



CHAPTER III

EXPERIMENTAL

3.1 Raw Materials

NR (STR-5L) was purchased from Thai Hua Chumpon rubber Co.,LTD. (Samutsakorn, Thailand). Reagent grade toluene and 3-chloropropionic acid (3-CPA) were provided from Fischer Scientific Ltd. and Fluka Chemie GmbH, respectively. The 99.99% oxygen-free hydrogen gas was supplied by Praxair Inc. (Samutprakarn, Thailand). The hydrogenation catalyst, $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$, was prepared in laboratory following the described by elsewhere (Esteruelas and Werner, 1986 and Esteruelas et al., 1988). Analytical grade thioacetic acid (TAA) from Fluka Chemie GmbH and 1,1'-azobis(cyclohexanecarbonitrile) (ACCN) from Aldrich were used as received. Methanol and sodium hydroxide (NaOH) were supplied from Fischer Scientific Ltd. (Auckland, New Zealand) and Ajax Finechem Ltd. (Lecicestershire, UK), respectively.

The rubber chemicals for the vulcanization process such as stearic acid from Imperial Industrial Chemicals (Thailand) Co. Ltd. (Pathumthani, Thailand), zinc oxide and sulfur powder from Pan Innovation Ltd. (Bangkok, Thailand), N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and tetramethylthiuram disulfide (TMTD) from Flexsys (Monsanto) (Cologne, Germany) and dicumyl peroxide (DCP) from Petch Thai Chemical Co. Ltd. (Bangkok, Thailand) were all commercial grade. Ethylene-propylene diene rubber (EPDM) of Nordel IP grade (7.5 wt% diene content) obtained from DuPont Dow Elastomers (Wilmington, USA) was used for the properties comparison.

3.2 Hydrogenation of Natural Rubber

The procedure for HNR preparation has been described in previous literature (Hinchiranan et al., 2009). A specific amount of NR (ca. 612.7 mM) was dissolved in 1,200 mL of toluene with a small amount of 3-CPA (5 mM). The hydrogenation of NR carried out in a 2 litre Parr reactor. The catalyst was weighed (ca. 105.8 μ M) into a small glass bucket and placed in the catalyst addition port within the reactor head. After assembling the reactor and purging the system by using hydrogen gas to remove oxygen, heating was initiated and stabilized at 140°C. The catalyst was then charged into the rubber solution using hydrogen pressure at 27.6 bar for 1 – 4 h depending on the desired hydrogenation level.

3.3 Functionalization of HNR

The preparation of functionalization of thioacetate and mercapto functional groups onto HNR backbone was described in the previous literature (Oliveira et al., 1999). The obtained HNR with 80% and 90% hydrogenation levels were further used for functionalization under nitrogen atmosphere as illustrated in Figure 3.1. For the preparation of the thioacetate-modified HNR (HNRTA), 10 g of HNR was dissolved in 250 ml of toluene. Then, TAA and ACCN used as initiators were added into the rubber solution with constant stirring rate at 80°C for desired reaction time. To terminate the reaction, the hot rubber solution was subsequently poured into ethanol. The resulting precipitate was washed several times with ethanol and dried under vacuum at room temperature.

The methanolysis of HNRTA was performed by dissolving 10 g of HNRTA in 250 ml of toluene at 50°C. Then, 15 ml of a methanolic solution of NaOH was slowly added into the rubber solution in order to avoid the formation of crosslinking during reaction which carried out under constant agitation rate for a given reaction time. To cease the reaction, 40 ml of 1 M of HCl solution was added into the reacted solution for neutralization. The mercapto-modified HNR (HNRSH) was precipitated and washed several times with ethanol and then dried under vacuum at room temperature.

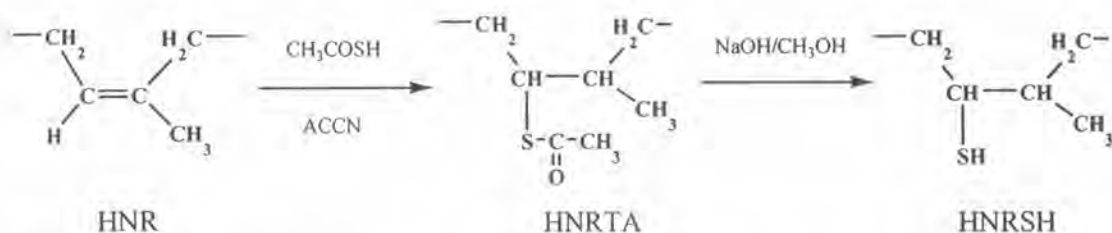


Figure 3.1 Scheme of HNR functionalization with thioacetate and mercapto groups.

3.4 Preparation of Blends

The formulation used for the preparation of the HNR/NR blends compared with EPDM/NR blends is given in Table 3.1. The typical preparation of HNR/NR blends was described in previous literature (Hinchiranan et al., 2009). To avoid the overcure effect of the NR phase, NR was blended with HNR using a two-roll mixing mill at room temperature. NR was masticated for 2 min before mixing with HNR and the compatibilizer (HNRTA and HNRSH). When the rubber blend was homogenized (ca. 7 min), the chemicals for vulcanization were added. The processing time after the addition of each component was ca. 2 min. For the blends of HNR/NR, two vulcanization systems such as conventional vulcanization (CV) and efficient vulcanization with peroxide (EPV) were employed. The amount of compatibilizers (HNRTA and HNRSH) was varied from 0-15 phr. The rheometric characteristics of blends were assessed at 150°C by using a Monsanto Rheometer MDR 2000. The blends were then vulcanized in a hydraulic compression mold at the obtained optimum cure time at 150°C.

3.5 Characterization Method

3.5.1 Fourier Transform Infrared Spectroscopic Analysis (FTIR)

Infrared spectra of HNRTA and HNRSH were collected on a Bio-Rad FTS 3000X spectrometer. Samples for FTIR analyses were prepared by casting rubber solution as thin films on a sodium chloride disk.

Table 3.1 Formulation of blend compounds.

Ingredients (phr) *	Vulcanization systems	
	CV	EPV
HNR** / NR	50/50	50/50
EPDM/ NR	-	50/50
Zinc oxide	3.0	3.0
Stearic acid	1.5	1.5
CBS	-	0.7
DCP	-	2.0
TMTD	-	1.5
Sulfur	3	-

* Parts per hundred of rubber by weight.

** >95%hydrogenation

3.5.2 ¹H-NMR Analysis

To confirm the FTIR results and to calculate the exact conversion of hydrogenation and functionalization, the content of functional group on the modified HNR was investigated by proton nuclear magnetic resonance spectroscopic analysis (¹H-NMR). ¹H-NMR spectra was obtained by dissolving 0.01 g of rubbers in CDCl₃ and recording the spectra using an Avance 300 MHz spectrometer (Bruker).

3.5.2.1 Determination of Hydrogenation Level

The final degree of hydrogenation of each experiment was evaluated using ¹H-NMR spectroscopy. The peak areas of the saturated protons (–CH₂– and –CH₃) in the range of 0.8 – 2.3 ppm and the unsaturated protons peak area at 5.2 ppm were measured in order to calculate the %hydrogenation using eq. 2.1:

$$\% \text{Hydrogenation} = \frac{A - 7B}{A + 3B} \times 100 \quad (2.1)$$

where A is the peak area of saturated protons and B is the peak area of unsaturated protons. An example for the %hydrogenation calculation is illustrated in Appendix B.1.

3.5.2.2 Determination of %Thioacetate in HNR

The actual content thioacetate functional group on the HNR structure was obtained by using $^1\text{H-NMR}$ spectroscopy. The level of thioacetate content could be calculated from the peak area of $-\text{CH-S-}$ at 3.6 ppm and the summation of peak areas between proton of $-\text{CH-S-}$ and the unsaturated proton at 5.2 ppm. The percentage of thioacetate in HNR was calculated using eq. 2.2:

$$\% \text{Thioacetate in HNR} = \left(\frac{b}{a + b} \right) \times 100 \quad (2.2)$$

where a is the peak area of unsaturated protons and b is the peak area of $-\text{CH-S-}$ proton. An example the thioacetate content calculation is illustrated in Appendix B.2.

3.5.2.3 Determination of % Methanolysis

The percentage of methanolysis of HNRTA samples was calculated from the integrated peak area from $^1\text{H-NMR}$ spectrum before (0) and after (t) methanolysis as described in Appendix B.3. The percentage of methanolysis was calculated following eq. 2.3:

$$\% \text{Methanolysis} = \left\{ 1 - \left[\frac{c_t}{b_t} \times \frac{b_0}{c_0} \right] \right\} \times 100 \quad (2.3)$$

where b is the peak area of $-\text{CH-S-}$ protons at 3.6 ppm and c is the peak area of proton of the methyl group in the thioacetate at 2.3 ppm.

3.5.3 Determination of Gel Content

The gel content in a rubber sample represents the amount of insoluble parts in the rubber samples dissolved in the toluene according to ASTM D 3616-95 (2000). The gel content can be calculated by using eq. 2.4 and eq. 2.5:

$$B = 4 \times A \quad (2.4)$$

$$\text{Gel (\%)} = \frac{(C - B)}{C} \times 100 \quad (2.5)$$

where A is weight of rubber solution (25 ml) after drying, B is weight of total dried sol and C is initial weight of rubber before dissolving in the solvent (100 ml).

3.5.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry of the modified-HNR samples was carried out on a Mettler Toledo DSC 822. The thermogram signal was derived from the temperature difference between the sample and the reference. Rubber samples (5 mg) placed in a crimped aluminium pan were cooled to -100°C with liquid nitrogen and then heated at a constant rate of $5^{\circ}\text{C}/\text{min}$ to 25°C . The glass transition temperature was calculated from the midpoint of the base-line shift of the DSC thermogram.

3.5.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the HNR samples before and after modification was performed on a Perkin-Elmer Pyris Diamond TG/DTA. The temperature was raised from room temperature to 700°C at a constant heating rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. The flow rate of nitrogen gas was controlled as $50 \text{ mL}/\text{min}$. The initial decomposition temperature (T_{id}) and the temperature at the maximum mass loss rate (T_{max}) were evaluated.

3.5.6 Cure Characterization

The cure characteristics of rubber blends were analyzed at 150°C using a Monsanto Rheometer MDR 2000 according to ASTM D5289-95. Test results were reported in terms of minimum torque (M_L), maximum torque (M_H), scorch time (t_{s2}) and optimum cure time (t_{c90}).

3.5.7 Determination of crosslink density

The cross-linking efficiency of the specimens was evaluated in terms of crosslink density using an equilibrium solvent swelling test method. The specimens (10 x 10 x 2 mm) with accurately weighted were immersed in toluene and allowed to swell in closed vessels for 7 days. Then, the surface of the swollen samples was quickly wiped and weighed (w_1). After drying at 40°C for 48 h, the dried rubber samples were weighed again (w_2) to determine the amount of absorbed toluene inside the samples. The volume fraction of polymer in the swollen specimens (v) was calculated using eq. 2.6:

$$v = \frac{w_2(\delta_r)^{-1}}{w_2(\delta_r)^{-1} + (w_1 - w_2)(\delta_s)^{-1}} \quad (2.6)$$

where δ_r and δ_s are the density of rubber and solvent, respectively (Sirqueira and Soares, 2003). The crosslink density of the specimens was calculated based on the Flory-Rhener equation (eq. 2.7):

$$-\ln(1 - v) + v + \chi v^2 = V_0 n \left[v^{1/3} - \frac{v}{2} \right] \quad (2.7)$$

where n is the number of elastically active chains per unit volume (mol/cm^3). V_0 is the molar volume of the solvent ($106.3 \text{ cm}^3/\text{mol}$ for toluene) and χ is the Flory-Huggins polymer solvent interaction term (0.39 for NR-toluene) (Sperling, 2006).

3.5.8 Mechanical Properties

The mechanical properties of vulcanized rubbers in terms of tensile properties and hardness were evaluated. The tensile properties of all vulcanizates rubbers were carried out on a Universal Testing Machine (LLOYD model LR5K) at 500 mm/min of the cross-head speed. This test method followed the standard method ASTM D 412. The elongation of specimens was obtained from the extensometer. The specimens were cut using a die C and the average of three specimens was considered as the representative value. The hardness measurement was performed using a Durometer Hardness System Model 716 and shore A following ASTM D 2240. Every specimen was tested in three times and the average results were reported as the hardness value of each rubber recipe.

3.5.9 Thermal Ageing Properties

The effect of thermal ageing on the mechanical properties of the blends was investigated in a hot air ageing oven at 100°C for 22 ± 2 h. At the termination of ageing time interval, the dumbbell-shape specimens were removed from the oven and cool at room temperature on a flat surface for 24 h before determination of the tensile properties according to ASTM D 412. The thermal ageing properties were calculated as percentage of properties retention following eq. 2.8.

$$\% \text{Retention} = \frac{\text{Properties after ageing}}{\text{Properties before ageing}} \times 100 \quad (2.8)$$

3.5.10 Ozone Resistance Test

The test of ozone resistance followed the standard test method JIS K 6301-1995 and Physical Testing Standards of Rubber developed Nishi and Nagano (1983). The specimens were cut to a size of $1.5 \times 8.0 \times 0.2$ cm and then exposed in an ozone cabinet (HAMPDEN, Northampton, England) with ozone concentration of 50 pphm (part per hundred million) at 40°C for 6, 24 and 48 h. Before exposure to ozone, the specimens were stretched by 20% using specimen holder for 48 h in the absence

of light and ozone-free atmosphere. The cracking on rubber surfaces was examined by using a CCD camera.

3.5.11 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties such as storage modulus and loss modulus of the rubber samples after the vulcanization process were examined using a GABO QUALIMETER EPLEXOR 25N with a tension mode. The temperature scan was run at an oscillation frequency of 10 Hz with a heating rate of 2°C/min. The vulcanized rubber samples were cut as strips with 10 mm width, 2.7 mm thickness and 10 mm length.