CHAPTER III

EXPERIMENTALS

3.1   Materials

High ammonia natural rubber latex (HA, 0.7%) with 60% dry rubber content (DRC) was purchased from the Rubber Research Institute of Thailand (Bangkok, Thailand). Oleic acid, potassium hydroxide (KOH; Fluka), sodium dodecyl sulfate (SDS; Fluka, >99.5%.), methyl methacrylate (MMA; Fluka, Purum), cumene hydroperoxide (CHPO; Fluka, purity ~80%), tetraethylenepentamine (TEPA; Fluka, purity ~85%), tetraethoxysilane (TEOS; Fluka, >98%) and γ-methacryloxypropyltrimethoxysilane (γ-MPS; Fluka, >98%) were used as received. The ammonia solution (25% v/v) was purchased from BDH, England.

3.2   Procedures

3.2.1   Preparation of NR graft with MMA, γ-MPS and TEOS

NR particles in the latex was grafted with MMA, γ-MPS and TEOS by *in situ* emulsion polymerization technique. The high ammonia natural rubber latex (30% DRC) was placed in a round bottom flask along with potassium hydroxide solution (10% w/v, 0.25 phr), and sodium dodecylsulfate solution (10% w/v, 1.0 phr). The latex mixture was stirred by a magnetic stirrer. It was then deoxygenated by bubbling nitrogen gas for approximately 15 min at room temperature. The stabilizer, oleic acid (10 phr) was added into the latex mixture while stirring for 15 min. The MMA and γ-MPS was then added continually in a proper order (the mixing order of γ-MPS was presented in Table 3.1) while stirring for 30 min to allow the monomer to absorb on the surface of latex particles. The mixture was heated up to 50°C, the initiator (CHPO) was then added. After 15 min of mixing, the amine activator (TEPA) was added. The bipolar redox initiating system was employed at 1:1 ratio (CHPO:TEPA) for a total amount of 1.0 phr. The reaction was allowed to proceed for

1 hr under continuous stirring and nitrogen atmosphere. TEOS was then added into the latex compound at room temperature with stirring for 15 min to obtain a homogeneous milky mixture, and was then filtered through a wire mesh to separate coagulated solid phase. The latex compound was poured in to a petri dish. The dish was then closed and seal with tape to reduce ammonia evaporation. The mixture was heated at 50°C, and a heating time varied from 1-5 days was carried out to complete the sol-gel process and the films was further dried at 50°C for another 48 hr. Formulations of the latex compound for the preparation of grafted NR are shown in Table 3.2.

Table 3.1 Mixing order of γ-MPS in the latex compound

Formula no.			
1	2	3	4
MMA ↓ γ-MPS r.t.,15 min ↓ 1stCHPO/TEPA 50°C, 1 hr	MMA ↓ 1stCHPO/TEPA 50°C, 1 hr ↓ γ-MPS 50°C, 1 hr	MMA ↓ 1stCHPO/TEPA 50°C, 1 hr ↓ γ-MPS 50°C, 15 min ↓ 2ndCHPO/TEPA 50°C, 15 min	MMA ↓ 1stCHPO/TEPA 50°C, 1 hr ↓ 2ndCHPO/TEPA r.t., 15 min ↓ γ-MPS r.t., 15 min

r.t. = room temperature

Tables 3.2 Formulations of the latex compounds for the preparation of grafted NR

No.	Code	NR (phr)[a]	MMA (phr)	γ-MPS (phr)	TEOS (phr)
1.	NR	100	-	-	-
2.	NR-g-MMA	85	17.65	-	-
3.	NR-g-MMA-TEOS	85	17.65	-	5,10,15
4.	NR-g-MMA-γ-MPS1	85	15.88	1.76	-
5.	NR-g-MMA-γ-MPS2	85	14.12	3.53	-
6.	NR-g-MMA-γ-MPS1-TEOS	85	15.88	1.76	5,10,15
7.	NR-g-MMA-γ-MPS2-TEOS	85	14.12	3.53	5,10,15

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

3.3   Characterization of NR grafted with MMA

3.3.1   Grafting efficiency

The conversion of MMA to PMMA was calculated using the following equation:

$$\text{Total MMA conversion} = \frac{\text{Weight of MMA charged}}{\text{Total weight of PMMA formed}} \times 100 \qquad (3.1)$$

Soxhlet extraction procedures were carried out to assess the extent to which the products contained free homopolymer and graft copolymer. The free NR was extracted by petroleum ether (60-80°C) for 48 hr. The residue was dried to a constant weight in an oven at 70°C. The residue was further extracted in the soxhlet using acetone (60°C) for 48 hr in order to remove the ungrafted or free PMMA. The residual weight after 2 extractions was therefore the weight of NR-g-MMA. %Grafting efficiency and %Grafted NR were calculated using:

$$\text{Grafting efficiency (\%)} = \frac{\text{Weight of total MMA added} - \text{weight of ungrafted MMA}}{\text{Weight of total MMA added}} \times 100 \quad (3.2)$$

The amount of grafted NR was therefore calculated by

$$\% \text{ Grafted NR} = \left(\frac{b}{a + b + c}\right) \times 100 \quad (3.3)$$

where a, b and c are the weights of the ungrafted NR, grafted NR and free-PMMA, respectively.

3.3.2 Chemical functional group of the grafted NR

The grafted NR film was dissolved in chloroform and a thin film was casted on a KBr cell. Functional groups of the grafted NR were detected by Fourior transform infrared spectrophotometer (Perkin Elmer model 1760x) in the range of 4000-400 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}.

3.3.3 Morphology of the grafted NR particles in latex

The latex was diluted with distilled water to obtain its DRC at 0.75% DRC (10 ml). A drop of 0.5% ruthenium tetroxide (RuO_4) was added into the diluted latex and stirred for 24 hr. Then one drop of the diluted latex was placed on a carbon-coated Formvar film deposited on a grid and dried overnight in a desiccator. Finally, the substrate grid was stained by RuO_4 vapor in a glass-covered dish at room temperature for 24 hr. Morphology of the grafted NR latex was studied using JEOL transmission electron microscope (JEM-2100) at 120 kV.

3.4 Silica content in the composites

The silica/NR composite films were cut into small pieces (50-60 mg) and placed in aluminum oxide cups. The sample films were 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 30 min to complete the oxidation and combustion. The silica content was calculated from the weight of the remaining ash by:

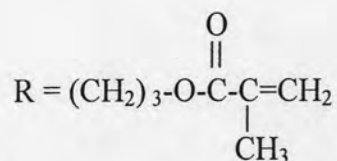$$\text{Silica content (phr)} = (W_1/W_2) \times 100 \qquad (3.4)$$

The conversion of silanes to silica was calculated using:

$$\text{Conversion (\%)} = (W_3/W_4) \times 100 \qquad (3.5)$$

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 equation. 3.4. W_4 was the theoretical amount of silica generated assuming a quantitative conversion of silanes to silica by Schemes 3.1 and 3.2.

$$Si(OCH_2CH_3)_4 + 2\ H_2O \longrightarrow SiO_2 + 4\ C_2H_5OH$$
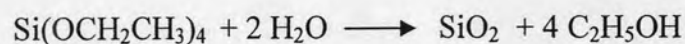
Scheme 3.1 Polymerization reaction of TEOS to silica

$$n\ R\text{-}Si(OCH_3)_3 + 1.5n\ H_2O \longrightarrow \left[R\text{-}SiO_{1.5}\right]_n + 3n\ CH_3OH$$

$$R = (CH_2)_3\text{-}O\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH_2$$

Scheme 3.2 Polymerization reaction of γ-MPS to alkylated silica

3.5 Morphology of silica particles in the composites

The SEM photographs were used to determine the dispersion and size of the silica particles in the rubber matrix. The NR composite films were fractured under liquid nitrogen. The samples were then sputter-coated with gold and the electron micrographs were taken on a scanning electron microscope (JEOL JSM-6480LV, SEM) at 15 kV, and a magnification of 2,000 and 10,000. The energy dispersive X-ray spectrometer (EDX) was also employed with an elevation angle of 35°.

3.6   Thermal Properties

The calorimetric studies were conducted on a differential scanning calorimeter (DSC 204 F1 Phoenix® differential scanning calorimetry). A rubber sample (~10 mg) was scanned from -100 to 220°C at a heating rate of 20°C/min under nitrogen atmosphere. The glass transition temperature (T_g) was taken as the midpoint of changes in the heat capacity and 2nd T_g was taken at the peak position.

Thermogravimetric analyses were studied by a thermal analyzer (NETZSCH STA 409C). A piece of rubber sample (~20 mg) was placed in an aluminium oxide crucible and the crucible was heated from 25 to 700°C at a scan rate of 20°C/min. The measurements were done under air atmosphere at the flow rate of 50 mL/min.

3.7 ^{29}Si-NMR Analysis

The ^{29}Si-NMR experiment was carried out to identify the local environments of the silicon atoms bridging structures in the NR composites. Solid-state ^{29}Si cross-polarization magic angle spinning (CP MAS). NMR spectra of the composites were collected at 59.6 MHz on Bruker DPX-300. Up to 10,000 scans was required to obtain the appropriate signal-to-noise ratio.

3.8   Swelling measurements

The composite films were cut to circular-shape specimens with a diameter of 2.0 cm. Thickness and diameter of the specimens were measured by digital calipers. The specimens of known weights were immersed in toluene at room temperature for 24 hr to allow swelling to reach their diffusion equilibrium. Then, the specimens were immediately blotted with filter paper. The degree of swelling was determined by the weight difference before and after the swelling as shown in eq. 3.6.

$$\text{Degree of swelling (\%)} = (W_s\text{-}W_d)/W_d \times 100 \qquad (3.6)$$

where, W_d and W_s were the dry (before swelling) and after equilibrium swelling weights of the NR sample, respectively.