

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals

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. *tert*-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.,

### 3.2 Instruments and Apparatus

#### 1. Batch Reactor

The apparatus consists of four parts as follows :

##### a) *Reactor*

The reactor is a high pressure batch stirred autoclave model 4551 from the Parr Instrumental Company with 3750 cm<sup>3</sup> stainless steel 316 cylindrical bomb, split ring closures and bomb heater. The reactor can work in a pressure range 0-2000 psi and in the temperature range of 0-450 °C.

##### b) *Reactor fittings*

The stirred reactor is equipped with convenient valves and fitting.

##### c) *Automatic temperature controller*

The controller used is model 4842 PID controller from Parr Instrumental Company. It is operated with a dual thermocouple. There are various enhancement modules to assist in monitoring and controlling the temperature, pressure, and stirring speed. The range of stirring speed can be adjusted in the range of 0-1000 rpm.

##### d) *Gas controller system*

The system consists of a nitrogen tank with a pressure regulator.

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2. Infrared Spectrophotometer.	: Perkin Elmer 2000 .
3. Mastersizer	: Malvern 1.1 Serial No 6209
4. Gel Permeation Chromatograph (GPC)	: Waters 150C
5. Scanning Electron Microscope (SEM)	: JSM 35CF
6. Transmission Electron Microscope(TEM)	: JEM 200CX
7. Two roll mills	: Lab Tech engineering company LTD.
8. Cutting machine	: Bosco
9. Injection molding mechine	: Boy 225
10. Differential Scanning Calorimeter (DSC)	: Netzsch DSC200
11. CHNS/O analyzer	: Perkin Elmer PE2400 Series 2
12. Universal testing machine	: Instron 4302
13. Impact testing machine	: Zwick 1435

### 3.3 Procedure

#### 3.3.1 Natural rubber latex analyses

##### *Natural Rubber latex*

The natural rubber latex consist of particles of rubber hydrocarbon and non-rubber constituents suspended in an aqueous serum phase. The composition of natural rubber latex is presented in Table 4.1. The molecular weight was analysed by the gel permeation chromatography and the GPC chromatogram of natural latex is shown in Figure 4.1. The particle size analysis was made by the Mastersizer and the average diameter and size distribution of rubber particle is shown in Figure 4.2.

### 3.3.2 Purification of monomers [21,22]

The styrene monomer (b.p. 145.2°C/760 mmHg) [20], 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 Na<sub>2</sub>SO<sub>4</sub>. The dried styrene monomer was distilled in the presence of CuCl<sub>2</sub> 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) [20], contained a trace of *tert*-butyl catechol as inhibitor. The acrylonitrile monomer was purified as above and distilled under reduced pressure (40°C/20 mmHg).

### 3.3.3 Preparation of Grafted Natural Rubber

The graft copolymer of styrene and acrylonitrile onto natural rubber was prepared by emulsion polymerization. The equipment for preparation is shown in Figure 3.1 and 3.2. The procedure for the preparation of graft natural rubber and characterization is summarized in Figure 3.3 which also shows the blending step of the graft natural rubber.

Natural rubber latex (300 g) was charged to a polymerization reactor along with 500 mL of water and 0.7 g of potassiumhydroxide as a buffer and were deoxygenated by bubbling nitrogen with stirring for at least 10 min. through the diluted. The nitrogen flow rate was then reduced to a low level before the addition 18 g of isopropanol as stabilizer and 2.7 g of sodiumdodecylsulfate as an emulsifier were added, after which the mixture was warmed to the reaction temperature, 2.7 g of potassiumpersulfate as an initiator was added. Then, the mixture of 60 % styrene monomer and 40 % of acrylonitrile monomer by weight was added. The reaction was then allowed to proceed for 8 hours. under continuous stirring. After the required reaction time, 1.0 g of a phenol antioxidant was added, then the reaction was stopped. The grafted 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

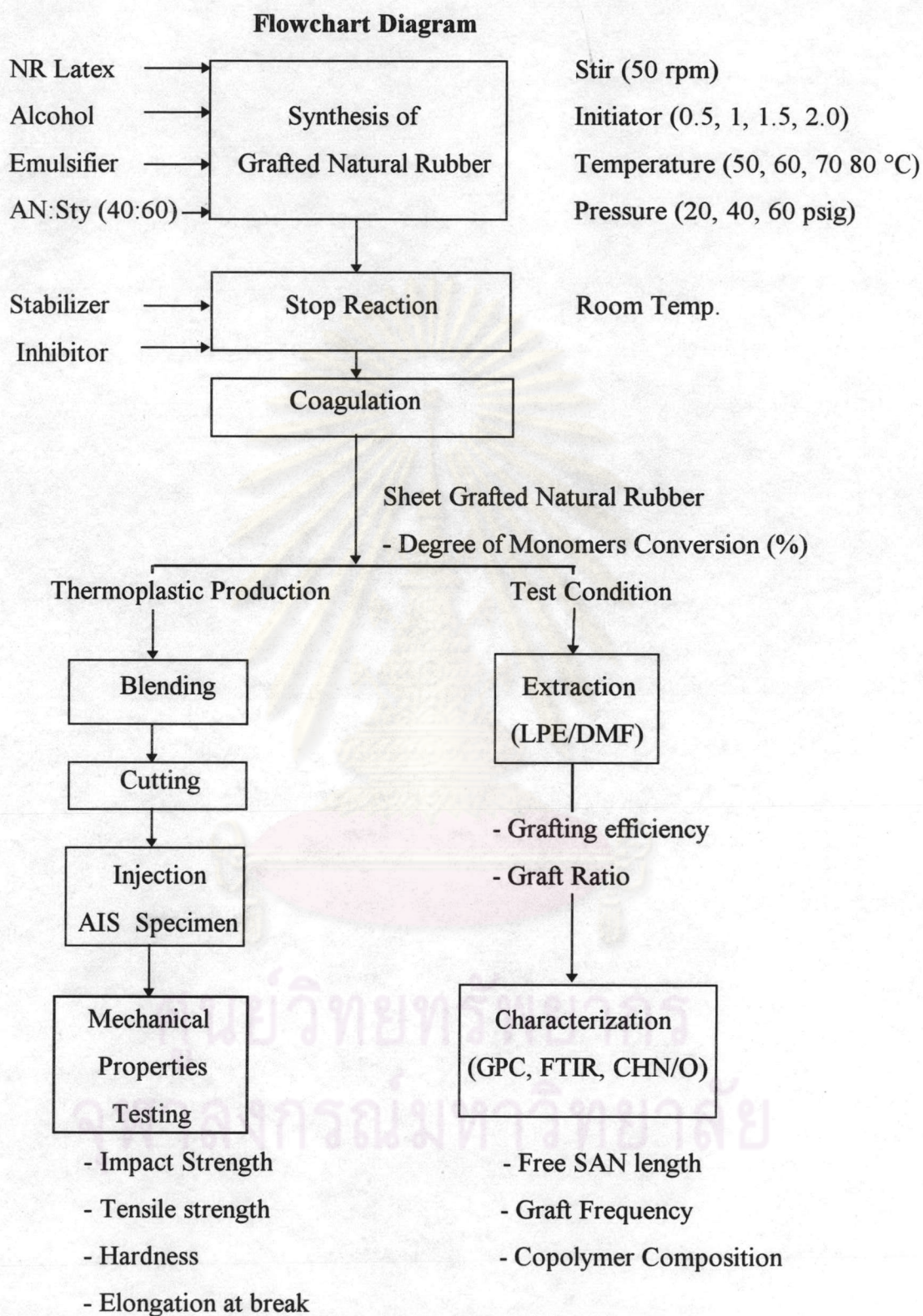
vacuum oven. The dried sheet was leached in deionised water to remove any water-soluble impurities from the rubber. The sheet was then returned to the vacuum oven until it was thoroughly dry.

In this experiment, the appropriate conditions for graft copolymerization were studied by varying the initiator concentration, reaction temperature and pressure (Table 3.1).

**Table 3.1.** The variation of parameters investigated in the graft copolymerization

Initiator (g/100 g of monomer)	0.5, 1.0, 1.5, 2.0
Temperature( °C)	50, 60, 70, 80
Pressure (psig)	0, 20, 40, 60

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**Figure 3.1.** Preparation of grafted natural rubber, characterization and blending.

### **3.4 Characterization**

#### **3.4.1 Determination of grafting efficiency and graft ratio**

The ungrafted copolymer and free natural rubber remaining in the reaction products could be removed by extraction. The ungrafted styrene-acrylonitrile copolymer was extracted by solvent extraction, using dimethylformamide as extracting solvent while free natural rubber was extracted by light-petroleum ether. 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.

#### **3.4.2 Determination of the morphology of grafted natural rubber latex**

The morphology of grafted natural rubber latex samples, was studied by a scanning electron microscope (SEM) and transmission electron microscopy (TEM).

#### **3.4.3 Determination of average molecular weight of free SAN**

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

Average molecular weight was determined by GPC. Operating at 30-40 °C and THF solvent. The flow rate was set at 10 ml/min. Both the UV and IR detectors were used.

#### **3.4.4 Determination of graft copolymer composition**

##### **a) Fourier-Transform Infrared-Spectrophotometry (FT-IR)[23,24]**

The grafted polymer samples were prepared by casting on KBr discs. From the FT-IR spectra the copolymer composition (acrylonitrile:isoprene:styrene)

was determined by peaks area of the specific function group of acrylonitrile, isoprene, and styrene monomer. The FT-IR spectra are shown in Appendix C.

#### b) CHN/O Analyzer

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

### **3.4.5 Determination of thermal properties of the grafted natural rubber**

The glass transition temperature,  $T_g$ , was measured using the differential scanning calorimeter (DSC). DSC 2000. Data were recorded at scanning rate of 10 C/min. against a baseline scan. Temperature ranges of the scans were -100 to 150 °C with nitrogen flow rate of 30 ml/min. and the sensitivity of 000/Rg500  $\mu$ V, under the nitrogen atmosphere. The weight of the specimens used was 10-20 mg.

### **3.5 Blending of grafted natural rubber and SAN**

The thermoplastic blends were prepared at different ratio of the grafted natural rubber and SAN (styrene acrylonitrile copolymer), 20:80, 30:70, 40:60 and 50:50 by weight.

#### Blending

The mixture at the required ratio was preheated on the two roll mill for about 5 min. The blending of grafted 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 back roll. Finally the blended sheet was removed out of the two roll mill and cut into the small chips by the cutting machine.



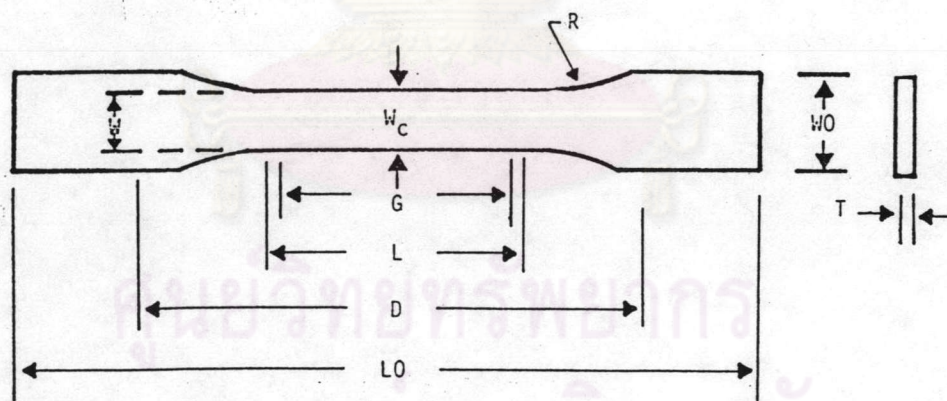
### Injection Molding

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.

### 3.6 Mechanical Testing

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

ASTM D638: Standard Test Method for Tensile Properties  
The test specimens dimension (type I ) is shown in Figure 3.4



W : 13 mm

W<sub>0</sub> : 19 mm

G : 50 mm

R : 76

L : 57 mm

L<sub>0</sub> : 165 mm

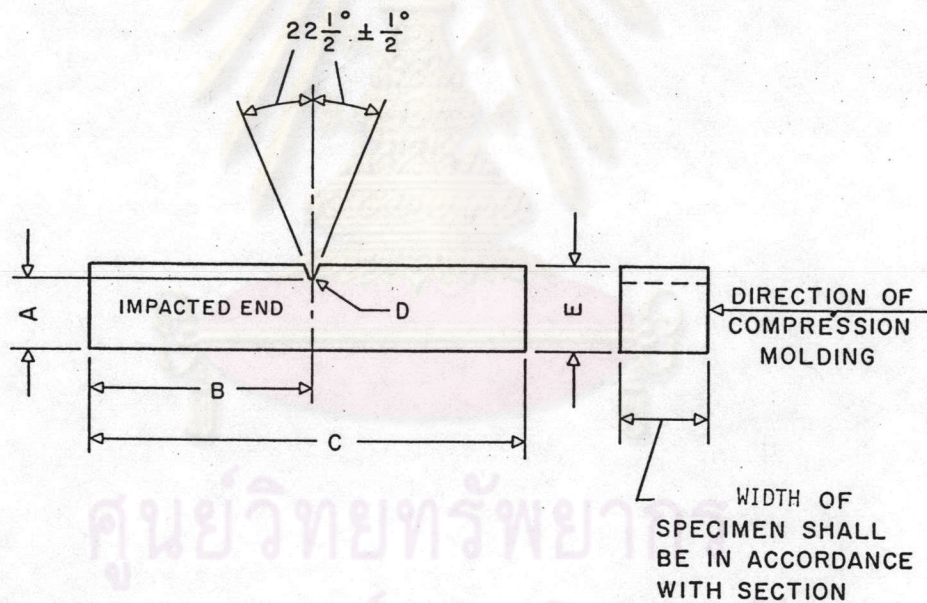
D : 115 mm

**Figure 3.2** Schematic of tensile test specimen (type I)

The tensile testing condition

Temperature	25.0	°C
Relative humidity	50	%
Speed of testing	10	mm/min.
Gage length	50	mm
Distance between grips	115	mm

ASTM D 256: Standard test method for impact resistance.  
The test specimens dimension for Cantilever Beam  
(Izode-type) test is shown in Figure 3.5



Unit : mm

A : 10.16 $\pm$ 0.05	D : 0.25 $\pm$ 0.05
B : 32.00 max, 31.50 min	E : 12.70 $\pm$ 0.15
C : 63.50 max, 60.30 min	

Figure 3.3 Schematic of Izod type test specimen.

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

Temperature :	25	°C
Relative humidity :	50	%
Pendulum capacity :	2.0	J
Depth of specimen :	10.16	mm

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 were not 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 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 five samples were tested to obtain a reliable average and standard deviation.