CHEPTER III

EXPERIMENTAL

3.1 Chemicals

1. Natural rubber latex, high ammonia grade: Thai Rubber Latex Corporation (Thailand) public, Co., Ltd.
2. Methyl methacrylate monomer, commercial grade: Siam Chemical Industry Co., Ltd., Thailand.
3. Vinyl *neo*-decanoate monomer, analytical grade: Aldich, Missouri, U.S.A.
4. Potassium persulfate, analytical grade: Fluka, Steinheim, Switzerland.
5. Sodium thiosulphate, analytical grade: Carlo Erba, Milano, Italy.
6. Tert-butyl hydroperoxide, analytical grade: Fluka, Steinheim, Switzerland.
7. Cumene hydroperoxide, analytical grade: Fluka, Steinheim, Switzerland.
8. Tetraethylene pentamine, analytical grade: Fluka, Steinheim, Switzerland.
9. Sodium dodecylsulfate, analytical grade: Carlo Erba, Milano, Italy.
10. Oleic acid, analytical grade: Merk, Honenbrunn, Germany.
11. Potassium hydroxide, analytical grade: BDH, Poole, England
12. Light petroleum ether, analytical grade: Lab Scan Asia Co., Ltd., Bangkok, Thailand.
13. Acetone, commercial grade: J.P.M. & Scientific, Bangkok, Thailand.
14. Sodium hydroxide, analytical grade: Carlo Erba, Milano, Italy.
15. Chloroform, HPLC grade: Lab Scan Asia Co., Ltd., Bangkok, Thailand.
16. Methanol, analytical grade: Lab Scan Asia Co., Ltd., Bangkok, Thailand.
17. Toluene, analytical grade: Lab Scan Asia Co., Ltd., Bangkok, Thailand.

3.2 Glassware

1. 4-Necked round bottom reactor, 500 cm^3 capacity
2. Condenser
3. Nitrogen gas tubing
4. Soxhlet extraction

3.3 Equipment

1. Fourier-Transform Infrared Spectroscopy	: Perkin Elmer model 1760x, U.S.A.
2. Transmission Electron Microscopy	: JEM-CX200, Japan
3. Gel Permeation Chromatograph	: Simadzu C-R7A plus, Japan
4. Differential Scanning Calorimeter	: NETZSCH200, Bararia, Germany
5. Nuclear Magnetic Resonance Spectroscopy	: Avance DPX-400, Germany
6. Ultracentrifuge	: Hitachi CR5B2, Japan
7. Vacuum oven	: Hotpack 273 700, P.A., U.S.A.

3.4 Procedure

3.4.1 Purification of Monomer

The methyl methacrylate monomer contained a trace amount of hydroquinone inhibitor. The MMA was washed with 10% aqueous sodium hydroxide solution, followed by washing with distilled water until the wash solution became neutral, and then dried with anhydrous sodium sulfate, and passed through an activated aluminum oxide column to remove the residual inhibitor. The purified MMA was stored in a refrigerator.

3.4.2 Preparation of Grafted Natural Rubber

Graft copolymers of methyl methacrylate onto natural rubber were prepared from the high ammonia natural rubber (HANR) latex by emulsion graft copolymerization. The equipment setup is shown in Figure 3.1. The initiation of graft copolymerization was started by three different redox systems, cumene hydroperoxide(CHPO)/tetraethylene pentamine(TEPA), tert-butyl hydroperoxide(TBHPO)/TEPA and potassium persulfate ($K_2S_2O_8$)/sodium thiosulfate($Na_2S_2O_3.5H_2O$). The procedure of preparation of graft natural rubber and the characterization are summarized in Figure 3.2.

a.) Preparation of Grafted Natural Rubber using CHPO/TEPA, and TBHPO/TEPA

The HANR latex (50g, DRC 60.04%) was placed in a round bottom reactor along with 100 cm^3 of distilled water of potassium hydroxide, 1 wt% of the dry rubber content was added as a buffer, and sodium dodecylsulfate (1 phr) as an emulsifier was then added

while stirring. The mixture was deoxygenated by bubbling the nitrogen gas for approximately 15 min at room temperature. The stabilizer, oleic acid (10 phr) was added, after 15 min of stirring, the MMA monomer (40, 60, 80, 100, or 120 phr) was then added continually while stirring for 30 min to allow the latex particles to attain swelling. The mixture was heated up to 30-60°C, the initiator (CHPO or TBHPO) was then added. After 15 min of mixing, the amine activator (10 wt% aqueous solution of TEPA) was added. The bipolar redox initiating system was employed at a ratio 1:1 (based on 0.5 to 2.0 phr). The reaction was then allowed to proceed for 4-10 hr under continuous stirring to complete the polymerization and then the reaction was stopped.

b.) Preparation of Grafted Natural Rubber using $K_2S_2O_8/Na_2S_2O_3$

The HANR latex (50g, DRC 60.04%) was placed in a round bottom reactor along with 100 cm^3 of distilled water of potassium hydroxide, 1 wt% of the dry rubber content was added as a buffer, and sodium dodecylsulfate (1 phr) as an emulsifier was then added while stirring. The mixture was deoxygenated by bubbling the nitrogen gas for approximately 15 min at room temperature. The stabilizer, oleic acid (10 phr) was added and the mixture was then heated up to 50-70°C. Potassium persulfate as an initiator was added. After 15 min of mixing, sodium thiosulfate ($Na_2S_2O_3.5H_2O$), 10 wt% aqueous solution was added. The bipolar redox initiating system was employed at a ratio of $K_2S_2O_8/Na_2S_2O_3$ 1:0.6 (based on 0.5 to 2.0 phr). Subsequently, a mixture of MMA and vinyl *neo*-decanoate monomer was added. The reaction was then allowed to proceed for 4-10 hr under continuous stirring to complete the polymerization and then the reaction was stopped.

All of grafted natural rubber latexes of NR-g-MMA was cast at room temperature in an open tray and transferred to a vacuum oven at 40°C for approximately 24 hr to

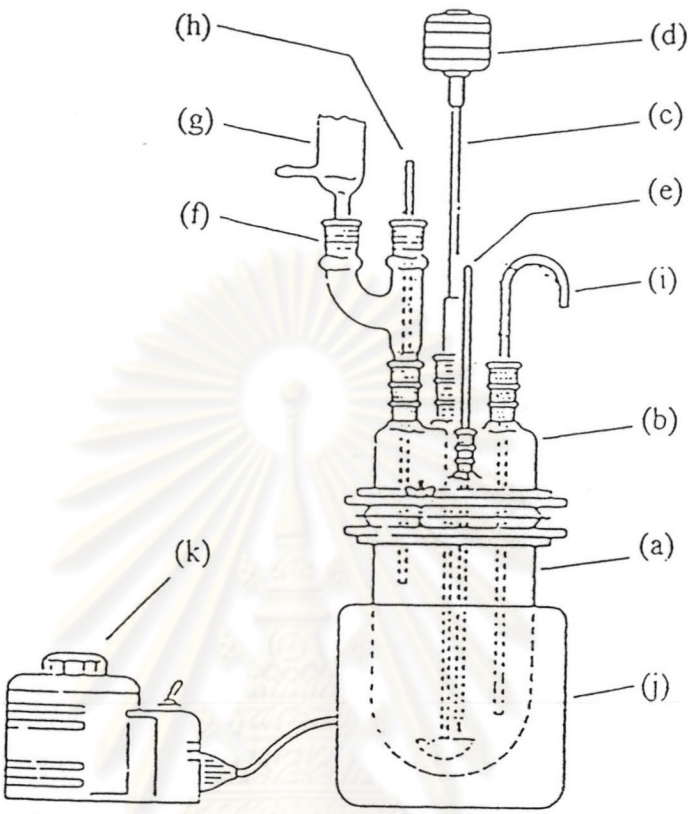

Figure 3.1 Apparatus for copolymerization of MMA monomer onto natural rubber latex.

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

remove any unreacted monomer. The dried sheet was then leached with distilled water to remove any water–soluble impurities. The sheet was then thoroughly dried in the vacuum oven.

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

Table 3.1 Experimental conditions for graft copolymerization

	CHPO or TBHPO	**$K_2S_2O_8$**
MMA/Vinyl *neo*-decanoate	100/0	90/10, 80/20, 70/30, 60/40
Initiator concentration (g/100g rubber)	0.5, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
Monomer content (g/100g rubber)	40, 60, 80, 100, 120	40, 60, 80, 100, 120
Reaction time (hr)	4, 6, 8, 10	4, 6, 8, 10

3.5 Characterization of the Grafted Natural Rubber

3.5.1 Determination of Conversion

The grafted natural rubber latex was cast in an open tray, dried in a vacuum oven at 40 °C, leached in distilled water, dried again in the vacuum oven. The degree of

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

3.5.2 Determination of Grafted Natural Rubber and Grafting Efficiency

The homopolymer and the graft copolymer in the reaction products could be determined by the soxhlet extraction. The free natural rubber was extracted in a soxhlet extractor by light petroleum ether for 24 hr while free poly(methyl methacrylate) was extracted by acetone for 24 hr. [20] The graft copolymer content was determined by the residual weight after extraction of homopolymer. The data obtained from this step were used to calculate the graft natural rubber. The details of all calculations are shown in Appendix A.

3.5.3 Determination of the Gel Content of Graft Copolymer

Gel contents were determined by treating 0.4 g of the graft copolymer with 20 cm^3 toluene, which had been kept without stirring for a week in the dark at ambient temperature. The gel fraction was collected as a bottom fraction obtained by centrifugation at 10,000 rpm for 30 min. The soluble fraction of graft copolymer was collected as a sol fraction, which was then precipitated with an excess amount of methanol. The collected gel and sol fractions were dried under reduced pressure at 40°C for a week. The gel content was determined from the masses of the gel and sol fractions.

3.5.4 The Morphology of Grafted Natural Rubber

The grafted natural rubber latex was diluted 400 times with distilled water. In a 2% aqueous solution of OsO_4, 1-2 drops were used to stain the rubber particles in 200 cm^3 of diluted latex for 1 day. A drop of latex was placed on the grid and dried. The morphology of the grafted natural rubber was photographed using the transmission electron microscopy (TEM model JEM-200CX) at 120 kV.

3.5.5 Determination of Average Molecular Weight of Grafted Natural Rubber

The molecular weight determination was carried out by gel permeation chromatography (GPC). The measurements were made using a ultraviolet-visible detector, and a pair of Showa Denko column (Shodex GPC K-806 M; 300 mm. x 8 mm. I.D.: packing with styrene divinylbenzene gel having a number of theoretical plate of 17,000) at 35°C. The HPLC grade chloroform was used as eluent at a flow rate of 1 $cm^3 min^{-1}$.

The GPC samples were prepared by dissolving the sol fraction of graft copolymer in chloroform, injecting the sample solution of 100 µl into GPC for analysis. The molecular weights of graft copolymer were obtained by the calibration lines using polystyrene standard samples supplied by Showa Denko (S-66.0) and the eluted volume.

3.5.6 Determination of Grafted Natural Rubber

After the solvent extraction of the grafted natural rubber, the grafted natural rubber was analyzed by FT-IR and NMR.

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

Functional groups of the grafted natural rubber were determined by Fourier Transform Infrared Spectrophotometer (Perkin Elmer model 1760x). The grafted natural rubbers samples were dissolved in toluene and cast on the KCl cell for IR investigation.

b.) Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR and ^{13}C-NMR)

The grafted natural rubber was swollen with $CDCl_3$. The ^{1}H-NMR and ^{13}C-NMR spectra of the solution were operated on the NMR spectrometer (AC-F200, 200 MHz and Avance DPX-400, respectively).

3.5.7 Thermal Properties of the Grafted Natural Rubber

Thermal behavior of the grafted natural rubber samples was examined by a differential scanning calorimeter (DSC) to obtain glass transition temperatures. The sample, 10-20 mg, was put into the aluminum pan and sealed. The measurements were carried out over a temperature range of −100 to 100 °C with a heating rate of 10°C min^{-1}, under the nitrogen atmosphere.

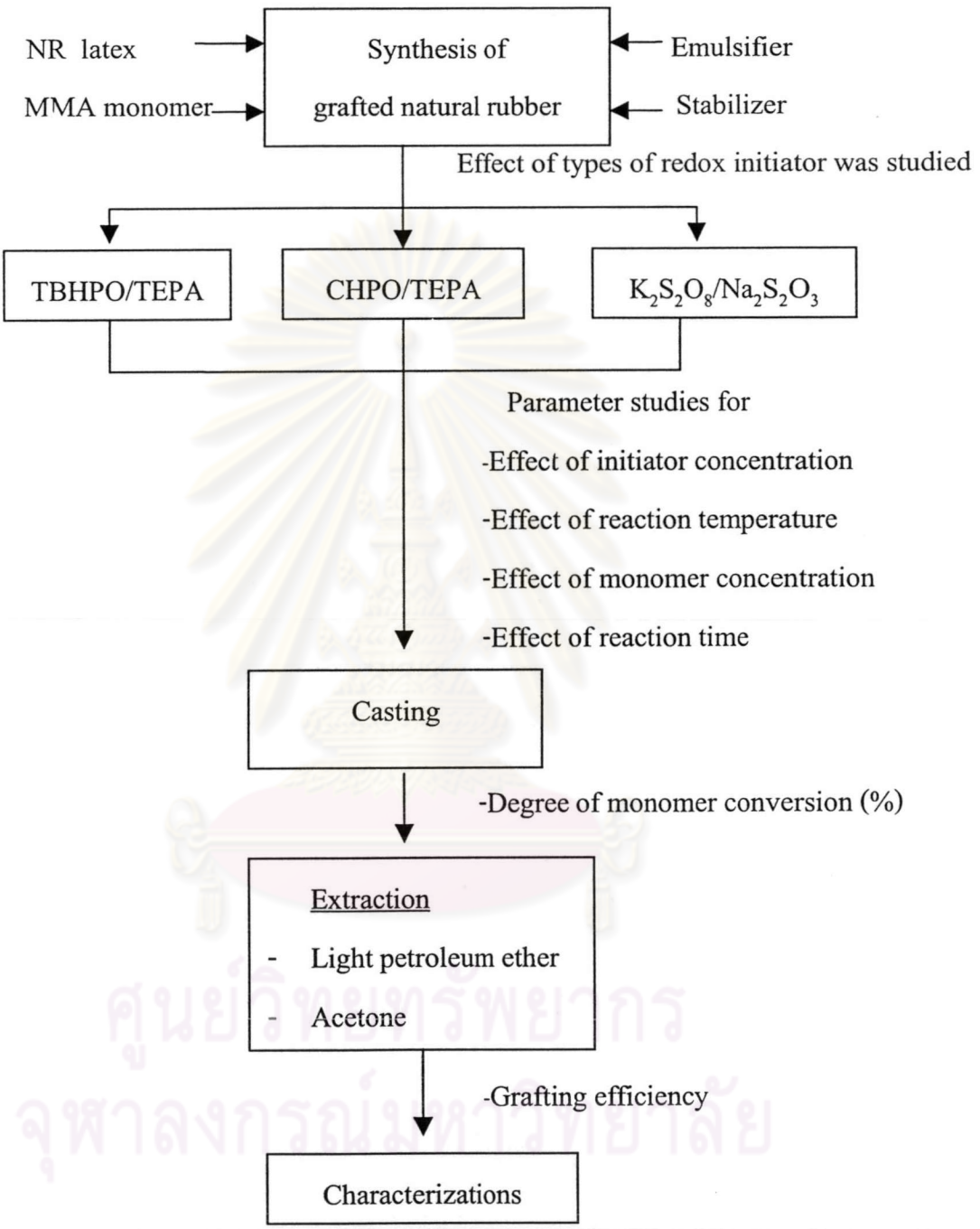

Figure 3.2 The overall schematic experimental process.