

CHAPTER III EXPERIMENTAL

3.1 Materials

Centrifuged NR latex with 60% dry rubber content was provided by the Rubber Research Institute of Thailand, Bangkok, Thailand. Sodium alginate (Carlo Erba Co., Ltd.) was used as a surface-active agent for the NR latex. Aniline monomer (Merck) was purified by vacuum distillation and stored at 4°C before polymerization. Ammonium peroxodisulfate (AR grade, Merck) and aqueous ammonia (25%, Merck) were used as received. *N*-methyl-2-pyrrolidone (NMP, Merck) was employed as a solvent for PANI. Hydrochloric acid (37% AR grade, Labscan) was used as the dopant. Dehydrated calcium chloride (Labscan) was used as a cross-linking agent for the sodium alginate. Commercial grade methanol and acetone were used without further purification.

3.2 Equipment

3.2.1 Fourier Transform Infrared (FTIR) Spectrophotometer

Fourier transformation infrared (FTIR) spectra of PANI, neat NR and composite fibers were recorded with a Thermo Nicolet Nexus 670 FTIR spectrometer equipped with an attenuated total reflectance (ATR) crystal accessory operating at 32 scans and a resolution of 4 cm⁻¹, covering a wavenumber range of 4000-650 cm⁻¹

3.2.2 Particle Size Analyzer (Malvern Instruments Ltd., Mastersizer X[®])

Particle size analyzer was used to measure the particle size of PANI powder with 100 mm Len size and active beam length was set to 2.4 mm.

3.2.3 Thermo Gravimetric-Dynamic Temperature Analyzer (TG-DTA)

Thermal stability and degradation temperature of neat NR, PANI and composite fibers were performed by a high resolution TG-DTA Pyris Diamond (Perkin Elmer). The samples were weighted in the range of 5-10 mg and loaded on a

platinum pan. The mass change with increasing temperature was monitored and recorded from 30°C to 700°C with a heating rate of 10°C/min under nitrogen flow.

3.2.4 Scanning Electron Microscope (SEM)

Surface and cross-sectional morphological studies of the fibers were carried out with a JEOL JSM-5200 scanning electron microscope (SEM) operating at an accelerating voltage of 15 kV with the magnifications of 100-7500 times. For the surface morphology, the fiber samples were cut into small pieces and adhered on brass-stub by using adhesive tape and were coated with thin layer of gold by using a JFC-1100E ion sputtering device. For the cross-sectional morphology, the fiber samples were fractured by immersing in liquid nitrogen and then gold-sputtered prior to microscopic analysis.

3.2.5 Universal Testing Machine

The mechanical properties of the composite fibers were measured following to ASTM D 2433 with an initial sample length of 20 cm. The measurements were carried out with a Lloyd Instrument model LR50K, the load cell used was 100 N, the displacement rate was 500 mm/min and the gauge length was set at 50 mm. The values quoted represent averages of 20 specimens.

3.2.6 Electrometer

DC electrical conductivity experiments were carried out with a two-point probe arrangement. Two grip probes, which were used to contact individual fibers, were coupled to Keithley electrometer model 6517A.

3.2.7 Custom-built Electromechanical Tester

Electromechanical actuation was investigated in terms of bending deformation. The transparent cell-box with a pair of parallel copper electrode plates were coupled with high DC voltage. The video digital camera was used to record the bending deformation.

3.3 Methodology

3.3.1 Polyaniline Synthesis

PANI was synthesized in its emeraldine base form (EB) according to the method described by Cao *et al.* (1989). Freshly distilled aniline (20.4 g) was

dissolved in aqueous HCl (1.5 M, 230 mL) and the solution was cooled to below 5°C using ice bath. After 30 min, a solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (25 g) in aqueous HCl (1 M, 250 mL) was added dropwise slowly into the mixture of aniline solution for 1 h. The solution was then vigorously stirred (~500 rpm) and maintained at temperature of 0-5°C for 4 h. The dark green emeraldine salt form of PANI that had precipitated from the reaction mixture was collected by filtering under reduced pressure and was washed repeatedly with a water/methanol mixture (80:20 v/v) until the filtrate was colorless and of neutral pH. The emeraldine salt (ES) form was converted into the emeraldine base form by stirring for 2 h in aqueous $(\text{NH}_4)\text{OH}$ (3%, 300 mL). The resulting dark blue emeraldine base powder was filtered off and washed with water until the filtrate was colorless and had a neutral pH. The dark blue powder was dried in a vacuum oven at ambient temperature for 48 h to yield 6.2658 g (30.71%) of the product.

3.3.2 Polyaniline/Natural Rubber Composite Fiber Spinning

For the preparation of spinning dopes, the NR latex (37.5 g) was mixed with the surface-active agent sodium alginate (5% w/w aqueous solution) in the ratio of 75:25 (w/w) (total amount of sodium alginate was 0.625 g) in order to achieve a viscosity appropriate for the spinning process (Peethambaran, 1990). After thoroughly mixing these components, PANI, in its emeraldine base form (EB) with an average particle size of 20.76 μm , was added and the dispersion was mechanically mixed. The PANI amount was adjusted so that its content in the solid blends was 0, 0.5, 1, 2, 5 and 10% w/w, respectively. During the mixing, 1.67 mL of 1% w/w PANI/NMP was added drop-wise in order to improve PANI dispersion in the NR dope. In the case of the neat NR reference fibers (comprising sodium alginate but no PANI), the spinning dope was prepared without NMP.

The spinning dopes thus prepared were extruded under nitrogen pressure (0.5 kg/cm^2) through a spinneret (30 holes with a 0.20 mm diameter) into a first coagulation bath consisting of a solution of calcium chloride (which cross-links the sodium alginate) in methanol (5% w/v) and the coagulated fiber bundles were subsequently drawn through a second bath containing neat methanol. The resulting fibers were subsequently straightened by applying uniaxial tension before the fiber bundles were collected on a take-up roller. The exact wind-up speed was not known,

but it was chosen such that only a slight tensional force was exerted to the fiber in the coagulation bath, just to keep them straightened. Samples used for further investigation were collected by cutting the strands (before take up through the take-up roller) to a length of ca. 25 cm. The fiber bundles thus obtained were fixated on a glass frame in order to keep them straight while they were subsequently immersed in methanol bath for 24 h and then dried in air.

3.3.3 Doping of Polyaniline/Natural Rubber Composite Fiber

To dope PANI, the dried fiber bundles were immersed for 24 h in an aqueous HCl solution (1M) and subsequently allowed to dry in air. Upon doping, the composite fiber bundles changed their color from blue to green, which is the characteristic color change associated with the doping of PANI (Stejskal, 1996), the color change was clearly visible in even for the samples with low PANI content (0.5 % w/w). The composite fibers were dried in a desiccator for 24 h.

3.3.4 Polyaniline/Natural Rubber Composite Fiber Characterization

3.3.4.1 *Structural Characterization*

The FTIR spectra of PANI, neat NR and composite fibers were recorded with Thermo Nicolet Nexus 670 FTIR spectrometer equipped with an attenuated total reflectance (ATR) crystal accessory operated at 32 scans at a resolution of 4 cm^{-1} by using deuterated triglycerinesulfate detector (DTGS) with specific detectivity of $1 \times 10^9\text{ cmHz}^{1/2}\text{w}^{-1}$.

3.3.4.2 *Morphology*

Scanning electron microscope was used to investigate the surface and cross-sectional morphology of fibers with the magnifications of 350-7500 times at an acceleration voltage of 15 kV.

3.3.4.3 *Thermogravimetric Analysis*

Thermal stability and degradation temperature of natural rubber, polyaniline and their blend fibers were compared.

3.3.4.4 *Linear Density*

Samples were cut into 20-cm length and weighed by using a digital electron balance with five-decimal point. The linear density of the fibers was expressed in tex-the mass, in grams, of one kilometer of fiber. The value quoted for each sample was the average value of 20 individual specimens.

3.3.4.5 Mechanical Properties

The tenacity and elongation at break of fibers were measured in the form of rubber thread according to ASTM D 2433. The 100 N load cell, cross-head speed of 500 mm/min and the gauge length of 50 mm were used. The test performed in standard atmosphere having a temperature of $23 \pm 1^\circ\text{C}$ and a relative humidity of $50 \pm 2\%$. All samples measure for their linear density as mentioned in the section 3.3.4.4. The value quoted for each sample was the average value of 20 individual specimens.

3.3.4.6 Electrical Conductivity Measurement

DC electrical conductivity experiments were carried out with a two-point probe arrangement. Two grip probes were used to contact individual fibers, and a circuit consisting of a power source that provided a constant voltage (V) and a current meter (Keithley model 6517A), was used to measure the resultant current (I). The specific conductivity σ (S/cm) was calculated according to equation (3.1) (Chandradekhar, 1999; Zhang, 2001):

$$\sigma = \frac{L_o \cdot I}{A_o \cdot V} \quad (3.1)$$

where L_o (cm) is the length of fiber between the two contacts (typically 2.50 cm), I (A) is the current driven through the sample, A_o (cm^2) is the cross-sectional area of the fiber (typically 0.0057 cm^2 for an average diameter of 0.085 cm), and V (V) is the applied voltage.

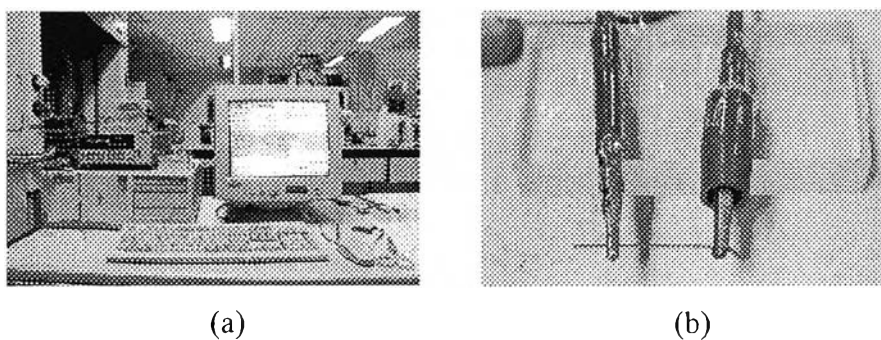


Figure 3.1 Equipments for electrical conductivity measurement; (a) Electrometer Keithley model 6517A (b) Two-point grip probe arrangement.

The strain-dependent conductivity experiment was carried out by the method reported by Chiang *et al.* (1997). Since the change of the cross-section area of the fibers upon uniaxial deformation is inversely proportional to the length after stretching L (cm) between the conducting grip probes, the conductivity (σ) can be determined as a function of strain ($\varepsilon = L/L_0 - 1$) by an experiment that is similar to the above, and using the equation (3.2):

$$\sigma = \frac{L^2 \cdot I}{V \cdot L_0 \cdot A_0} \quad (3.2)$$

The equation is derived from under the assumption that the final volume of the fiber does not change upon stretching.

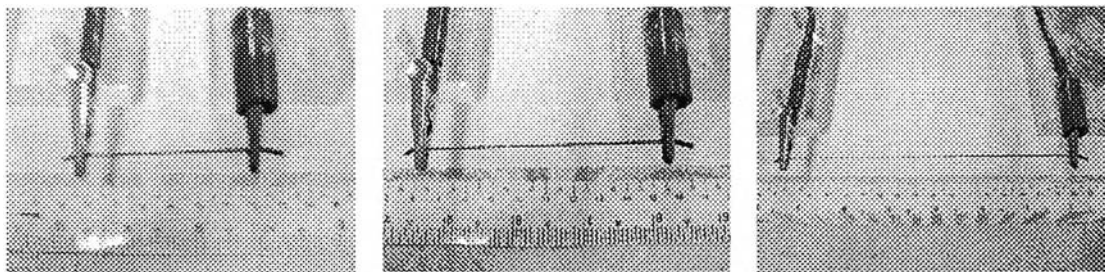


Figure 3.2 Two-point grip probe method for strain-dependent conductivity measurement.

3.3.4.7 Electromechanical Testing

Electromechanical actuation was investigated in terms of bending deformation. The composite fiber was vertically suspended into silicon oil between a pair of parallel copper electrode plates. High DC voltage was applied in a non-contact mode through copper electrodes, placed 2.50 cm apart (Figure 3.4). The electric response of the fiber was recorded by a video digital camera; the deflection and required voltage were analyzed by a video camera analyzer. All the measurements were carried out at ambient temperature.

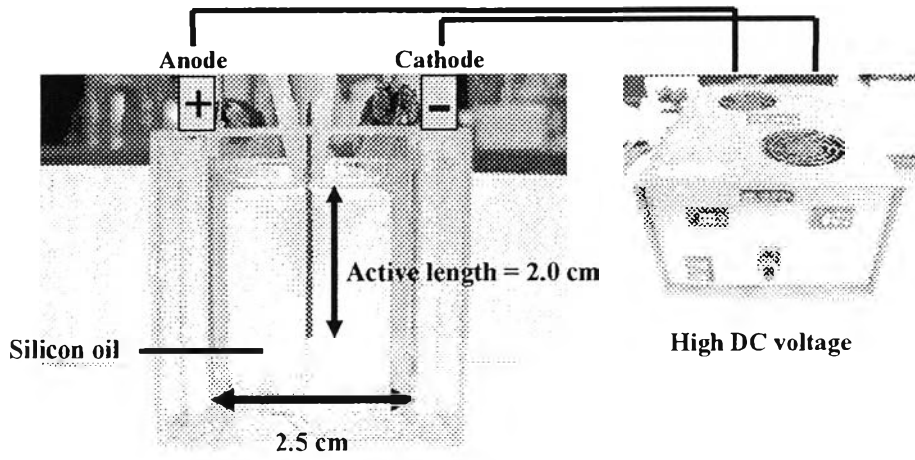


Figure 3.3 Experiment set-up for the electromechanical Testing.