

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Natural rubber latex : Thai Rubber Latex Corporation
(Thailand) Co.Ltd
2. Tergitol NP10 : Union Carbide
3. Glacial acetic acid : Merck
4. Sulfuric acid : Merck
5. Hydrogen peroxide 50% : Merck
6. Sodium hydrogencarbonate : Merck
7. Diethylenetriamine : Fluka
8. Ethylenediamine : Merck
9. Hexane : Merck
10. Methylene chloride : Merck
11. Chloroform : Merck
12. Ethanol : Merck
13. Acetone : Merck
14. Toluene : Merck
15. Sodium acetate : Merck

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3.2 Instruments and Apparatus

1. Mechanical stirrer : Janke & Kunkel, RE 16
2. Magnetic stirrer : Model 34532, Snijderes, CU
3. Compression molding : Lab Tech Engineering, RRI
4. Tensile tester : Instron Calibration laboratory, RRI
5. Two-roll mill : Lab Tech Engineering, RRI
6. Rheometer : Lab Tech Engineering, RRI
7. Infrared Spectrophotometer : Perkin Elmer, Nicolet (Impact 410)
8. Nuclear Magnetic Resonance Spectrometer : Bruker, ACF 200 MHz
9. Gas Chromatography-Mass spectrometry : Fisons GC8000/MS Trio 2000 with a DB-wax fused silica column (30 m x 0.22 mm)

3.3 Experimental Procedure

3.3.1 Preparation of peracetic acid [10]

In 250 ml conical flask, a desired amount of glacial acetic acid (100 ml) and sulfuric acid (2 ml) was added. Then 50% H₂O₂ (55 ml) were added dropwise and stirred at 10°C for 1 hour.

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3.3.2 Preparation of epoxidised natural rubber (ENR) [10]

3.3.2.1 Preparation of 25%ENR.

In one litre conical flask, natural rubber latex (60% dry rubber content) (250 ml) and distilled water (200 ml) were added. The latex was then stabilized with tergitol NP 10 (3% by weight of natural rubber latex, 5.4 g) and stirred for 9 hours at room temperature. The stabilized natural rubber latex was poured into one litre glass reactor and equipped with a mechanical stirrer. Then peracetic acid (18 ml) was added dropwise and stirred at 20-25 °C for 2.5 hours.

3.3.2.2 Preparation of 50%ENR.

In one litre conical flask, natural rubber latex (60% dry rubber content) (250 ml) and distilled water (200 ml) were added. The latex was then stabilized with tergitol NP 10 (3% by weight of natural rubber latex, 5.4 g) and stirred for 9 hours at room temperature. The stabilized natural rubber latex was poured into one litre glass reactor and equipped with a mechanical stirrer. Then peracetic acid (25 ml) was added dropwise and stirred at 20-25 °C for 2.5 hours.

3.3.3 Natural rubber (NR) and ENR characterization

During the epoxidation, latex samples were taken at 30, 60, 90, 120 min and isolated by pouring into 50% (v/v) aq ethanol. The coagulum was washed to remove free acid and other residues and then pressed into a thin sheet (thickness 1-2 mm). The thin sheet was soaked in 1% Na₂CO₃ solution for 24 hours at room temperature, washed with distilled water until pH was 7 and then dried at 80°C to constant weight before characterization.

3.4 Characterization

3.4.1 IR-spectroscopy [10]

The liquid natural rubber (LNR) and epoxidised natural rubber (ENR) were characterized as films by Perkin Elmer system 2000 FTIR spectrophotometer.

3.4.2 ¹H-NMR spectroscopy [10]

Samples for ¹H-NMR analysis were prepared by dissolving the material in deuterated chloroform with tetramethylsilane as internal reference. The epoxidation level of ELNR was calculated using the equation shown below :

$$\text{mol \% epoxidation} = \frac{100 * [A_{2.70}]}{A_{5.14} + A_{2.70}}$$

A_{2.70} : The integrated area of the proton adjacent to epoxide ring at 2.70 ppm

A_{5.14} : The integrated area of the olefinic proton at 5.14 ppm

3.5 Preparation of membrane

3.5.1 Crosslinked epoxidised natural rubber using *p*-phenylenediamine [30].

The *p*-phenylenediamine was ground into a finer powder before use. The rubber and compounding ingredients were mixed on an open-2-roll mill, and then cured by compression molding between two stainless sheets of thickness 0.1 mm at 120°C 24 N/cm², for 30 min. The formulations for preparing crosslinked ENR using *p*-phenylenediamine are shown in Table 3.1.

Table 3.1 Formulation of crosslinked ENR using *p*-phenylenediamine

Chemical	Formulation									
	1	2	3	4	5	6	7	8	9	10
1. ENR 25% (phr)	99	98	97	96	95	-	-	-	-	-
2. ENR 50% (phr)	-	-	-	-	-	99	98	97	96	95
3. <i>p</i> -phenylenediamine powder (phr)	1	2	3	4	5	1	2	3	4	5

3.5.2 Crosslinked epoxidised natural rubber using ethylenediamine and diethylenetriamine [31,32].

The latex was neutralized with sodium hydrogen carbonate. The amine was added dropwise to epoxidised natural rubber, and the mixture was maintained at room temperature (30°C) for 24 hours. Then the mixture was poured into petri dish and dried at room temperature for 24 hours and at 80 °C for 5 hours. The rubber was pressed by compression molding under the pressure 120 kg/cm².

The films were prepared and subjected to various investigations as following:

1. Effect of amines concentration

The membranes were prepared by varying amine and concentration of 0, 1, 2, 3, 4, and 5 phr.

2. Effect of curing temperature

These effects were investigated by varying the curing temperature of 100, 105, 110, 115, and 120 °C to obtain the appropriate temperature of compression.

3.5.3 Preparation of amine crosslinked ENR membranes.

Crosslinking Procedure

The amine mixed ENR were cured by hot press process. The mold was brought to curing temperature in the closed press and held at this temperature for at least 15 min before the uncured pieces were inserted. The press was opened, then the uncured pieces were inserted into the mold. The press was closed in the minimum

time possible. Precautions were then taken to prevent excessive cooling by contact with cool metal surfaces or by exposure to air drafts. The mold was held under a pressure of 120 kg/cm² (1700 psi) on the cavity areas during curing. After the required vulcanization time, the press was opened. The cured sheets were removed from the mold and cooled on metal surface by using water cooling for 10 to 15 min. The cured sheets were conditioned at 23 ± 2 °C for at least 16 hours and for no greater than 96 hours before preparing and testing.

Preparation of sheets

The amine mixed ENR were placed on flat, dry, clean metal surface. Then the pieces were cut (4.5±1.5 mm) shorter in width and length than the corresponding dimensions of the mold cavity.

3.6 Membrane characterization

3.6.1 The gel content

The gel content was measured in toluene using a standard method (ASTM D 415)

3.6.2 Tensile property (ASTM D 412-87)

The tensile strength, tensile modulus, and elongation at break of rubber compound were measured in a universal testing (Instron Corporation Series IX) according to ASTM D 412-87. The dimension of the tensile specimen in this experiment is type C as shown in Figure 3.1 and Table 3.2.

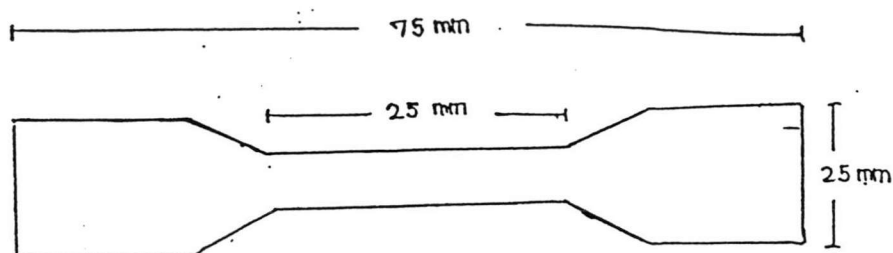


Figure 3.1 Tensile strength specimen type C

Table 3.2 The dimension of tensile specimen

Dimension	Type C (mm.)
A. Overall length (minimum)	75
B. Width	12.5 ±1.0
C. Length of narrow portion	25.0 ±1.0
D. Width of narrow portion	4.0 ±0.1
E. Transition radius outside	8.0 ±0.5
F. Transition radius inside	12.5 ±1.0

The tensile testing condition

Temperature	25°C
Humidity	60%
Test length of dumb-bells	20 ± 0.5 mm.
Cross head speed	500 mm/min
Full scale load range	5.0 KN

3.6.3 Solvent swelling [27]

A specimen was cut from cured sheets and weighted about 0.1g then it was immersed in the test solvent (100 ml), for 22 hours at ambient temperature according to ASTM D 471. After the immersion test has proceeded for the required length of time, the specimen was removed. Loose liquid was quickly removed by blotting with filter paper and the swollen weight was immediately measured. Calculation the percent change in mass is as follows :

$$\Delta M, \% = [(M_2 - M_1) / M_1] * 100$$

Where : ΔM = change in mass, %

M_1 = initial mass of specimen, g

M_2 = mass of specimen after immersion, g

Test solvent: toluene, hexane, chloroform, methylene chloride, methanol and acetone

3.6.4 Study effect of thickness of membrane

The membranes were prepared by varying thickness of 0.1, 0.2, 0.3, 0.4, 0.5 mm to obtain the appropriate thickness for solvent swelling. Test method was same solvent swelling test method.

3.6.5 Permeability [27]

The permeabilities of various solvents were investigated by measuring the weight loss of small vials containing with the solvents, and covered by a membrane 0.1 mm and tightly capped with aluminium.

3.7 Permeability of chloroform and ethanol mixture

3.7.1 Permeability of pure chloroform and pure ethanol

Small vials were contained by chloroform and ethanol (5 cm^3), covered by membrane 0.1 mm and then tightly capped with aluminium. The capped vials were kept at 30°C , measured the weight loss of the vials and then determined amount of chloroform and ethanol remaining in the vial at 1, 6, 12, 24, 48 h using GCMS.

3.7.2 Permeability of chloroform and ethanol mixture

Small vials were contained by the mixture of chloroform and ethanol (75:25, 50:50 and 25:75 ratio) (5 cm^3), covered by membrane 0.1 mm and then tightly capped with aluminium. The capped vials were kept at 30°C , measured the weight loss of the vials and then determined amount of chloroform and ethanol remaining in the vial at 1, 6, 12, 24, 48 h using GCMS.