

CHAPTER III

EXPERIMENTAL

3.1 Materials

1. High-ammonia natural rubber (HANR) latex
: Thai Rubber Latex and Cooperation (Thailand) Co. Ltd.
2. Gelatin from porcine skin
: Chemical grade; Fluka
3. Gum Arabic
: Chemical grade; Fluka
4. Titanium (IV) oxide (TiO_2)
: Analytical grade; Riedel-de Haen
5. Sulfur
: Chemical grade; DYNA Trade Co. Ltd.
6. Zinc oxide (ZnO)
: Chemical grade; Fluka
7. Zinc diethyl dithiocarbamate (ZDEC)
: Chemical grade; Aldrich
8. Sodium hydroxide
: Chemical grade; Merck
9. Potassium hydroxide
: Chemical grade; Merck
10. Toluene
: Analytical grade; Carlo Erba
11. Glacial acetic acid
: Analytical grade; Carlo Erba

12. Formaldehyde solution
: Analytical grade; Lab-Scan
13. Methanol
: Analytical grade; Merck
14. Soybean oil was obtained commercially.

3.2 Instruments

1. Ultraviolet light
: Daavlin PW, UVB 220 (UVB Psorawand) (290-315 nm)
2. Ultraturrax
: IKA Works, model T18 basic
3. Ubbelohde viscometer
: Sibata, model 2613-001
4. Fourier Transform Infrared Spectrophotometer (FT-IR)
: Perkin Elmer, model 1760X
5. Attenuated Total Reflection Infrared Spectrophotometer (ATR-IR)
: Bruker, model Vector 33
6. Scanning Electron Dispersive X-ray Microscopy (SEM-EDX)
: JEOL, model JSM – 5800LV
7. X – ray diffractometer
: JEOL, model JDX – 8030
8. Universal testing machine
: Hounsfield, model H10KM

3.3 Procedure

3.3.1. Purification and determination of gel content of natural rubber

HANR latex 5 mL was poured into a glass/aluminum mold ($5 \times 5 \times 1 \text{ cm}^3$) and covered with aluminum foil. The latex was dried in the dark at ambient temperature for 2 days. The dried latex sheet was dissolved in dried toluene. The solution was kept without stirring in the dark at ambient temperature for 3 days. The gel fraction was collected as a bottom fraction by vacuum filtration. The solution fraction of rubber was collected as a sol fraction, which was later precipitated with an excess amount of methanol. The dried rubber obtained after precipitation was called fractionated rubber.

3.3.2. Molecular weight determination of natural rubber by solution viscometry

The stock rubber solution ($2.1 \times 10^{-3} \text{ g/mL}$) was prepared by dissolving fractionated rubber 0.2 g in 100 mL dried toluene, which was stirred for 2 days in the dark at ambient temperature. The stock rubber solution 6 mL and 2 mL toluene ($1.6 \times 10^{-3} \text{ g/mL}$) were added into Ubbelohde tube at 25°C . The solution level was brought up above a (see Figure 2.5) using rubber bulb. The time at which the solution moved down from a to b was measured. The same procedure was repeated for each concentrations by a stepwise addition of 2 mL toluene to obtain rubber concentration of 1.3×10^{-3} , 1.1×10^{-3} , 9×10^{-4} and $8 \times 10^{-4} \text{ g/mL}$, respectively. Viscosity-average molecular weight (\bar{M}_v) was determined using Mark-Houwink equation.

3.3.3. Oxidative degradation of natural rubber in the presence of TiO_2 powder under accelerated condition

The rubber solution ($2.1 \times 10^{-3} \text{ g/mL}$) was prepared by dissolving 0.2 g fractionated rubber in 100 mL dried toluene, which was stirred for 2 days in the dark at ambient temperature. TiO_2 powder 0.01, 0.1, 0.2 and 1 g (0.05, 0.5, 1 and 5%w/v) was added into 50 mL beaker containing 20 mL rubber solution and a magnetic bar. The solution was kept stirring while exposed to ultraviolet light for a desired period of time

(15 – 120 min). The solution was then filtered to separate TiO_2 powder before subjected to molecular weight determination using solution viscometry.

3.3.4. Preparation of microparticles containing TiO_2 powder

Gelatin and gum arabic solution 5%(w/v) were prepared separately at 47 °C by dissolving 2.5 g gelatin or gum arabic in 50 mL deionized water. TiO_2 powder (1.5 g) was mixed with 10 mL soybean oil in 600 mL beaker at room temperature. Gelatin solution 5%(w/v) 50 mL at 47 °C was added into the mixture. The emulsion was homogenized at 14,000 rpm for 2 min. Gum arabic solution 5%(w/v) 50 mL at 47 °C was added into the suspension. pH of the suspension was reduced to 3.5 by 10% acetic acid followed by an addition of 80 mL warm water (47 °C). The suspension was homogenized at 14,000 rpm for 30 min. The system was cooled down to 5 °C and left for 30 min before 3 mL formaldehyde was added. 10% sodium hydroxide was added to the suspension to elevate pH to 8.5. After agitation continued for 30 min, the temperature was increased to 50 °C. Microparticles were subjected to freeze-drying for 1 day before characterized by scanning electron microscopy.

3.3.5. Oxidative degradation of rubber sheet containing TiO_2 powder and TiO_2 microparticles

TiO_2 powder 0.005, 0.025, 0.05 or 0.25 g (0.1, 0.5, 1 or 5%w/w) or TiO_2 microparticles 0.025, 0.05, 0.15 or 0.25 g (0.5, 1, 3 or 5%w/w) was mixed with 5 g HANR latex by stirring. The mixture was poured into a glass/aluminum mold and covered with aluminum foil. The latex was dried in the dark at ambient temperature for 2 days. The rubber sheets ($5 \times 5 \times 1 \text{ cm}^3$) were exposed to ultraviolet light for a desired period of time (60-150 min) or sunlight for 1 – 4 days. The rubber sheet was dissolved in 50 mL dried toluene. The solution was kept without stirring in the dark at ambient temperature for 3 days. The solution was then filtered by vacuum filtration to separate TiO_2 powder or microparticles along with gel fraction. Viscosity-average molecular weight of rubber sol fraction was determined using solution viscometry.

3.3.6. Preparation of vulcanized rubber sheets

HANR latex 100 mL was first stabilized by adding 10%(w/v) potassium hydroxide at 50°C. 2 g of 50%(w/v) sulfur dispersion, 1 g of 50%(w/v) zinc oxide dispersion and 1 g of 50%(w/v) zinc diethyl dithiocarbamate (ZDEC) were then added into the latex. The latex mixture was then warmed up to 50 °C for 3 hours before 1 g of TiO₂ powder or TiO₂ microparticles were added. The latex mixture was poured into a dumb-bell shaped mold. The dimension of dumb-bell test pieces is shown in Table 3.1. The compounded latex sheet was obtained after drying in the dark at ambient temperature for 2 days. The vulcanized sheets were prepared by heating the compounded sheets at 100 °C for 30 min. The vulcanized sheets were exposed to sunlight for 5 – 15 days. Oxidative degradation was studied by monitoring mechanical properties. Degraded rubber sheets were analyzed by attenuated total reflection-infrared spectroscopy (ATR-IR) and scanning electron microscopy (SEM).

3.3.7. Mechanical testing

The tensile strength and elongation at break of vulcanized rubber sheets (5 specimens/sample) were measured using a universal-testing machine according to ASTM D 412-87. The condition for tensile testing is illustrated in Table 3.2. The dumb-bell test pieces (type D) have the outline shown in Figure 3.1.

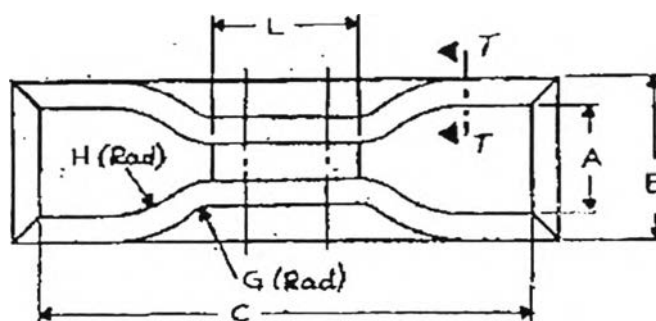


Figure 3.1 Schematic of tensile specimen

Table 3.1 Dimension of dumbbell test pieces (type D) prepared for mechanical testing

Dimension	(mm)
(A) Width of ends	16 ± 1
(C) Overall length (minimum)	100
(G) Transition radius outside	14 ± 1
(H) Transition radius inside	16 ± 2
(L) Length of narrow portion	33 ± 2

Table 3.2 The condition for tensile testing

Temperature	25 °C
Humidity	60%
Crosshead speed	500.00 mm/min
Gauge length	20.0 mm