

## CHAPTER III

### EXPERIMENT

#### 3.1 Materials

The Rubber samples shown below were from the rubber industries in Thailand

1. Cup lumps; Tong Thai Technical Rubber Co.,LTD ( Chantaburi,Thailand)
2. STR5L, STR5, STR10, STR20; Teck Bee Hang Co.,LTD ( Rayong,Thailand.)
3. DPNR; Rayong Bangkok Rubber Co.,LTD ( Rayong, Thailand)
4. Smoke1, Smoke2, Smoke3, Smoke4, Smoke5; Mitthai Nakorn Co.,LTD  
(Nakorn srithumaraj, Thailand)

#### 3.2 Chemicals

1. Acetic acid for synthesis : Merck
2. Propionic acid for synthesis : Merck
3. Butyric acid for synthesis : Merck
4. Isobutyric acid for synthesis : Merck
5. Pentanoic acid for synthesis : Merck
6. Isovaleric acid for synthesis : Merck
7. Benzalkonium chloride, AR grade : Fluka
8. Zeolite 13X, commercial grade : Estern Cegate
9. Activated carbon powder, AR grade : Fluka

10. Sodium dodecyl sulphate, AR grade : APS Ajax Finechem
11. Chitosan Mw. 700,000, commercial grade : SeaFresh company
12. Cyclodextrin , AR grade : Aldrich
13. Zinc oxide (ZnO), commercial grade : DYNA Trade Co., Ltd.
14. Tetramethyl thiuram disulphide(TMTD) , commercial grade : Sunny World (1989) Co., Ltd.
15. Steric acid , commercial grade : Imperial (Thai) Co., Ltd.
16. Sulfur, commercial grade : DYNA Trade Co., Ltd.
17. Methyl Valerate, AR grade : Merck

### 3.3 Instruments and Apparatus

1. Vial 100 ml. for Headspace technique
2. Gas Chromatography : Hewlett Packard (HP)  
Model 6890 series, Australia
3. Gas Chromatography / Mass Spectrometry: Finigan MAT GCQ™, U.S.A.
4. Rheometer : Monsanto MDR2000
5. Tensile testing machine : Instron Corporation Series IX  
Automated Materials Testing  
System6.05 Model 1011, U.S.A.
6. Hardness testing machine : Durometer Hardness system  
(shore A) Model 716, U.S.A.
7. Specific gravity testing machine : Denver Instrument Company A-  
160 Densitech II, U.S.A.
8. Two-roll mill : Labtech Engineering, Thailand
9. Gas tight syringe : SGE Amani Co., Ltd, Australia

10. Column for GC : HP-20M capillary column  
25.0m x 0.2mm id. coated with  
0.2  $\mu$ m film of polyethylene  
glycol, Australia
11. Column for GC/MS : DB-5 capillary column 30m x  
0.25mm id.; coated with 0.25 $\mu$ m  
film of (5% phenyl)methyl  
polysiloxane and ZBWAX  
capillary column 30 m.x 0.32  
mm id.; coated with 0.25  $\mu$ m  
film of polyethylene glycol

### 3.4 Characterization of Mal-odor from Natural Rubber

#### 3.4.1 Headspace Technique:

The volatile components, which cause the mal-odor from natural rubber, were collected from natural rubber samples that were trapped in 100 ml vial(Figure3.1). 10 to 15 g of samples were used. Before GC characterization, all sample were heated up to 60°C for 2 hour in the oven.

#### 3.4.2 Gas Chromatography: Condition for GC characterization

The 0.5 ml volatile components that were collected from the rubber samples via a syringe was injected into a Hewlett Packard (HP) Model 6890 series gas chromatography equipped with a Flame Ionization Detector (FID) and HP-20M (Carbowax 20M) capillary column. The column temperature was programmed from

35°C (2mins) to 150°C at the rate of 10°C/min for all runs. The injector and detector temperature were 200°C. Helium and nitrogen were used as the carrier gas and make up gas, respectively at flow rate of 2.00 mL/min.

### **3.4.3 Gas Chromatography / Mass Spectrometry: Condition for GC/MS**

The volatile components, which were collected from rubber samples, were analyzed using an Finigan MAT GCQ<sup>TM</sup> Gas chromatography/Mass Spectrometry. The column was DB-5 MS capillary column. The column temperature was programmed from 40°C (2mins) to 200°C(5 mins) at the rate of 10°C/min for all runs. The transfer line temperature was 275°C. Helium was used as the carrier gas at the velocity of 30cm/sec. MS conditions were as follows: Mass range in this condition was 40-180 amu. Electron multiplier voltage was 1300 V. The ion source temperature was 200°C. Another column that was used was ZB-Wax capillary column: column temperature was programmed from 35°C (6mins) to 180°C (5 mins) at the rate of 10° C/min in all runs. The injector temperature was 200°C. The velocity of helium carrier gas was 50 cm/sec. The transfer line temperature was 240°C. For mass spectrometer, the conditions were set as followed: electron multiplier voltage was 1550 V, the ion source temperature was 200°C and mass rang was 40-180 amu.

### **3.5 Reduction of Mal-odor**

STR5 and Smoke3 were selected as representative samples to study. To study the intensity of mal-odor as a function of time, each sample was injected for once a week during 5 week period.

1  $\mu\text{L}$  methyl valerate was added into rubber samples, STR20 and Smoke5 as an internal standard. The samples were heated up to  $60^{\circ}\text{C}$  for 2 hours and were injected into GC to compare the quantity of volatile and standard.

Odor-reducing substances used were sodium dodecyl sulphate (SDS), benzalkonium chloride, chitosan, carbon black, zeolite13X and cyclodextrin. These substances were mixed with rubber samples: STR20 and Smoke5 using two-roll mill in the ratio of 1.5 or 5.0 phr. The volatile components, which were collected from rubber samples mixed with odor-reducing substances, were analyzed by GC using an optimized condition.

In order to determine odor reduction efficiency as a function of time, 5 samples were prepared for each odor-reducing substance and each sample was analyzed after being kept for a desired period of time (0, 1, 2, 3 and 4 weeks). Five controlled samples (without odor-reducing substances) were also analyzed for comparison.

### **3.6 Mechanical Testing**

The vulcanized rubber sheets were prepared by compression molding before mechanical testing. The formulation of compound rubber was shown in Table3.1.

**Table 3.1** Compounding rubber formulas

<b>Ingredient</b>	<b>Quantity of mix (phr.)</b>
Natural rubber sample	100
Sulfur	3.5
Zinc oxide	6.0
Steric acid	0.5
TMTD	0.5
<b>Odor-reducing substances:</b>	
Carbon black	1.5, 5.0
Chitosan	1.5, 5.0
Zeolite 13X	1.5, 5.0
SDS	1.5, 3.0

The temperature and time used for curing rubber compounds were 150°C and 4-5 mins, respectively. Mechanical properties of the vulcanized rubber were investigated by following the ISO and the ASTM test methods as follows:

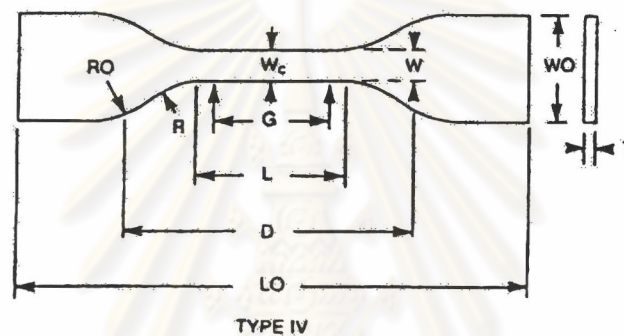
### **3.6.1 Tensile Stress- Strain Properties (ASTM D412 DIE C)**

The properties of vulcanized rubber, which were determined by the method are the tensile strength, the elongation at break and the stress at a given elongation (modulus). The vulcanized rubber was stamped with a compress air sample cutter

(Model SDAP-100-N) using a dumbbell die “C”. The stress-strain curve of samples was measured at the following condition.

The tensile testing condition:

Temperature	25 °C
Humidity	60 %
Sample Rate	10.00 pts/sec
Crosshead speed	500 mm/min



W : 6 mm	WO : 19 mm	G : 25 mm	R : 14 mm	T : 4 mm or under
L : 33 mm	LO : 115 mm	D : 65 mm	RO : 25 mm	

**Figure 3.1** Schematic diagram of tensile test specimen (Type IV)

### 3.6.2 Hardness Properties (ASTM D 2240)

The Durometer Hardness System Model 716 was used for measuring the hardness of vulcanized rubber sheets. The specimen was of at least 6 mm. in thickness unless it was known that the results were equivalent to the 6 mm. values. The specimen was composed of plied pieces to the necessary thickness. The surfaces of the specimen were flat and parallel over sufficient area to permit the pressure foot to contact the specimen. The lateral dimensions of the specimen were measured at least 12 mm from any edge. The condition in this testing are shown as follows:

Temperature	25° C
Relative humidity	50 %
Number of pieces plied	3 pieces

### **3.6.3 Specific Gravity properties (ISO 2781)**

The vulcanized samples were cut into square pieces (3x3 cm). The Densitech II Instrument Model A-160 was used to measure specific gravity of samples. In this study, water was used instead of oil.

### **3.7 Olfactometry Testing**

20 people (20-35 years old) were subjected to olfactometry testing. Rubber samples (STR20 and Smoke5) with odor-reducing substances were prepared by the previously described method. Pure rubber samples (STR20 and Smoke5) were put in five 250 mL bottles (1, 5, 10, 15 and 20g) as references for odor testing. Each bottle therefore represented one odor intensity. 10 g of rubbers mixed with odor-reducing substances were put in 250 mL bottles. The odor of rubber mixed with odor-reducing substances was compared with the references. Each test person then recorded the number of reference bottles that gave lower odor intensity as the mixed samples.