



CHAPTER III EXPERIMENTAL

3.1 Materials

In this research, the natural rubber latex used as the substrate for electrochemical polymerization was provided by Rubber Research Institute, ~60% DRC.

The anionic surfactant, selected in this experiment was Sodium Dodecyl Sulfate (SDS). A schematic of the chemical structure of SDS is shown in the Figure 3.1. SDS was purchased from Aldrich Chemical Company, Ltd. with 99% purity^[89]. According to Rosen (1996) the CMC of SDS was determined to be $\sim 1.58 \times 10^{-3}$ mol/dm³ at 25°C.

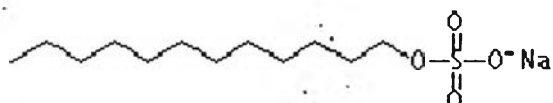


Figure 3.1 Schematic of SDS.

Hydrochloric acid used as doping agent and for adjusting PH.

The pyrrole monomer (Aldrich) was first purified by distillation at 131°C and thereafter stored and refrigerated at 4°C before using in polymerization. Pyrrole monomer : purum 97% GC, Mr =67.06, bp =120-131°C, d_{4}^{20} =0.970.

The thiophene monomer (Fluka) was first purified by distillation and thereafter stored refrigerated at 4°C before using in polymerization. Thiophene monomer: purum 98% GC, Mr= 84.14, bp=82-84 °C, d_{4}^{20} =1.063 contain 0.2% benzene.

3.2 Equipment

NR latices were purified by centrifugation at 10000 rpm/20 min with two cycles at 20°C by centrifugator, Hermle Z383K. A particle size analyzer (Mastersizer X) was used to measure the particle size of the NR latex particles (45 mm lens, active beam length 2.4 mm). A thermogravimetric-differential thermal analyzer (Perkin Elmer, Pyris Diamond) was used to study the thermal stability and the decomposition temperature. The morphology of the conductive polymer were observed by scanning

electron microscopy (JEOL JSM-5200) and transmission electron microscope (TEM) (JEOL JEM-2100) at 200 kV. SEM digitized photographs were obtained with a magnification range between 1000-5000x using an acceleration voltage of 15 kV. Tensile testing was carried out using a Lloyd LRX universal testing machine under ASTM D882-91 and an Instron universal testing machine under ASTM 638M-91a. Surface and volume resistivity were measured by using a resistivity Test Fixture (Keithley Model 8009) and an electrometer/high resistance meter (Keithley 6517A). The structure determined by FTIR absorptions using the horizontal attenuated total reflection accessories (Nexus 670, HATR flat plate system with 45 °C ZnSe crystal) to measure the spectra of materials. The density of the specimens was measured using the Sartorius approach, model :YDK01.

All of the above instruments and ASTMs are summarized in the Tables 3.1 and 3.2, respectively.

Table 3.1 Parameters to be measured for admicelled rubber properties

Parameters	Instrument / Technique
Prepared and purified natural rubber	-Hot plate and magnetic stirrer -Centrifugator, Hermle Z383K (at 10000 rpm/20 min) (ASTM 1076-02)
Particle Size	-Particle Size Analyzer (Mastersizer X Ver 2.15) (45 mm lens, active beam length 2.4 mm)
Thermal properties and amount of polymer formed	Thermogravimetric Analyzer (Perkin Elmer, Pyris Diamond) Thailand co.,ltd
Surface morphology	Scanning electron microscope (SEM) (JEOL JSM-5200) with magnification range between 1000-5000 times using voltage 15 kv
Atomic morphology	Transmission electron microscope (TEM) (JEOL JEM-2100)

Tensile testing	-Lloyd LRX Universal Testing Machine (ASTM D882-91) -Instron Universal Testing Machine under (ASTM638M-91a)
Functional group	Fourier Transform Infrared Spectroscopy (FTIR) (Nexus 670, HATR flat plate system with 45°C ZnSe crystal)
Surface and volume conductivity	Resistivity Test Fixture (Keithley Model 8009) and Electrometer/High Resistance Meter (Keithley 6517A). (ASTM D257-99)
Density	Sartorius approach, model :YDK01

Table3.2 Rubber compound test method

Property	Method	Instrument
Tensile properties (Max stress, MPa Elongation to break, % modulus, MPa)	ASTM 638M-91a ASTM D882-91	Instron Model 1011 Lloyd Instruments LS 500
Hardness, Shore A and Shore D	ASTM D2240	Lever Loader Model 716

3.3 Methodology

3.3.1 Particle Size Measurement

The particle sizes of the natural rubber was determined by a particle size analyzer, Masterizer X version 2.15 (Malvern Instruments Ltd.). The lens used in this experiment was 45 mm for particle size 0.1-80 μm and active beam length was set at 24 nm. The sample was placed in a sample cell across a laser beam. This machine analyzes the average particle size and standard size distribution from the laser beam depending on the beam length parameter. Consequently, the specific surface area is calculated from the particle diameter with the assumption of constant volume of spherical particle.

A droplet of surfactant was added in a stirring water chamber in order to help the distribution of natural rubber in water. After that, 0.03 vol% of natural rubber aqueous solution was suspended in a stirring water chamber.

3.3.2 Preparation of the Rubber in Surfactant as Bilayer Forming

The rubber latex has a 60%wt dried solid content. Rubber latex (4-8 g) was mixed with 50 ml distilled water and centrifuged two times at 20°C, 10000 rpm for 20 minutes to removed dissolved impurities. The 25 g of latex was separated in 10 ml dilute water. Then the rubber latex was mixed with surfactant solution, SDS, 16 mM, in 490 ml dilute water to obtain a 500 ml total volume, then using HCl to maintain the pH of the solution at 3.0, which is the pH below the point of zero chart. Then, it is stirred four hours (Chantarak, S. 2006)¹² to overnight to let the surfactant molecules form the bilayer at the surface of the rubber particles.

3.3.3 Preparation of Conductive Natural Rubber by Electrochemical Method

The pyrrole or thiophene solution, (20–800 mM, 0.69–27.66 ml), was added and left for 1 hour. Next, the apparatus for electrolysis was set up and the aqueous solution was poured into the reaction bottle. Then, an additional current was passed through the solution containing the pyrrole or thiophene monomer at various voltages (1-15 V). While the current was applied across the cell, pyrrole, thiophene polymerized on the rubber latex solution by forming the admicellar structures and conductive natural rubber was deposited on the cathode electrode (copper with a diameter of around 3x10 cm) as shown in Figure 3.2.

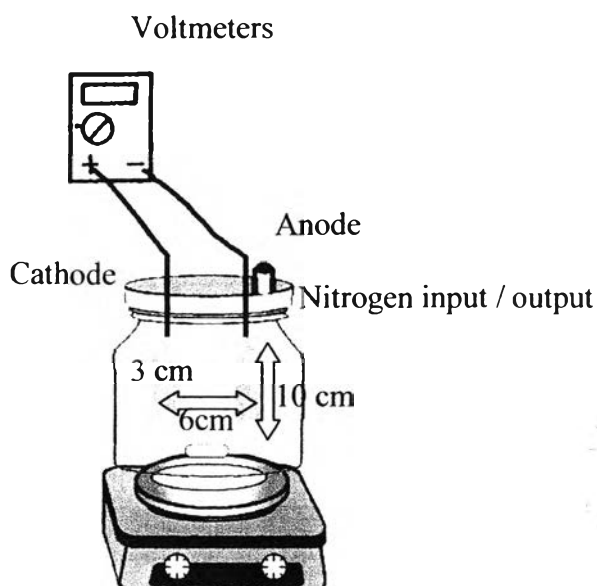


Figure 3.2 Apparatus for admicelled polymerization with electrolysis. It consists of a reaction bottle and cover, cathode and anode electrodes, voltmeter, ammeter, current supply, hot plate, and magnetic stirrer.

At each hour, the electro-polymerization, both pH, mass on the electrode were checked and the new electrode was replaced. At the same time, the pH of the samples was checked and adjusted to $\text{pH} < 3.0$ at all times. Because pH below the point of zero charge (PZC): surface exhibit (+) : Anionic surfactant can adsorb

pH at $\text{EM} = 0$: Point of zero charge

pH at $\text{EM} < 0$: surface exhibit (+) : Anionic surfactant can adsorb

pH at $\text{EM} > 0$: surface exhibit (-) : Cationic surfactant can adsorb

A higher amount of surfactant can adsorb and improve the coating of the pyrrole and thiophene monomer. It can result in higher conductivity properties.

Next, the dark solid rubber on the working electrode was washed off with water and taken to determine the weight, followed by drying in a vacuum oven at 70°C for 12 hours to obtain a black sheet with a constant weight. The weight was again determined. The solution color changed from white to black and finally clears for polypyrrole. However, the color of polythiophene was changed from cream to brown.

3.3.4 Morphological study

There are two steps for the morphological study. Firstly, studying the admicellar formation during the application of various voltages by using a transmission electron microscope (TEM, JEOL 2100). TEM was operated by using the electron instead of light. The solution samples were taken by using the grid at randomly position. Then, specimens were looked at the views screening of TEM. TEM can operate by using the light source at the top of the microscope; it emits electrons through the vacuum in the column of the microscope. At the bottom of the microscope the unscattered electrons hit a fluorescent screen, which gives rise to a shadow image of the specimen with its different parts displayed in varied darkness according to their density, as shown in Figure 3.3. The image can be studied directly by the operator or photographed with a camera in different sizes (Table 3.3).

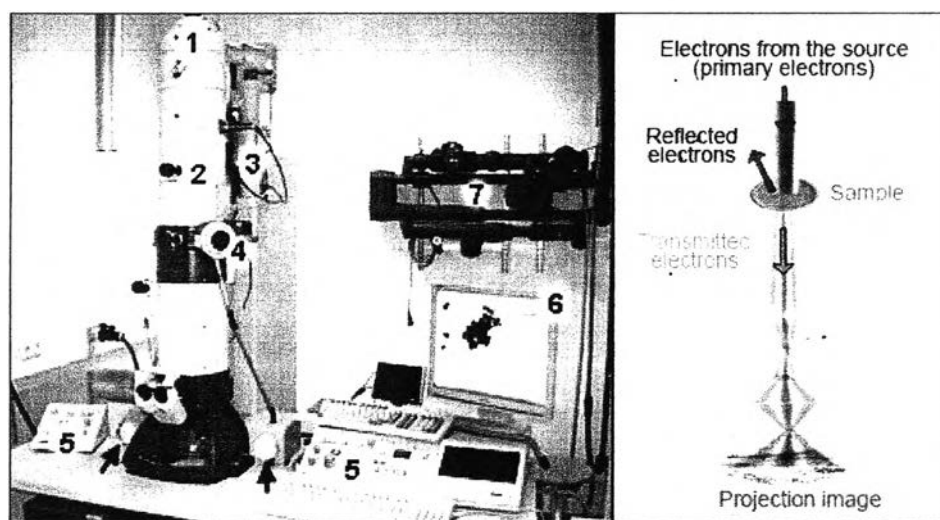


Figure 3.3 Transmission electron microscope (TEM)

1. Electron cannon in the upper part of the column.
2. Electro-magnetic lenses to direct and focus the electron beam inside the column.
3. Vacuum pump system.
4. Opening to insert a grid with samples into the high-vacuum chamber for observation.
5. Operation panels (left for alignment; right for magnification and focus; arrows for positioning the object inside the chamber).
6. Screen for menu and image display.
7. Water supply to cool the instrument.

Table 3.3 A comparison between the particle size and magnification

Size of particles	Magnification
2 μm	2000-3000
1 μm	4000-5000 6000-10 K 12K -25 K
0.5 μm	30K -40 K
0.2 μm	50K -80 K
100 nm	
50 nm	100K-250K
20 nm	300K-400K
10 nm	
5 nm	500 K -800K
2 nm	1 M -4.5 M

Secondly, the morphological structure after polymerization was studied. This study can confirm the morphology of the coating by SEM. Samples were made into small pieces and adhered on brass stubs by using adhesive tape in order to study the coating of polymers. The remaining samples were out into liquid nitrogen and then broken immediately and adhered to brass stubs by using adhesive tape in order to study the cross-section of polymers. Next, the samples on the stubs were painted with a thin layer of gold. The morphologies of the admicelled rubbers were observed by a scanning electron microscope (SEM, JOEL model JSM-5200). SEM digitized photographs were obtained with a magnification range between 1,000–5,000x using an acceleration voltage of 15 kV.

3.3.5 Thermal properties measurement

Thermal stability, moisture content, and degradation process of the admicelled rubbers were studied by a thermogravimetric-differential thermal analyzer (Perkin Elmer, Pyris Diamond), TG-DTA. The samples weighed 10-18 mg and were put in a platinum pan. The instrument was set to operate at temperatures

from 30 to 600°C at a heating rate of 10°C/min under nitrogen atmosphere, 100 ml/min.

3.3.6 FT-IR Observation

The IR absorption of the admicelled rubber films with a thickness of 0.3–0.8 mm obtained by compression at 160°C under pressure 30 tons for 15 min were determined using the horizontal attenuated total reflection accessories for the FTIR (Nexus 670, HATR flat plate system with 45 °C ZnSe crystal) to measure the spectra of materials. The spectra were recorded in the absorbance mode in a wavenumber range of 400-4000 cm^{-1} . The sample spectra were recorded by using air as a background.

The KBr technique was used to prepare the powder sample of pure PPy and pure PTh. They were prepared by grinding the powdered PPy/ PTh with the KBr powder. The mixture was molded in special dies under a pressure of 10 tons. The sample spectrum was recorded by using KBr as a background.

3.3.7 Mechanical properties measurement

The tensile strength test uses two clamps to hold the testing strip. When secured, the testing strip is pulled apart with a specified force. The yield point and/or breaking point is then measured (Figure 3.4).

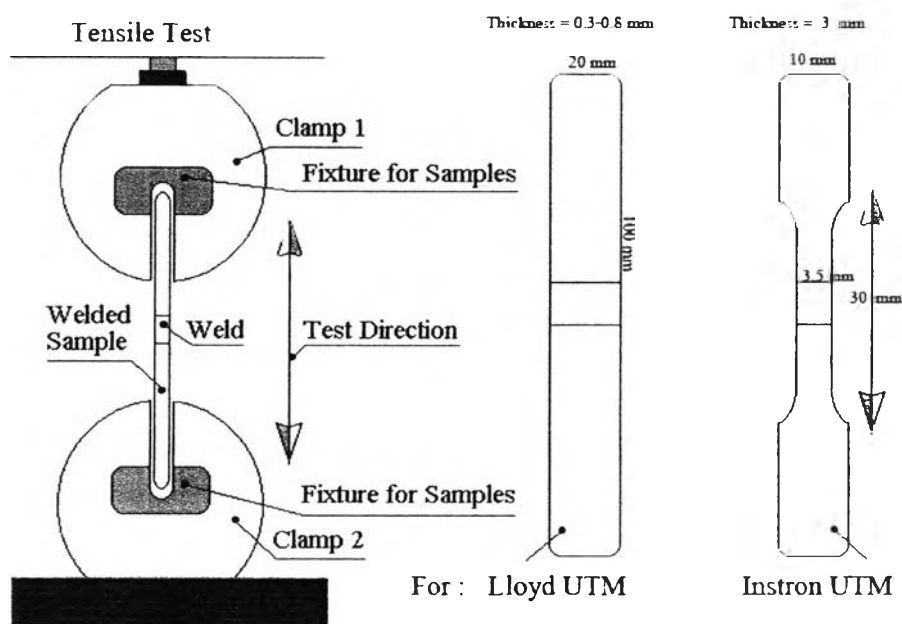


Figure 3.4 Preparation samples for tensile test.

The mechanical properties were determined for two specimen types. One type, the specimen has a dimension of 20x100 mm (thickness 0.3-0.8 mm). The test were prepared from compression molding. The test followed ASTM D822-91 with a crosshead speed of 50 mm/min, a guage length of 50 mm, and a load cell 500 N under room temperature using a Lloyd Universal Testing Machine, model :LRX. The test was repeated 5 times.

The other type is a dumbbell shaped specimen, which has a thickness larger than 3 mm, the specific sample size (Figure3.4) were cut by using a pneumatic punch following ASTM D638M-91a. The samples were tested by using an Instron Universal Testing Machine with a crosshead speed of 50 mm/min, a gauge length of 13 mm, and load cell 100 kN under room temperature. The test was repeated 5 times.

3.3.8 Shore A and Shore D hardness Measurement

The flat specimen was placed on the plate. Then, the maximum height of the indenter was adjusted so that the tip of the indenter was approximately 10 mm above the test specimen. The unit was locked in position and the pointer was set to zero. The durometer probe was carefully, but fairly quickly and uniformly, lowered onto the test specimen. Then, initial shore hardness values were obtained by the pointer reading. According to ASTM D2240, the following conditions should be complied with :

- The test specimen should be at least 6 mm thick.
- The indenter should be at least 12 mm away from any edge of the specimen.
- At least 5 hardness readings should be taken per specimen.
- The instantaneous hardness reading on the dial gauge should be taken
- Only hardness values ranging between 10 and 90 are acceptable for shoreA.
- If the value is greater than 90, the shore D test should be used instead (Figure 3.5).

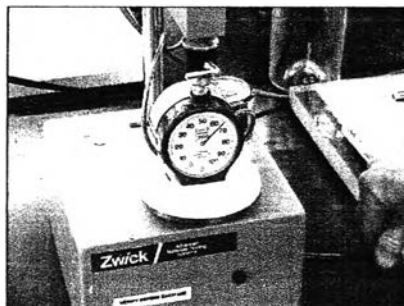


Figure 3.5 ShoreA and ShoreD hardness measurement.

3.3.9 Conductivity measurement

The admicelled rubber films from compression molding (thickness 3 - 4 mm) were cut into a round shape six inches in diameter and tested for their surface and volume resistivity by using a Keithley 8009 Resistivity Test Fixture and a Keithley 6517A Electrometer/High Resistance Meter (Figure 3.6). The dc voltage from 0.1 to 15 volts was applied to the specimen placed in the Keithley 8009 test fixture. Then, the current was read and the surface and volume resistivity were determined.

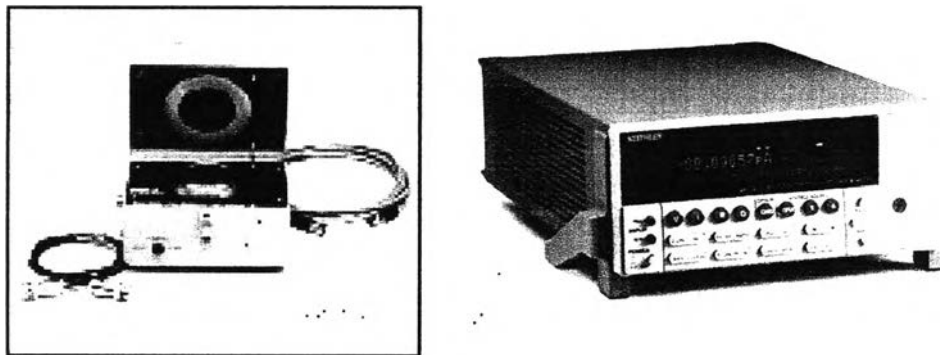


Figure 3.6 Photos of the Keithley 8009 Resistivity Test Fixture (left) and the Keithley 6517A Electrometer/High Resistance Meter (right).

The resistance, R , of the films was calculated using Eq.3.1, the volume resistivity, surface resistivity, and the conductivity were found using Eqs.3.2, 3.3, and 3.4, respectively (see appendix B):

$$R = \frac{V}{I} \quad (3.1)$$

$$\rho_v = \frac{22.9V}{tI} \quad (3.2)$$

$$\rho_s = \frac{53.4V}{I} \quad (3.3)$$

$$\sigma = \frac{1}{\rho_v} \quad (3.4)$$

where R is the resistance (watts), V is the voltage (volts), I is the current (amperes), ρ_v is the volume resistivity (ohm centimeters), ρ_s is the surface resistivity (ohm), t is the film thickness (centimeters), and σ is the conductivity (siemens per centimeter).

3.3.10 Density measurement

The density of the specimens was measured using the Sartorius approach, model:YDK01, where the sample is weighed in air and then in water by a balance with a reproducibility better than 10 μg . Each measurement represented the average of at least 3 specimens.

Density of H₂O 0.9964 (from table at 25°C)
temperature 27.5

$$\text{Eq} \quad d = \frac{w_a \times d_{H_2O}}{(w_a - w_f) \times 0.99983} + 0.0012 \dots \text{g/cm}^3 \quad (3.5)$$

$$G = W(a) - W(fl) \quad (3.6)$$

Where: w_a = weight of solid in the air; w_f = weight of solid in the liquid;

G = buoyancy of the glass plummet; d = density

Pycnometer method is applicable to determinate the PPy particle density. This procedure is simple by using a know volume bottle, typically 25 ml. The measurement was done at 27.5°C.

$$\text{Solid sample of PPy} \quad \text{Sp.gr. } 27.5/27.5^\circ\text{C} = \frac{a \times d}{a + w - b} \quad (3.7)$$

where: a = mass of solid ; b = mass of pycnometer filled with water + solid at 23°C ;

e = mass of Pycnometer; d = sp.gr. 23/23°C of liquid;

w = mass of pycnometer filled with water