

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals

1. Natural rubber latex, High ammonia : Revertex (Thailand) Ltd.
2. Methyl methacrylate monomer, : Siam Chemical Industry Co., Ltd.  
Commercial grade
3. Potassium persulfate, AR grade : Fluka
4. Potassium hydroxide, AR grade : BDH
5. Sodium dodecylsulfate, AR grade : Merck
6. Light petroleum ether, AR grade : Univar
7. Acetone, AR grade : Univar
8. Sodium hydroxide, AR grade : EKA
9. Aluminum oxide, for chromatography : Fluka
10. Acetic acid, AR grade : Univar
11. Poly(methyl methacrylate) resin, : TPI Polyacrylate Co., Ltd.  
MF#001

#### 3.2 Glasswares

1. 4-Necked round bottom reactor, 500 cm<sup>3</sup> capacity
2. Condenser
3. Nitrogen gas tubing
4. Soxhlet

### 3.3 Equipment

- |  |                                       |
|--|---------------------------------------|
| 1. Fourier-Transform Infrared Spectroscopy | : Perkin Elmer model 1760x.<br>U.S.A. |
| 2. Transmission Electron Microscopy        | : JEM-CX200, Japan                    |
| 3. Two-roll mill                           | : Lab Tech Engineering,<br>Thailand   |
| 4. Crushing machine                        | : Bosco Engineering,<br>Thailand      |
| 5. Compression molding machine             | : Lab Tech Engineering,<br>Thailand   |
| 6. Durometer Hardness                      | : Shore model 716, U.S.A.             |
| 7. Dynamic Mechanical Analyzer             | : Perkin Elmer model 7e,<br>U.S.A.    |
| 8. Tensile testing machine                 | : Instron model 1011, U.S.A.          |
| 9. Universal testing machine               | : Lloyd, U.K.                         |
| 10. Scanning Electron Microscope           | : JSM-6400, Japan                     |

### 3.4 Procedure

#### 3.4.1 Purification of Monomer

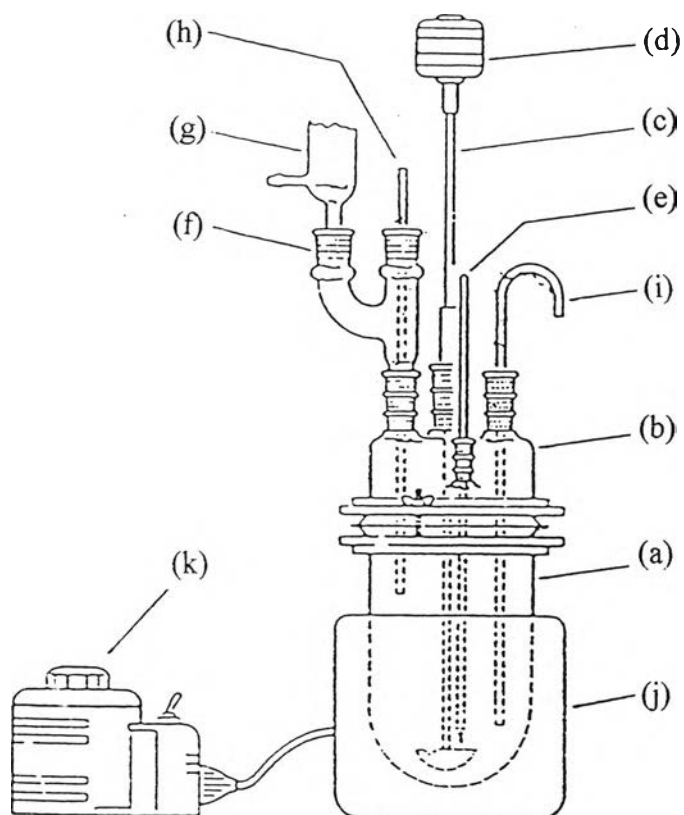
Methyl methacrylate (MMA) was washed with 10 wt% aqueous sodium hydroxide solution followed by distilled water washes until neutral, and then dried using anhydrous sodium sulfate, and passed through an activated aluminum oxide column to remove the residual inhibitor. The purified MMA was stored in the refrigerator.

### 3.4.2 Preparation of Graft Natural Rubber

Graft copolymers of natural rubber with methyl methacrylate were prepared from the high-ammonia natural rubber (HANR) latex by emulsion graft copolymerization. The equipment setup is shown in Figure 3.1.

The HANR latex (50g, DRC 61.20%) was placed in a round bottom reactor along with 100 cm<sup>3</sup> of distilled water, of the potassium hydroxide 0.25 wt.% of dry rubber content (phr) was added as buffer, and 1.0 phr of sodium dodecylsulfate as an emulsifier was then added while stirring. The mixture was deoxygenated by bubbling the nitrogen gas for approximately 30 min at room temperature. The MMA monomer (40, 60, 80, 100, 120 phr) was then added continually while stirring for 15 min to allow the latex particles to attain swelling. Potassium persulfate as an initiator 0.5 - 2.0 phr were added when the reaction was carried out at temperature between 50-70°C. The reaction was then allowed to proceed for 4 -10 hours under continuous stirring to complete the polymerization and then stop reaction. The obtained graft copolymer latex of NR-g-MMA was cast at room temperature on open trays. Once dry, the sheet was removed from the tray and transferred to the oven at 70°C for approximately 24 hr to remove any traces of monomer that may be retained. The dried sheet was then leached with distilled water to remove any water-soluble impurities from the rubber. Finally the sheet was then returned to the oven until it was thoroughly dry.

An appropriate condition for graft copolymerization could be obtained through varying the initiator concentration, reaction temperature, monomer concentration and reaction time as shown in Table 3.1.



**Figure 3.1** Apparatus for copolymerization of MMA monomer onto NR latex.

- |                            |                         |
|----------------------------|-------------------------|
| (a) Reaction kettle bottom | (b) Reaction kettle top |
| (c) Stirrer                | (d) Motor               |
| (e) Thermometer            | (f) Adapter             |
| (g) Condenser              | (h) Nitrogen-inlet tube |
| (i) Sampling               | (j) Water bath          |
| (k) Variable transformer   |                         |

**Table 3.1** Experimental conditions for graft copolymerizations.

Rubber content (g)	100
Initiator concentration, (g/100g rubber content, phr)	0.50, 0.75, 1.00, 1.50, 2.00
Reaction temperature (°C)	50, 55, 60, 70
Monomer concentration (g/100g rubber content, phr)	40, 60, 80, 100, 120
Reaction time (hr)	4, 6, 8, 10

### 3.5 Characterization of The Grafted Natural Rubber

#### 3.5.1 Determination of Conversion

The conversion of graft copolymerization was determined by the percentage increase of rubber weight. The details of all calculations are shown in the Appendix A.

#### 3.5.2 Determination of Grafted Natural Rubber and Grafting Efficiency

Soxhlet extraction procedures were carried out to assess the extent to which the products contained free natural rubber and graft copolymer. The free natural rubber was extracted in a soxhlet extractor by light petroleum ether for 24 hr while free poly(methyl methacrylate) was treated with acetone for 24 hr [30]. The grafted natural rubber used for soxhlet extraction was approximately 2 g. After each extraction, the percentage of the materials extracted was calculated. The details of all calculations are shown in the Appendix A.

### **3.5.3 Determination of The Morphology of Grafted Natural Rubber**

First, the grafted natural rubber latex was diluted 400 times with distilled water. Then a 2% aqueous solution of  $\text{OsO}_4$  1-2 drops stained the rubber particles in  $200 \text{ cm}^3$  of diluted latex for 1 day. Second, a drop of each diluted latex was placed on a carbon-coated Formvar film deposited on a grid and dried in the dessicator. Morphology of the grafted natural rubber latex was studied using the transmission electron microscopy (TEM model JEM-200CX ) at 120 kV.

### **3.5.4 Determination of Grafted Natural Rubber Composition**

Composition of grafted natural rubber were determined by Fourior Transform Infrared Spectrophotometer (Perkin Elmer model 1760x). The grafted natural rubber films were made by dissolving in chloroform and casting on KBr cell.

### **3.5.5 Determination of Dynamic Mechanical Properties of Grafted Natural Rubber**

Dynamic mechanical properties were measured on a Dynamic Mechanical Analyzer (Perkin Elmer 7e) and a liquid nitrogen cooling system. A frequency of 1 Hz was applied to the test piece (12 mm length, 4 mm wide, 3 mm thick) from  $-120$  to  $+110^\circ\text{C}$  and at heating rate of  $10^\circ\text{C}$  per min. The output data from the apparatus was recorded and calculated with a computer.

## **3.6 Preparation of Grafted Natural Rubber/PMMA Blends**

The mixing roll temperature was kept constant at  $165^\circ\text{C}$ . The PMMA pellets were fed to the two-roll mill for 3 minutes and then blended with grafted natural

placed into a mill again at 165°C for 4 minutes until the surface of blend was smooth. Finally, the sheets were pressed into a preheated mold at 170°C by compression molding and pressure of 120 kg/cm<sup>2</sup> for 10 min. After pressing, the mold was transferred to a water cooled press for 10 min. The compositions of grafted natural rubber and PMMA blends are shown in Table 3.2.

**Table 3.2** Grafted natural rubber (GNR) and PMMA composition.

Composition	
GNR60/PMMA	GNR100/PMMA
100/00	100/00
70/30	70/30
60/40	60/40
50/50	50/50

GNR60 = Grafted natural rubber of MMA 60 phr in natural rubber latex.

GNR100 = Grafted natural rubber of MMA 100 phr in natural rubber latex.

### 3.7 Mechanical Testing

The mechanical properties of the grafted natural rubber and PMMA blends were determined according to the ASTM test methods.

### 3.7.1 Hardness (ASTM2240-97)

The test specimen shall be at least 6 mm. in thickness. The lateral dimensions of the specimen should be sufficient to permit measurements at least 12 mm. from any edge unless it is known that identical results are obtained when measurements are made at a lesser distance from an edge. The surfaces of the specimen should be flat and parallel over a sufficient area to permit the presser foot to contact the specimen.

The specimen was placed on a hard, horizontal surface. The durometer was hold on a vertical position with the point of the indenter at less of 12 mm from any edge of the specimen. The presser foot was applied to the specimen as rapidly as possible, without shock, the foot was kept parallel to the surface of the specimen. Just sufficient pressure was applied to obtain a firm contact between the presser foot and the specimen, the scale reading is to be taken within 15 s. The condition in testing was shown as follows.

Temperature	25°C
Humidity	60%

One measurement was made at each of five different points distributed over the specimen of at least 6 mm apart using the median of these measurements for the hardness value.

### 3.7.2 Tensile Properties (ASTM D638-97)

Tensile properties of the samples were measured at 25°C and humidity of 60% using dumbbell-shaped test pieces (Type IV) as illustrated in Figure 3.2. The specimens were wire cut from a 3.0 mm-thick sheet. The testing was performed on a tensile testing machine (Instron model 1011) with a crosshead speed of 50 mm/min.



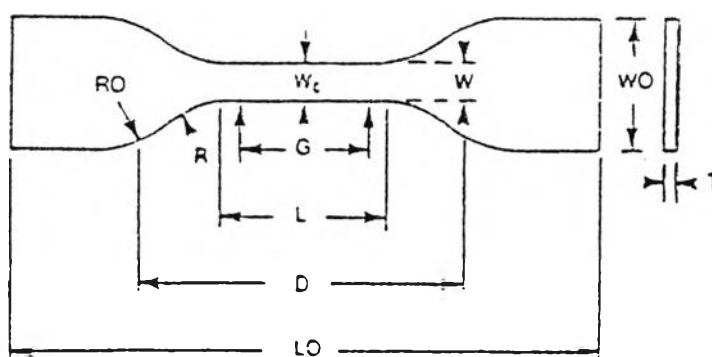
### 3.7.3 Tear Strength (ASTM D624-98)

The test specimen should conform in shape according to Die C in Figure 3.3. The thickness of the test specimen was 3 mm. The tests of the specimens were measured at 25°C and humidity of 60%. A crosshead speed of the universal testing machine (Lloyd) at 500 mm/min was used.

### 3.7.4 Scanning Electron Microscopy (SEM) studies

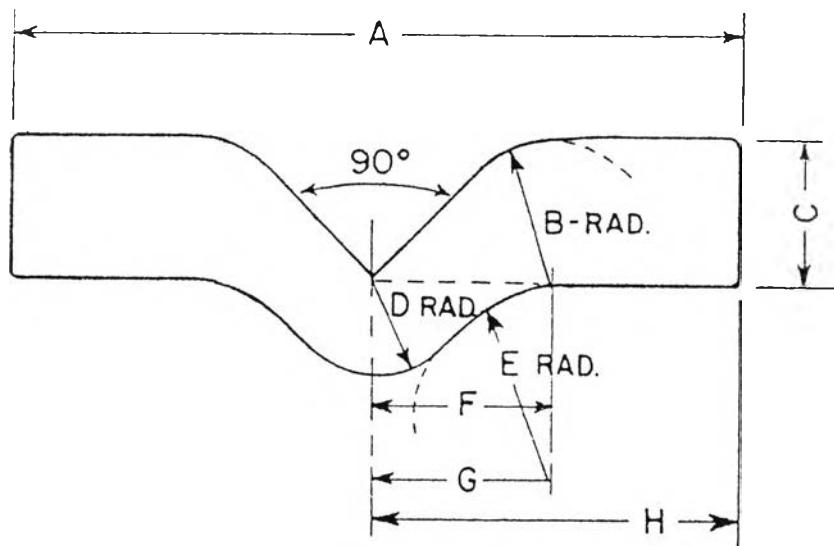
The SEM was used to investigate the fracture surface of the grafted natural rubber/PMMA blends from the tensile properties test. Samples for SEM were mounted on a SEM stub using a double-side tape and the fractured specimens were coated with gold. The SEM (model JSM-6400) was operated at 20 kV.

The overall schematic experimental process as shown in Figure 3.4.



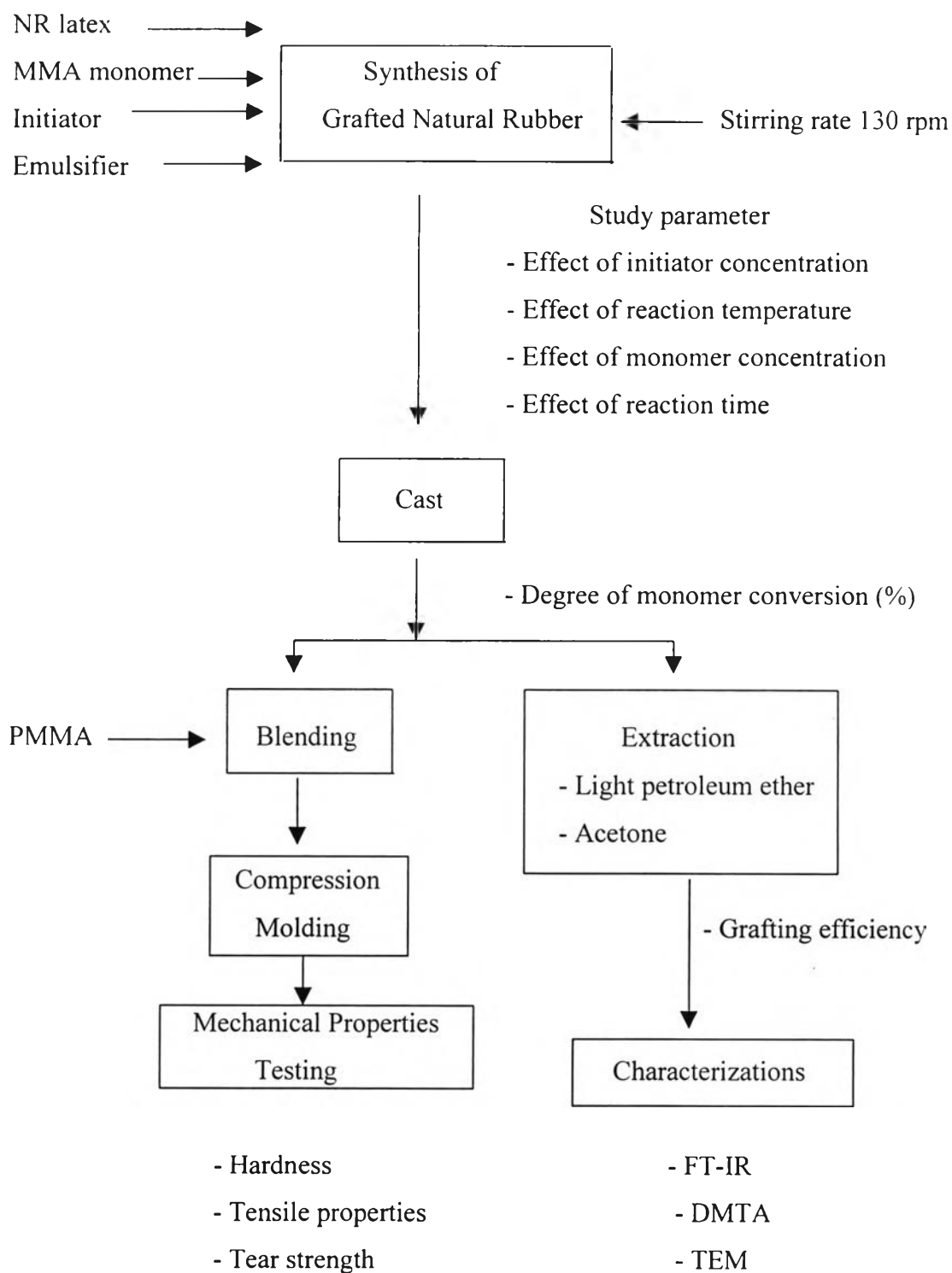
W: 6 mm      W<sub>0</sub>: 19 mm      G: 25 mm      R: 14 mm      T: 4 mm or under  
 L: 33 mm      L<sub>0</sub>: 115 mm      D: 65 mm      R<sub>0</sub>: 25 mm

**Figure 3.2** Schematic diagram of tensile test specimen (Type IV).



A: 102 mm    B: 19 mm    C: 19 mm    D: 12.7 mm  
E: 25 mm    F: 27 mm    G: 28 mm    H: 51 mm

**Figure 3.3** Schematic diagram of tear test specimen (Die C).



**Figure 3.4** The overall schematic experimental process.