

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals

1. Natural rubber latex, high ammonia : Thai Rubber Latex Corporation  
(Thailand) Public Co., Ltd.
2. Styrene monomer, commercial grade : Eternal Resin Co., Ltd.
3. Glycidyl methacrylate monomer, commercial grade : The Kouyoh Trading Co., Ltd.  
Tokyo, Japan.
4. Potassium hydroxide, AR grade : BDH
5. Sodium dodecylsulfate, AR grade : APS Ajax Finechem
6. Isopropanol, AR grade : BDH
7. Cumene hydroperoxide : Fluka
8. Tetraethylene pentamine : Fluka
9. Light petroleum ether, AR grade : Lab Scan Analytical Sciences
10. Acetone, AR grade : BDH
11. Toluene, AR grade : Univar
12. Sodium hydroxide, AR grade : Akzo Nobel
13. Sodium sulfate anhydrous, AR grade : Merck
14. Chloroform-d for NMR : Aldrich
15. Zinc oxide : DYNA Trade Co., Ltd.
16. Stearic acid : Imperial (Thai) Co., Ltd.
17. Tetramethyl thiuramdisulphide : Sunny World (1989) Co., Ltd.
18. Sulphur : DYNA Trade Co., Ltd.
19. STR 5L (Standard Thai Rubber 5L) : Thai Hua Yangpara Co., Ltd.

20. Poly (Methyl Methacrylate) pellet, MF#001 : TPI Polyacrylate Co., Ltd.

### 3.2 Glasswares

1. 4-Necked round bottom reactor, 500 cm<sup>3</sup> capacity
2. Condenser
3. Nitrogen gas tubing
4. Thermometer adapter
5. Extraction apparatus
6. Round bottom flask
7. Extractor
8. Dimorth condenser
9. Other general laboratory glassware

### 3.3 Equipments

1. Fourier-Transform Infrared Spectrometer : Nicolet (Impact 410), England
2. Transmission Electron Microscope : TEM-200CX, Japan
3. Nuclear Magnetic Resonance Spectrometer : DPX-400
4. Two-roll Mills : Lab Tech Engineering, Thailand
5. Compression Molding Machine : Lab Tech Engineering, Thailand
6. Cutting Machine : Dumbbell Co., Ltd, Japan
7. Dynamic Mechanical Analyzer : Perkin Elmer Model 7e, U.S.A.
8. Tensile Testing Machine : Instron Model 1011, U.S.A.
9. Universal Testing Machine : Lloyd, U.K.
10. Durometer Hardness : Shore A Model 716, Shore Instrument & MFG. Co., Ltd., U.S.A.
11. Impact Testing Machine : Izod-Charpy Impact Tester

12. Scanning Electron Microscope : JEOL, Model JSM-5800 LV,  
Japan

### 3.4 Procedure

#### 3.4.1 Purification of Monomer

The styrene monomer (b.p. 145.2°C/760 mmHg), contained a trace amount of hydroquinone as inhibitor. The inhibitor was removed by washing with 10% NaOH solution. The styrene monomer washed with distilled water until neutral and then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The purified styrene monomer was stored in the refrigerator. The glycidyl methacrylate monomer (b.p. 189°C/760 mmHg) was used as received and stored in the refrigerator.

#### 3.4.2 Preparation of Grafted Natural Rubber

The graft copolymer of natural rubber with styrene (St) and glycidyl methacrylate (GMA) were prepared by emulsion graft copolymerization. The high ammonia natural rubber (HANR) latex (50 g, DRC 60.03%) was charged to 500 cm<sup>3</sup> round bottom reactor with 100 cm<sup>3</sup> of distilled water and the sodium dodecylsulfate 1.5 wt.% of dry rubber content (phr) was added as emulsifier. The 1.5 g of isopropanol as stabilizer and potassium hydroxide was added as buffer to maintain the pH of system at 10. The mixture was stirred in nitrogen atmosphere at room temperature for at least 30 min. The monomer mixture of 70% of St and 30% of GMA by weight was added to the reactor, then tetraethylene pentamine (TEPA), TEPA was used to activate the cumene hydroperoxide; (CHPO:TEPA = 1:1 w/w) were added. The HANR latex was swollen with the monomer mixture for 1 hour before adding initiator at reaction temperature. The reaction was then allowed to proceed for 10 hours under continuous stirring to complete the polymerization and then stop the reaction. The obtained graft copolymer

latex was cast on open trays at room temperature. The gross polymer was removed, washed and dried in vacuum oven at 40°C for 24 hours. The complete experimental procedure is summarized in Figure 3.1. The experimental variables used for the graft copolymerization are shown in Table 3.1.

**Table 3.1** Experimental Variables for Graft Copolymerization

Rubber content (g)	100
Initiator concentration, (g/100 g rubber content, phr)	0.5, 1.5, 2.5, 5
Reaction Temperature (°C)	50, 60, 65, 70
Monomer concentration, (g/100 g rubber content, phr)	50, 75, 100, 125, 150
Reaction Time (h)	4, 8, 10

### 3.5 Determination of the Grafted Natural Rubber

#### 3.5.1 Determination the Conversion of Graft Copolymerization

The conversion of graft copolymerization was determined by the percentage increase of rubber weight. The calculations are as following equation 3.1.

$$\text{Total Conversion (\%)} = \frac{\text{Total weight of polymer formed}}{\text{Weight of monomer charged}} \times 100 \quad (3.1)$$



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

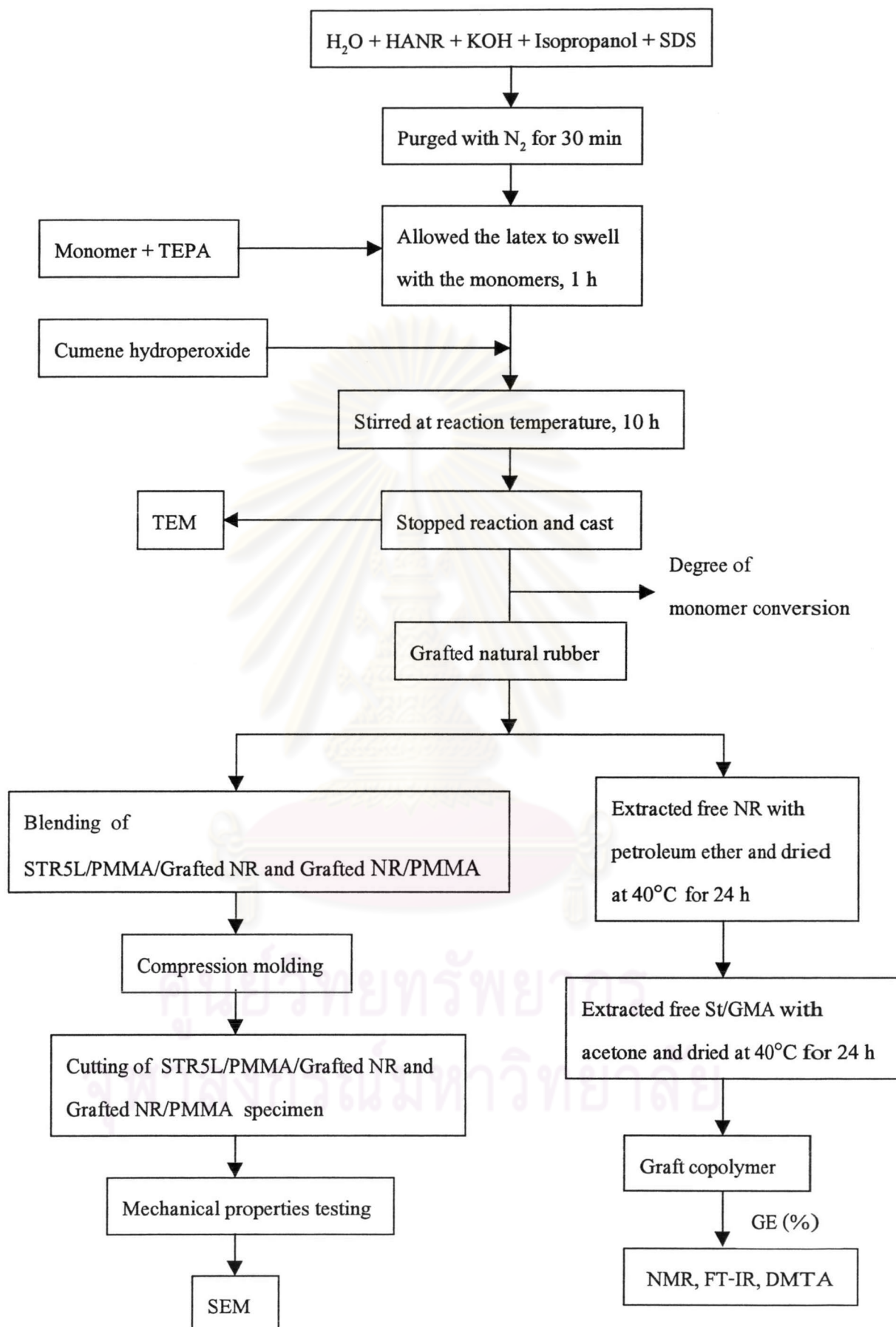
The amount of grafted natural rubber, free natural rubber, free St/GMA in the product could be determined by soxhlet extraction. The free natural rubber was extracted by light petroleum ether (60-80°C) for 24 hours, while free St/GMA was extracted by acetone for 24 hours [13, 16]. The grafted natural rubber content was determined by the residual weight after extraction of homopolymer. The grafting efficiency is defined as the mass of grafted St/GMA divided by the total St/GMA produced. All of calculations are as following equations 3.2 and 3.3.

$$\% \text{ Grafted Natural Rubber} = \frac{b}{a + b + c} \times 100 \quad (3.2)$$

Where

- a** is the weight of free rubber determined by soxhlet extraction with light petroleum ether for 24 hours.
- b** is the weight of grafted copolymer determined from the residual weight after extraction of free homopolymers.
- c** is the weight of free St/GMA determined by soxhlet extraction with acetone for 24 hours.

$$\% \text{ Grafting Efficiency} = \frac{\text{the weight of polymer as grafted copolymer}}{\text{the total weight of polymer formed}} \times 100 \quad (3.3)$$



**Figure 3.1** The Overall Schematic Experimental Process

### 3.5.3 Determination of the Morphology of Grafted Natural Rubber

The grafted natural rubber latex was diluted 400 times with distilled water to a concentration of 0.05 wt.%. In 1 cm<sup>3</sup> of this solution, 2% aqueous OsO<sub>4</sub> solution was added, and allowed to stain the natural rubber in the grafted natural rubber for overnight. The latex was placed on a grid and dried [23]. The morphology of the graft copolymer was examined by a transmission electron microscopy technique (TEM model JEM-200CX) and the accelerating voltage was 100 kV.

### 3.5.4 Characterization of Graft Copolymer Product

After the solvent extraction of grafted natural rubber product, the grafted natural rubber (NR-g-St/GMA) was characterized. The solution after the extraction by petroleum ether and the solution after the extraction by acetone were analyzed by FT-IR and NMR spectroscopy.

#### a. Fourier-Transform Infrared Spectroscopy (FT-IR)

Sample after the solvent extraction of grafted natural rubber product (dissolved by using chloroform as a solvent), solution after the extraction by petroleum ether and solution after extraction by acetone were casted onto NaCl cell [21]. The spectra of all samples were operated on the Nicolet Infrared Spectrophotometer (Model Impact 410) after 128 scans at resolution of 4 cm<sup>-1</sup>.

#### b. Nuclear Magnetic Resonance Spectroscopy (NMR)

The grafted natural rubber was swollen in CDCl<sub>3</sub>. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were operated on the NMR spectrometer (DPX-400). From <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectrums, the copolymer composition was determined by the signal area of the specific functional group of styrene, isoprene and glycidyl methacrylate [22].

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

The dynamic mechanical properties of grafted natural rubber were measured on a dynamic mechanical analyzer (Perkin-Elmer 7e) with a liquid nitrogen cooling system. The Parallel Plate mode was used in a temperature range of  $-80$  to  $+20^{\circ}\text{C}$  at a heating rate of  $5^{\circ}\text{C min}^{-1}$  and at a frequency of 1 Hz.

### **3.6 Preparation of STR5L/PMMA/Grafted Natural Rubber Blends**

The STR5L and 5 to 20 phr of grafted natural rubber (NR-g-St/GMA) content were mixed at room temperature by using two roll-mill. The PMMA pellets were fed into two roll-mill for 15 min and then blended with the STR5L and grafted natural rubber for 5 min. The mixing-roll temperature was kept constant at  $165^{\circ}\text{C}$ . The milled sheets were cut and fed into the mill again and blended for 5 min. In the case of vulcanization, 6 phr zinc oxide (activator), 0.5 phr stearic acid (activator), 0.5 phr tetramethyl thiuramdisulphide (accelerator) and 3.5 phr sulphur (vulcanizing agent) were blended with STR5L/PMMA/grafted natural rubber at  $70^{\circ}\text{C}$  for 5 min. The compounding formulations of the blends are shown in Table 3.2. The thin sheets from the two roll-mill were then pressed by compression molding at  $170^{\circ}\text{C}$  at pressure  $150\text{ kg/cm}^2$  for 15 min, after pressing the mold was transferred to a water cooled press for 15 min. The sheet thickness was 3 mm. The sheet was cut into the standard specimens according to the ASTM test method.



**Table 3.2** Compounding Formulations

Ingredients	1	2	3	4
1. STR5L	70	50	70	50
2. PMMA	30	50	30	50
3. Zinc oxide (phr)	-	-	6	6
4. Stearic acid (phr)	-	-	0.5	0.5
5. Tetramethyl thiuramdisulphide (TMTD) (phr)	-	-	0.5	0.5
6. Sulphur (phr)	-	-	3.5	3.5
7. Grafted natural rubber content (phr)	0,5,10,15 and 20	0,5,10,15 and 20	0,5,10,15 and 20	0,5,10,15 and 20

### 3.7 Preparation of Grafted Natural Rubber (NR-g-St/GMA)/PMMA Blends

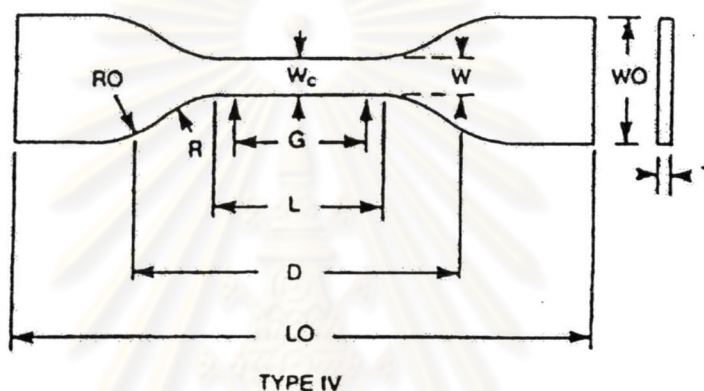
The mixing roll temperature of two roll-mill was kept constant at 165°C. The PMMA pellets (0, 30, 40, 50 phr) were fed to the two-roll mill for 15 min and then blended with 100, 70, 60 and 50 phr of grafted natural rubber (NR-g-St/GMA) for 5 min. The sheets were pressed into a preheated mold of compression molding at 170°C 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 sheet thickness was 3 mm. The sheet was cut into the standard specimens according to the ASTM test method.

### 3.8 Mechanical testing

Mechanical properties of the STR5L/PMMA/grafted natural rubber (NR-g-St/GMA) and grafted natural rubber (NR-g-St/GMA)/PMMA blends were measured by following the ASTM test methods as follows:

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

Tensile properties of the samples was measured at 25°C and humidity of 60% using dumbbell-shaped test pieces (Type IV) as illustrated in Figure 3.2. The specimens were 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 500 mm/min.

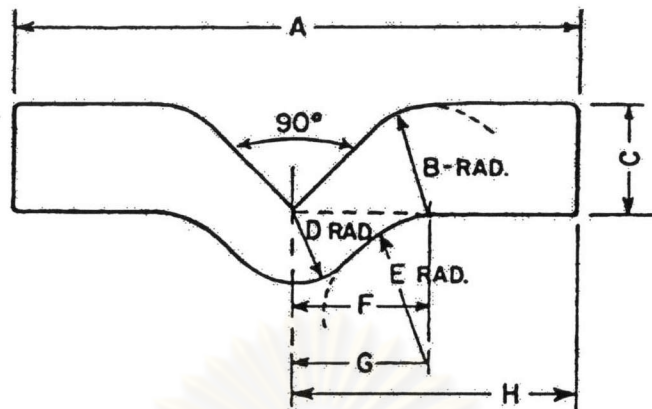


W : 6 mm    WO : 19 mm    G : 25 mm    R : 14 mm    T : 4 mm or under  
 L : 33 mm    LO : 115 mm    D : 65 mm    RO : 25 mm

**Figure 3.2** Schematic Diagram of Tensile Test Specimen (Type IV)

### 3.8.2 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 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.



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)

### 3.8.3 Hardness (ASTM D2240-97)

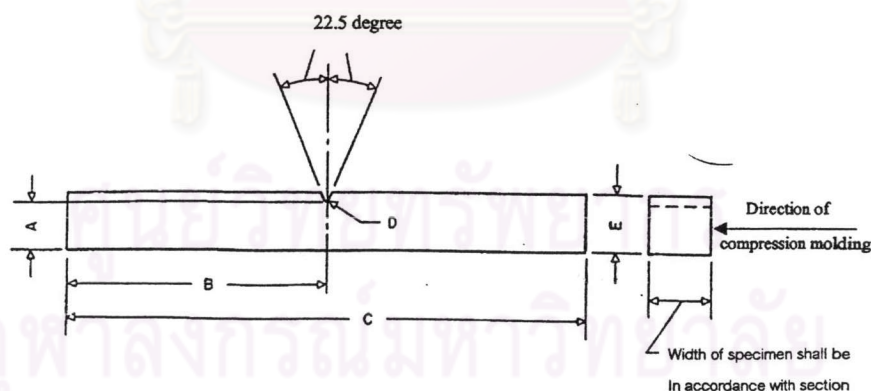
The test specimen shall be at least 6 mm in thickness. A specimen may be composed of plied pieces to obtain the necessary thickness. The lateral dimensions of the specimen shall be sufficient to permit measurements at least 12 mm from any edge. The surfaces of the specimen shall be flat and parallel over a sufficient area to permit the presser foot to contact the specimen over an area having a radius of at least 6 mm from the indenter point.

The specimen was placed on a hard, horizontal surface. The durometer was hold on a vertical position with the point of the indenter at least 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 specimen. After the presser foot was in firm contact with the specimen, the scale reading was to be taken within 15 s. The condition in testing was as follows, temperature of 25°C and humidity of

60%. One measurement was made at five different points distributed over the specimen of at least 6 mm apart and the median of these measurements was used as the hardness value.

### 3.8.4 Impact Energy (ASTM D256)

The test specimen should conform to the dimensions and geometry of Figure 3.4. The machine used in the present investigation was Izod-Charpy Impact Tester. The width of each specimen was measured in the region of the notch with a micrometre caliper and recorded its average width along with its identifying markings. The test specimen was put in a horizontal position so that it will be impacted edgewise at its center on the face opposite the notch for notched specimens. The breaking energy of the specimen was estimated and a pendulum of suitable energy was selected. The pendulum was released and the excess energy remaining in the pendulum was recorded after breaking the specimen, together with a description of the appearance of a broken specimen. The average impact energy was calculated in the group of specimens.



Unit : mm.

A :  $10.16 \pm 0.05$

D :  $0.25 \pm 0.05$

B : 32.00 max., 31.50 min.

E :  $12.70 \pm 0.05$

C : 63.50 max., 63.30 min.

**Figure 3.4** Dimensions of Simple Beam, Charpy Type, Impact Test Specimen



### 3.9 Oil Absorption

The vulcanized STR5L/PMMA blends at ratio of 70/30 and at ratio of 50/50 with various grafted natural rubber content (diameter 1.90 cm.) were completely immersed in lubricant oil (benzene engine) for 1 week. The samples were wiped with tissue paper to remove surface oil before weighting. The weight of the sample was recorded and the calculation of the change in mass is as follows (ASTM 471-79) :

$$\text{Change in mass (\%)} = (M_2 - M_1) / M_1 \times 100$$

Where  $M_1$  = initial mass of specimen, g and

$M_2$  = mass of specimen, g, after immersion

### 3.10 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) was used to investigate the fracture surface of the STR5L/PMMA/grafted natural rubber (NR-g-St/GMA) blends and the grafted natural rubber (NR-g-St/GMA)/PMMA blends from the tensile properties test. Samples for SEM were mounted on a SEM stub using a double-side tape and the fracture specimens were coated with gold. The SEM (JEOL model JSM-5800LV) was operated at 15 kV.