



CHAPTER III

EXPERIMENTAL SECTION

3.1 Studies on preparation and purification of liquid natural rubber

3.1.1 Determination of dry rubber latex content (DRC) [19]

To rubber latex (10 g), 20 mL of water was added, with stirring, then 6 % acetic acid solution was added dropwise with constant stirring until the latex became viscous and set to a mass. To complete the coagulation, the beaker was placed on a hot water-bath until the clear serum was observed. All the small pieces of rubber lump were collected and washed several times with water and pressed into a thin sheet. The rubber sheet was allowed to dry in an oven at 70 ± 2 °C for 20 h and was left to cool to room temperature in a desiccator. The rubber product was weighed and % DRC was calculated .

$$\% \text{ DRC} = m_1 / m_0 \times 100 \quad (3.1)$$

where m_0 = initial weight of rubber latex in gram

m_1 = final weight of rubber sheet in gram

3.1.2 Method of preparation

The liquid natural rubber (LNR) was prepared from rubber latex of 30 % DRC (diluted from centrifuged concentrated latex of about 60 % DRC) using the equipment shown in Figure 3.1.

To 300 mL rubber latex was added, with stirring, Teric 16 A 16 (1 % wt/wt of DRC). The mixture was stirred to allow homogenization and then allowed to stand overnight at room temperature before filtering into a 500 mL reaction kettle that was immersed in an oil-bath at 80°C. 10 % (wt/wt of DRC) phenylhydrazine was slowly added, with stirring, to the resulting latex. After a homogeneous dispersion of phenylhydrazine in the latex, compressed air was bubbled into the reaction mixture. The reaction was allowed to take place for a required period of time, then the supplied air was stopped. The product was precipitated from excess methanol. After the precipitate settled, the methanol solution was decanted. The precipitated rubber was allowed to dry in an oven at 80°C for 18 h. This LNR appeared as a transparent and dark brown viscous liquid.

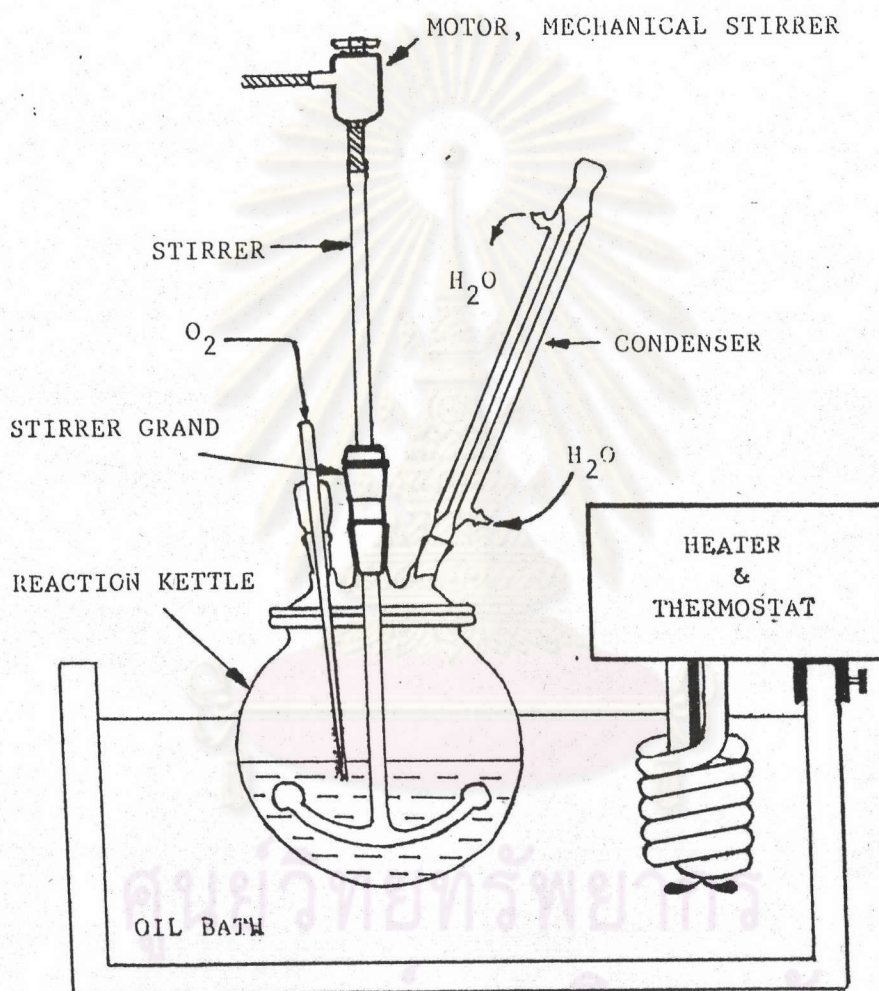


Fig 3.1 Apparatus used for the preparation of liquid natural rubber.

LNR with different molecular weight was prepared by varying the depolymerization time as listed in Table 3.1.

Table 3.1 Preparation of LNR at different depolymerization time

No	Conc of phenylhydrazine (wt/wt of DRC)	depolymerization time, h
1	0	0
2	10	1
3	10	3
4	10	5
5	10	10
6	10	15
7	10	20
8	10	30

3.1.3 Purification of LNR

The crude LNR was repurified to remove the remaining latex stabilizer, phenylhydrazine, and some non-rubber constituents such as fatty acid, sterols, quibrachitol, etc. by dissolving LNR in toluene; then

the rubber solution was filtered and precipitated from excess methanol. The liquid was decanted off and the precipitated rubber was dried in an oven at 80°C for 18 h.

In order to obtain the purified product, LNR was repurified once more by using the same procedure mentioned previously, but a mixed solvent of methanol/acetone (3/1 v/v) was used instead of pure methanol. The purified LNR was allowed to dry in an oven at 80°C for 18 h and consecutively dried in an oven under reduced pressure at 80 °C for 15 h. The purified LNR was weighed and the percentage yield of the product was calculated.

IR (neat): 3050 (m, ν =C-H), 2950, 2850 (s, ν CH₃)
1660 (m, ν C=C), 840 cm⁻¹ (m, =C-H)

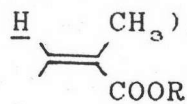
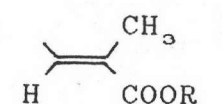
¹H NMR (CCl₄): δ 1.70 (s, 3H, -CH₂-C(CH₃)CH-CH₂-)
2.03 (s, 2H, -CH₂-C(CH₃)CH-CH₂-), 2.08 (d, 2H, -CH₂-C(CH₃)CH-CH₂-)
and 5.20 (s, 1H, -CH₂-C(CH₃)CH-CH₂-)

3.2 Preparation of 2-ethoxyethyl methacrylate

The preparation method of Sittattrakul [20] was used with some modification. A 1-L round-bottom flask equipped with a Dean Stark trap coupled to a water-cooled

condenser was charged with 84.4 mL (86.09 g, 1.0 mol) of freshly purified methacrylic acid, 106.6 mL (99.13 g, 1.1 mol) of purified 2-ethoxyethanol, 2.0 g concentrated sulfuric acid, 0.1 g (4.5×10^{-4} mol) of 2,6-di-tert-butyl-p-cresol, 0.1 g (5.0×10^{-4} mol) of phenothiazine and 250 mL of purified benzene. The mixture was heated to reflux in an oil bath at 100°C for 12 h. The by-product, water, was removed during the refluxing period in a yield of about 18 mL. After cooling to room temperature, benzene was removed by a rotary evaporator. The residue was washed with 5% sodium bicarbonate solution until the wash was basic to litmus paper, then washed again with water. The organic extract was dried over anhydrous sodium sulphate, filtered and distilled under reduced pressure to give 127 g (0.8 mol) of colorless product. (bp $90^\circ\text{C} / 20$ mm Hg)

IR (neat) : 2975, 2875 (s, νCH_3), 1720 (s, $\nu\text{C=O}$), 1640 (m, $\nu\text{C=C}$), 1240, 1040 (s, νas and νs , C-O-C), 1160 and 1120 cm^{-1} (s, b, C-O-C).

^1H NMR (CCl_4): δ 1.2 (t, J = 7.0 Hz, 3H, R-O- CH_2 - CH_3), 1.8 (s, 3H, CH_2 -C(CH_3)-COO-R), 3.53 (q, J = 7.0 Hz, 2H, R-O- CH_2 - CH_3), 3.63 (t, 2H, R-O- CH_2 - CH_2 -O- CH_2 - CH_3), 4.26 (t, 2H, R-O- CH_2 - CH_2 -O- CH_2 - CH_3), 5.55 (m, 1H, ), 6.10 (m, 1H, )

3.3 Preparation of graft copolymer

3.3.1 General procedure

Graft copolymer of LNR and 2-ethoxyethyl methacrylate (2-EEMA) was prepared by solution polymerization. The equipment set-up is shown in Figure 3.2.

To anhydrous copper sulphate (8.0 mg, 2.0×10^{-3} M), N,N-dimethyl aniline (6.06 mg, 2.0×10^{-3} M), concentrated sulfuric acid (1.84 mg, 7.5×10^{-4} M) and 10 mL purified CCl_4 in 50 mL reaction flask was added a solution of liquid natural rubber (0.8515 g, 5.0×10^{-1} M) in 15 mL purified CCl_4 and freshly purified 2-ethoxyethyl methacrylate (2.9662 g, 7.5×10^{-1} M). The mixture was stirred under nitrogen at room temperature for 1 h before it was refluxed in an oil bath at 80°C for 30 h with stirring while the flow of nitrogen was continued to blanket the reaction mixture. The resulting mixture was allowed to cool to room temperature and the separation process was followed.

In order to find an appropriate condition for grafting, a series of reaction mixtures were set up by varying composition of reagents and catalysts and reaction conditions as listed in Table 3.2.

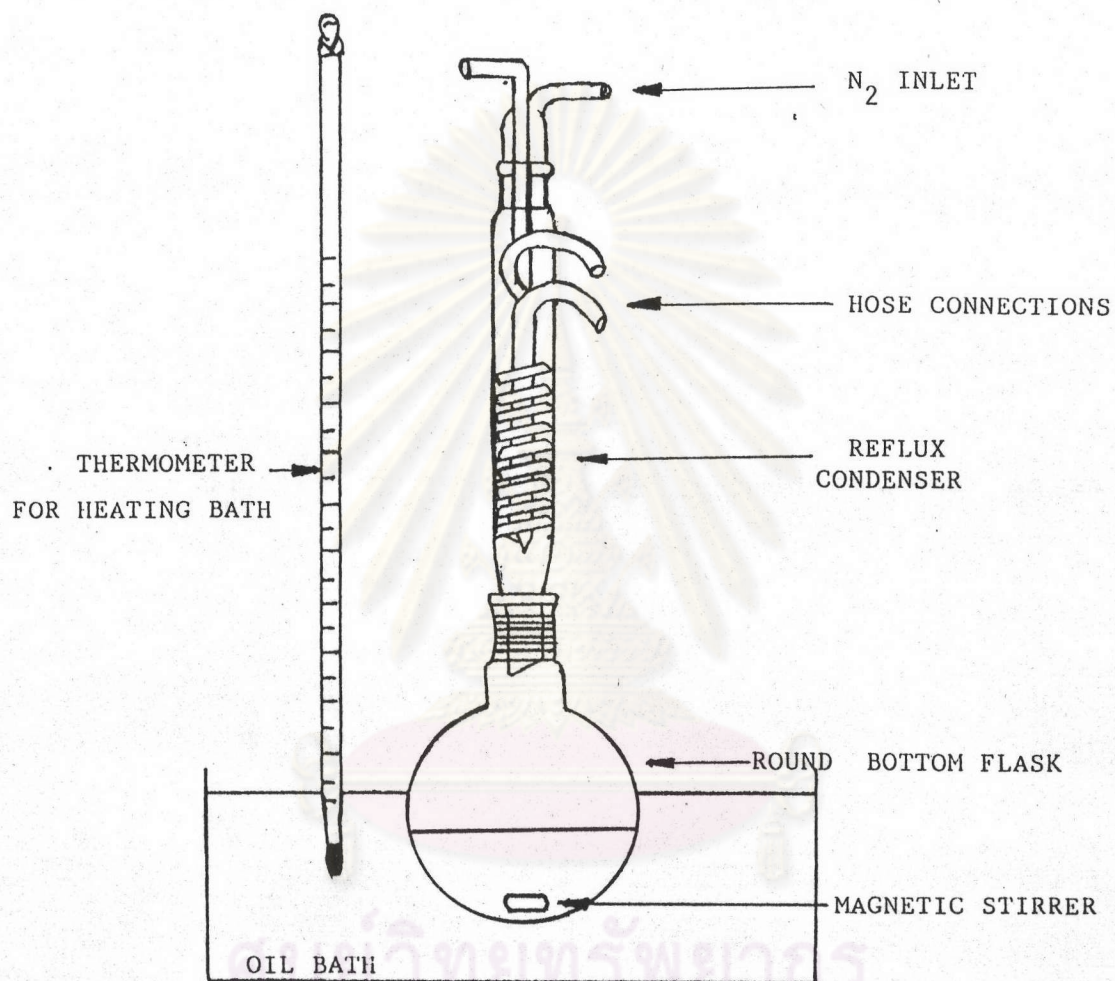


Fig 3.2 Apparatus used for the preparation of graft copolymer.

Table 3.2 Composition of reagents, catalysts and reaction conditions for the preparation of graft copolymer.

Items	Composition / reaction conditions
1. Liquid natural rubber ($\bar{M}_v = 3.3 \times 10^4$)	0.5 M
2. 2-Ethoxyethyl methacrylate	0.1 - 2.5 M
3. N,N-dimethyl aniline	1.0×10^{-3} - 1.0×10^{-2} M
4. Copper salt	1.0×10^{-3} - 1.0×10^{-2} M
5. Conc H_2SO_4	0.0 - 5.0×10^{-3} M
6. Temperature	40 - 100 °C
7. Time	15 - 60 h
8. Type of copper salt	anhydrous copper sulphate, anhydrous copper chloride, copper acetylacetonate, copper acetate monohydrate and copper bromide
9. Type of solvent	carbon tetrachloride, toluene, chloroform and tetrahydrofuran

3.3.2 Separation of homopolymer

The resulting mixture was diluted with a small amount of purified carbon tetrachloride and then filtered. The homopolymer was separated by adding the filtrate dropwise into excess hexane and the solution was centrifuged for 15-20 minutes before the precipitated product was separated by decantation. The decantation contained grafted natural rubber. The homopolymer product was repurified by dissolving it in carbon tetrachloride and the solution was precipitated from excess hexane. The precipitated product was dried in vacuo at 40°C for 24 h before it was characterized by IR and NMR spectroscopy.

IR (neat) : 2975, 2875 (s, ν CH₃), 1730 (s, ν C=O), 1240, 1040 (s, ν as and ν s, C-O-C), 1160 and 1120 cm⁻¹ (s, b, C-O-C)

¹H NMR (CCl₄): δ 1.20 (t, 6H, -CH₂-C(CH₃)-COOCH₂CH₂-O-CH₂-CH₃), 1.67, 1.97 ([s,s], 2H, -CH₂-C(CH₃)-R), 3.53 (m, 4H, R-CH₂-CH₂-O-CH₂-CH₃), 4.13 (s, b, 2H, R-O-CH₂-CH₂-O-CH₂-CH₃)

3.3.3 Separation of grafted natural rubber

The combined decantate was evaporated to dryness by using a rotary evaporator and the residue was consecutively dried in vacuo at 40°C for 24 h. The unreacted monomer remaining in the grafted natural rubber can be removed by twice soaking the crude product with 20 mL of mixture of methanol/H₂O (3/1 v/v) at 40°C overnight. The solution was separated by decantation and the residue was dried in vacuo at 40°C for 24 h. The purified grafted copolymer was weighed and characterized by IR and NMR spectroscopy.

IR (neat) : 3000, 2900 (s, ν CH₃), 1740 (s, ν C=O), 1675 (m, ν C=C), 1250, 1050 (s, ν as and ν s, C-O-C), 1170, 1130 (s, b, C-O-C) and 850 cm⁻¹ (m, =C-H)

¹H NMR (CCl₄): δ 1.2 (m, 6H, R- $\overset{\overset{|}{\text{C}}}{\text{C}}(\text{CH}_3)\text{-COO-C}_2\text{H}_4\text{-O-CH}_2\text{-CH}_3$), 1.67 (s, 4H, RCH=C($\overset{\overset{|}{\text{C}}}{\text{C}}\text{H}_3$) $\overset{\overset{|}{\text{H}}}{\text{C}}\text{-H-CH-R'}$), 1.97 (s, 2H, R'- $\overset{\overset{|}{\text{H}}}{\text{C}}\text{-CH-}\overset{\overset{|}{\text{C}}}{\text{C}}(\text{CH}_3)=\text{CH-R}$), 2.06 (d, 2H, R'- $\overset{\overset{|}{\text{C}}}{\text{C}}\text{-C}(\text{CH}_3)\text{CH-CH}_2\text{-R}$), 3.50 (m, 4H, R-R'-COO-CH₂- $\overset{\overset{|}{\text{C}}}{\text{C}}\text{-O-CH}_2\text{-CH}_3$), 4.03 (s, b, 2H, R-R'-COO- $\overset{\overset{|}{\text{C}}}{\text{C}}\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$) and 5.03 (s, b, 1H, R'- $\overset{\overset{|}{\text{C}}}{\text{C}}\text{-C}(\text{CH}_3)\overset{\overset{|}{\text{H}}}{\text{C}}\text{-CH}_2\text{-R}$)

The extent of grafting was calculated from the following equation:

$$\% \text{ grafting} = \frac{\text{weight of graft copolymer} - \text{weight of LNR}}{\text{weight of LNR}} \times 100 \quad (3.2)$$

3.4 Characterization and testing of the products

3.4.1 General procedure for molecular weight determination of LNR [21]

In a 25 mL-beaker, 0.25 g of purified LNR was dissolved in 20 mL of purified toluene and then filtered through a sinter glass funnel into a 25 mL-volumetric flask. The volume was filled to the mark with purified toluene and thoroughly mixed. 13 mL of this rubber solution was pipetted into an Ubbelohde viscometer which was set-up vertically in a 25°C viscometer bath. After temperature equilibration, the time required for the solution to flow from the upper mark to the lower mark was measured. The average of three measurements was taken as the flow time (t) of polymer solution. The flow time of pure solvent (t_0) was determined in a similar manner. The other measurements at lower concentration of rubber solution were made by dilution method. 2 mL of

purified toluene was added into the first solution in the viscometer and then mixed thoroughly. After allowing the solution temperature to be equilibrated, the flow time of this solution was measured. This procedure was performed again on three other concentrations. For each of the polymer solutions studied, the specific viscosity (η_{sp}) was calculated. To obtain $[\eta]$ for the LNR, plot of η_{sp}/c vs c and linear extrapolation of the plot to $c = 0$ was performed. The molecular weight of LNR can be calculated by using the Mark-Houwink relationship .

3.4.2 General procedure for adhesion testing

The Thai Industrial Standards, " Rubber-based adhesive " (TIS, 521-2527 (1984)) [22] method of testing was followed. Adhesion strength by stripping method (peeling test) was used in this investigation.

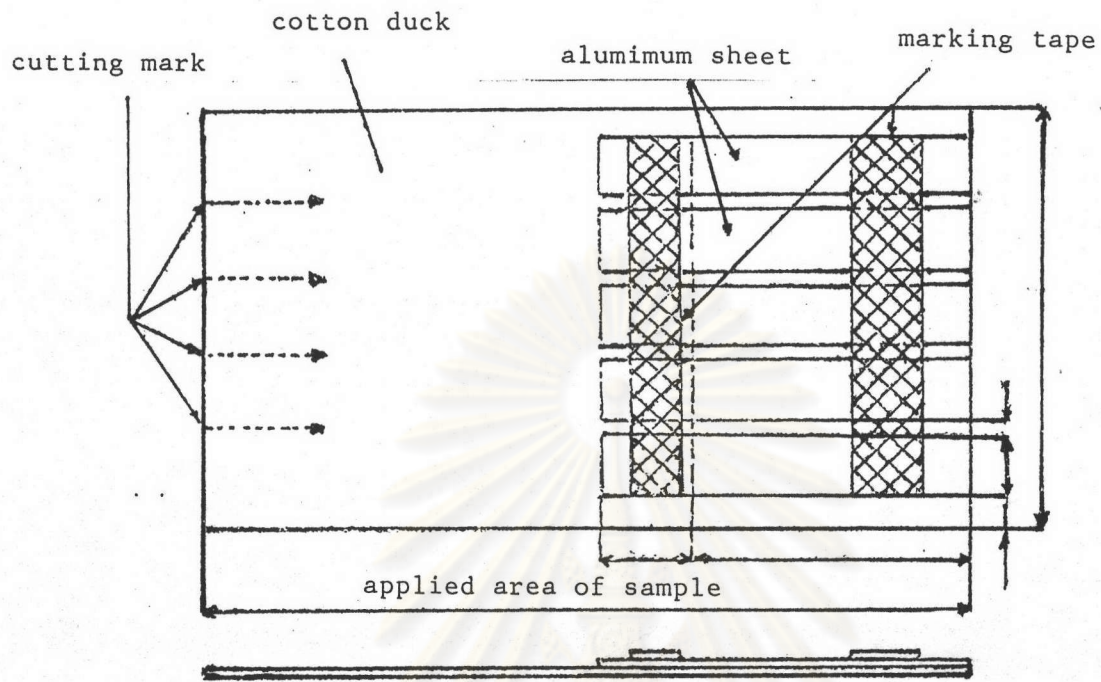
(a) Preparation of test specimens

A group of 5 strips of aluminum sheet, 150 x 25 x 1.6 mm, was polished with a wire brush and then was washed free of dirt and oil by carbon tetrachloride. After the aluminum sheet was dried thoroughly, the test adhesive was applied by brushing

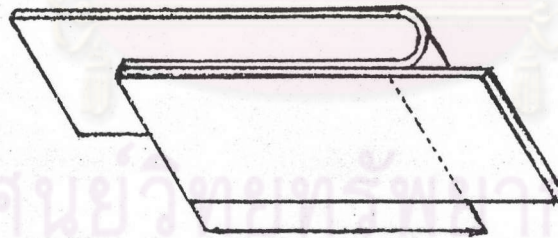
to form a film of about 0.025 mm in thickness. A 312 x 25 mm medium-textured cotton-duck was bonded together with the adhesive-applied aluminum sheet after allowing the surface-drying of the thin film. The specimen was pressed and rolled before it was allowed to age for 24 h. The cutting process was performed and then the testing procedure was followed. Figure 3.3 a shows the preparation of test specimens.

(b) Testing procedure

One side of the test specimen was clamped to a tensile testing machine and the other side was turned back (180 degrees) to the assigned point of the cotton-duck (as illustrated in Figure 3.3 b.) and clamped. The separation force required for three points in every 25 mm on the test specimen was measured with the rate of 50 mm/minute, omitting 25 mm in the first and the last point of the sample. The average of the three measurements was expressed as the force in newton/25 mm. This procedure was performed again on the other four samples in the group and the average of the five measurements was taken as the adhesion strength in peeling of a sample.



(a) a group of test specimens



(b) a test specimen

Fig 3.3 Test specimens for adhesion strength in stripping method : a. preparation of a group test specimens, b. a test specimen