

CHAPTER III EXPERIMENTAL

3.1 Surface Characterization

3.1.1 Materials

3.1.1.1 *Concentrated Natural Rubber Latex (NRL)*

NRL used in this study was received by Rubber Research Institute of Thailand. It was used as received. Its properties are shown:

Total solid content (TSC)	62.11%
Dry rubber content (DRC)	60.71%
Non rubber context	1.40%
Mechanical stability time at 55% TSC	650 seconds
Volatile fatty acid number (VFA)	0.086
Potassium hydroxide number	0.80
pH	9.51
Magnesium content	16 ppm

3.1.1.2 *Linear Polydimethylsiloxane*

Polydimethylsiloxane $\text{-(Si(CH}_3\text{)}_2\text{O)-}$ used in this study was 365, 35% Dimethicone Normal Formularly, received by Dow Corning (Thailand) Limited. Its density is 0.99 g/cm^3 . It was used as received.

3.1.1.3 *10% Potassium hydroxide (KOH)*

Potassium hydroxide was purchased from Merck. This material is opaque pellet and used as stabilizer. It was used as received.

3.1.1.4 *Vulcanizing Agents*

Vulcanizing agents including 50% sulphur (S), 50% zinc diethyldithiocarbamate (ZEDC), 50% zinc oxide (ZnO), and 40% sodium

dibutyldithiocarbamate (SDBC) were received from Rubber Research Institute of Thailand. They were used as received.

3.1.1.5 50% Wingstay-L (W-L)

Wingstay-L was used as antioxidant, received from Rubber Research Institute of Thailand. It was used as received.

3.1.1.6 35% Coagulant Solution of Calcium nitrate

Calcium nitrate was received from Rubber Research Institute of Thailand. It was used as received.

3.1.1.7 Ethylene glycol (EG)

Ethylene glycol (HOCH₂CH₂OH), boiling point 196-198°C was purchased from Lab-Scan Analytical Science and Baker Analyzed Reagent. It was distilled in a fractional distillation set at 200°C under nitrogen gas and stored under nitrogen gas before use.

3.1.2 Instruments

3.1.2.1 Fourier Transform Infra Red Equipped with Attenuated Total Reflection (FTIR-ATR)

FTIR spectrometer that used in this studied was Bruker FT-IR spectrometer with a deuterated triglucinesulfate detector (DTGS) with a specific detectivity (D^*) of $1 \times 10^9 \text{ cmHz}^{1/2} \text{ W}^{-1}$. IR spectra of rubber surface regions were obtained by using Attenuated Total Reflection. Crystal cell used in this study is zinc selenide (refractive index 2.4) to give a total 16 reflection. The penetration depth (d) calculated by equation 3.1 is 1.63 μm .

$$d = \frac{2\lambda}{\pi n_1 \sin^2 \theta} \quad (3.1)$$

where λ is selected wavelength (in this case, λ is $9.78 \times 10^{-4} \text{ cm}$)

π is 22/7

n_1 is refractive index of zinc selenide crystal

θ is 45

n_{21} is ratio of refractive index of polydimethylsiloxane to refractive index of zinc selenide crystal

n_2 is refractive index of polydimethylsiloxane (n_2 is 1.4034).

Each value is placed in equation 3.1,

$$d = \frac{9.78 \times 10^{-4}}{2 \times 22/7 \times 2.4 (\sin^2 45 - (1.4034/2.4)^2)^{1/2}}$$

$$d = 1.63 \times 10^{-4} \text{ cm}$$

$$d = 1.63 \text{ } \mu\text{m}$$

Frequency was range from 4000 to 400 cm^{-1} with the resolution of 4 cm^{-1} .

3.1.2.2 Contact Angle Measurements

Drop of ethylene glycol was photographed by Nikon FM2 camera after 3 minutes of contact. Then film was scanned by Nikon LS-1000 film scanner and contact angle was measured by Photoshop version 5.0.

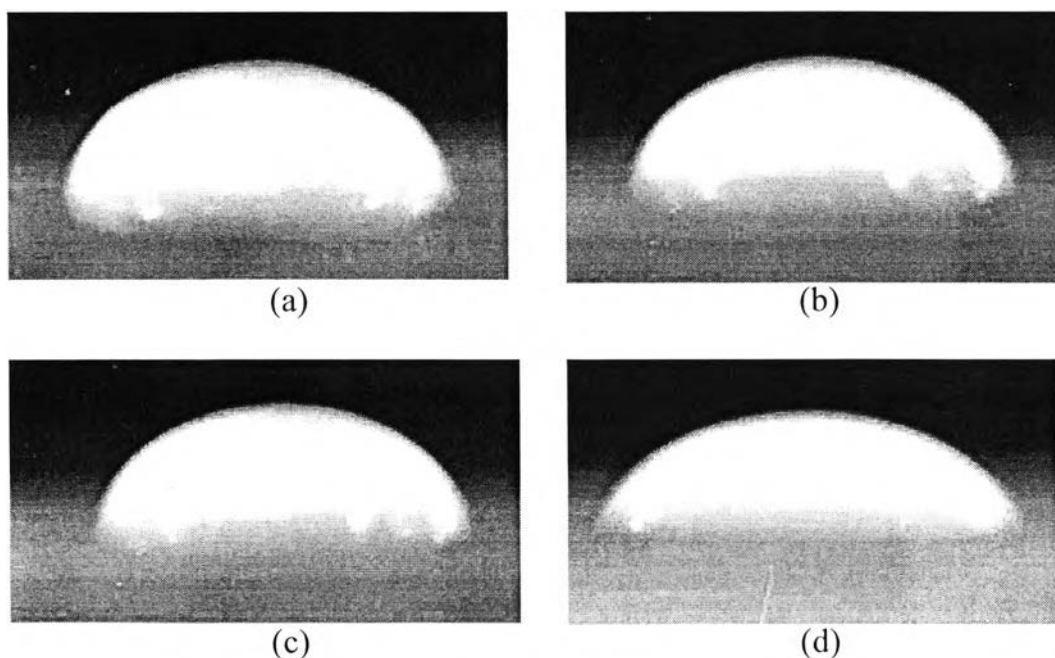


Figure 3.1 Photograph of ethylene drop on rubber surface of: (a) CPD sheet (b) CSE5 sheet (c) CPD film and (d) CSE5 film.

3.1.2.3 Thermogravimetric Analyzer

Thermal property was characterized by using a PERKIN-ELMER 7 Series Thermal Analysis System from 50°C to 850 °C. Heating rate was at 20°C/min under N₂ atmosphere.

3.1.2.3 Scanning Electron Microscope with Electron Dispersive Detector (SEM-EDS)

Scanning electron microscope is a practical technique used for studying morphology of polymers and identification of the elemental constituents of the area of the specimen. This technique uses electron beam, usually from tungsten filament, to interact with solid surface. When electron beam impinges the surface, three types of interaction may occur i.e., backscattered electron, secondary electron and X-ray photon.

To qualify and quantify the element at the surface, electron dispersive detector was used. SEM, JEOL 6400 with a magnification range of 35 – 200,000 times was used for this study. The magnification of the images was 2000 at 15 kV.

3.1.3 Procedure

3.1.3.1 Preparation of Samples

There were two types of samples: vulcanized rubber sheets and films.

a) Vulcanized rubber sheet

Vulcanized rubber sheets were prepared by thoroughly mixing NRL, PDMS and other additive, as indicated in Table 3.1. There were five samples; CPD for compounded NRL without PDMS; CSE5, CSE10, CSE15, CSE20 for compounded NRL with PDMS of 5, 10, 15, 20 parts per hundred of rubber (phr) respectively.

Table 3.1 Formulation for vulcanized rubber sheet.

Material	Compound				
	CPD	CSE 5	CSE 10	CSE 15	CSE 20
60% NRL	100	100	100	100	100
10% KOH	0.2	0.2	0.2	0.2	0.2
35% PDMS	0	5	10	15	20
50% S	0.65	0.65	0.65	0.65	0.65
50% W-L	0.60	0.60	0.60	0.60	0.60
50% ZDEC	0.70	0.70	0.70	0.70	0.70
50% ZnO	1.00	1.00	1.00	1.00	1.00
40%SDBC	0.12	0.12	0.12	0.12	0.12
Distilled	Add to	Add to	Add to	Add to	Add to
Water	32%TSC	32%TSC	32%TSC	32%TSC	32%TSC

They were matured at room temperature for three days. Then these compounded NRL of 1.2 grams were poured into petridish (15x60 mm). After that they were dried in the hot air oven at 60°C for 13 hours and vulcanized at 100°C for 10 minutes. The obtained sheet had thickness of ranging from 0.88 to 1.00 mm, measured by thickness gauge.

b) Vulcanized rubber films

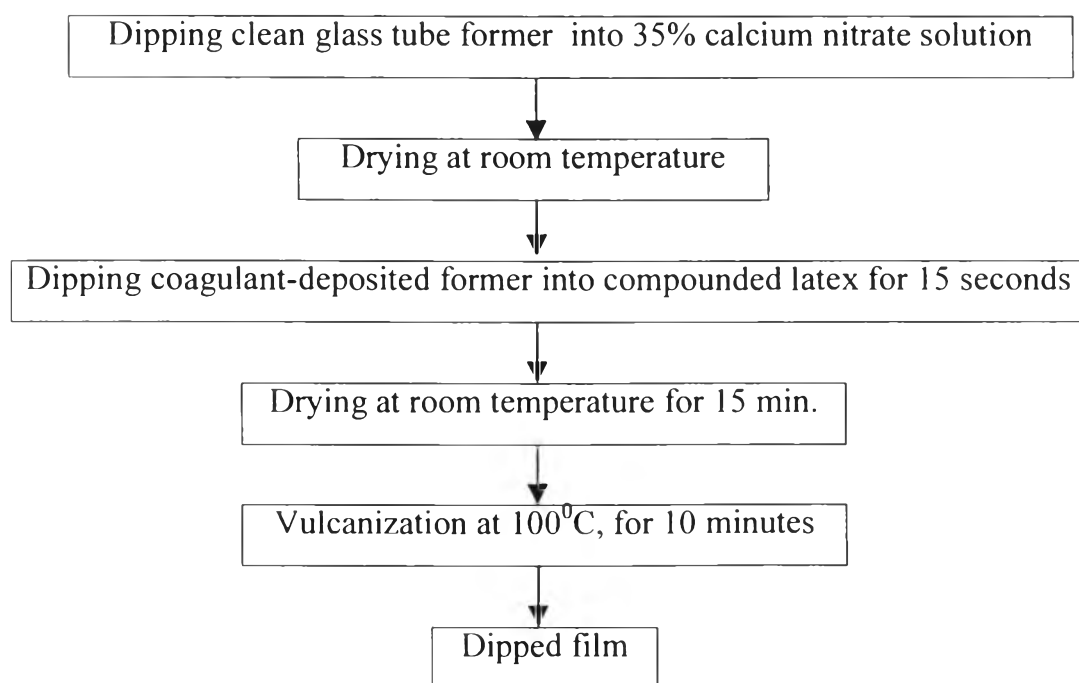
Vulcanized rubber films were prepared by thoroughly mixing NRL, PDMS and other additive, as indicated in Table 3.2. There were two samples; CPD for compounded NRL without PDMS; CSE5 for compounded NRL with PDMS of 5 phr.

Table 3.2 Formulation for vulcanized rubber film.

Material	Compound	
	CPD	CSE5
60% NRL	100	100
10% KOH	0.20	0.20
35% PDMS	0	5
50% S	0.65	0.65
50% W-L	0.60	0.60
50% ZDEC	0.70	0.70
50% ZnO	1.00	1.00
40%SDBC	0.12	0.12
Distilled Water	Add to 40%TSC	Add to 40%TSC

They were matured at room temperature for three days.

Dipped films were constructed by the following chart:

**Figure 3.1** Flow diagram of vulcanized rubber film.

The obtained film had thickness of ranging from 0.18 to 0.20 mm, measured by thickness gauge.

3.1.3.2 Spectroscopic Studies

Both sides of sample surfaces were placed on zinc selenide crystal to obtain a total of 16 reflections.

3.1.3.3 Contact Angle Measurements

Ethylene glycol of 20 microliters was dropped on horizontal surface of the sample placed on platen state. The contact angles at both sides of the drop were measured after 3 minutes of contact. Average values for three drops were taken as representative of the rubber surface.

3.1.3.4 Thermogravimetric Analysis

Thermogravimetry was applied to investigate the degradation of the samples. Samples were heated from 50°C to 850°C at a rate of 20°C/min under N₂ atmosphere.

3.1.3.5 Scanning Electron Microscopy-EDS

The vulcanized rubber sheet and vulcanized rubber film samples were interacted with electron beam and detected with electron dispersive detector without sample coating.

3.1.4 Aging Condition

Both vulcanized rubber sheet and vulcanized rubber film samples were heated at 70°C for 7 days in hot air oven. Then these samples were characterized by FTIR-ATR, thermogravimetric analyzer and SEM according to 3.1.3.2, 3.1.3.4 and 3.1.3.5 respectively.

3.2 Mechanical Studies

3.2.1 Materials

The same materials as used for surface characterization were also used for mechanical studies.

3.2.2 Instruments

3.2.2.1 *WABASH Compression Press*

Compression press with load 30 and 1.5 tons was used to press two pieces of vulcanized rubber sheet and vulcanized rubber film, having the side exposed to air (outside) in contact to each other, for 10 minutes respectively. No temperature was used.

3.2.2.2 *LLOYD LR5K*

LLOYD with load cell 500 N was used to do T-peel test and tensile test. In this study, T-peel test and tensile test of specimens were tested according to ASTM D 1876-95 and ISO 37 respectively.

3.2.3 Procedure

3.2.3.1 *Preparation of Samples*

a) Vulcanized rubber sheet

Vulcanized rubber sheets for T-peel test and tensile test were prepared by pouring compounded NRL, as given in Table 3.1, of 150 grams and 65 grams into glass plate of 9x12 inches and 6x6 inches for T-peel test and tensile test respectively. They were allowed to set at room temperature for 4 days and were vulcanized in hot air oven at 100°C for 10 minutes.

For T-peel test, the obtained sheet was 9 inches wide, 12 inches long and about 0.035-0.039 inches thick. Two pieces of sheet were bonded only approximately 9 inches of their length. Then they were cut into 2.5 cm wide and backed with cotton cloth. Load for vulcanized rubber sheet was 30 tons for 10 minutes.

For tensile test, the obtained sheet was 6 inches wide, 6 inches long and about 0.035-0.039 inches thick. It was cut into dogbone.

b) Vulcanized rubber film

The preparation of vulcanized rubber films for tensile test and T-peel test was similar to that for surface characterization. For peel test, two-piece samples of 2.5 cm width, backed with cotton cloth on one side surface were compressed with WABASH compression press. Load for vulcanized rubber films was 1.5 tons for 10 minutes.

3.2.3.2 T-peel Test

T-peel test was performed on LLOYD LR5K. It incorporated these features, i.e., load cell 500 N, crosshead speed 254 mm/min and gauge length 80 mm, and 25 mm for vulcanized rubber sheets and vulcanized rubber films respectively. At least three tests shall be tested for each sample.

3.2.3.3 Tensile Test

Tensile test was performed on a LLOYD LR5K. It incorporated these features, i.e., load cell 500 N, crosshead speed 500 mm/min, and gauge length 25 mm. At least three tests were carried out for each sample.

3.2.4 Aging Condition

Both vulcanized rubber sheet and vulcanized rubber film samples were aged at 70°C for 7 days in hot air oven. Then they were subjected to tensile test as in 3.2.3.3. For T-peel test, two pieces of aged samples having the side exposed to air in contact were pressed by compression press at 30 tons for vulcanized rubber sheet and 1.5 tons for vulcanized rubber film for 10 minutes followed by T-peel test according to 3.2.3.2.