

CHAPTER III

EXPERIMENTAL



Chemicals

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| 1. Natural rubber latex | : Thai rubber latex corporation. |
| 2. Styrene monomer | : Scientific |
| 3. Acrylonitrile monomer | : Scientific |
| 4. Potassium persulfate | : Fluka |
| 5. Sodium dodecyl sulfate | : Fluka |
| 6. <i>tert</i> -Dodecyl mercaptan | : Fluka |
| 7. Isopropanol | : Aldrich |
| 8. Phenol | : Fluka |
| 9. Phosphoric acid | : Fluka |
| 10. Sulfuric acid | : Fluka |
| 11. Sodium hydroxide | : Merck |
| 12. Sodium sulfate | : Carlo Erba |
| 13. Light petroleum ether (b.p. 60-80°C) | : Merck |
| 14. Dimethyl formamide | : Fluka |
| 15. SAN | : Thai Petrochemical Industrial
Co. Ltd., |

Glasswares

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

Equipments

- | | |
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| 1. Infrared Spectrophotometer. | : Perkin Elmer 1706X . |
| 2. Mastersizer | : Malvern 1.1
Serial No 6209 |
| 3. Gel Permeation Chromatograp (GPC) | : Waters 150C |
| 4. Scanning Electron Microscope (SEM) | : JSM 35CF |
| 5. Transmition Electron Microscope(TEM) | : JEM 200CX |
| 6. Two roll mills | : Labtech Engineering
Model LRM200 |
| 7. Cutting machine | : Labtech Engineering
Model LRM 110 |
| 8. Differential scanning calorimeter (DSC) | : Netzsch DSC200 |
| 9. CHNS\O analyzer | : Perkin PE2400
Series 2 |
| 10. Universal testing machine | : Instron 4302 |
| 11. Impact testing machine | : Zwick 1435 |
| 12. Hardness testing machine | : Matsuzaws DXT-1 |
| 13. Flexural testing machine | : Zwick 5102.100/00 |

Procedure

1. Purification of Monomers [20]

The styrene monomer (b.p. 145.2 °C/760 mmHg), contained a trace 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 Na₂SO₄. The dried styrene monomer was distilled in presence of CuCl₂ under reduced pressure (50-60 °C/20 mmHg). Finally, the pure styrene monomer was stored under nitrogen atmosphere in a refrigerator.

The acrylonitrile monomer (b.p. 78 °C/760 mmHg), contained a trace of *tert*-butyl catechol as inhibitor. The acrylonitrile monomer was purified by following the same procedure as the styrene monomer purification and distilled under reduced pressure (40 °C/20 mmHg).

2. Preparation of Graft Natural Rubber

The graft copolymer of styrene and acrylonitrile onto natural rubber was prepared by emulsion graft polymerization. The equipment setup is shown in Figure 3.1. The procedure of preparation of graft natural rubber and the characterization is summarized in Figure 3.2. Figure 3.2 also shows the blending step of the graft natural rubber.

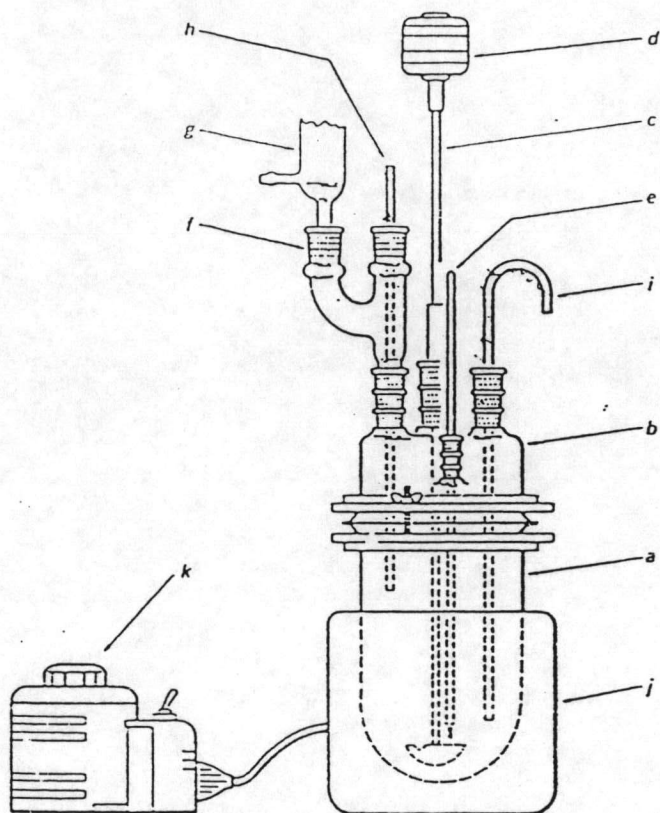


Figure 3.1. Apparatus for graft emulsion polymerization of monomeric styrene and acrylonitrile onto latex natural rubber [21]

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

Flowchart Diagram

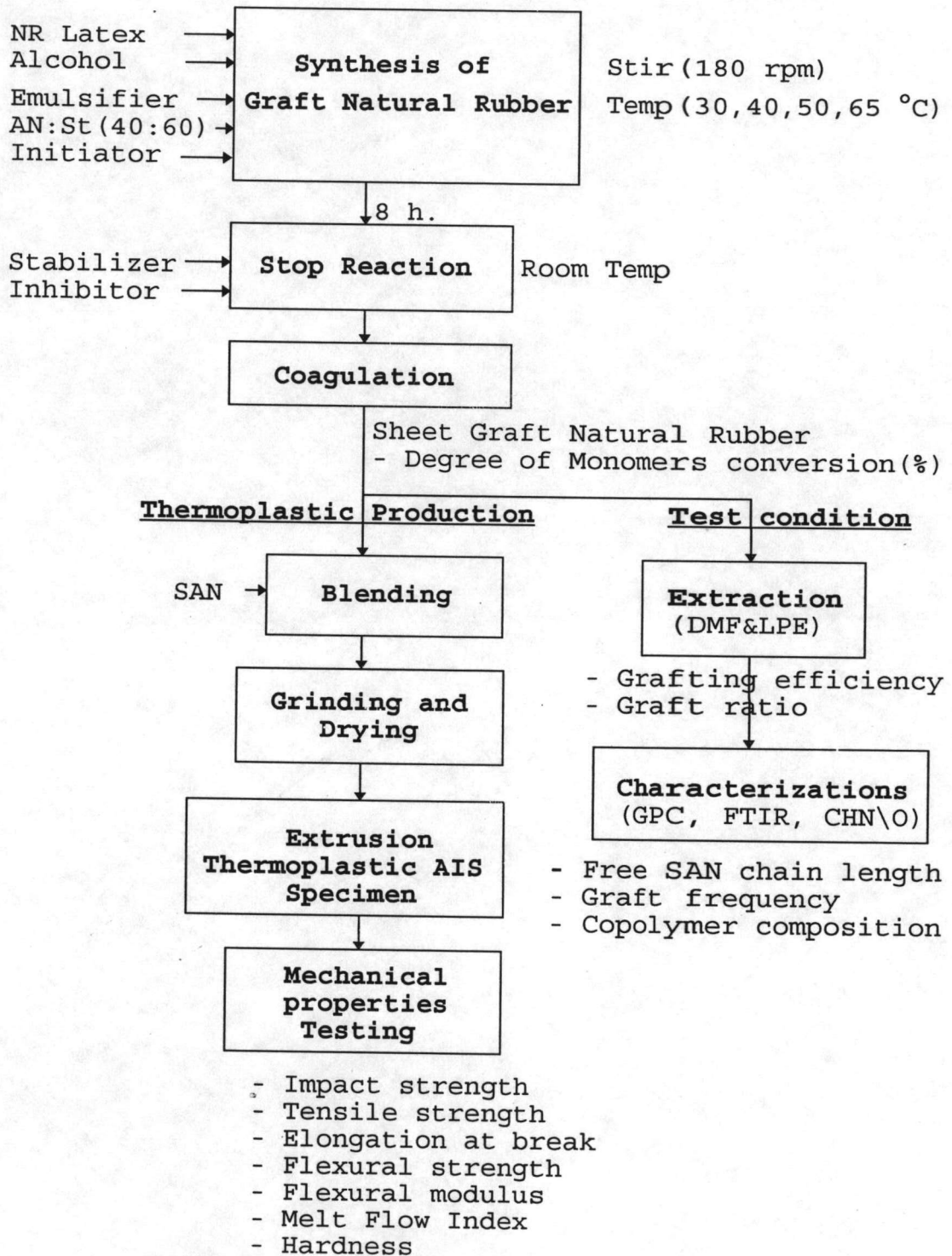


Figure 3.2. Diagram of preparation of graft natural rubber, characterization and blending.

500 ml of water and 0.7 g of potassium hydroxide as an buffer were placed in a 1000 ml bottom reactor fitted with a reflux condenser and nitrogen inlet tube. 300 g of natural rubber latex containing 60.04 % solid was introduced into a mixture at room temperature. The mixture was stirred under of nitrogen atmosphere at room temperature for ten minutes and continuous stirring. Isopropanol (18 g) as stabilizer and 1.8-3.6 g of sodium dodecylsulfate as an emulsifier were added, the mixture was then warmed up to 30-65 °C. After that 100 g of 2.7 % potassiumpersulfate aqueous solution was added. Subsequently, the mixture of 60% of styrene and 40% of acrylonitrile monomers by weight was added. The amount of monomer per 100 g of rubber content was varied such as 30, 50, 75, 100, 150 and 200. The reaction mixture was stirred at constant temperature for 8 hours. After the required reaction time, 1.0 g of phenol as an antioxidant was added, then the reaction was stopped. The graft natural rubber latex was coagulated by casting together with drying. Finally, the sheet of rubbers were obtained, the rubber sheets were dried at 70 °C in vacuum oven.

In order to find an appropriate condition for graft copolymerization, a series of experiments were performed by varying the ratio of monomers to dried solid rubber content, emulsifier concentration and reaction temperature as shown in Table 3.2

Table 3.1. The ranges of parameters investigated in the graft copolymerization.

Monomer (g/100g rubber)	30, 50, 75, 100, 150, 200
Emulsifier (g/100g rubber)	1.0, 1.5, 2.0
Reaction temperature (°C)	30, 40, 50, 65

3. Determination of grafting efficiency

The ungrafted copolymer and free natural rubber remaining in the reaction products could be removed by the extraction process. The ungrafted styrene-acrylonitrile copolymer was extracted by solvent extraction, using dimethyl formamide as extracting solvent while free natural rubber was extracted by lightpetroleum ether [22]. Data obtained from this step were used to calculate the grafting efficiency and graft ratio. The details of all calculations are shown in the Appendix A and C.

Characterization

1. Determination of the core shell of graft natural rubber latex

The core shell formed of graft natural rubber latex samples were investigated by using a Scanning Electron Microscope (SEM) model JSM 35CF and Transmission Electron Microscope (TEM) model JEM 200CX.

2. Determination of Average molecular weight of free SAN

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

Average molecular weight was determined by using GPC model 150C., Waters., operating at 30-40 °C with styragel column Series of 10^3 , 10^4 and 10^5 °A, respectively in the THF solvent. The flow rate was regulated at 1.0 ml/min and using IR detector.

3. Determination of Copolymer Composition

3.1 Fourier Transform Infrared-Spectrophotometry (FTIR) [23, 24]

Infrared (FTIR) Spectra of grafted polymers were operated on the Perkin-Elmer Infrared Spectrophotometer model 1760X. The grafted polymer samples were prepared by casting on NaCl cell. From the FTIR spectra the copolymer composition (acrylonitrile:isoprene:styrene) was determined by peaks area of the specific functional group of acrylonitrile, isoprene, and styrene monomer. Detailed method of measurement and calculation are described in Appendix D

3.2 CHN\O Analyzer

The Elemental Analyzer, model PE2400 Series 2 of Perkin Elmer was used to measure and calculate the copolymer composition. Detailed methods of calculation are described in Appendix E.

4. Differential Scanning Calorimetry (DSC) [25, 26]

The graft natural rubber samples were investigated with a Netzsch Differential Scanning Colorimeter model DSC200. The measurements were carried out over a temperature range of -150 to 300 °C with the heating rate of 10 °C/min., the $N_{2(g)}$ flow rate of 30 ml/min and the sensitivity of 000/Rg500 μ V, under the nitrogen atmosphere. The weight of specimens used was about 10-20 mg.

Blending of graft natural rubber and SAN

The thermoplastic blends were prepared at different ratio of the graft natural rubber and SAN (Styrene acrylonitrile copolymer), 2:8, 3:7, 4:6 and 5:5 by weight.

Blending

The mixture at the required ratio was preheated on the two roll mill for about 5 min. The blending of graft natural rubber and SAN were homogenized on the two roll mill for 10 min. The temperature of the mixing rolls were maintained constant at 180 °C for the front roll and at 170 °C for the back roll. Finally the blended sheet was removed out of the two roll mill and cut into the small chips by the cutting machine.

Injection Molding

The polymer chips with 0.1 %wt of silicone oil feed to the hopper of injection molding machine, the small standard bars and a sheet for the test specimens were obtained. The temperature of injection heating zone and nozzle were 200-250 °C.



Mechanical Testing [27]

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

ASTM D 256: Standard test method for impact resistance.

The test specimens dimension for Cantilever Beam (Izod Type) test is shown in Figure 3.3

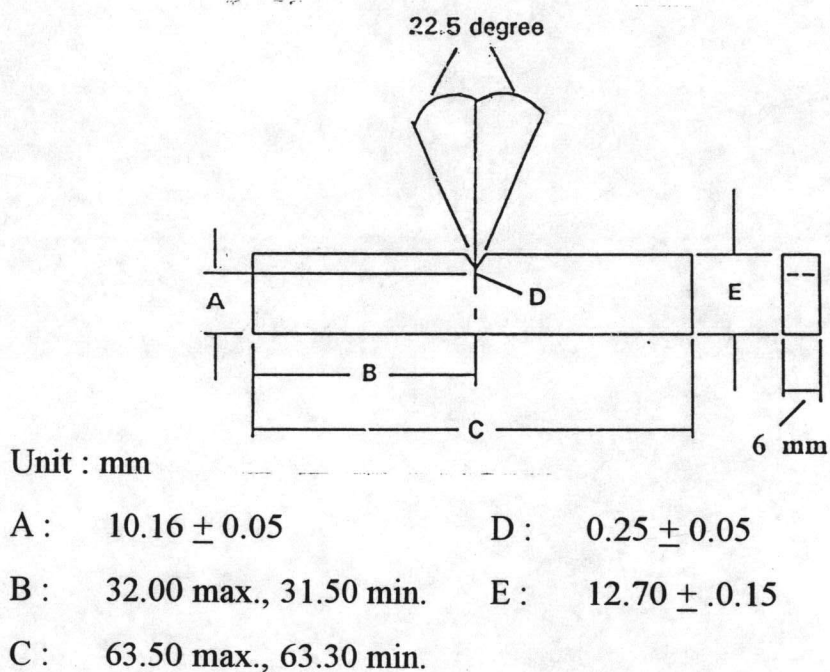
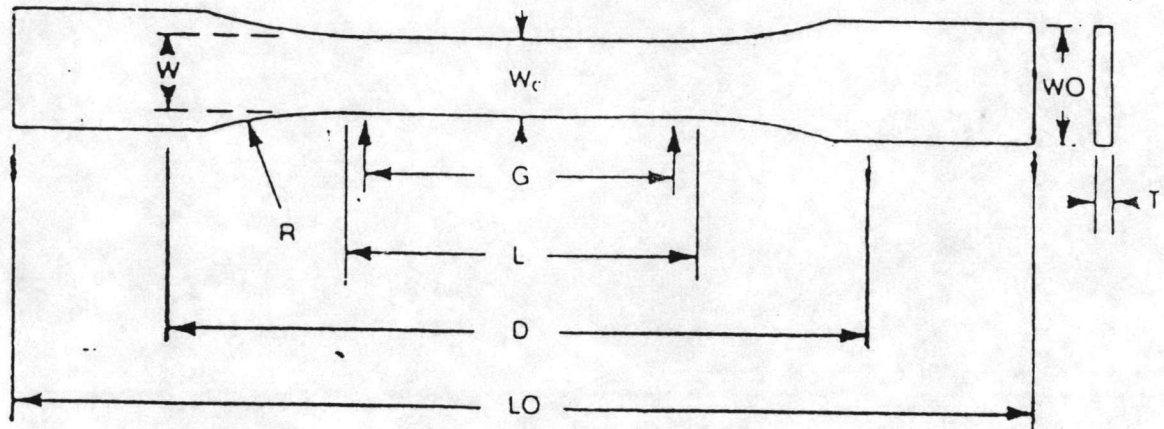


Figure 3.3. Schematic of Izod type test specimen.

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

Temperature :	23.0	°C
Relative humidity :	50	%
Depth of specimen :	10.16	mm
Pendulum capacity :	11.0	J

ASTM D638 : Standard test method for tensile properties.
 The test specimens (type I) dimension is shown
 in Figure 3.4



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

Figure 3.4. 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 D648 : The test method for heat distortion temperature.

At least two test specimens were used. The specimen was 127 mm (5 in.) in length, 13 mm (1/2 in.) depth and by any width from 3 mm (1/8 in.) to 13 mm (1/2 in.). Tolerances on dimensions (for highly reproducible work) were of the order of +0.13 mm (0.005 in.) over the length of the specimen.

The test specimens were conditioned at 23 ± 2 °C (73.4 ± 3.6 °F) and 50 ± 5 % relative humidity for not less than 40 h prior to testing in accordance with Procedure A of Practice D618 for those tests where conditioning is required.

ASTM D790 : Standard test method for flexural properties.

The recommended specimen for molding material was 127 by 12.7 and by 3.2 mm (5 by 1/2 by 1/8 in.) tested flatwise on a support span, resulting in a support span to depth ratio of 16 (tolerance +4 or -2). Thicker specimens were avoided if they exhibited significant shrink marks or bubbles when molded.

The test specimens were conditioned at 23 ± 2 °C (73.4 ± 3.6 °F) and 50 ± 5 % relative humidity for not less than 40 h prior to testing in accordance with Procedure A of Practice D618 for those tests where conditioning is required.

ASTM D785 : Standard test method for Rockwell 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 parallel 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 adage.

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 conditions in testing were shown as follows :

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

All of the properties measured, at least three samples were tested to obtain a reliable average and standard deviation.