

CHAPTER VIII
CONDUCTIVITY BEHAVIOR AFFECTED BY STRETCHING
DOPED NR FILM

8.1 Abstract

Admicelled NR|PPy and Admicelled NR|PTh were prepared by using electrochemical method. The electrical conductivity of PPy and PTh were stretched and measured conductivity by using two-point probe under N₂ atmosphere. The stretching increments were stepped to 0.50 – 5 mm, corresponding to strain 0.55-5.55%, respectively. A dc voltage from 0.1 to 15 volts was applied to the specimen. It demonstrated that the conductivity increased with low strain due to the improvement of alignment of polypyrrole and polythiophene but the conductivity decreased significantly when continuing to stretch the film to larger strain. The opportunity of this study could be made the actuator more intelligent which contacted the human physical body or powers assist devices to generate the contraction motion. The major advantage of this actuator has more flexible and light weight.

8.2 Introduction

Conducting polymers can exhibit significant levels of electrical conductivity suitable for use in electronic devices, batteries, functional electrodes, electrochromic devices, optical switching devices, sensors, and so on. Research interest in the development of conducting polymers such as polyaniline, polypyrrole, polythiophene, polyphenylene, etc. has increased tremendously because of the versatility of their applications [1-5]. Attempts have been made to produce composites or blends of conducting polymer films with some insulating polymer in order to overcome the drawbacks such as poor processability and the lack of essential mechanical properties exhibited by these polymers [6]. In this technique, a host of insulating polymers, namely, poly(vinylalcohol) [6,7], poly(styrenesulphonate) [8], polycarbonate [9], poly(methyl methacrylate) [10], rubber [11], polyimide [12], *etc.*, have been combined with a number of conducting polymers such as polypyrrole, polyaniline, polythiophene, *etc.*, in aqueous or organic medium to produce conducting polymer composites which will have the conducting properties of the conducting polymer with some of the superior mechanical properties of the host insulating polymer.

In the last decades, several soft actuators with the change in volume of intrinsically conducting polymers during redox process have been studied extensively [13,14]. This volume change can be expressed as electrochemomechanical deformation. Most of the actuators have a bilayer or a tri-layer configuration [15-16]. In a single actuating film is affixed to a second, electromechanically inert layer. Bi-actuators use two conjugated polymer films attached to either side of a passive film, such as an adhesive tape. In these configurations, the electrochemically inert layer can increase the strength, however, also provides extra weight and volume of the actuator. Recently, Takashima and coworkers [17,18] reported a bi-ionic actuator (BIA) consists of only two layers of polypyrrole films, which is driven by cooperative bending associated with the anion driven (anodic expansion) and the cation driven (anodic contraction). Although the bending actuation of the actuator has been enhanced because of bi-ionic

contributions, the mechanical strength of the conducting polymer films was relatively weak.

Furthermore, during the process, the ions and solvent molecules were inserted and de-inserted into the film repeatedly and changed the morphology of the film of a compact film into a porous one. As a result, the mechanical strength of the actuator decreased dramatically.

In this paper, we report an actuator consists of NR/PPy, NR/PTh without doping and NR/PPy, NR/PTh with doping of conducting polymer films. The two layers of polypyrrole act as bi-ionic driving layers for actuation. The polythiophene (PTh) layer is electrically conductive and acts as a current collector. Furthermore, the PPy and PTh were electrochemically synthesized and it had an excellent high tensile strength and good flexibility as explain more detail in chapter 4-5 [19-20]. Thus, the PPy and PTh might be provided the actuator with an excellent mechanical support.

8.3 Experimental

8.3.1 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 for this experiment was Sodium Dodecyl Sulfate (SDS). A schematic of the chemical structure of SDS is shown in Figure 3.1. SDS was purchased from Aldrich Chemical Company, Ltd. with 99% purity^[20]. According to Rosen (1996) the CMC of SDS was determined to be $\sim 1.58 \times 10^{-3}$ mol/dm³ at 25 °C. Hydrochloric acid used as doping and adjust PH. The pyrrole monomer (Aldrich) was first purified by distillation at 131°C and 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. Thiophene monomer: purum 98% GC, Mr= 84.14, bp=82-84°C, d_{4}^{20} =1.063 contain 0.2% benzene. Iodine (I₂) was a reagent grade which was stored over silica gel in desiccator.

8.3.2 Equipments

NR latices were purified by centrifugation at 10000 rpm/20 min with two cycles at 20 °C by centrifugator, Hermle Z383K. The density was tested by Sartorius approach, model: YDK01. Functional groups were determined by Fourier Transform Infrared Spectroscopy (FTIR) (Nicolet 670, HATR flat plate system with 45°C ZnSe crystal) PERKIN ELMER 1760X. Particle Size Analyzer (Mastersizer X) was used to measure the particle size of NR latex particles (45 mm lens, active beam length 2.4 mm). Thermogravimetric-Differential Thermal Analyzer (Perkin Elmer, Pyris Diamond) was used to study the thermal stability and the decomposition temperature. The morphology of the admicelled latex films were observed by Scanning Electron Microscopy (JOEL 5200) and Transmission electron microscope (JEOL JEM-2100). Tensile testing was carried out using Lloyd LRX Universal Testing Machine under ASTM D882-91 and Instron Universal Testing Machine under (ASTM638M-91a). The hardness shoreA and ShoreD was observed by Lever Loader, model 716. Surface and volume resistivity were measured by using Resistivity Test Fixture (Keithley Model 8009) and Electrometer/High Resistance Meter (Keithley 6517A).

8.3.3 Preparation the sample

Concentrated natural rubber latex (4-8 g) was mixed with 50 ml distilled water and centrifuged two times at 20°C, 10000 rpm for 20 minutes. The 25 g of cream was separated and added in 10 ml distilled water. Then the rubber latex was mixed with surfactant solution, SDS, 16 mM, and make up volume to 500 ml (including amount of Pyrrole and Thiophene at various concentration 20-800 mM) by distilled water. HCl was added to maintain the pH of the solution at 3.0, which is the pH below the point of zero charge [11]. Then, it is stirred four hours to let the surfactant molecules form the bilayer at the surface of the rubber particles.

The pyrrole solution (20–800 mM, 0.79–27.66 ml) or thiophene solution (20–800 mM, 0.79–31.66 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 though the solution containing the pyrrole monomer at various voltages and the solution was purge with N₂ to prevent the

oxidation in the system. As the current was applied across the cell, pyrrole was polymerized in the rubber latex solution at the cathode. The rubber was also pulled to cathode during polymerization and finally conductive natural rubber occurred on the cathode, the copper has a dimension of 3.5x7 cm.

After the electro-polymerization has started, the pH and mass on the electrode are checked every hour and the electrode was replaced. The pH was adjusted to 3.0 by HCl. After the polymerization was complete, the dark solid rubber on the working electrode was washed with water to remove the surfactant, followed by drying in a vacuum oven at 70°C for 12 hours and black sheet with a constant weight was obtained. The solution changed from white to black and finally to clear solution. In order to obtain the best synthesized conditions, factors such as applied potential (voltage), time, %yield and pH were studied. Mass can also be controlled by these factors. The voltage was applied by using an adaptor (0-30 Voltage, 3A, Kenji-model: K01). The average electrode sizes were about 3.5 x 7cm.

8.3.4 Conductivity measurement

The admicelled rubber films from compression (thickness 0.3-0.8 mm) were cut into a round shape with 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. A 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 (ASTM D-257).

The resistance, R , of the films was calculated using Eq. 1, the volume resistivity, surface resistivity and the conductivity were found using Eqs. 2, 3 and 4, respectively:

$$R = \frac{V}{I} \quad (1)$$

$$\rho_v = \frac{22.9V}{tI} \quad (2)$$

$$\rho_s = \frac{53.4V}{I} \quad (3)$$

$$\sigma = \frac{1}{\rho_v} \quad (4)$$

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).

The samples, thin films (original gauge length = 90 mm, width = 20 mm, thickness = 0.3-0.8 mm) were stretched and measured conductivity by using two-point probe under N_2 atmosphere. The stretching increments were stepped to 0.50 – 5 mm, corresponding to strain 0.55-5.55%, respectively. The probes were connected to a source meter (Keithley, Model 6517A) for a constant voltage source and for reading current. The geometric correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing. The geometric correction determined by using standard material; silicon wafer chip (SiO_2) with known specific resistivity. The conductivity of the films was calculated using Eq. (5) and (6):

$$R_s = CF \times \frac{V}{I} \quad (5)$$

$$\sigma = \frac{1}{R_s \times \pi \times r} \quad (6)$$

where R_s is the sheet resistivity (ohms), CF is the correction factor which is 2.70 and r is the probe's radius which is 0.192 cm.

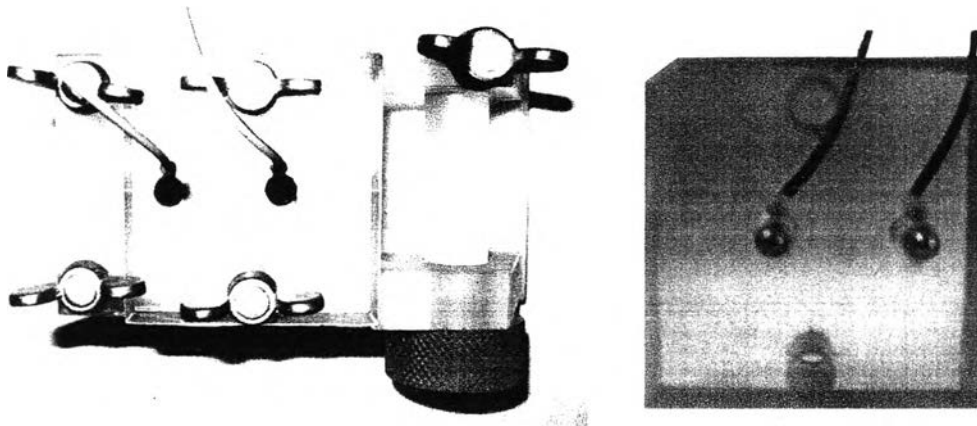


Figure 8.1 Schematics of a two-point probe base (left) and probes (right).

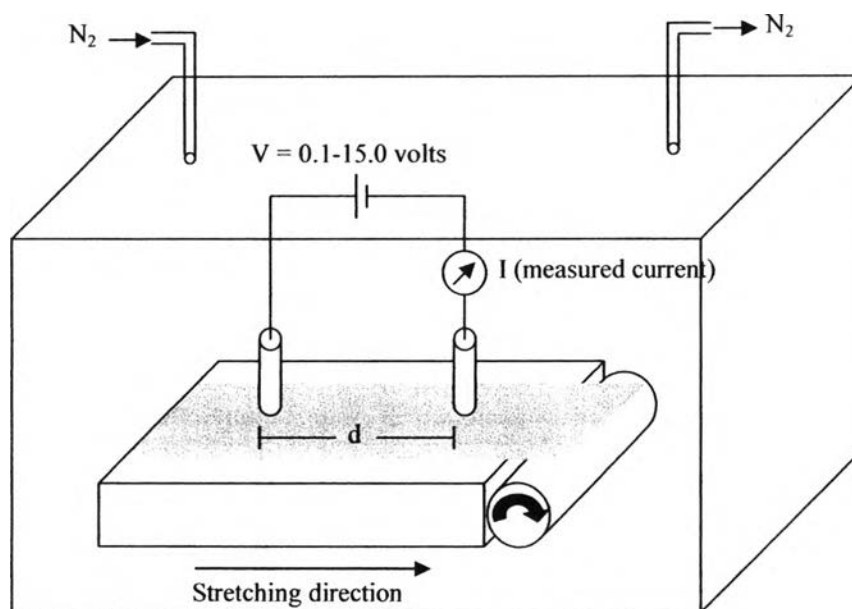


Figure 8.2 Diagram of a conductivity measurement using two-point probe.

8.4 Results and discussion

The conductivity of the thin stretched admicelled rubbers films (thickness 0.30-0.90mm) at different distance in low strain region was investigated. It demonstrated that the conductivity increased with low strain due to the improvement of alignment of polypyrrole and polythiophene but the conductivity decreased significantly when continuing to stretch the film to larger strain, because the particle contacts and the path ways of charge carrier were disconnected. This result is similar to silicone rubber/polypyrrole composites, studied by Vilcakova J., et al.(2004,[21]), that the change in electrical conductivity during deformation results from particle displacement which affects the conductivity paths in the material. The conductivity of samples is continually decreases with further extension due to the disrupt of PPy or PTh network over rubber particles. The increasing amount of PPy or PTh show more brittleness (reducing elongation) to the material. It also obtained the higher in their conductivity due to the increasing amount of monomer to abstract electron.

Figure 8.3-8.4 shows the characteristics of the soft displacement sensor incorporated in the intelligent actuator. The characteristics of this sensor also depend on the velocity of the deformation because of the viscoelasticity of rubber

(Shuichi.W, (2005)[22]). Samples of high conductivity show the softest film decreases at the beginning then increases with continued stretching due to the improvement of alignment of monomer. Then, conductivities were decreased significantly when stretch the film to larger strain. This related to the polyaniline/styrene-butadiene-styrene composites studied by Xie-H.-Q. and Ma Y.-M. (1999,[23]).

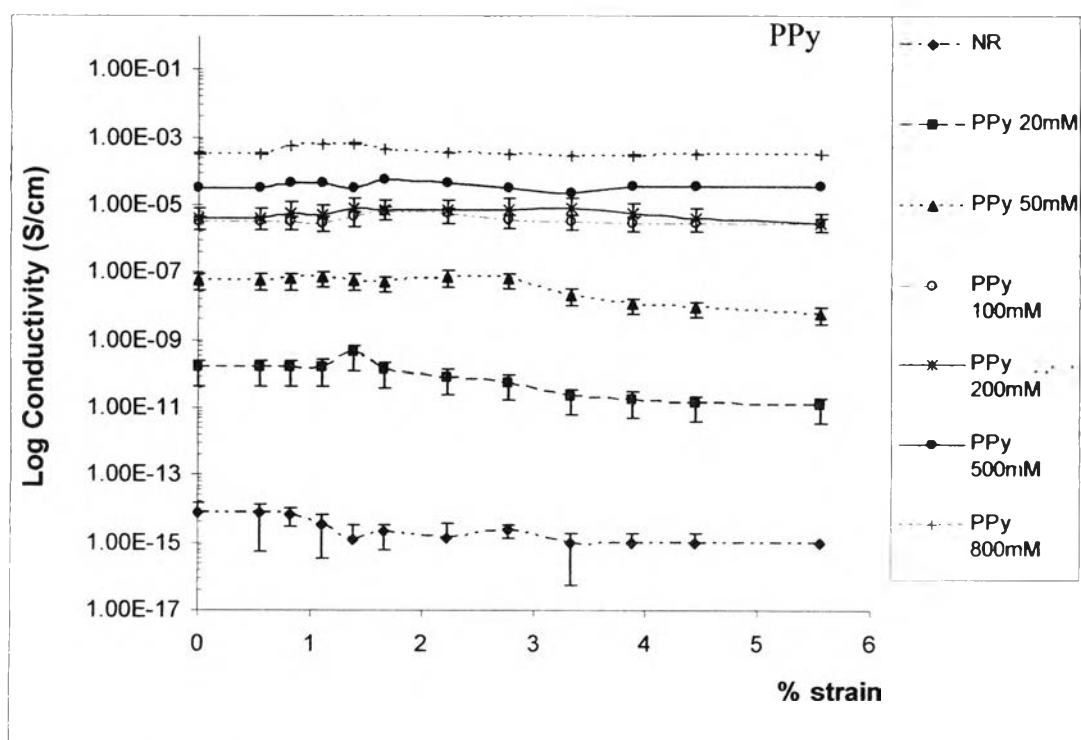


Figure 8.3 Effect of stretching on volume conductivity of the admicelled rubbers/PPy (Apply dc 0.1-15 volt) under N₂ atmosphere.

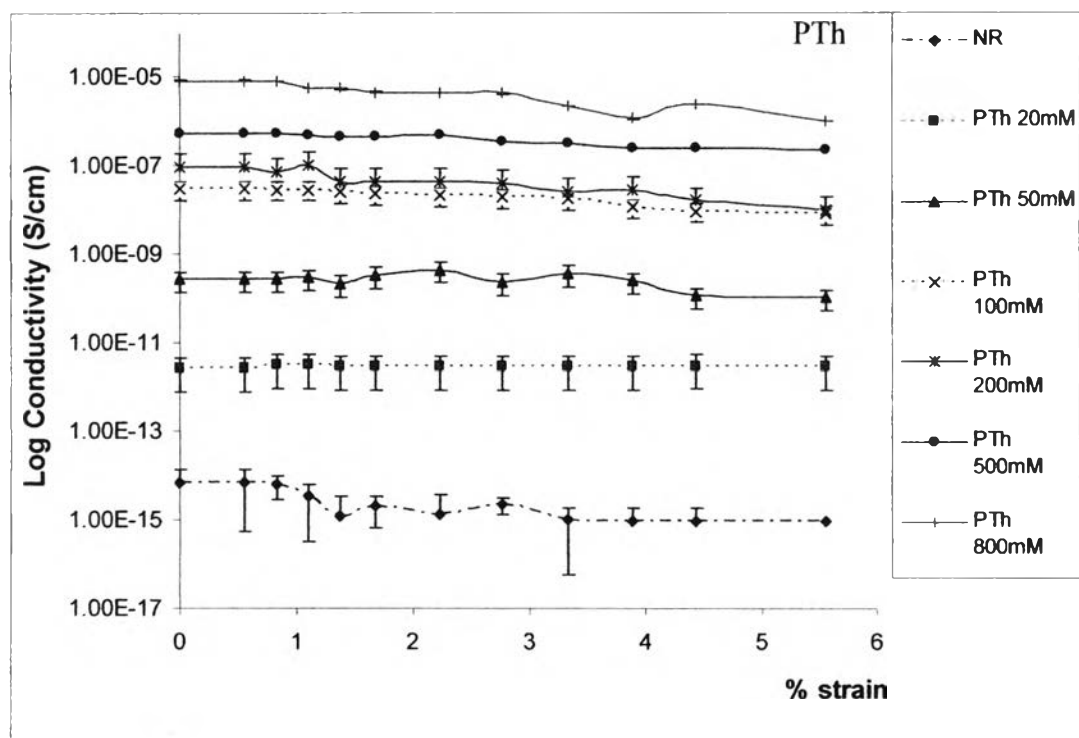


Figure 8.4 Effect of stretching on volume conductivity of the admicelled rubbers|PTh (Apply dc 0.1-15 volt) under N_2 atmosphere.

Table 8.1 Effect of stretching on volume conductivity of admicelled rubber|PPy at various to PPy contents

% strain (ϵ)	NR	PPy (mM)					
		20	50	100	200	500	800
(%)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)
0.56	7.17E-15	1.49E-10	5.99E-08	3.10E-06	3.79E-06	3.11E-05	3.19E-04
0.83	6.51E-15	1.51E-10	6.19E-08	3.23E-06	5.90E-06	4.12E-05	5.19E-04
1.11	3.38E-15	1.52E-10	7.23E-08	2.91E-06	4.90E-06	4.11E-05	6.19E-04
1.38	1.18E-15	4.20E-10	6.12E-08	4.30E-06	7.79E-06	3.11E-05	6.31E-04
1.67	2.05E-15	1.31E-10	5.14E-08	6.41E-06	6.79E-06	5.23E-05	4.12E-04
2.22	1.38E-15	8.01E-11	7.39E-08	5.35E-06	7.30E-06	4.12E-05	3.41E-04
2.77	2.28E-15	5.54E-11	6.34E-08	3.61E-06	7.40E-06	3.11E-05	3.09E-04
3.33	9.84E-16	2.13E-11	2.19E-08	3.31E-06	7.90E-06	2.23E-05	2.67E-04
3.88	9.10E-16	1.73E-11	1.13E-08	2.90E-06	5.40E-06	3.33E-05	2.84E-04
4.44	9.32E-16	1.34E-11	9.02E-09	2.81E-06	4.00E-06	3.61E-05	2.94E-04
5.56	9.58E-16	1.19E-11	5.91E-09	2.79E-06	2.90E-06	3.51E-05	3.00E-04

Table 8.2 Effect of stretching on surface conductivity of admicelled rubber|PPy at various to PPy contents

% strain (ϵ)	NR	PPy (mM)					
		20	50	100	200	500	800
(%)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)
0.56	2.46E-15	2.30E-10	3.94E-09	1.63E-06	1.03E-06	3.07E-05	3.83E-04
0.83	3.46E-15	2.13E-10	4.13E-09	1.85E-06	1.23E-06	4.12E-05	3.97E-04
1.11	3.60E-15	2.03E-10	4.31E-09	1.95E-06	1.33E-06	4.39E-05	4.01E-04
1.38	3.16E-15	1.98E-10	4.23E-09	1.78E-06	9.30E-07	3.97E-05	3.77E-04
1.67	2.25E-15	2.23E-10	4.41E-09	1.33E-06	9.65E-07	3.23E-05	3.89E-04
2.22	1.66E-15	2.43E-10	3.21E-09	1.40E-06	9.33E-07	2.97E-05	2.13E-04
2.77	1.26E-15	1.30E-10	1.23E-09	1.54E-06	9.53E-07	1.03E-05	1.23E-04
3.33	1.13E-15	9.30E-11	9.95E-10	1.11E-06	9.34E-07	9.30E-06	9.13E-05
3.88	1.02E-15	8.17E-11	8.54E-10	1.30E-06	9.10E-07	9.10E-06	9.13E-05
4.44	1.03E-15	8.13E-11	6.12E-10	1.21E-06	8.03E-07	8.17E-06	8.30E-05
5.56	1.05E-15	6.24E-11	4.51E-10	9.30E-07	8.33E-07	8.31E-06	7.81E-05

Table 8.3 Effect of stretching on volume conductivity of admicelled rubber|PTh at various to PTh contents

% strain (ϵ)	NR	PTh (mM)					
		20	50	100	200	500	800
(%)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)
0.56	7.18E-15	2.52E-12	2.57E-10	2.86E-08	8.94E-08	5.35E-07	8.26E-06
0.83	6.51E-15	3.13E-12	2.64E-10	2.85E-08	7.14E-08	5.12E-07	8.12E-06
1.11	3.38E-15	3.10E-12	2.89E-10	2.83E-08	9.96E-08	4.77E-07	5.62E-06
1.38	1.18E-15	2.80E-12	2.11E-10	2.51E-08	4.41E-08	4.56E-07	5.43E-06
1.67	2.05E-15	2.93E-12	3.31E-10	2.34E-08	4.32E-08	4.66E-07	4.48E-06
2.22	1.38E-15	2.91E-12	4.32E-10	2.11E-08	4.12E-08	4.77E-07	4.23E-06
2.77	2.28E-15	2.89E-12	2.31E-10	1.89E-08	3.94E-08	3.57E-07	4.21E-06
3.33	9.84E-16	2.89E-12	3.51E-10	1.78E-08	2.51E-08	3.23E-07	2.11E-06
3.88	9.10E-16	2.81E-12	2.40E-10	1.11E-08	2.76E-08	2.34E-07	1.12E-06
4.44	9.32E-16	2.99E-12	1.10E-10	9.13E-09	1.56E-08	2.35E-07	2.30E-06
5.56	9.58E-16	2.75E-12	9.88E-11	8.13E-09	9.25E-09	2.21E-07	9.81E-07

Table 8.4 Effect of stretching on surface conductivity of admicelled rubber|PTh at various to PTh contents

% strain (ϵ)	NR	PTh (mM)					
		20	50	100	200	500	800
(%)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)	(S/cm)
0.56	2.46E-15	1.85E-12	1.41E-11	1.31E-08	1.40E-08	2.77E-07	2.61E-06
0.83	3.46E-15	9.50E-13	9.10E-12	9.12E-09	1.63E-08	2.13E-07	2.11E-06
1.11	3.60E-15	9.10E-13	5.12E-12	8.91E-09	2.12E-08	2.21E-07	1.21E-06
1.38	3.16E-15	9.90E-13	5.22E-12	8.75E-09	3.14E-08	2.71E-07	1.41E-06
1.67	2.25E-15	9.31E-13	4.95E-12	8.53E-09	3.11E-08	2.13E-07	1.26E-06
2.22	1.66E-15	7.11E-13	4.33E-12	7.91E-09	2.14E-08	2.14E-07	1.91E-06
2.77	1.26E-15	6.12E-13	4.11E-12	5.11E-09	2.31E-08	2.13E-07	9.26E-07
3.33	1.13E-15	4.15E-13	2.15E-12	3.21E-09	2.14E-08	1.77E-07	9.12E-07
3.88	1.02E-15	3.25E-13	2.11E-12	1.12E-09	2.44E-08	9.70E-08	8.67E-07
4.44	1.03E-15	1.85E-13	1.45E-12	1.21E-09	1.14E-08	8.12E-08	8.19E-07
5.56	1.05E-15	1.85E-13	1.13E-12	1.02E-09	9.40E-09	7.13E-08	7.12E-07

8.5 Conclusion

The conductivity of the stretched admicelled rubbers at different distance in low strain region was investigated. It demonstrated that the conductivity increased with low strain due to the improvement of alignment of polypyrrole and polythiophene but the conductivity decreased significantly when continuing to stretch the film to larger strain, because the particle contacts and the path ways of charge carrier were disconnected.

8.6 Acknowledgements

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