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 Rubber Research Institute of Thailand. Tetraethoxysilane (TEOS) and ammonia solution (NH_3) were obtained from Fluka. Bis-(3-triethoxysilylpropyl)tetrasulfide (TESPT) was supplied by JJ-Degussa (Thailand) Co., Ltd. Zinc oxide (ZnO) was obtained from Univentures Public Co., Ltd. Stearic acid was obtained from Imperial (Thailand) Co., Ltd. Mercaptobenzothiazole disulfide (MBTS), tetramethyl thiuram disulfide (TMTD) amd montaclare (antioxidant) were obtained from Reliance Technochem (Flexsys) Co., Ltd. Sulfur (S) was obtained from Loxley Public Co., Ltd.

3.2 Procedures

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

The NR latex was placed in a wide-mouth glass container. The TEOS and TESPT of the required amount were added into the latex with stirring at 800 rpm by a mechanical stirrer (IKA RW20 DZM.n). The stirring was allowed to proceed for 10-15 minutes to obtain a homogeneous milky mixture. The mixture was immediately poured into a glass bowl and tightly closed with a wrapping film. Then, it was left in a 50 °C oven for 5-10 days to let the sol-gel reaction to proceed. 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 a 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.

3.2.2 Preparation of NR-Silica Vulcanizates

Formulation for sulfur vulcanization is given in Table 3.1. The compound was mixed by a two-roll mill at a temperature of about 70 °C. The cure characteristics of the rubber compounds were determined with a Rotorless curemeter (Monsanto MDR 2000) at 150 °C in accordance with ASTM D5289. The curing was carried out in a compression molding machine (Model V75h-18-BPX, Serial number 9593) with a compression pressure of 1.5 MPa and 150 °C for the optimum cure time obtained from the curemeter. The vulcanized composite sheets with ca. 2 mm. thick were obtained.

Table 3.1 Compound formulation

Ingredient	Quantity (phr[a])
NR	100.0
ZnO	3.0
Stearic acid	2.0
TMTD	0.3
MBTS	1.0
Sulfur	2.0
Montaclare	1.0
Silica	Variable
TESPT	Variable

[a]phr = part per 100 grams of rubber

3.2.3 Measurement of Mechanical Properties

After the vulcanization, 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 grain direction whereas the tear properties were measured perpendicular to the grain direction. Hardness was measured using Durometer Hardness System (Shore A) Model 716 according to ASTM D2240. Measurements are made of five different points distributed over the specimen. The median of these measurements is used as the hardness value. Dynamic mechanical properties were measured using DMA/SDTA861e (Mettler Toledo) at a frequency of 1 Hz and a heating rate of 3 °C/min. Test specimen dimension was 5 mm long, 4 mm wide and 2 mm thick. The shear mode was used.

3.2.4 Determination of Silica Content

A weighed sample (ca. 50 mg) of silica-NR composites was placed in an aluminum oxide cup and heated under air atmosphere, from 0 °C to 850 °C in a high temperature oven (Carbolite GM 11/7). The temperature was then held for 15 min at 850°C. The silica contents were calculated from the weight of remaining ash by Eq. 3.1.

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

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

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

where W_1 was the weight of silica in the sample, and W_2 was the weight of 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 quantitative conversion of silanes to silica by

$$n\ R{-}Si(OR')_3 + 1.5n\ H_2O \rightleftharpoons \left[R{-}SiO_{1.5}\right]_n + 3n\ R'OH$$

TEOS : $R = OC_2H_5$, $R' = C_2H_5$

TESPT : $R = (CH_2)_3S_4(CH_2)_3Si(OC_2H_5)_3$, $R' = C_2H_5$

3.2.5 Determination of the Crosslink Density

Crosslink density was determined using an indirect method, namely a swelling test with toluene. The rubber vulcanizates were immersed in toluene at room temperature for 3 days. From the differences in sample masses, the degree of swelling (Q) was calculated using the correlation:

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

where M_o and M were the masses of the sample before and after swelling, respectively.

3.2.6 Microscopic Analysis

Dispersion of silica

The rubber vulcanizate was 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). SEM photographs were used to determine the degree of silica dispersion.

Size analysis of silica particles

Ultra-thin films of rubber-silica vulcanizate (~100 nm thick) were prepared using a cryogenic microtome (Leica EM KMR2) set at -70 ºC. 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 Silica-Rubber Composites

Silicon-29 cross-polarization magic angle spinning (CPMAS) NMR spectra of the rubber composite were collected at 59.6 MHz on Bruker DPX-300. Up to 10,000

scans were carried out to obtain appropriate signal-to-noise ratios. This method was used to determine the extent of reaction between silica and silane coupling agent.

3.2.8 The Design of Two-Level Factorial Experiments

In this study, three factors: TEOS, TESPT and added ammonia content, were evaluated. Thus, this resulted in a total of 2^3 or 8 runs. It was performed to evaluate three principal effects and four interaction effects of each factor on the properties of NR-silica composite. The amount of TEOS, TESPT and added ammonia at low and high levels are shown in Table 3.2.

Table 3.2 Factors and levels used in the experimental design

Factor	Unit	Level	
		(Low = -1)	(High = +1)
TEOS content (T)	phr	10	50
TESPT content (C)	phr	1	5
Added ammonia solution (N)*	%	0	2.5

*The amount shown are "added amount" only. All latex already has 0.7% NH_3 from the manufacturer.

Values for main and interaction effects were calculated from the factorial design results. Both types of effects were calculated using the Eq. 3.4.

$$Effect = \hat{y}_+ - \hat{y}_- \qquad \textbf{Eq. 3.4}$$

where $\hat{y}_+$ and $\hat{y}_-$ are the averaged values for the responses at the high and low levels of each factor. From the three factors studied, up to 7 averaged effects can be analyzed; three main effects (T, C, and N), three binary effects (TC, TN, and CN), and one combined effect (TCN). For main effects, the averages simply refer to the results at the high (+) and the low (-) levels, independent of the level of the other

factors. For a binary interaction, $\hat{y}_+$ is the average of results for two factors at high-high and low-low levels, whereas $\hat{y}_-$ is the average of the results when one of the factors involved is at a high level and the other is at a low level. For a tertiary interaction, $\hat{y}_+$ is the average of results which have a + sign for the three-factor, whereas $\hat{y}_-$ is the average of the results which have a – sign for the three-factor interaction. The sign of three-factor interaction is obtained from multipling the sign of the two-factor interactions with the sign of the other factor.

In this study, three replicate experiments were performed, whose standard errors (E) in the effect values were calculated by Eq. 3.5.

$$E = \left(\frac{\sum V}{2N}\right)^{1/2} \qquad \textbf{Eq. 3.5}$$

where V is the variance of three replicates and N is the number of experiments performed. The standard error was used to determine which factor was significant. If the effect value was larger than the standard error, that effect had a significant influence on the tested property.

3.2.9 Q-Test for Rejection of Outliers [33]

Q-test is a simple statistical tool to determine if a data point that is very different from the other data points in a set and can be rejected. Only one data point may be discarded using the Q-test. If $Q_{calculated}$ is larger than $Q_{critical}$, the outlier can be discarded with 90% confidence.

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

Table 3.3 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