

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Centrifuged natural rubber latex with 60% solid content was kindly supplied by the Rubber Research Institute (Thailand) and Goodyear Tire & Rubber Co (United States of America). The compounding ingredients viz. potassium hydroxide, zinc oxide, calcium carbonate, zinc diethyl dithiocarbamate (ZDEC), wingstay-L, and sulfur were purchased from the Rubber Research Center, Kasetsart University (Thailand) and were used as received. Sulfur monochloride ( $S_2Cl_2$ ) was purchased from Aldrich Co. and was used as received. Benzene, toluene and methanol (all Merck grades) were utilized as the solvent for the solution cross-linking reactions, swelling, and deswelling experiments, respectively. Pyrrole monomer with 97% purity was supplied by Aldrich Co. and was stored in a refrigerator at 4°C prior to use. Dodecyl sulfate sodium salt (SDS) was purchased from Aldrich Co. Pristine sodium montmorillonite ( $Na^+$ -MMT), with a cation exchange capacity (CEC) of 115 and 145 meq/100g was kindly supplied by Kunimine Industries Co., Ltd. and Nanocor Inc., respectively.

### 3.2 Methodology

#### 3.2.1 Preparation of Concentrated NR Latex/Clay Aerogel Composites and Their Characterizations

##### 3.2.1.1 *Aerogels Preparation*

A conventional vulcanization (CV) system was conducted for pre-vulcanizing the rubber latex, as listed in Table 3.1. The latex was mixed with the compounding ingredients using a homogenizer at 70°C for 30 min. Then, the pre-vulcanized latex was kept in tight plastic bottles for 24 hr. To prepare the composites, a 1 wt% dispersion of pristine clay was added in various amounts with vigorous stirring for 2 hr, followed by homogenizing stirring for 30 min at room temperature to ensure good mixing of the aqueous solutions. The coarse particles

were filtered out, and the solution viscosity was checked using a Brookfield viscometer (Model: DV III). Then, the aqueous solutions were immediately frozen within cylindrical glass shells at the temperature of liquid nitrogen. After freezing, the shells were attached to a lyophilizer (freeze-dryer) maintained at  $-54^{\circ}\text{C}$  in a vacuum of less than 400 mtorr. This process usually took 36 h to entirely sublime the ice out. The control for these samples was the prevulcanized NR latex.

**Table 3.1** Formulation of the rubber compound

Ingredients	Dry (parts by weight)	Wet (parts by weight)
60 % Natural rubber latex	100.0	166.67
10 % Potassium hydroxide solution	0.5	5.0
50 % Zinc oxide dispersion	1.0	2.0
50 % Calcium carbonate dispersion	10.0	20.0
50 % Sulfur dispersion	1.0	2.0
50 % ZDEC dispersion	0.75	1.5
50 % Wingstay-L dispersion	1.0	2.0
1 % Clay dispersion	1.0, 2.0, 3.0	100.0, 200.0, 300.0

Two vulcanization methods were used: (1) thermal curing and (2) microwave curing. For the thermal method, the samples were cured in an oven at  $100^{\circ}\text{C}$  for 20 min. This is because the higher cure temperature could cause the changing of color in vulcanizates. For the microwave method, the samples were cured in a microwave oven—power: 100–850 W; wavelength: 12.24 cm; frequency: 2450 MHz; and magnetron: OM75P(31)—under the same vulcanization temperature as the thermal curing. To achieve the optimum conditions, trial and error experiments were done: an infrared heat sensor gun was used for detecting the temperature of the chamber immediately after stopping the irradiation at a particular power and time.

The results indicated that irradiation with a power of 450 W for 3 min gave a vulcanization temperature of 100°C. It should be noted that a longer cure time might cause overcuring of the samples.

### 3.2.1.2 Characterizations

Elemental analysis of the pristine clay and the nanocomposites was carried out by X-ray fluorescence using an Oxford Model ED2000. The excitation source was an X-ray tube with thin silver as the primary filter, operating at a tube voltage of 35 kV.

The absorbance spectra of a 1 wt% clay aqueous suspension in distilled water and 0.4M H<sub>2</sub>SO<sub>4</sub> were recorded on a UV/vis spectrophotometer 2550 (Shimadzu) scanning in the range of 200–600 nm at room temperature. Experiments were performed in a 1 cm quartz cuvette.

The viscosity measurement of the nanocompounds was carried out with a Brookfield viscometer, Model RVDV-III. The experiments were performed by varying the size and speed of the spindle in order to achieve a shear stress close to 100%. Then, the viscosity data were collected. Shear rate and shear stress can be calculated by using the following equations:

$$\dot{\gamma} = \frac{2\omega(R_c)^2(R_b)^2}{\chi^2(R_c^2 - R_b^2)} \quad , \quad (3.1)$$

$$\tau = \eta \cdot \dot{\gamma} \quad , \quad (3.2)$$

where  $\dot{\gamma}$  is the shear rate,  $\omega$  is the angular velocity of the spindle,  $R_c$  and  $R_b$  are the radii of the container and the spindle, respectively,  $\chi$  is the radius at which shear rate is calculated (normally the same value as  $R_b$ ), and  $\eta$  and  $\tau$  are viscosity and shear stress, respectively.

X-ray diffraction patterns were taken with an X-ray diffractometer, Bruker AXS Model D8 Discover. The X-ray beam was Ni-filtered Cu K $\alpha$  ( $\lambda = 0.154$  nm), and the radiation operated at a tube voltage of 40 kV and a tube current of 40 mA. The samples were scanned in a step mode at a scan rate of 1.5°/min from  $2\theta = 1$ –20°. The interlayer spacing ( $d_{001}$ -spacing) was calculated via the Bragg equation:

$$\lambda = 2d \sin \theta \quad , \quad (3.3)$$

where  $\lambda$  is the X-ray wavelength,  $d$  is the interlayer spacing, and  $\theta$  is the diffraction angle.

The morphology was determined using a scanning electron microscope (JEOL, Model JSM5200). The samples were fractured in a liquid nitrogen bath and coated with gold under vacuum. All SEM digitized photographs were taken at an acceleration voltage of 15 keV with a magnification range between 75 and 2000x.

Hardness was determined by a Shore A durometer according to ASTM D-2240. Five determinations of hardness at five different positions on the specimen were taken and averaged.

The curing behavior was investigated at 150, 160, 170, and 180°C using a Monsanto moving die rheometer (MDR2000) (Rubber Research Center, Kasetsart University, Thailand), operating at a 0.5° arc.

The crosslink densities of the vulcanizates from both methods were determined using a toluene-swelling method, as prescribed in ASTM D-6814-02. The vulcanizate samples were cut into squares (1 cm wide and 3–5 mm thick) and weighed before being swollen in toluene until equilibrium swelling, which normally took 72 h. The crosslink density was calculated by using the Flory–Rehner equation:

$$v_e = \rho_d / M_c = - [\ln(1-V_r) + V_r + \chi_1 V_r^2] / [V_1(V_r^{1/3} - V_r/2)] \quad . \quad (3.4)$$

where  $M_c$  is the average molecular weight between the network crosslinks,  $v_e$  is the network chain density ( $\text{molcm}^{-3}$ ),  $V_r$  is a volume fraction of rubber in a swollen network,  $V_1$  is the molar volume of toluene ( $106.3 \text{ cm}^3 \text{ mol}^{-1}$ ), and  $\chi_1$  is the Flory–Huggins interaction parameter between toluene and polymer (0.391):

$$V_r = [(W_d - W_f) / \rho_d] / [((W_d - W_f) / \rho_d) + (W_s / \rho_s)] \quad , \quad (3.5)$$

where  $W_d$  and  $W_s$  are the weight of dry rubber and the weight of solvent adsorbed by the sample, respectively,  $W_f$  is the weight of the filler in the sample,  $\rho_d$  is the density of the rubber ( $0.92 \text{ gcm}^{-3}$ ), and  $\rho_s$  is the density of toluene ( $0.867 \text{ gcm}^{-3}$ ).

Differential scanning calorimetry (DSC) measurements were carried out with a NETZSCH model DSC 204 F1. The weight of the uncured and cured samples was in the range of 5–10 mg. The thermal scan was performed from

30°C to 250°C at a heating rate of 10°C/min under nitrogen atmosphere to determine the vulcanization behavior of the uncured and cured composites. The heat of vulcanization was calculated by integrating the area under the exothermic signal.

A Perkin-Elmer Pyris Diamond TG/DTA was used for determining the thermal stability of the composites. The weight of the samples was in the range of 15–20 mg. The samples were heated at a heating rate of 10°C/min from 30°C to 600°C in a nitrogen atmosphere.

### 3.2.2 Preparation of Diluted NR Latex/Clay Aerogel Composites and Their Characterizations

#### *3.2.2.1 Aerogels Preparation*

As received 60 wt% rubber latex was first diluted to 30 wt% with distilled water, and was used as a raw material for preparing the pre-vulcanized latex. The pre-vulcanization was conducted using the same procedure as described above. In a second 2 liter container, 20 g of Na<sup>+</sup>-MMT was blended with 1000 g distilled water under vigorous stirring for 2 h in order to wet out the Na<sup>+</sup>-MMT, and then the mixture was mixed at high speed for 30 min using a homogenizer to create a 2wt% Na<sup>+</sup>-MMT dispersion. Afterwards, the designated amount of Na<sup>+</sup>-MMT dispersion was slowly added into the pre-vulcanized latex under vigorous stirring for 2 h, followed by homogenizing stirring for another 30 min at room temperature.

Aqueous solutions obtained in this manner were poured into 2.5 cm diameter cylindrical glass vials for making cylindrical test specimens and were subsequently frozen in a -80°C freezer. The frozen samples were then transferred to a Scanvac freeze-dryer with a condenser temperature of -108°C and subjected to very high vacuum (< 0.1 mbar) in order to sublime the ice. After 3 days in the freeze-dryer, the samples were removed and then cured in an oven at 150°C for 30 min. Control samples were made according to the above-mentioned procedure without the incorporation of Na<sup>+</sup>-MMT.

#### *3.2.2.2 Characterizations*

X-ray diffraction patterns were recorded in the range of  $2\theta = 1\text{--}40^\circ$  (interval of  $0.02^\circ$ ) on a Bruker AXS Model D8 Discover X-ray diffractometer, with Ni-filtered Cu  $K\alpha$  ( $\lambda = 0.154$  nm) radiation operated at 40 kV and 40 mA.

The morphological features of the composites were investigated using a JEOL, Model JSM5200 scanning electron microscope.

The cure characteristics of the composites were determined at four different temperatures ranging from 150 to  $180^\circ\text{C}$  using a torque rheometer (ODR). The kinetic parameters viz. specific rate constant ( $K$ ) and apparent activation energy ( $E_a$ ) were calculated from the torque–time curves.

A gravimetric procedure was adopted to monitor the swelling behavior of the composites. The thickness and initial weight of the samples were taken prior to the swelling experiment. Samples were then immersed in 80 ml toluene at  $25^\circ\text{C}$  and filtered out at regular intervals of time using a mesh sieve. The swollen samples were then drained on the sieve to remove the adhering solvent, and weighed immediately on the electronic balance. The solvent adsorption ( $Q_1$ ) and the swelling kinetics were determined on the basis of the mass changes. The crosslink density and thermodynamic parameters were also computed using the Flory–Rehner and Flory–Huggins equations, respectively.

Compression testing was carried out using a Universal Testing Machine (LLOYD LR 100K) at a constant strain rate of 10 mm/min according to ASTM D575-91. Five samples of each composition were tested, and the compressive moduli were calculated from the slopes of the linear portions of the stress–strain curves.

Dynamic mechanical analyses were conducted on a TA Instruments Q800 DMA machine fitted with a tensile testing head in the temperature ranging from  $-80^\circ\text{C}$  to  $+130^\circ\text{C}$  at a rate of  $3^\circ\text{C}/\text{min}$ . A static force was applied to ensure that the samples were taut between the tensile grips, and the measurement was conducted at the fixed frequency of 10 Hz and the amplitude of 25  $\mu\text{m}$ .

Rheological measurements were carried out on a Rubber Process Analyzer (RPA 2000, Alpha Technologies) under the oscillatory shear. All studies were conducted at the temperature of  $150^\circ\text{C}$ . Dynamic strain sweep tests were initially performed for strains between 0.28 and 140% at a constant frequency

of 0.63 rad/s in order to assess the limits of the linear viscoelastic regime. Dynamic frequency sweeps were performed over the frequency range of 0.1-100 rad/s at the constant strain amplitude of 5%.

### 3.2.3 Preparation of Solution Cross-Linked NR/Clay Aerogel Composites and Their Characterizations

#### *3.2.3.1 Aerogels Preparation*

A 10 wt% clay aqueous suspension was initially prepared by blending 2.75 g of Na<sup>+</sup>-MMT with 27.5 ml of DI water on the high speed setting of a Waring model MC2 mini laboratory blender for ~1 min. Appropriate amounts of NR latex and DI water were then added with gentle mechanical stirring to create the NR/clay hydrogels comprising 5 wt% clay gel and different concentrations of NR, ranging from 2.5 to 10 wt%. For instance, 2.4 g of NR latex and 29 ml of DI water were mixed with the 10 wt% clay gel to produce 2.5 wt% NR/5 wt% clay dispersions. Once thoroughly mixed, the combined solutions were transferred to the cylindrical PS vials and immediately frozen in a solid carbon dioxide/ethanol bath (~-80°C), before being dried for 4 days in the chamber of a VirTis Advantage EL-85 lyophilizer with a shelf temperature of 25°C and an ultimate chamber pressure of 10 μbar. As noted, wt% herein refers to the weight percentage of each component in the parent aqueous dispersion/gel, and the clay weight fraction was kept constant at 5 wt% due to the fact that the only clay aerogel that was sufficiently strong to allow the determination of its compressive modulus, was the one obtained from the 5 wt% clay gel (Gawryla, 2009a).

#### *3.2.3.2 Solution Cross-Linking Process*

Benzene solution of S<sub>2</sub>Cl<sub>2</sub> was chosen for conducting the solution cross-linking of the NR/clay aerogel composites (so-called 'NR aerogels'). Two sets of experimental conditions were performed: (A) as for the 2.5 wt% NR aerogels, S<sub>2</sub>Cl<sub>2</sub> concentration was varied between 0.25 and 5 % (v/v), and the reactions were conducted at a given temperature ( $T_{\text{prep}}$  of either -18 or 18°C); (B) as

for the 5 and 10 wt% NR aerogels, the  $S_2Cl_2$  concentration and  $T_{\text{prep}}$  were kept constant at 1% (v/v) and  $-18^\circ\text{C}$ , respectively.

In a typical experiment, the aerogel samples were immersed in an excess benzene solution of  $S_2Cl_2$  of different concentrations. Preliminary studies showed that the aerogels immediately absorbed benzene to attain their equilibrium states. Thus, after 1 min of the immersion time, the samples together with the external solution were transferred to either a thermostated room ( $T_{\text{prep}}$  of  $18^\circ\text{C}$ ) or a freezer ( $T_{\text{prep}}$  of  $-18^\circ\text{C}$ ), and the cross-linking reactions were allowed to proceed for 24 hr. Thereafter, the samples were taken out of the solution and were extracted with an excess of toluene at room temperature to wash out the soluble polymer and the unreacted  $S_2Cl_2$ . Finally, they were placed in methanol overnight, during which methanol was refreshed several times, and dried under vacuum at  $40^\circ\text{C}$ . As noted, all the neat and cross-linked samples were kept in an acrylic desiccator before testing in order to prevent any moisture absorption.

### 3.2.3.3 Characterizations

Densities of the NR aerogels before and after the solution cross-linking were calculated by measuring the mass and dimensions using a Mettler Toledo AB204-S analytical balance and digital caliper, respectively.

Compression testing was conducted on the cylindrical specimens ( $\sim 20$  mm in diameter and height) using an Instron model 5565 universal testing machine, fitted with a 1 kN load cell, at a constant crosshead speed of  $1\text{ mm min}^{-1}$ . The compressive modulus and toughness at a given strain were determined from the slope of the linear portion and the integrated area of the stress–strain curve, respectively.

Samples for electron microscopy (SEM) were prepared by sputter-coating the fractured monoliths with a thin layer of palladium ( $\sim 50$  Å). Imaging, elemental mapping as well as the energy dispersive X-ray (EDX) analyses were performed using a Quanta 3D 200i FE-SEM at an acceleration voltage of 5 kV.

Thermal properties were examined using a TGA Q500 (TA instruments) under a nitrogen flow ( $40\text{ ml min}^{-1}$ ). Approximately 5 mg of samples



were placed in a platinum pan and heated from ambient temperature to 600°C at a rate of 10°C min<sup>-1</sup>.

The swelling capacity of the NR aerogels before and after the solution cross-linking was determined by following the weight and diameter of the samples immersed in toluene for at least 24 hr. The equilibrium weight and volume swelling ratios, denoted as  $q_w$  and  $q_v$ , respectively, were calculated using the following equations:

$$q_w = \frac{m_{tol}}{m_{dry}} \quad (3.6)$$

$$q_v = \left( \frac{D_{tol}}{D_{dry}} \right)^3 \quad (3.7)$$

where  $m_{tol}$  and  $m_{dry}$  are the weights of the equilibrium swollen and dry NR aerogels, respectively, and  $D_{tol}$  and  $D_{dry}$  are the corresponding diameters. As noted, in order to dry the equilibrium swollen NR aerogels, they were first transferred into methanol overnight and then dried under vacuum.

The pore volume ( $V_p$ ) of the networks was estimated through uptake of methanol of the NR aerogels. Since methanol is a nonsolvent for NR, it only enters into the pores of the aerogel networks. Thus,  $V_p$  (ml pores in one gram of dry aerogel network) was calculated as:

$$V_p = \frac{(m_M - m_{dry})}{d_M m_{dry}} \quad (3.8)$$

where  $m_M$  is the weight of the NR aerogels immersed in methanol after 24h, and  $d_M$  is the density of methanol (0.792 g ml<sup>-1</sup>).

The cross-link density of the NR aerogels was determined in-situ from the equilibrium swelling measurements at room temperature, on the basis of Flory–Rehner theory, which assumes a phantom model to describe the elastic behavior of the swollen network.

### 3.2.4 Fabrication of the Semiconducting Nanomaterials and Their Characterizations

#### 3.2.4.1 *Admicelle Formation*

25 g of centrifuged NR latex was dispersed in distilled water in a reaction vessel containing a magnetic stirring bar. Then, a 1 wt% clay aqueous suspension was poured into the solution to achieve the clay contents between 1 and 7 phr with continuous stirring for 24 hr (the total volume of distilled water was 500 ml); after that 2.31 g of anionic surfactant (SDS) was added to the system while stirring for 2 hr before adjusting the pH. To maximize the admicelle formation, hydrochloric acid (HCl) was used to adjust the pH of the system to below the PZC of NR (normally adjusted to 3.0).

#### *3.2.4.2 Monomer Adsolubilization and Electrochemical*

##### *Polymerization*

In a typical experiment, the pre-cooled pyrrole monomer was introduced into the equilibrated mixture, and the system was left at room temperature for 1 hr to allow for the monomer adsolubilization in the SDS admicelle. To initiate the polymerization, a constant potential of 9 V was applied to the reaction mixture using 2 cm × 10 cm copper plates as both cathode and anode electrodes. After 2 hr of polymerization, a dark admicelled rubber was synthesized and deposited at the anode electrode. Due to a corrosion effect, both electrodes were changed every 2 hr. The polymerization reaction was recorded from the start of applying a constant potential until nothing was deposited on the anode electrode. At the end of the experiment, the collected materials were twice washed with distilled water to remove the outer layer of SDS, and then dried in a vacuum oven at 70°C for 24 hr. Finally, compression molded sheets having a thickness of 3 mm were prepared for further investigation by a hydraulically operated press at 160°C for 15 min.

As a comparison, the control samples comprising various concentrations of pyrrole between 100 and 800 mM were synthesized using the same preparation method as mentioned above, without adding any pristine clay into the system.

#### *3.2.4.3 Characterizations*

The PPy film formed on the rubber surface was identified by a Horizontal attenuated total reflection-Fourier transform infrared spectroscopy

(HATR-FTIR). Nexus 670 spectrometer. The spectra were recorded with 32 scans over a wave number range of 600–4000  $\text{cm}^{-1}$  using air as a background.

X-ray diffraction patterns were recorded in the range of  $2\theta = 1\text{--}30^\circ$  (by steps of  $0.02^\circ$ ) on an X-ray diffractometer, Bruker AXS Model D8 Discover, with Ni-filtered Cu  $K\alpha$  ( $\lambda = 0.154$  nm) radiation operated at a tube voltage of 40 kV and a tube current of 40 mA.

The morphological features of the nanocomposites were investigated using a scanning electron microscope (JEOL, Model JSM5200). The SEM micrographs were taken at an acceleration voltage of 15 keV with a magnification of 3500.

A zero A H-7650 TEM (Hitachi High-Technologies Co., Japan), operating at an acceleration voltage of 100 kV, was used to study the dispersion of the silicate layers within the nanocomposites. Before being examined, some of the mixture collected during the electropolymerization was suspended in distilled water under sonication for 5 min to get a well-dispersed suspension. After that, a droplet was deposited on a 300 mesh copper grid and left for drying overnight. In the case of sectioning, the small specimens were cryogenically cut into ultrathin pieces of about 75 nm thick with a diamond knife using a LEICA ULTRA CUT and were collected on the same copper grids.

The thermal analyses were carried out using a Perkin-Elmer Pyris Diamond TG/DTA under nitrogen atmosphere. The temperature program was set from  $30^\circ\text{C}$  to  $600^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$ . The kinetics of thermal decomposition of the resulting materials was studied.

Hardness tests were performed using a Shore A durometer according to ASTM D-2240. Tensile tests were conducted following ASTM D638M-91a with a Universal Testing Machine (LLOYD LR 100K). The conditions used for the measurements were room temperature, a crosshead speed of 50 mm/min, and a gauge length of 15 mm. Five specimens were tested and taken in an average.

Dynamic mechanical analyses were performed on a dynamic mechanical analyzer (DMA, GABO-EPLEXOR QC 25) using a constant frequency of 10 HZ and a temperature range of  $-80^\circ\text{C}$  to  $+130^\circ\text{C}$ . The measurements were

carried out under tension mode with a static strain of 0.5% and a dynamic strain of 0.1%.

The DC electrical conductivity ( $\sigma_{dc}$ ) was measured at room temperature by the two-point probe technique using a Keithley 8009 Resistivity Test Fixture. The voltage was applied across the sample, and the current was read by an electrometer. The volume electrical conductivity was calculated via the following equations:

$$R = \frac{V}{I}, \quad (3.9)$$

$$\rho_v = \frac{22.9V}{tI}, \text{ and} \quad (3.10)$$

$$\sigma_{dc} = \frac{1}{\rho_v}, \quad (3.11)$$

where  $R$  is the resistance (ohms,  $\Omega$ ),  $V$  is the voltage (volts),  $I$  is the current (amperes, A),  $\rho_v$  is the volume resistivity (ohm centimeters,  $\Omega\text{cm}$ ),  $t$  is the sample thickness (cm), and  $\sigma_{dc}$  is the volume conductivity (siemens per centimeter,  $\text{Scm}^{-1}$ ).