specimens.

Tensile properties were measured along the machine direction whereas the tear properties were measured perpendicular to the machine direction. Hardness was measured using Durometer Hardness System (Shore A) Model 716 according to ASTM D2240. Measurements are taken from five different points distributed over the specimen. The median of these measurements is used as the hardness value. Abrasion resistances were measured using HAMPEN Model APH-40 according to DIN 53516. The individual sample values were averaged from six specimens.



(a) (b)

(c) (d)

Figure 3.1 Instruments of mechanical test: (a) tensile tester; (b) tear tester; (c) hardness tester; (d) abrasion tester.

3.2.5 Swelling Measurements of NR-Silica Vulcanizates

Swelling test were performed on a uniform cut from the compression-molded rubber samples with a dimension of 50x20x2 mm by the immersion/gain method in pure toluene at room temperature for three days to allow the swelling to reach diffusion equilibrium. Then, the test piece was taken out and rapidly removed by blotting the solvent with filter paper. From the differences in sample masses, the degree of swelling (Q) was calculated using the correlation by Eq.3.3:

$$\%Q = \frac{M - M_o}{M_o} \times 100 \qquad \text{Eq. 3.3}$$

where M_o is the initial mass of specimen (g) and M is the mass of specimen (g) after immersion. The swelling ratio is a direct measurement of the degree of crosslinking [12].

3.2.6 Microscopic Analysis

Dispersion of silica

Both of the *in situ* silica-filled NR composite and vulcanizate were fractured under liquid nitrogen. The samples were then sputter-coated with gold and the photographs were taken on a JEOL JSM-6400 scanning electron microscope (SEM). The SEM photographs were used to determine the degree of silica dispersion.

Size analysis of silica particles

Ultra-thin films of *in situ* silica-filled NR vulcanizate (~100 nm thick) were prepared using a cryogenic microtome (Leica EM KMR2) set at -70 °C. The specimens were placed on a copper grid and stained with osmium tetraoxide (OsO_4) vapor for 12 h. The staining enhanced the contrast for the microscopic viewing of the composites. The thin film sections were analyzed on a JEOL JEM-2010 transmission electron microscope (TEM). The accelerating voltage was 200 kV.

3.2.7 NMR Analysis of NR-Silica Vulcanizates

Solid-state ^{29}Si cross-polarization magic angle spinning (CPMAS) NMR spectra of the rubber vulcanizate were collected at 59.6 MHz on Bruker DPX-300. Up to 10,000 scans were carried out to obtain the appropriate signal-to-noise ratio. This method was used to characterize modified silica generated *in situ*.

3.2.8 Q-Test for Rejection of Outliers

Results of silica content, degree of swelling (%), and mechanical properties are expressed as the mean ± SD. Experiments were performed at least three times and results of representative experiments are presented. Q-test is utilized to determine whether a data point can be rejected when it is very different from the other data points in a set. Only one data point is discarded by using the Q-test. If $Q_{calculated}$ is larger than $Q_{critical}$, the outlier can be discarded with 90% confidence [29].

$$Q_{calculated} = \frac{[\text{outlier} - \text{value closest to the outlier}]}{[\text{highest value} - \text{lowest value}]}$$

Table 3.2 Q-test decision level at a 90% confidence interval.

Number of values	3	4	5	6	7	8	9	10
$Q_{critical}$	0.94	0.76	0.64	0.56	0.51	0.47	0.44	0.41