

CHAPTER III

EXPERIMENTAL

3.1 Chemical

1. Natural rubber latex : Thai rubber latex Corporation.
2. Styrene monomer : Scientific Co.
3. Methyl methacrylate monomer : Scientific Co.
4. Potassium persulfate : Fluka
5. Sodium dodecyl sulfate : Fluka
6. *tert*-Dodecyl mercaptan : Fluka
7. Isopropanol : Aldrich
8. Phenol : Fluka
9. Acetic acid : Fluka
10. Sodium hydroxide : Merck
11. Potassium hydroxide : Merck
12. Sodium sulfate : Carlo Erba
13. Light petroleum ether (b.p. 60-80 °C) : Merck
14. Acetone : Merck
15. PVC (SG 660) : Thai Plastic and Chemical (Public Co.) Ltd.
16. MBS : Thai Plastic and Chemical (Public Co.) Ltd.
17. Lead sulfate : Thai Plastic and Chemical (Public Co.) Ltd.
18. Steric acid : Thai Plastic and Chemical (Public Co.) Ltd.

3.2 Glassware

1. 4-Necked bottom reactor 1000 cm³
2. Liebig condenser
3. Nitrogen gas tube
4. Other general laboratory glassware

3.3 Equipment

1. Fourier-Transform Infrared Spectrometer : Perkin Elmer 2000
2. Nuclear Magnetic Resonance Spectrometer : Bruker AC-F200
3. Gel Permeation Chromatograph : Waters 150C
4. Scanning Electron Microscope : JSM 35CF
5. Transmission Electron Microscope : JSM 200CX
6. Two roll mills : LabTech. Engineering
7. Cutting machine : Yasuda 189-PFN
8. Compression molding : LabTech. Engineering
LP20
9. Differential Scanning Calorimeter : Netzsch DSC 200
10. Elemental analyzer : Perkin PE 2400 Series 2
11. Universal testing machine : Instron 4206
12. Impact testing machine : Yasuda 258-D
13. Hardness testing machine : Zwick

3.4 Procedure

3.4.1 Purification of monomer

The styrene monomer (b.p. $145.2^{\circ}\text{C}/760\text{ mmHg}$), contained a trace amount of hydroquinone as inhibitor. The inhibitor was removed by washing with 1.0% NaOH solution. The styrene monomer was then washed with distilled water and then dried with anhydrous Na_2SO_4 . The dried styrene monomer was distilled in presence of CuCl_2 under reduced pressure ($50\text{-}60^{\circ}\text{C}/20\text{ mmHg}$). Finally, the pure styrene monomer was stored under nitrogen atmosphere in a refrigerator.

The methyl methacrylate monomer (b.p. $98^{\circ}\text{C}/760\text{ mmHg}$), contained a trace amount of hydroquinone as inhibitor. The methyl methacrylate was purified by following the above procedure as for styrene monomer purification, and distilled under reduced pressure ($40^{\circ}\text{C}/20\text{ mmHg}$).

3.4.2 Preparation of Graft Natural Rubber

The graft copolymer of styrene and methyl methacrylate onto natural rubber was prepared by emulsion graft copolymerization. The equipment setup is shown in Figure 3.1. The procedure of preparation of graft natural rubber and the characterization is summarized in Flow diagram 1.

Water (500 cm^3) and 0.7 g of potassium hydroxide as a buffer were placed in a 1000 cm^3 bottom reactor fitted with a reflux condenser and nitrogen inlet tube. Natural rubber latex (300 g) was introduced into the mixture at room temperature. The mixture was stirred in nitrogen atmosphere at room temperature. Isopropanol (18 g) as stabilizer and 0.9–4.5 g of sodium dodecylsulfate as an emulsifier were subsequently added, the mixture was then warmed up to $40\text{-}70^{\circ}\text{C}$, 0.9–3.6 g of potassium persulfate as an initiator was added. Subsequently, the mixture of 25% of styrene and 75% of methyl

methacrylate by weight was added. The amount of mixed monomer solution per 100 g of rubber content was varied as 50, 75, 100, 125, and 150. The reaction mixture was stirred at the constant temperature for 8 hours. Then, 1.0 g of phenol as an antioxidant was added to stop reaction. The grafted natural rubber latex was coagulated. The resulting crumb was filtered, washed, and dried at 70°C in a vacuum oven.

In order to obtain an appropriate condition for graft copolymerization, a series of experiments as performed by varying the ratio of monomer to dried solid rubber content, emulsifier concentration, initiator concentration, and reaction temperature as shown in Table 3.1.

Table 3.1 Parameters investigated in the graft copolymerization.

Monomer (g/100g rubber)	50, 75, 100, 125, 150
Emulsifier (g/100g rubber)	0.5, 1.0, 1.5, 2.0, 2.5
Initiator (g/100g rubber)	0.5, 1.0, 1.5, 2.0
Reaction temperature (°C)	40, 50, 60, 70

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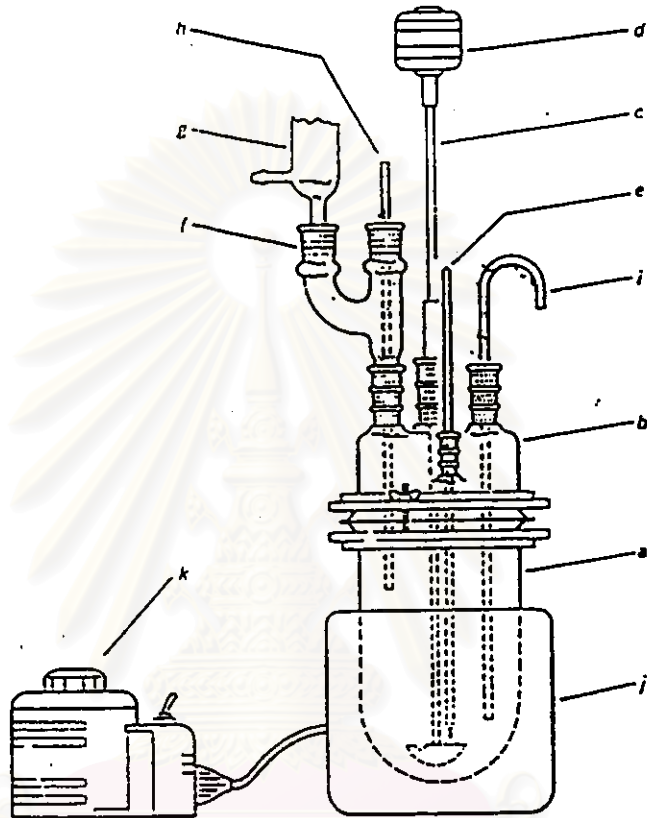
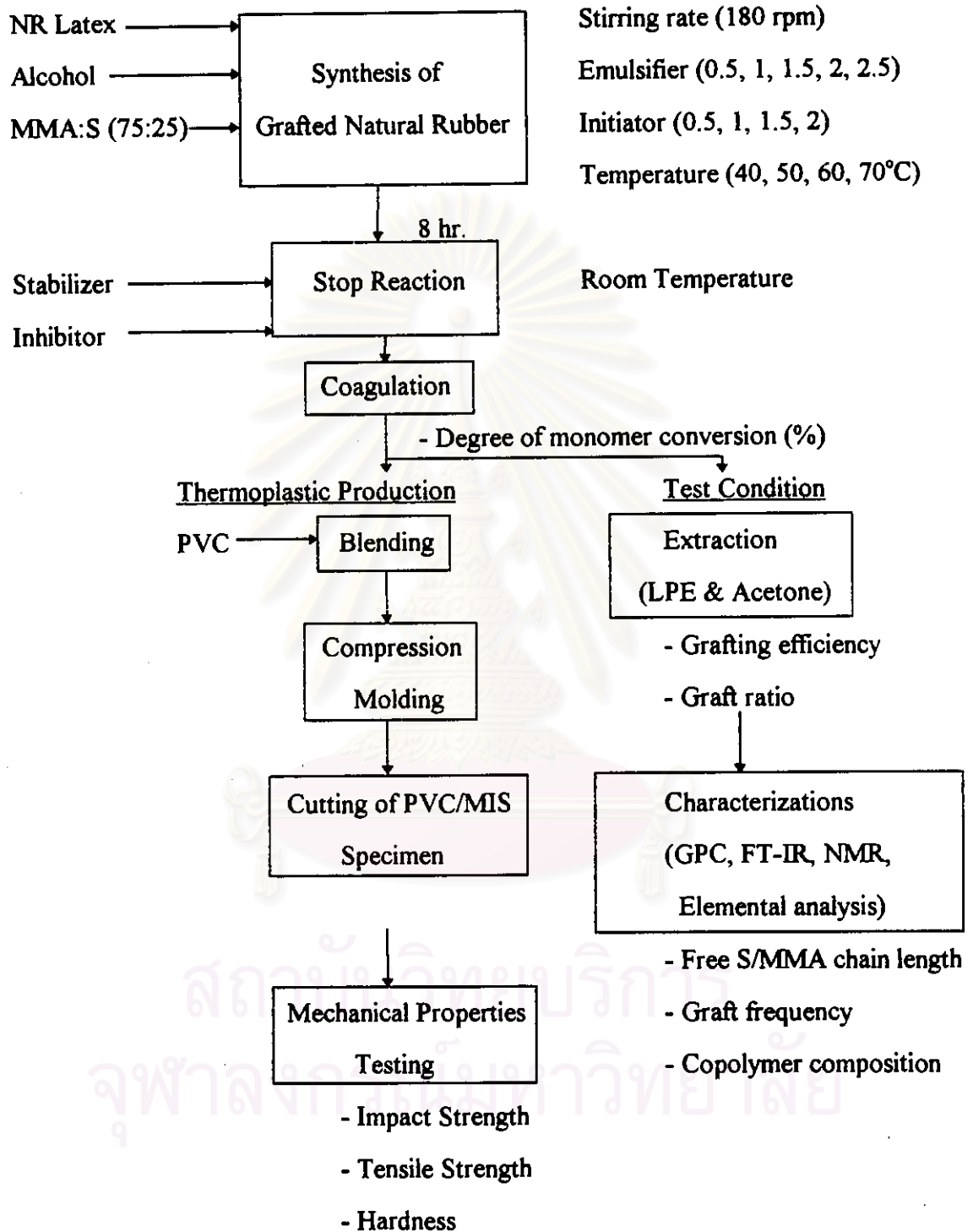


Figure 3.1 Apparatus for emulsion graft copolymerization of monomer styrene and methyl methacrylate onto natural rubber latex [29].

- | | |
|-----------------------------|--------------------------|
| (a) reaction kettle bottom | (g) condenser |
| (b) reaction kettle top | (h) nitrogen-inlet tube |
| (c) stainless steel stirrer | (i) sampling tube |
| (d) air motor | (j) water bath |
| (e) thermometer | (k) variable transformer |
| (f) adapter | |



Flow diagram 1 Experiment scheme of preparation of grafted natural rubber, Their blends with PVC and mechanical testing.

3.5 Characterization

3.5.1 Determination of grafting efficiency and graft ratio

The ungrafted copolymer and free natural rubber remaining in the reaction products could be removed by the extraction process. The ungrafted styrene-methyl methacrylate copolymer was extracted by solvent extraction, using acetone as extracting solvent while free natural rubber was extracted by light-petroleum ether. The data obtained from this step were used to calculate the grafting efficiency and graft ratio. The details of all calculations are shown in Appendix B [20].

3.5.2 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 cm³ of this solution a 2% aqueous OsO₄ solution was added, and allowed to stain the natural rubber in the grafted natural rubber for 1 hour. The latex was placed on a grid and dried. The morphology of the graft copolymer was examined by a transmission electron microscopy technique (TEM model JEM 35CF) [17].

3.5.3 Determination of average molecular weight of free S/MMA

The GPC solution of free S/MMA was prepared by dissolving 10 mg of the polymer into 100 cm³ of THF, the solution was agitated and then filtered with a microfilter.

Average molecular weight was determined by using GPC Waters model 150C., operating at 30-40°C with the special column in the THF solvent. The flow rate was regulated at 10 ml/min. Both the UV and IR detectors were used [20].

3.5.4 Determination of graft copolymer composition

After the solvent extraction of grafted natural rubber product, the composition of grafted natural rubber (NR-g-S/MMA) was analyzed by FT-IR, NMR, and CHO analyzer [17,22].

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

Infrared (FT-IR) spectra of grafted natural rubber were operated on the Nicolet Infrared Spectrophotometer model Impact 410. The grafted natural rubber sample was prepared by casting on KBr cell [17].

b) Nuclear Magnetic Resonance Spectroscopy (NMR)

The grafted natural rubber was swollen with CDCl_3 . The $^1\text{H-NMR}$ spectra were operated on the NMR spectrometer Model AC-F200 (200MHz). From the $^1\text{H-NMR}$ spectra, the copolymer composition (styrene-isoprene-methyl methacrylate) was determined by the signals area of the specific functional group of styrene, isoprene, and methyl methacrylate. Detailed method of measurement and calculation are described in Appendix D [17].

c) Elemental Analyzer

Elemental Analyzer, Perkin Elmer model PE 2400 series 2 was used to measure and calculate the copolymer composition. Detailed methods of calculation are described in Appendix E [22].

3.5.5 Determination of thermal properties of the grafted natural rubber

The grafted natural rubber sample was investigated with a Netzsch Differential Scanning Calorimeter model 2000. The measurements were carried out over a temperature range of -100 to 150°C with a heating rate of 10°C/min., the nitrogen flow rate of 30 cm³/min and the sensitivity of 000/Rg500 μV, under the nitrogen atmosphere. The weight of specimens used was about 10-20 mg [25].

3.6 Grafted natural rubber and PVC blends

The powders of the PVC compound and 5 to 20 phr grafted natural rubber were mixed at room temperature. The PVC compound was composed of 100 phr PVC (K value = 66), 3.5 phr lead sulfate (heat stabilizer), and 1.0 phr steric acid (lubricant). The mixture was mixed by, a roll milling at 180°C for 5 min. The thin sheets from the two roll mill were then pressed by compression moulding at 190°C for 10 min; the sheet thickness was 3 mm. The sheet was cut into the standard specimens according to the ASTM test method [21].

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3.7 Mechanical Testing

Mechanical properties of the thermoplastic blends were measured by following the ASTM test methods as follows :

ASTM D256 : Standard test method for impact resistance.
The test specimens dimension for Cantilever Beam (Izod Type) test is shown in Figure 3.2.

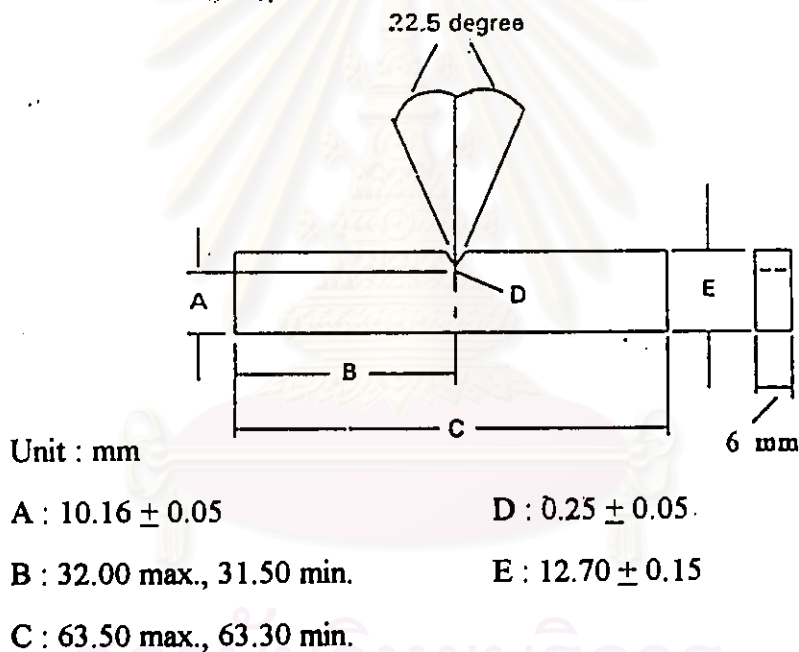
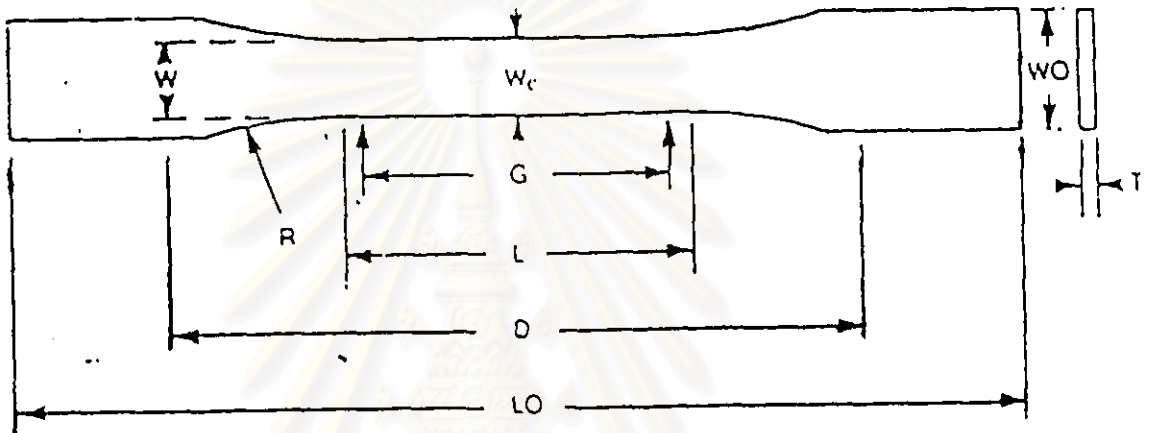


Figure 3.2 Schematic of Izod type test specimen.

The machine parameters and testing conditions of the impact test were listed below :

Temperature :	23°C
Relative humidity :	50%
Depth of specimen :	10.16 mm
Pendulum capacity :	21.6 J

ASTM D638 : Standard test method for tensile properties.
 The test specimens (type I) dimension is shown
 in Figure 3.3.



W : 13 mm	W ₀ : 19 mm	G : 50 mm	R : 76
L : 57 mm	L ₀ : 165 mm	D : 115 mm	

Figure 3.3 Schematic of tensile test specimen (type I)

The tensile testing conditions were as follows :

Temperature :	23.0°C
Relative humidity :	50.0%
Speed of testing :	5 mm/min.
Distance between grips :	115 mm
Gage length :	50 mm

ASTM D 2240 : Standard test method for Shore hardness

For the assignment of the specimen for hardness testing, the test specimen was of at least 6 mm in thickness. The surface of the specimen was flat and over a sufficient area to permit the presser foot to contact the specimen. For materials having hardness values above 50 Type D Durometer, the thickness of the specimen was of at least 3 mm and measurements should not be made closer than 6 mm to any edge.

According to the thickness assignment, the test specimens in this experiment were composed of plied pieces to obtain the necessary thickness. The type D Durometer was used in this experiment. The condition in testing were shown as follows :

Temperature :	25°C
Relative humidity :	50%
Number of pieces plied :	2 pieces

For all of the properties measured, at least five samples were tested to obtain a reliable average and standard deviation.

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