

# CHAPTER III

## EXPERIMENTAL

### 3.1 Materials

1. Concentrated and high-ammonia NR latex (Thai Rubber Latex Corporation (Thailand) Public Co., Ltd. and Rubber Research Institute of Thailand )
2. NR block STR5L (Teck Bee Hang Co., Ltd)
3. Silica: Hi-Sil 255-S (F-10-02), PPG-Siam Co., Ltd (Thailand), particle size is  $56.09 \pm 35.08 \mu\text{m}$  (from SEM analysis)

### 3.2 Chemicals

1. Tetraethoxysilane (TEOS) : Fluka
2. Ammonia solution ( $\text{NH}_3$ ) : Fluka
3. Zinc oxide (ZnO) : Univentures public Co., Ltd.
4. Stearic acid : Imperial (Thailand) Co., Ltd.
5. Tetramethyl thiuram disulfide (TMTD) : Flexsys Co., Ltd.
6. Mercaptobenzothiazole disulfide (MBTS) : Flexsys Co., Ltd.
7. Sulfur : Loxley public Co., Ltd.
8. Wingstay L (Antioxidant) : Goodyear Co., Ltd.
9. Styrene monomer : Fluka

### 3.3 Instruments and Apparatus

1. Mechanical stirrer : IKA RW 20 DZM.n (Germany)
2. Two-roll mill : Model R11-3-FF (Tokyo, Japan)

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| 3. Rheometer                               | : Monsanto MDR2000 (USA)   |
| 4. Mooney viscometer                       | : Visc. Tech. (USA)  |
| 5. Tensile testing machine                 | : Instron Corporation Series IX<br>Automated Materials Testing<br>System 6.05 Model 1011 (USA) |
| 6. Tear testing machine                    | : LLOYD Instruments LS 500<br>(USA)  |
| 7. Hardness testing machine                | : Durometer Hardness system<br>(Shore A) Model 716 (USA)                                       |
| 8. Compressed air sample cutter            | : Model SDAP-100-N Intro<br>Enterprise Co., Ltd. (USA)   |
| 9. Compression molding hydrolic            | : Model V75h-18-BPX, Serial<br>9593 (USA)  |
| 10. Scanning electron microscope (SEM)     | : JEOL, Model JSM-6400 (Japan)   |
| 11. Transmission electron microscope (TEM) | : JEOL, JEM -1220 (Japan)  |
| 12. High temperature oven                  | : Carbolite GM 11/7 (England)  |

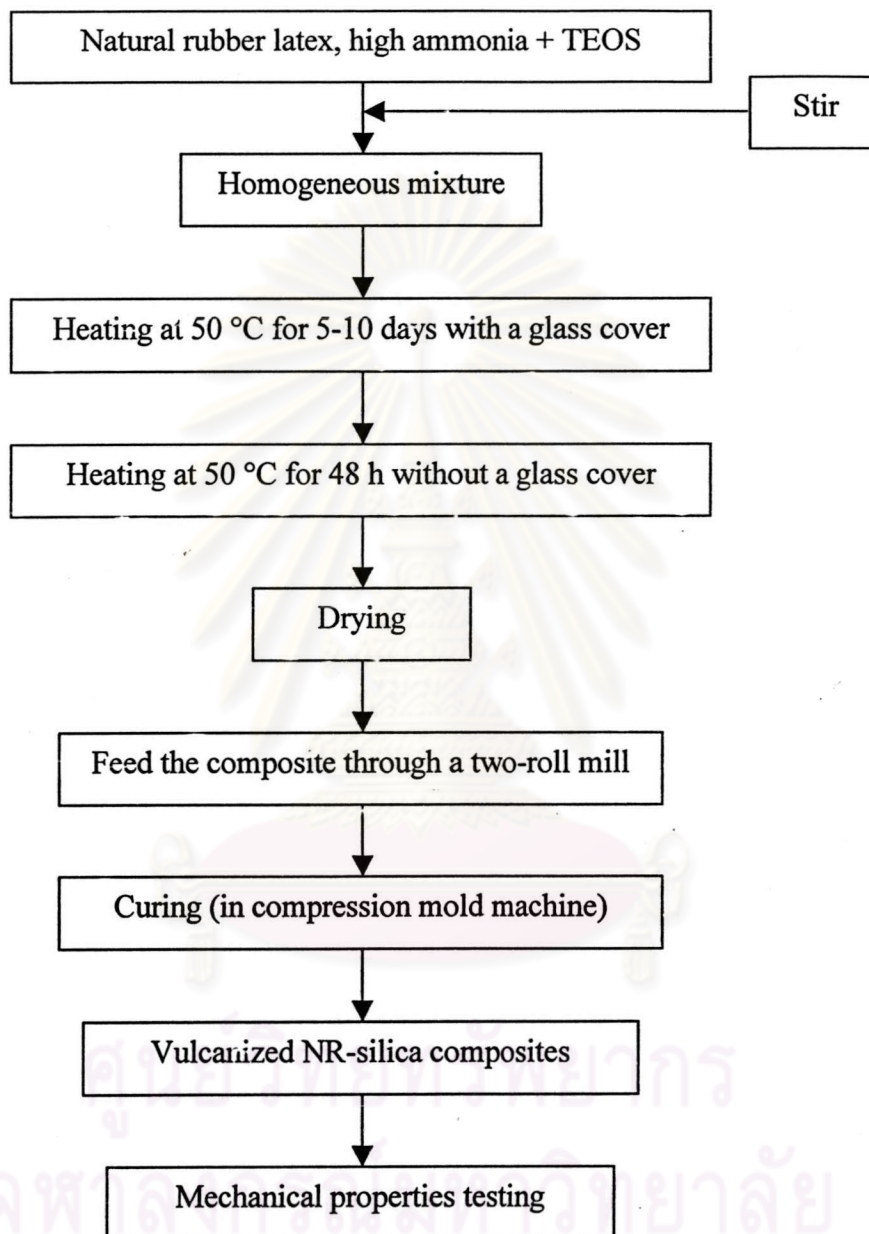
### 3.4 Methods

#### 3.4.1 *In situ* Generation of the Silica in NR Matrix

The silica was generated in the natural rubber matrix by a method shown in Scheme 3.1, with a detail explanation as follows

The concentrated natural rubber latex (DRC 60%, NH<sub>3</sub> 0.7%) was placed in a wide-mouth glass container or beaker. TEOS of the required amount was added into the latex with stirring at 750-800 rpm by a mechanical stirrer. 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 wrapping film. The bowl was left in a 50 °C oven to let the sol-gel reaction to proceed. After 5-10 days, the lid was opened and the composite was left in the oven for another 48-hour period at 50 °C. The silica filled rubber was further dried in vacuum at 50 °C for 48 h. 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.



**Scheme3.1** Experimental scheme for the preparation of NR-silica composite



### 3.4.2 Determination of the Silica Content

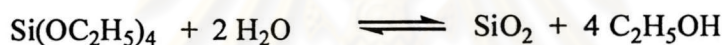
A piece of NR-silica composite (ca. 50 mg), prepared from the method in 3.4.1, was placed in an aluminum oxide cup and heated under air atmosphere, from 0 °C to 850 °C in an oven. The temperature was then held for 15 min at 850 °C. The silica content was calculated from the weight of remaining ash by Eq. 3.1.

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

The conversion of TEOS to silica was also calculated using Eq. 3.2.

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

Where  $W_1$  was the weight of residue ash, and  $W_2$  was the initial weight of the sample.  $W_3$  was the weight of *in situ* generated silica in the sample, which was obtained from Eq. 3.1.  $W_4$  was the theoretical weight of silica being generated assuming quantitative conversion of TEOS into silica by



### 3.4.3 Vulcanization of NR-silica composite

The recipe of the compound rubber is presented in Table 3.1. Detailed procedure is as follows.

The *in situ* silica-NR composite was fed to the two-roll mill having a preset temperature of 70 °C. Then, all materials were added slowly to the rubber. The mixing proceeded until homogeneous compound was obtained. The sheet was cut off the roll and placed on a flat, dry, clean place. Small pieces were removed to test for Mooney viscosity and cure meter before vulcanization. The sheet was then placed into a preheated square-shape mold for compression at 150 °C and a pressure of 150 kg/cm<sup>2</sup> for a prescribed time. The vulcanized composite sheets of ca. 2 mm thickness were obtained. The composite prepared by mixing STR5L with silica powder was also prepared by the same vulcanization method stated earlier.

**Table 3.1** Formulation of compound NR-silica composite for *in situ* silica and mechanically mixed silica.

Materials	Quantity (phr)
ZnO	3.0
Stearic acid	2.0
TMTD	0.3
MBTS	1.0
Sulfur	2.0
Wingstay L	1.0

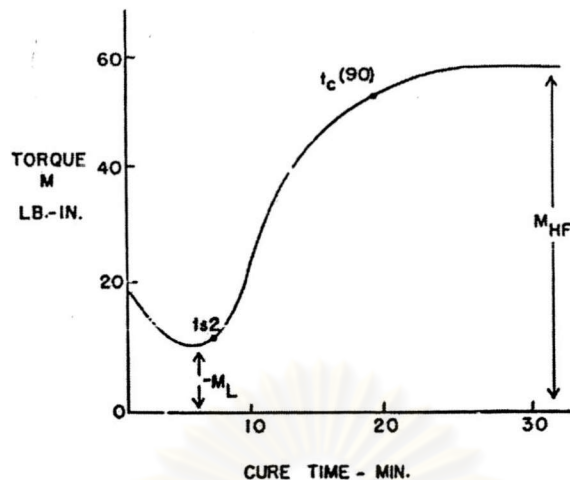
#### 3.4.4 Determination of Curing Behavior and Mechanical Properties

Determination of curing behavior and mechanical properties of vulcanized NR-silica composites were investigated by following the ASTM test methods as follows:

##### Rotorless Cure Meter (ASTM D5289)

The moving-die rheometer (Monsanto MDR2000) was used for determining vulcanization characterization of the rubber compounds.

A test specimen of vulcanized rubber compound is cut into a circular form. A sample shall be 30 mm in diameter and 11.5 mm in thickness. It is then placed in a die cavity which is closed under positive pressure and maintained at the vulcanization temperature. The cavity is formed by two dies, one of which is oscillated through a rotary amplitude. This action produces a torsion strain in the test piece and torque which depends on the stiffness (shear modulus) of the rubber compound. The envelope curve, which is defined as the amplitude of the oscillating force or torque, is continuously recorded as a function of time. The stiffness of the rubber test piece increases as vulcanization proceeds. The time required to obtain a vulcanization curve (Fig. 3.2) is a function of the test temperature (150 °C) and the characteristics of the rubber compound. The test results reported are normally chosen from the following parameters: minimum ( $M_L$ ) and maximum ( $M_{HF}$ ) torque in dN.m unit, scorch time ( $t_{s2}$ ) and cure time ( $t_c(90)$ ) in min.



**Figure 3.1** A typical vulcanization curves which attains an equilibrium torque

#### Mooney Viscometer (ASTM D1646)

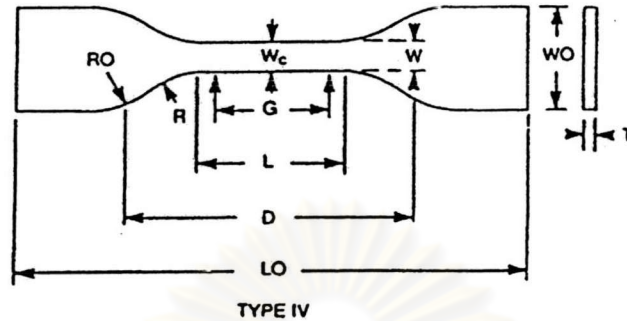
A Mooney viscometer measures the effect of temperature and time on the viscosity of rubber. The test specimen consists of two pieces which completely fill the test chamber. One piece is placed above the rotor and the other beneath it. The rubber is squeezed into the cavity under considerable pressure and temperature. The rotor is continuously rotated at 2 rpm in one direction for a specified time. The resistance to this rotation offered by the rubber is measured in arbitrary torque units as the Mooney viscosity (MV) of the specimen. The viscometer is adjusted so that it will read zero torque when run empty, and  $100 \pm 0.5$  when a torque of  $8.30 \pm 0.02$  N-m is applied to the rotor shaft. The temperature for viscosity determination is  $100^\circ\text{C}$ . The sample is allowed to warm up for one minute after the platens are closed. The motor is then started and reading taken at 4 min.

#### Tensile Properties (ASTM D412)

Tensile strength, elongation and modulus are determined. The vulcanized rubber is stamped with a compressed air sample cutter into a dumbbell shape (Type IV) as illustrated in Fig. 3.2. The specimens are cut from a 2.0 mm thick rubber sheet. The testing is performed on a tensile testing machine. Results reported for each sample are averages of 6 specimens. Measurement condition is as follows:



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



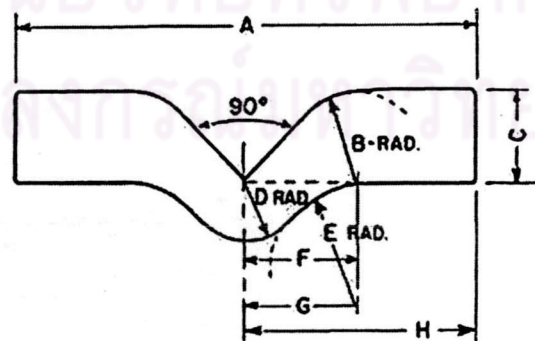
W : 6 mm	W <sub>0</sub> : 19 mm	G : 25 mm	R : 14 mm	T : 4 mm or under
L : 33 mm	LO : 115 mm	D : 65 mm	RO : 25 mm	

**Figure 3.2** A schematic of the specimen for tensile test (Type IV)

#### Tear Strength (ASTM D624)

The vulcanized rubber is stamped with a compressed air sample cutter (Model SDAP-100-N) using a "Die C" (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 shall be sharpened to provide a sharp corner. The sample thickness is 1.9-2.0 mm. Results reported for each sample are averages of 6 specimens. The tear testing condition is shown as follows:

Temperature	25 °C
Humidity	50 %
Crosshead speed	500 mm/min
Full scale load range	500 N



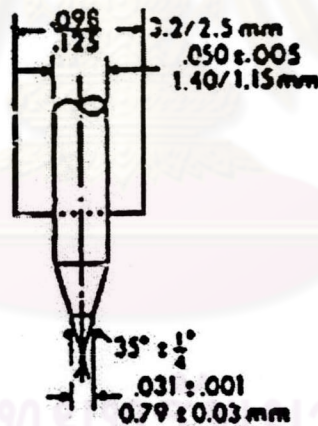
**Figure 3.3** A schematic diagram of tear test specimen (Die C).

### Hardness (ASTM D2240)

For the assignment of the specimen for hardness testing, the test specimen is at least 6 mm in thickness. In this experiment, the test specimens are composed of plied pieces to obtain the necessary thickness. Type A Durometer is used to measure the hardness.

The specimen is placed on a hard and horizontal surface. The presser is held on a vertical position with the point of the indenter at least 12 mm from any edge of the specimen. The presser is applied to the specimen. After the presser foot is in firm contact with the specimen, the scale reading is taken within 30 s. Measurements are made at five different points distributed over the specimen. The median of these measurements is used as the hardness value. The conditions of testing are as follows:

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



**Figure 3.4** A schematic of indenter for type A Durometers.

### **3.4.5 Scanning Electron Microscopy**

The NR-silica composite sheet was frozen in liquid nitrogen and then fractured. The sample was placed on the double sided sticky tape on a specimen stub and sputtered with gold before viewing. Morphology of the composite of the fractured surface was obtained by using SEM.



### 3.4.6 Transmission Electron Microscopy

The NR-silica composite was embedded in polystyrene to make the specimens harder. The specimen was cut to be a small piece and placed in osmium tetroxide (OsO<sub>4</sub>) vapor for 24 h in order to stain the NR phase. The staining not only enhanced the contrast for the microscopic viewing of the composites but also hardened the rubber phase. The specimens were prepared to be ultra-thin films using a microtome. The specimen was placed on a copper grid, which was coated with Formvar<sup>®</sup>. The thin film sections of NR-silica composite was also observed by TEM. The accelerating voltage was 80 kV.

### 3.4.7 The Design of Two-Level Factorial Experiments

Factorial design is widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response. For an experiment having k independent factors, each was studied at “low” and “high” levels. The low level is coded as -1 and the high level is coded as +1.

In this study, a 2<sup>3</sup> design requires a total of 8 runs. It is performed to evaluate three main effects and five interaction effects of each factor on the mechanical properties of NR-silica composite. The three factors are TEOS content, added ammonia solution, and gelation time. Details 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
Added ammonia solution (N)	%	0	2.5
Gelation time (G)	Days	5	10

Values for main and interaction effect are calculated using the Eq. 3.3.

$$\text{Effect} = \bar{y}_+ - \bar{y}_-$$

**Eq. 3.3**

Where  $\bar{y}_+$  and  $\bar{y}_-$  are average values for the responses at high and low levels of each factor. For principal effects the averages simply refer to the results at the high (+) and the low (-) levels, independent of the level of the other factors. For binary interaction,  $\bar{y}_+$  is the average of results for two factors at high-high and low-low levels, whereas  $\bar{y}_-$  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. Generally, high-order interactions are calculated using the Eq.3.3 by applying signs obtained by multiplying those for the factors involved, (+) for high and (-) for low levels.

In this study, replicate experiments are also performed, whose standard errors (E) in the effect values are calculated by Eq. 3.4.

$$E = \{\Sigma(SD) / 2N\}^{1/2} \quad \text{Eq. 3.4}$$

Where SD is the standard deviation of two replicate and N is the number of experiments performed.

The standard error is used to determine which factor is likely to be important. In this research, the estimated effects are calculated from 2 repeated experiments. Therefore standard error from the 2 experiment sets are used to determine which effect is significant. If the effect value is larger than the standard error, that effect has a significant influence on the tested property.

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