CHAPTER III

EXPERIMENTAL METHODS

3.1 Purification of Pyrrole Monomer

Pyrrole, from Fluka, was purified by distillation under reduced pressure at 50-70^{o}C/mmHg. It was kept under nitrogen atmosphere at 4^{o}C before used.

3.2 Preparation of Natural Rubber Sheet

The natural rubber sheet was prepared by the electrodecantation method. The equipment setup is shown in Figure 3.1. The sheet can be grown to various thickness on the working electrode of the cell with different voltage and time during which a current is applied across the cell. The parameters investigated in the preparation of natural rubber sheet are shown in Table 3.1.

Table 3.1 Preparation of natural rubber sheet with various voltage and time at room temperature.

Voltage (volt)	1 - 10
Coagulation time (minute)	4 - 60

3.3 Preparation of Conductive Natural Rubber by Electrochemical Method.

Incorporation of polypyrrole onto the prepared natural rubber films was carried out in an electrochemical cell. This is shown in Figure 3.2 (see section 1st method).

The cell (Figure 3.1) was used for the electrochemical preparation of a multi-component system incorporating polypyrrole onto prepared natural rubber sheet. In the preparation, 20 ml of various $LiClO_4$ concentration in methanol was added to the reaction bottle. After 0.05 M pyrrole monomer was added to the reaction bottle, coagulated natural rubber sheet on the palladium (Pd) working electrode, was placed in the reaction bottle. An additional current was passed though the solution containing pyrrole monomer at various voltage. While the current was applied across the cell, pyrrole polymerized on the rubber sheet and conductive natural rubber occurred on the working electrode. The conductive natural rubber sheet was

subsequently washed with methanol, from Fluka, until methanol solution was colorless. The conductive natural rubber sheet was washed with acetone again. Samples were stored in either : (i) in the vacuum dried desiccator at room temperature; and (ii) in open air (in contact with moisture at atmospheric condition).

In order to find an appropriate condition for the preparation of conductive natural rubber, a series of experiments were performed by varying $LiClO_4$ concentration, voltage, reaction time, reaction temperature and atmospheres as detailed in Table 3.2.

Table 3.2 The variation of parameters investigated in the production of conductive natural rubber.

$LiClO_4$ concentration [M]	0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0
Reaction voltage (volt)	1 to 5
Reaction time (minute)	1 to 10
Reaction temperature (^oC)	0, 10, 25, 55, 60
Reaction atmospheres	Nitrogen Gas Flow and Open Air

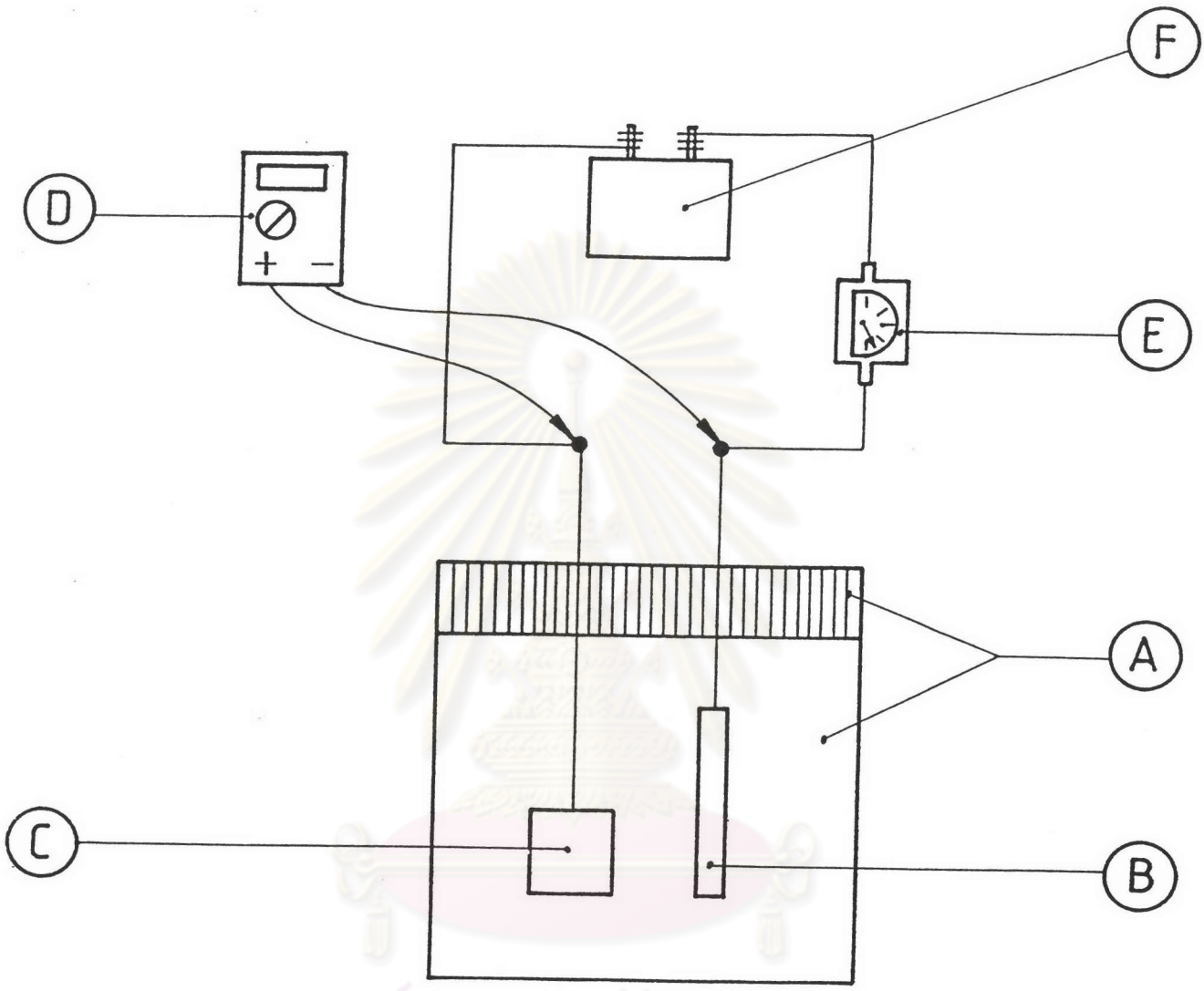

Figure 3.1 Apparatus for conventional electrolysis.

A) Reaction bottle and cover

B) Cathode electrode

C) Anode electrode

D) Voltmeter

E) Ammeter

F) Current supply

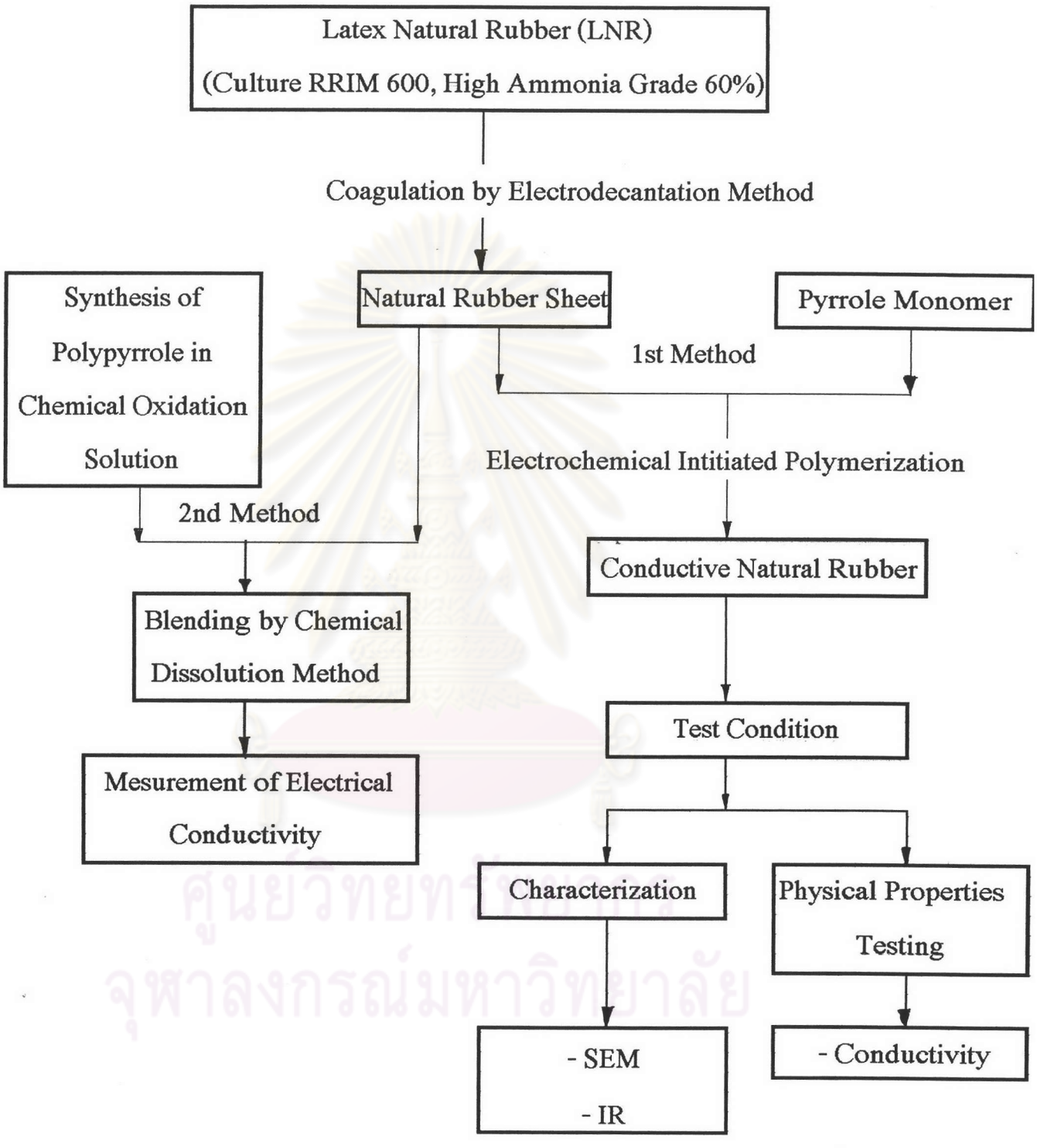

Figure 3.2 Preparation of conductive natural rubber and characterization.

3.4 Preparation of Conductive Natural Rubber byChemical Dissolution.

The procedure of preparation of conductive natural rubber by chemical dissolution method shown diagramatically in Figure 3.2 utilized equipment setup in Figure 3.3 [26]. Thanawadee (1993) studied the synthesis of polypyrrole by chemical oxidation polymerization, Ferric chloride solution in methanol was added into 100 ml three - neck glass reactor equipped with mechanical stirrer, gas inlet tube for bubbling the oxygen - free nitrogen, calcium chloride tube and a septum. Oxygen-free nitrogen gas must be passed though silica gel, pyrrogallol and concentrated sulfuric acid before flowing to the $FeCl_3$ solution at 0°C for 1 h. After that 1 ml of distilled pyrrole monomer was injected under vacuum through septum by syringe into solution with continuous stirring. The polymerization was carried out at 0°C for 20 minutes. A black powder formed almost instantaneously, and as the reaction progressed the color of the solution turned from rusty organic to green. The polymerization reaction was quenched by adding copious amount of solvent (methanol) in order to dilute $FeCl_3$ solution. The polymer power was filtered and washed with methanol until the filtrate was colorless and contained no Fe (II), as indicated by testing with KSCN. The polymer powder was washed with acetone and vacuum dried in a desiccator at room temperature.

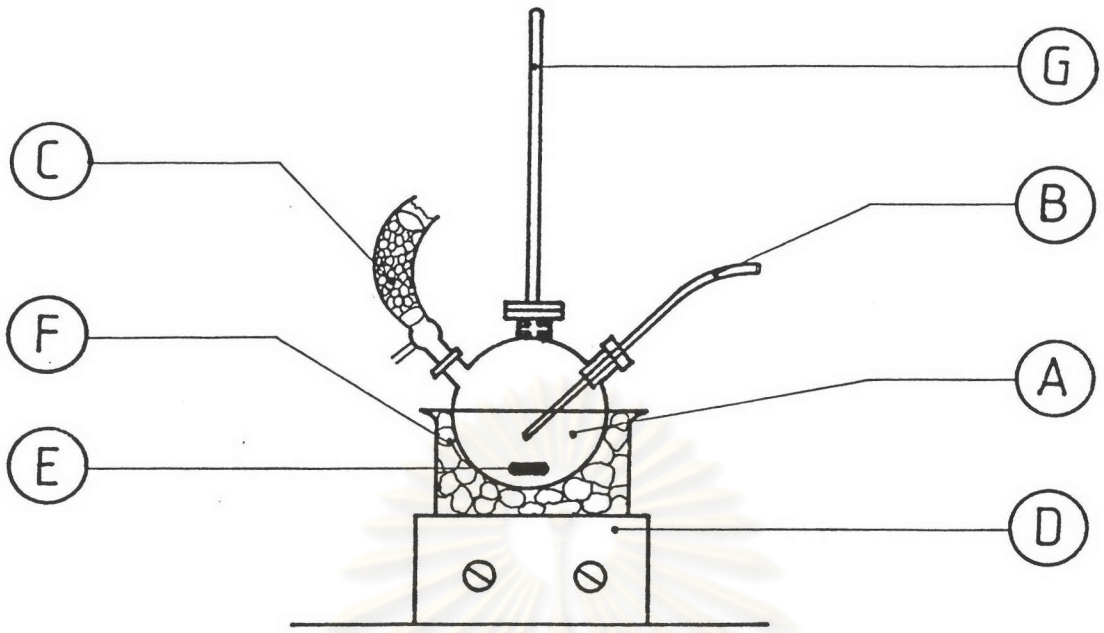

Figure 3.3 Apparatus for chemical solution method [26].

A) 3 - Neck round - bottom flask

B) Nitrogen - inlet tube

C) Drying tube

D) Mechanical stirrer

E) Magnetic bar

F) Ice - bath

G) Stand and Clamp

After that the dissolution of natural rubber sheet with toluene solvent, powder polypyrrole was added in a 500 ml beaker. The mixture was stirred at 50°C for 24 h. Several blends were prepared with the amount of polypyrrole per 1 gram of mixture varied as 10, 30, 50 70 and 90 %w. The sheet of conductive natural rubbers were obtained by pouring the mixture on a plate and let toluene evaporated off. The rubber sheets were dried at 50°C

in vacuum oven. After that CNR was pressed into disc form and conductivities were measured (see section 3.5).

3.5 Determination of Electrical Conductivity of Conductive Natural Rubber [see Appendix A].

The electrical conductivity of prepared conductive natural rubber by electrochemical method was measured by Van der Pauw method immediately after preparation at room temperature. But for prepared conductive natural rubber by chemical oxidation method, polymer composites film (polypyrrole and NR) was first pressed into disc form ($\varnothing$ = 1.20 cm) by hydraulic press at 2 ton for 10 minute in special evacuable die. After that the conductivities of these pressed disc composites were measured by Van der Pauw method at room temperature.

3.6 The Decay Conductivity of Disc Polymer Conductive Natural Rubber Sheet.

Samples of conductive natural rubber sheet, as obtained in section 3.3, were first measured for their conductivities, then they were separately kept in open air and dry air (in desiccator). The samples were tested several times for their conductivities as time passed for 150 days.

3.7 The Stability of the Conductivity of Conductive Natural Rubber Sheet in Acid or Base Solution.

Conductive natural rubber sheets, as obtained in section 3.3, were separately exposed to sulfuric acid solution and sodium hydroxide solution. The concentration of each solution was varied from 0.25 M to 1.00 M. The samples were kept in the solution at room temperature for 7 days, then they were washed with deionized water and kept to dry in a desiccator under reduced pressure. The conductivity of each sample was measured by Van der Pauw method and recorded.

3.8 Determination of the Morphology of Conductive Natural Rubber Sheet.

Samples of conductive natural rubber sheet, as obtain in section 3.3, were taken for morphology studies using a Scanning Electron Microscope (SEM) model JSM 200 CX. Pictures of these samples were taken at the magnifications of 1000 and 3500 times.