

# CHAPTER III

## EXPERIMENTAL

### 3.1 Chemicals

Cashew nut shell liquid (CNSL) was a gift from the 25 Industrial Products Co., Ltd. Natural rubber (grade STR20) was purchased from Thai Hua Co., Ltd. The chemicals for vulcanization, such as N-cyclohexylbenzothiazole-2-sulfenamide (CBS), naphthenic oil, stearic acid and carbon black were obtained from the Rubber Research Institute. Formaldehyde was purchased from Lab Scan. Resorcinol was purchased from Sigma. Elemental sulfur, and zinc oxide were purchased from Fisher. Diethylenetriamine and petroleum ether were purchased from Fluka. Calcium hydroxide and deuterated chloroform were purchased from Merck. Ethyl acetate, hexane, methanol, toluene and propylene glycol were commercial grade.

### 3.2 Instruments and Apparatus

Infrared (IR) spectra were recorded using a Nicolet Impact 410 spectrometer.  $^1\text{H}$  NMR (200 MHz) and  $^{13}\text{C}$  NMR (50 MHz) were recorded on a Bruker ACF-200 spectrometer and the solvent used was  $\text{CDCl}_3$ . Sulfur content was determined using a LECO SC-132 sulfur analyzer. Non-productive compounds were mixed by a Kneader Machinery internal mixer. Vulcanization ingredients were added to the compounds on a Lab Tech Engineering two-roll mill. Cure characteristics at 150 °C for 30 min and arc 0.5° were determined using a Monsanto rheometer MDR2000. Sheets and test specimens were vulcanized by Lab Tech Engineering TP-400 compression molding. Tensile measurements were carried out using a Instron Calibration Laboratory 1445 tensile tester. Hardness was determined using a Zwick hardness testing machine. Rebound resilience was determined using a Zwick rebound tester.

### 3.3 Experimental Procedures

#### 3.3.1 Preparation of CPS

##### 3.3.1.1 Preparation of Cardanol from CNSL [26-29]

CNSL was decarboxylated to give cardanol in the presence of calcium hydroxide as a catalyst. Calcium hydroxide (4 g) and hexane (200 ml) as solvent were charged into 1000 ml 2-neck round bottom flask, equipped with condenser and thermometer 200 g of natural CNSL. The mixture was refluxed at temperature of 120 °C with stirring for 3 hours. The reaction was stopped and the mixture was cooled down. Calcium hydroxide was filtrated. After evaporation of the solvent, decarboxylated CNSL was obtained. IR and NMR spectra of the resulting product shown in Figures A.2-A.10 indicate that the carboxylic acid group was removed completely.

Decarboxylated CNSL (60 g), formaldehyde (19.4 g) and diethylenetriamine (2.57 g) were mixed in methanol (200 ml). An exothermic reaction took place after mixing the reactants. After 30 minutes, two phases were formed. The upper phase was a slightly red solution. The lower phase was solidified and dark in color. The upper phase was decanted and treated with water (40 ml) followed by extraction with petroleum ether. The petroleum ether extract was distilled to recover hydrocarbon solvent. A reddish residue of cardanol (45 g, 80% w/w) was obtained.

##### 3.3.1.2 Synthesis of CPS

Cardanol (70 g) and excess elemental sulfur (40 g) were added to a 250 ml beaker. Toluene or propylene glycol were used as a solvent for a reaction temperature of 110 or 185 °C, respectively, according to the boiling point of each solvent. At other temperatures, no solvent was used. The mixture was heated to a desired temperature in a range of 110-185 °C and stirred for 2 hours. The reaction mixture became viscous resin. After stopping the reaction, the viscous resin was diluted with ethyl acetate with stirring for a half an hour. The diluted mixture was stood for at least 3 hours to let non-reacted elemental sulfur precipitate. Then the mixture was filtrated and centrifuged to get rid of excess elemental sulfur. The diluted mixture was evaporated. Dry weight of the dilution was calculated. Sulfur content in CPS was determined

using a sulfur analyzer. In order to determine suitable reaction time to give highest sulfur content in CPS, the reaction times were varied 3, 4 and 5 hrs. To calculate weight of CPS [25], approximately 1.5 g of a sample was poured into a weighing bottle and the bottle was placed in an oven maintained at 135 °C for 1 hr. Then, it was taken out of the oven and was allowed to cool down in a desiccator. The mass was weighed and the content of nonvolatile resin was calculated to an integral number by the equation below.

$$N = D/S \times 100$$

Where  $N$  is the content of nonvolatile matter (%),  $D$  the mass of sample after drying (g), and  $S$  the mass of sample (g).

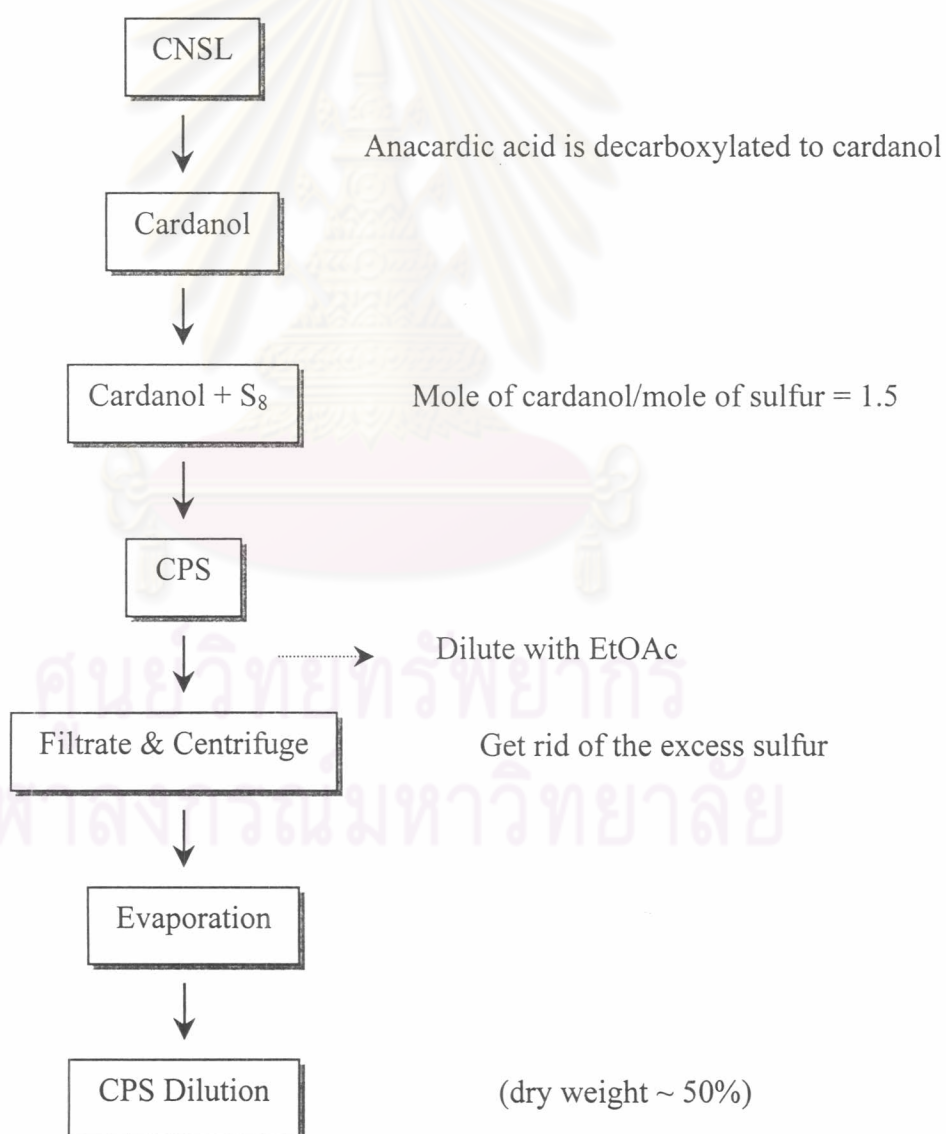


Figure 3.1 Experiment scheme of CPS preparation.

### 3.3.1.3 Characterization of CPS

The product, cardanol polysulfide (CPS), is a dark brown resin. The characterization of cardanol and CPS was carried out by FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Deuterated chloroform ( $\text{CDCl}_3$ ) was used as a solvent for recording the NMR spectra. All spectra are presented in Appendix C. Sulfur content in CPS was determined by a sulfur analyzer occurring to ASTM D 1552-95 [30] using oxygen gas pressure of 400 psi, instrument gas pressure of 400 psi, and furnace temperature 1350 °C.

### 3.3.2 Preparation of Rubber Compounds

#### 3.3.2.1 Preparation of Non-productive Compounds

Non-productive compound, is rubber containing additives in the absence of vulcanization ingredients. Rubber additives used in this research are resorcinol, naphthenic oil, carbon black, stearic acid and zinc oxide. The amount of each additive in rubber, was used as same as that in the commercial non-productive compound, as shown in Table 3.1. The unit of the amount of an additive in grams of the additive per 100 grams of rubber or parts of the additive per 100 parts of rubber (phr).

In this research, the amounts of conventional rubber additives used in typical amounts. The non-productive compound were mixed by a banbury mixer using the following conditions; rotor speed of 43 rpm, mixing temperature of 110 °C, and mixing time of 6 min.

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**Table 3.1** Ingredients in non-productive compound

Ingredients	Quantity of mix (phr)
Natural rubber (STR20)	100
Resorcinol	1.1
Naphthenic oil	3.5
Carbon black	24
Stearic acid	2
ZnO	3
	133.6

### 3.3.2.2 Preparation of Productive Compounds

Vulcanization ingredients were added to non-productive compound and mixed by a two-roll mill using the following conditions, friction ratio of 1:1.2, temperature of 70 °C, mastication time for non-productive compound of 2 min, and mixing time of 8 min.

CPS was used to partially replace sulfur by controlling the total sulfur at 2 phr. Normally, the amount of a sulfur donor, which was used to replace sulfur, is estimated from active sulfur. The CPS has 28 %wt of sulfur content but the amount of active sulfur cannot be determined. Thus 28 %wt of sulfur in CPS was used to calculate the required level of sulfur. The amounts of CPS in product in compounds were varied at 1.79, 3.57, 5.36 and 7.14 phr.

Table 3.2 shows vulcanization ingredients of rubber compounds used in this work. For studying the effect of CPS when using combination between sulfur and sulfur donor for vulcanization, condition B as shown in Table 3.2 was chosen to represent this system. The amounts of CPS were varied from 0 to 6 phr while sulfur content was kept constant at 1.5 phr (series B). For studying the effect of CPS when only a sulfur donor for vulcanization, condition E was chosen to represent this system. The amounts of CPS were varied from 0 to 15 phr without any sulfur in productive compound (series E).

**Table 3.2** Vulcanization ingredients of rubber compounds

Compounds	Vulcanization ingredients (phr)		
	CBS	sulfur	CPS
A	1.5	2.0	-
B	1.5	1.5	-
B1	1.5	1.5	1.79
B2	1.5	1.5	4.0
B3	1.5	1.5	6.0
C	1.5	1.0	-
C1	1.5	1.0	3.57
D	1.5	0.5	-
D1	1.5	0.5	5.36
E	1.5	-	7.14
E1	1.5	-	9.0
E2	1.5	-	12.0
E3	1.5	-	15.0

### 3.4 Determining Vulcanization Characteristics of the Rubber Compounds

Vulcanization characteristics and vulcanization curves were determined using a Monsanto rheometer MDR2000 according to ASTM D 2084-95 [31]. The conditions of testing used are the following, temperature 150 °C, testing time 30 min, and arc 0.5°.

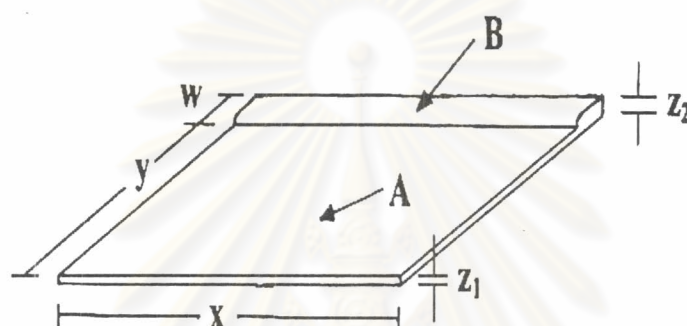
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### 3.5 Preparation of Vulcanized Sheets

#### 3.5.1 Preparation of Sheets

##### 3.5.1.1 Preparation of Sheets for Tensile Tester and Hardness Tester

For preparation of sheets, the unvulcanized rubbers were cut with specific dimension as shown in Figure 3.2. Then the unvulcanized rubbers were dried and cut smoothly to avoid flashing-over resulting from point discharges, or burning inside the unvulcanized rubbers.



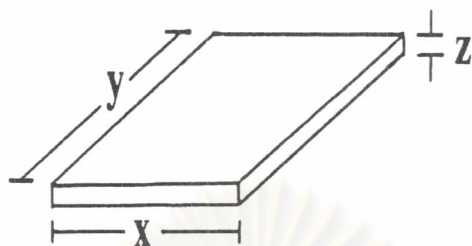
w	=	1 cm
x	=	10 cm
y	=	8 cm
z <sub>1</sub>	=	2 mm
z <sub>2</sub>	=	4 mm

**Figure 3.2** Vulcanized sheet for tensile and hardness tests.

As seen in Figure 3.2, the vulcanized sheet is subdivided into 2 parts, A and B. Part A (2 mm in thickness) is used for a tensile test and part B (top cap, 4 mm thickness) for a hardness test.

### 3.5.1.2 Preparation of Sheets for Rebound Resilience Test

For the preparation of sheets for rebound resilience, the green rubbers were cut with specific dimension as shown in Figure 3.3.



x	=	8 cm
y	=	10 cm
z	=	6 mm

**Figure 3.3** Vulcanized sheet for rebound resilience test.

### 3.5.2 Vulcanization Procedures

The vulcanized rubber sheets were prepared by the compression molding. The mold was preheated to avoid the long curing times at relatively low temperatures, which are necessitated by the poor thermal conductivity of rubber. The mold was brought to curing temperature (150 °C) in the closed press and held at this temperature for at least 20 min before the green rubber pieces were inserted. After preheating the mold, green rubbers were inserted into the mold and the press was closed. The mold was held under a pressure of 120 kg cm<sup>-2</sup> (1700 psi) on the cavity at 150 °C to a required vulcanization time for each pieces. The vulcanized sheets were conditioned at 23 ± 2 °C for at least 16 hours before preheating and testing.

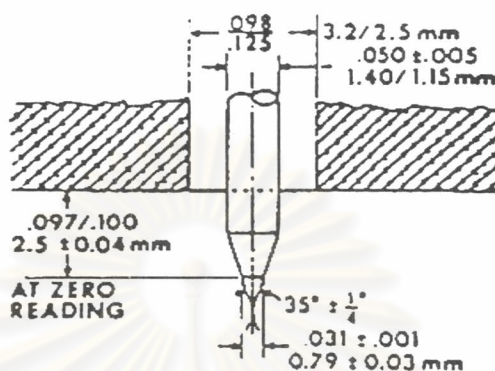
### 3.6 Mechanical Testing

The mechanical properties of the rubber compounds were determined using ASTM and ISO test methods as described in following sections.



### 3.6.1 Durometer Hardness

Hardness was determined according to ASTM D 2240-95 [32]. The top cap of vulcanized sheets was used to observe hardness. The shape of the indenter is shown in Figure 3.4.



**Figure 3.4** Indentor for type A durometer. Reproduced from [32].

The test specimens for this research were 4 mm in thickness. The minimum requirement for the thickness of the specimen is dependent on the extent of penetration of indenter into the specimen. For materials having hardness above 50, type A durometer was used. The thickness of the specimen was at least 3 mm.

The surface of the specimen was flat and parallel over a sufficient area to permit the presser foot to contact the specimen. Placed the specimen on a hard, horizontal surface. Hold the durometer in a vertical position with the point of the indenter at least 12 mm from any edge of the specimen. Apply the presser foot to the specimen as rapidly as possible, without shock, keeping the foot parallel to the surface of the specimen. The conditions testing used are the following, temperature of 25 °C, and relative humidity of 60 %.

For all of the properties measured, at least 5 samples were tested to obtain the median of the values.

### 3.6.2 Tensile Tester

Tensile measurements were determined according to ISO 37:1994 [33]. The tensile tester is basically a simple device. The tensile strength, the elongation and the stress at a given elongation (modulus) were determined. Figure 3.5 shows schematic of the test specimen (type 1).

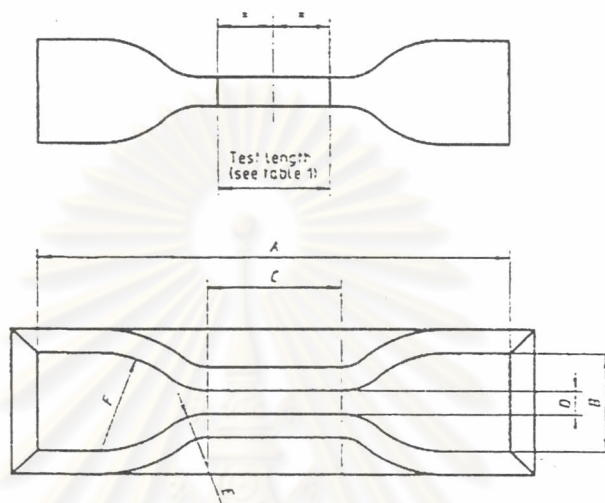


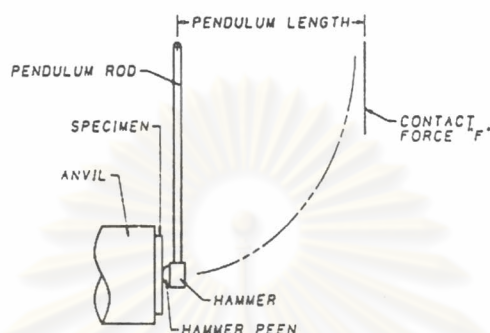
Figure 3.5 Schematic of tensile test specimen (type 1). Reproduced from [33].

<i>Dimension</i>	<i>Type 1 (mm)</i>
A	Overall length (minimum) 115
B	Width of ends $25.0 \pm 1.0$
C	Length of narrow portion $33.0 \pm 2.0$
D	Width of narrow portion $6.0 \pm 0.4$
E	Transition radius outside $14.0 \pm 1.0$
F	Transition radius inside $25.0 \pm 2.0$

The conditions of tensile testing used are the following temperature of 25 °C, relative humidity of 60 %, speed of testing 500 mm min<sup>-1</sup>, and test length 6 cm.

### 3.6.3 Rebound Resilience

Rebound resilience was measured at room temperature according to ASTM D 1054-91 [34]. Deflection is determined by measuring the depth of penetration of the rebound ball into the rubber block under testing. Figure 3.6 shows the testing device for rebound resilience.



**Figure 3.6** Schematic representation of a testing device. Reproduced from [34].

Specimen with a thickness of  $12.5 \pm 0.5$  mm and a diameter of  $41 \pm 12$  mm was used. Give particular attention to a smooth surface and plane parallelism. A stacking of no more than three cylindrical discs of finished parts is possible, requiring no cementing or lubrication, or both, between specimens. This stacking, however, is permissible only in the case of plane parallel discs of uniform thickness over the entire area. The specimen should contain no fabric or any other reinforcing materials. At least two samples were tested. The test was performed at a temperature of  $23 \pm 2$  °C.

After the specimen has been placed on the anvil in the holder and the thermal conditioning completed, the pendulum is allowed to fall six times from the horizontal position onto the same place on the specimen and caught each time before it strikes the sample once more. The first of these three blows constitute the mechanical conditioning of the specimen. The rebound resilience is read on the fourth, fifth, and sixth strokes. The median of the three readings is recorded.

### **3.7 Accelerated Aging**

Aging of test specimens were determined according to ASTM D 573-88 and ISO 188-1982, respectively [35, 36]. Accelerated aging was tested to describe a procedure to determine the influence of elevated temperature on physical properties of vulcanized rubber. They are designed to ultimate the relative resistance of yellow rubbers to deterioration with the passage of time.

Specimens of vulcanized rubber are exposed to the deteriorating influence of air at specified elevated temperatures for known periods of time, after which their physical properties are determined. These are compared with the properties determined on the original specimens.

#### **3.7.1 Preparation of Test Pieces**

The vulcanized sheets were cut into dumbbell-shaped specimens. The test pieces shall be measured before heating but, whenever possible, marking should be carried out after heating as some marking inks can effect the aging of the rubber.

#### **3.7.2 Aging Procedure**

The specimens for aging were placed in the air oven after they had been preheated to  $100\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  for 1 and 3 days. The test pieces shall be stationary, free from strain, freely exposed to air on all sides and not exposed to light. Start the aging interval at the time the specimens are placed in the oven and continue for a measured time interval. At the termination of the aging interval, the specimens from the oven were removed and the cooled down to room temperature on a flat surface, and allow them to rest not less than 16 hrs nor more than 96 hrs before determination of the physical properties. After aging tests, their mechanical properties were measured and compared with those of original specimens. Calculations of % reversion of properties changing are shown in Appendix D.