CHAPTER III

EXPERIMENTALS

3.1 Materials

High ammonia natural rubber latex with 60% weight content of dry rubber (DRC) incorporated 0.7% NH_3 was purchased from the Rubber Research Institute of Thailand. Liquid dispersion of vulcanizing agents was donated from Polymer Innovation Co., Ltd., Nonthaburi Thailand. Tetraethoxysilane (TEOS, >98%), vinyltriethoxysilane (VTOS, >98%), ethyltriethoxysilane (ETOS, >97%), methacryloxypropyltrimethoxysilane (MPS, >98%) were purchased from Aldrich Germany. Ammonia solution was purchased from BDH, England.

3.2 Procedures

3.2.1 Preparation of pre-vulcanized NR latex

NR latex (60%DRC) was diluted with 0.7% v/v ammonia solution to obtain a 30%DRC latex. It was then mixed with vulcanizing agents, as shown in Table 3.1. The mixture was stirred at 500 rpm by mechanical stirrer for 2 hr at room temperature.

Table 3.1 Vulcanizing agents formulation.

Ingredients	Amount (phr[a])
Natural rubber	100
Sulfur	2.5
ZMBT	0.5
ZDEC	1.5
ZnO	2.0
K5010L-50D	1.0

[a] phr = part per hundred part of rubber by weight.

After that, for single silane system, a predetermined amount of TEOS, VTOS, ETOS or MPS was added to the latex compound with stirring for 10–15 min to obtain a homogeneous milky mixture. Finally, the mixture was filtered through a wire mesh screen to separate coagulated solid (about 5% weight of latex compound). The silane-latex mixture was matured at room temperature for 1 day before it was used in a dipping process.

Table 3.2 Variation of silane amount for *in situ* generation of silica in NR latex.

Code	Silane amount (phr)			
	TEOS	VTOS	ETOS	MPS
VNR	-	-	-	-
30T	30	-	-	-
25T	25	-	-	-
20T	20	-	-	-
15T	15	-	-	-
30V	-	30	-	-
30E	-	-	30	-
30M	-	-	-	30
25T5V	25	5	-	-
20T10V	20	10	-	-
15T15V	15	15	-	-
25T5E	25	-	5	-
20T10E	20	-	10	-
15T15E	15	-	15	-
25T5M	25	-	-	5
20T10M	20	-	-	10
15T15M	15	-	-	15

For mixed silanes system, a predetermined amount of TEOS was first added to the latex compound with stirring. After maturated at room temperature for 24 hr, a predetermined amount of VTOS, ETOS, or MPS was mixed with the latex mixture. A cross condensation between the hydrolysis products of the two different silanes is possible, and it occurs mainly on the surface of the particles [27]. The homogeneous milky mixture of silane-latex was maturated for an additional 24 hr before it was used in the dipping process. During the maturation period, the reaction of silane slowly took place in the presence of water and base in the latex (detailed discussion is in Chapter IV). The variation of silane amount added into the NR latex was listed in Table 3.2.

3.2.2 Dipping process

A clean glass cylinder (Figure 3.1, diameter = 40 mm) was coated with 20% (w/v) calcium nitrate coagulating solution to make a film former. The former was slowly dipped into the maturated latex mixture for 20 sec. The coated former was then heated in an oven at 80°C for 24 hr to complete the vulcanization and sol-gel process of the added silanes. In average, the rubber film thickness was 0.15 mm.

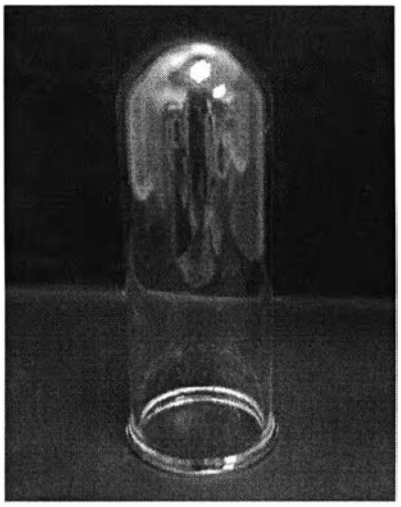

Figure 3.1 A glass cylinder used as a former for rubber dipping process.

3.3 Characterization of the NR/silica dipped films

3.3.1 Silica content in the composites

The silica content was determined by cutting the NR/silica dipped films into small pieces (~50 mg). After an exact weight was determined, the sample was heated at 850°C for 15 min in an oven. The weight of the remaining ash was calculated for the silica content by equation 3.1 and 3.2

$$\text{Weight of silica in the sample } (W_1) = W_a - W_0 \qquad (3.1)$$

where W_a is the weight of sample's ash, and W_0 is the weight of ash from silica-free sample (VNR),

$$\text{Silica Content} = 100\ (W_1/W_2) \qquad (3.2)$$

where W_1 is the weight of silica in the sample, W_2 the weight of the organic rubber.

The conversion of the silane to silica was calculated using equation 3.3 [5, 7],

$$\text{Conversion (\%)} = 100\ (W_3/W_4) \qquad (3.3)$$

W_3 is the obtained amount of the *in situ* generated silica in the sample, and W_4 is the theoretical amount of generated silica based on the added amount of silane in the latex. The results reported were averaged from three specimens.

3.3.2 Microscopic Analysis

3.3.2.1 Scanning electron microscope (SEM)

A scanning electron microscope (SEM) was used to analyze the fractured surface of the NR/silica dipped films. The samples were fractured under liquid nitrogen. The fractured samples were then sputter-coated with gold. The photographs were taken on a JOEL JSM-6480LV SEM. The SEM photographs were used to estimate the degree of silica particle dispersion. Measurements were done at 15 kV at 1,000 and 10,000 magnifications. Energy dispersive X-ray spectrometer (EDX) detector was carried at an elevation angle of 35° in order to determine atomic type on the analyzed surface.

3.3.2.2 Transmission electron microscope (TEM)

JOEL transmission electron microscope (JEM-2100) was used to examine the morphology of rubber particles after the *in situ* silica particles were generated in the latex. The silane-latex mixture was diluted with distilled water to obtain a DRC of 0.75%. The diluted latex sample was deposited onto a carbon-coated Formvar film grid and allowed to dry overnight in a desiccator. The substrate grid was finally stained by exposed to RuO_4 vapor in a glass-covered dish at room temperature for 24 hr.

3.3.3 Thermal properties (TGA)

Thermogravimetric analyses were performed in a thermal analyzer NETZSCH STA 409C. A piece of sample (~20 mg) was placed into an aluminium oxide crucible and scanned from 25 to 900°C at a rate of 20°C/min. The measurements were done under air atmosphere at the flow rate of 50 mL/min. Weight changes versus temperature were recorded.

3.3.4 Mechanical properties

3.3.4.1 Tensile Strength

Tensile properties were measured with Hounsfield H10KS universal testing machine (Hounsfield, Redhill, UK), according to JIS K6251-8 at a grip length of 10 mm, and crosshead speed of 500 mm/min. The NR/Silica dipped films were cut into dumbbell shape specimens using die cutter as (Figure 3.2). Each data point was an average value obtained from measurement of four specimens.

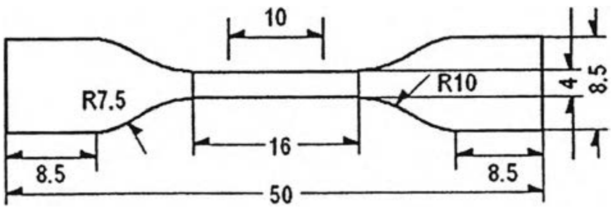

Figure 3.2 Schematic diagram of tensile test specimen (JIS K6251-8).

3.3.4.2 Tear Strength

The tear properties were measured using a Hounsfield H10KS universal testing machine, according to ASTM D624-91. The specimens were cut using die C as shown in Figure 3.3. The gauge length was 70 mm and the crosshead speed was 500 mm/min. The values reported for each sample were averaged from three specimens.

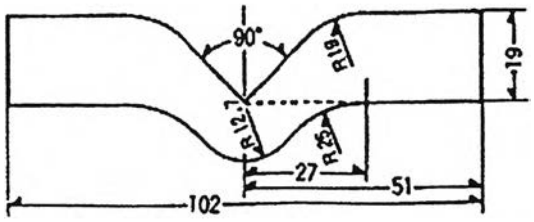

Figure 3.3 Schematic diagram of tear test specimen (ASTM D624 Die C).

3.3.4.3 Tension Set

The NR/Silica dipped films were cut into the size of 5x60 mm as shown in Figure 3.4. Two lines which were about 10 mm apart were marked on the sample. The distance between the two lines was measured by a vernier caliper. The sample was extended until distance the between the two lines was twice that of the original length, and was held for 10 min. After that, the sample was allowed to retract for 10 min. The final distance between the two lines was measured.

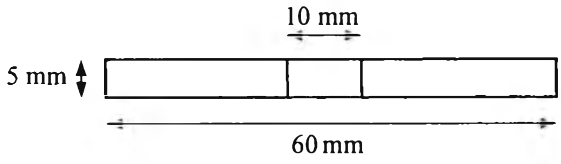

Figure 3.4 Schematic diagram of tear test specimen.

The tension set was calculated using the following equation

$$\text{Tension set (\%)} = 100\,((L_f - L_i)/L_i) \qquad (3.4)$$

where L_i is the initial distance between two lines, and L_f is the final distance between two lines.

3.3.5 Swelling measurements of NR/Silica composites

Circular specimens with diameter of 30 mm were cut out from the NR/Silica dipped films. Specimens of known weight were immersed in toluene at room temperature for 24 hr to allow the swelling to reach diffusion equilibrium. Then, the specimens were immediately blotted with filter paper. Their weights were then determined. From the differences of sample masses, the degree of swelling was calculated by

$$\text{Degree of swelling (\%)} = 100\,((W_6 - W_5)/\,W_5) \qquad (3.5)$$

where W_5 is the initial weight of the sample, and W_6 is the final (swollen) weight of the sample.