CHAPTER III
EXPERIMENTAL

3.1 Instruments and Chemicals

3.1.1 Instruments

(1) Air Oven (Fisher Scientific, Thailand)

(2) Banburymixer, C.W. Brabender Instruments,USA.

(3) Compression moulding,V75H-18-BPX,Wabash MPI, USA.

(4) Energy dispersive X-ray Analysis (EDAX), JEOL JSM-6460LV, USA.

(5) FTIR spectrophotometer (Perkin Elmer Spectrum one), German.

(6) Hardness Shore A, Durometer PN 71500, USA.

(7) Mooney Viscometer, EKT-2001M, Ektron, Taiwan.

(8) Oscillating Disk Rheometer (ODR), EKT-100H, Ektron, Taiwan.

(9) Scanning electron microscope (SEM) JEOL JSM-6460LV, USA.

(10) Two-roll mill, R11-3FF Kodaira Seisakusho, Japan.

(11) Universal Testing Machine, Instron Model 4301, USA.

(12) X-ray Diffraction (XRD Bruker AXS), German.

3.1.2 Chemicals

(1) Carbon black, High-abrasion furnace black (HAF, N330) Commercial grade, Thailand.

(2) Ethanol; CH_3CH_2OH, AR grade, Lab Scan., Ireland.

(3) *Jatropha curcas* oil, fatty acid was obtained from the Office of Agricultural Research and Development Region 3 Khon Kaen, Thailand

(4) Methanol; CH_3OH, AR grade, Lab Scan., Ireland.

(5) *N*-(1,3-dimethylbutyl)-*N*-phenyl-p-Phenylenediamine; 6PPD, Commercial grade, Thane, India.

(6) Natural Rubber, Ribbed Smoked Sheets; RSS#3. Thaihua, Thailand.

(7) N-cyclohexyl -2- benzothiazole sulfenamide; CBS. Commercial grades, Thane, India.

(8) Sodium hydroxide; NaOH, AR grade, Ajax Chemicals, Australia.

(9) Stearic acid, Commercial grade, Imperial, Thailand.

(10) Styrene Butadiene Rubber; SBR-1502. BSTE, Thailand.

(11) Sulfur; S. Commercial grade, Ajex, Australia.

(12) Tetramethylthiuram disulfide; TMTD. Commercial grade, Thane, India.

(13) Toluene; $C_6H_5CH_3$, AR grade, Carlo Erba, Italy.

(14) Zinc oxide; ZnO. Commercial grade, Global, Thailand.

(15) Zinc sulphate; $ZnSO_4{:}7H_2O$. AR grade, Lab scales, Ireland.

3.2 Preparation and characterization of zinc soap

3.2.1 Preparation of zinc soap

Zinc soap was prepared by metathesis technique involving two steps: hydrolysis and precipitation. 9.2 g of the *Jatropha curcas* oil was first by dissolved in 50 mL of boiling ethanol followed by treatment of the mixture with 20 mL of 20% (w/v) sodium hydroxide solution. To this mixture, 100 mL of 30% (w/v) solution of the zinc sulphate was slowly added with continuous stirring. The precipitated soap was washed with 100 mL deionised water several time and then were dried in a vacuum oven.

3.2.2 Determination of zinc soap

The morphology of the zinc soap of *Jatropha curcas* oil prepared by metathesis methods was determined using a scanning electron microscope coupled with a secondary electron imaging (SEI) detector. Samples were coated with gold using the sputtering technique. EDX analyser was used to determine metal content of the soap samples. Data were collected from 10 randomly chosen points and the average weight percent of the elements calculated.

The infrared spectra of *Jatropha curcas* oil and zinc soap were obtained using transmission technique. The range of the spectra was 400 - 4000 cm^{-1} and the KBr disc method was used to obtain pellets for analysis.

X-ray Diffraction was used to investigate the purity and crystalline form of the elements present in the soap sample. The operating conditions were 45 kV and 40 mA, Cu Kα radiation, λ 1.54 Å. The measurements were performed in the range of 2θ values of 5 - 70° with a scan speed of 0.06° s^{-1}.

3.3 Compounds mixing and characterization

3.3.1 Preparation of rubber compounds.

Mixing of rubber compounds was carried out using a two-lobe rotor laboratory Banbury mixer of 1.5l capacity (Stewart Bolling, USA) in two stages (master batch and final batch) and chemical content was based on the NR and SBR content. The information of the materials used in this study was summarized in Table 3.1-3.4, respectively.

Table 3.1 Formulation used to study the effect of zinc soap in rubber compounds.

Material	Amount (phr)
NR, SBR	100
Zinc oxide	5
Stearic acid	2
Carbon black	40
Zinc soap	Variable (0, 2.5, 5, 7.5, 10, 15)
6PPD[a]	1
TMTD[b]	0.5
CBS[c]	1.5
Sulfur	2.5

Table 3.2 Formulation used to study the effect of zinc soap in NR/SBR rubber blends.

Material	Amount (phr)
NR	75, 50, 25
SBR	25, 50, 75
Zinc oxide	5
Stearic acid	2
Carbon black	40
Zinc soap	Variable (0, 2.5, 5, 7.5, 10, 15)
6PPD[a]	1
TMTD[b]	0.5
CBS[c]	1.5
Sulfur	2.5

Table 3.3 Formulation used to study the effect of *jatropha curcas* oil and paraffinic oil in rubber compounds.

Material	Amount (phr)
NR, SBR	100
Zinc oxide	5
Stearic acid	2
Carbon black	40
Jatropha curcas oil	Variable (0, 1, 3, 5, 7, 9)
paraffinic oil	Variable (0, 1, 3, 5, 7, 9)
6PPD[a]	1
TMTD[b]	0.5
CBS[c]	1.5
Sulfur	2.5

Table 3.4 Formulation used to study the effect of *jatropha curcas* oil and paraffinic oil in NR/SBR blends.

Material	Amount (phr)
SBR	75, 50, 25
NR	25, 50, 75
Zinc oxide	5
Stearic acid	2
Carbon black	40
Jatropha curcas oil	Variable (0, 1, 3, 5, 7, 9)
paraffinic oil	Variable (0, 1, 3, 5, 7, 9)
6PPD[a]	1
TMTD[b]	0.5
CBS[c]	1.5
Sulfur	2.5

[a] = *N*-(1,3-dimethylbutyl)-*N*-phenyl-p-phenylenediamine.
[b] = Tetramethylthiuram disulfide.
[c] = *N*-cyclohexyl -2- benzothiazole sulfonamide

Master batch was done by setting the temperature at 90 °C and rotor speed at 60 rpm. First, the rubber was masticated for 3 min. Then, zinc oxide, stearic acid, carbon black (N330), process oil (paraffinic oil and/or *Jatropha curcas* oil) and the anti-degradants (6PPD) were added. After the power integrator (PI) indicated achievement of 0.32 kWh, the master batch was dumped. The dump temperature of the master batches was found to be within 140 - 150 °C. The master batches were sheeted out in a laboratory two-roll mill. Further mixing of the master batches were carried out after a maturing period of 8 h.

For final batch mixing, the temperature was kept at 60 °C and rotor speed at 30 rpm. The earlier prepared master batch was mixed with accelerator, and sulfur. The batch was dumped at a PI reading of 0.12 kWh. The dump temperature of the batches was found to be within 95 - 105 °C. The final batches were also sheeted out on a laboratory two-roll mill.

3.3.2 Cure measurements and vulcanization

Cure parameters were determined using an oscillating disk rheometer (ODR) according with ASTM D2048, at a temperature of 150 °C. From the rheographs, the scorch time, t_{s2}, optimum cure time, t_{c90}, and minimum and maximum torque, S_{max} and S_{min}, respectively, and delta torque, ΔS, were obtained. Test sheets were then moulded using a hydraulic press with electrically heated platens to their full cure at 150 °C and for the optimum cure times as determined from the ODR.

Mooney viscosity, ML (1+4) at 100 °C, from Alpha Technologies, USA in according with ASTM D1646. For a stress relaxation test, 1 min preheat time, 4 min test time, 2 min decay time and 1 s hold off time was used and percentage drop in Mooney viscosity was reported.

3.3.3 Testing of rubber vulcanizates

3.3.3.1 Mechanical characterization (Tensile and Tear strength)

Vulcanized sheet were prepared by compression molding, and the dumb-bell shaped specimens were punched out from a molded sheet by using ASTM Die C. The tests were done by means of a universal tensile testing machine under ambient condition (25 ± 2 °C), following the ASTM D412 and ASTM D624. The moduli at 100%, tensile strength, tear strength and elongation at break (%) was measured at room temperature. The initial length of the specimens was 25 mm and the speed of the jaw separation was 500 mm/minutes. The values of tensile strength, modulus, percentage elongation at break and tear strength are recorded directly from the digital display at the end of each test.

3.3.3.2 Hardness test

The hardness test of rubber is the relative resistance of a surface to indentation by an indicator of a specified dimension under a specified load.

The hardness of the vulcanisate was determined by adopting the standard dead load method described in ASTM D2240. The standard dead load method of measurement covers rubbers in the range of 30-85 International Rubber Hardness Degrees (IRHD).

3.3.3.3 Equilibrium swelling test

The vulcanizate having a thickness of 1.2 mm was cut into rectangular shape with weight about 0.7 g. Free organic materials were first extracted from the sample for 12 h using acetone as a solvent according to ASTM D471. Then, the sample was dried in a vacuum oven at room temperature. The sample was immersed in 100 mL toluene for 7 days. The swollen sample was removed from the toluene and the excess toluene was blotted with a paper towel. Then, the swollen sample was placed in a clean weighing bottle and weighed accurately. The swelling ratio (Q) was determined using equation (3.1). The value of swelling ratio of each vulcanizate was the average of three specimens:

$$Q = \frac{W_S - W_U}{W_U} \quad \ldots (3.1)$$

where W_S is the weight of swollen sample and W_U is the weight of extracted and dried sample before swelling.

3.3.3.4 Thermal ageing resistance

The thermal ageing properties were carried out by placing uncut tensile specimens in air circulating oven at 100 °C for 22 h. Then, following the ASTM D573, the specimens were cooled at room temperature for at least 18 h before testing. The tensile properties (100% modulus, tensile strength and elongation at break) of aged specimens were determined in the same manner as the unaged specimens. Relative tensile properties were calculated using equation (3.2) and they are employed to represent the thermal ageing resistance of various rubber vulcanizates.

$$\text{Relative tensile properties} = \frac{P_{aged}}{P_{unaged}} \quad \ldots (3.2)$$

where P_{unaged} and P_{aged} are tensile properties of unaged and aged specimens, respectively.

3.3.3.4 Scanning electron microscopy

Cryogenic fracture surfaces were prepared for observing filler dispersion. The morphology of tensile fractured surface was examined through observation was carried out using a Scanning electron microscope (SEM). The samples were coated with a thin gold layer under vacuum condition.