

Electrical Conductive Polymer Film

By

DAN YANG

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This thesis is approved by the following members of the Final Oral Review Committee:

Dr. Young-Gi Kim, Committee Chairperson, Department of Chemistry, Delaware State University

Dr. Cherese Winstead, Committee Member, Department of Chemistry, Delaware State University

Dr. Andrew Goudy, Committee Member, Department of Chemistry, Delaware State University

Dr. Mohammad Khan, External Committee Member, Department of Physics and Engineering, Delaware State University

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Electrical Conductive Polymer Film

Dan Yang

Faculty Advisor: Dr. Young-Gi Kim

ABSTRACT

We report a conformal coating of thin electronic film using polyaniline (PANI), for which a highly bulk dopant, dinonylnaphthalenesulfonic acid (DNNSA), was used for synthesizing the electrically conductive polymer. Corresponding polymer was observed to show enhanced processability in organic solvents. Additional solution doping with *m*-cresol was found to be helpful for decreasing the surface resistance of the polymer film. The electrical resistance of corresponding films was observed to be $60.3 \text{ } \Omega/\square$ after post film doping processes were applied.

The polymer layer was coated on a flexible aramid paper (NOMEX[®], DuPont) varying the coating conditions for finding a sweet spot. Resultant polymer coats on the conformal substrate were observed to show promising surface resistance ($140 \text{ } \Omega/\square$) showing any disadvantage in the mechanical integrity.

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LIST OF ABBREVIATIONS AND SYMBOLS

DNPA DNNSA doped Polyaniline

DNPA_{mc} DNPA doped with *m*-cresol

DNPA_{tm} DNPA doped with thymol

DNNSA Dinonylnaphthalenesulfonic acid

PANI Polyaniline

CHAPTER 1

INTRODUCTION

1.1 Background of the Problem

1.1.1 Energy Storage

The performance of organic polymer energy and electronic devices has steadily increased through the past decades.^{1,2} Electrically conducting polymer is one of the main polymers of the application area. During the period, portable electronic devices attracted research interest especially for energy storage device.³ The trends of applications in the energy storage device are to be more flexible, light, portable and improved efficiency.⁴ Currently existing energy conversion storage device is various including fuel cell, battery, and capacitor. Due to the different mechanisms of the charge accumulation in supercapacitor, the storage and delivery of charges happen quickly which leads to improved power density compared with all other kinds of electronic devices.⁵⁻⁷ Chemical dopings on the conducting polymers have demonstrated promising pathway for showing dramatic increment in electrical conductivity.^{8,9} In my research, experimental and theoretical clarification steps were attempted to elucidate the characteristics of the doped electrical conducting polymer, for applying into flexible energy storage devices.

1.1.2 Conducting Polymer

The conductive polymer is a conductive organic macromolecule. Such compounds may have a metal conductivity or may be a semiconductor. The greatest advantage of conductive polymers is their workability, mainly through dispersion.¹⁰ Intrinsic conductive polymers (ICP)

and extension of π - conjugation along the polymer backbone, and their electrical conductivity can be changed by several orders of magnitude from semiconductor to doped metal state.^{11,12} The conjugated polymers considered to have promising characteristics including light weight, flexibility and low cost.^{13,14} However, the polymers have several limitations to use for practical application. For examples, the polymer was reported to have lack of solubility because of the inherent rigid conjugation of polymer backbone.¹⁵ It decreases process ability when it is exposed to solvent. When we consider this polymer layer for the alternative electrode, inferior mechanical integrity may limit the performance of corresponding energy and electronic devices.^{16,17} In addition, compared to other classes of conductor, it was reported to show a limited electrical conductivity.¹⁸⁻²⁰

1.1.2.1 PANI

Among conducting polymers, polyaniline (PANI) is expected to be a good candidate for electrodes because of its high capacitance, less-expensive fabrication cost, and environmental stability.²¹ However, due to the shortcoming of mechanical stability in charge discharge process, it is difficult to get high cycle stability of device with only utilization of PANI. It is necessary for application of composite materials to enhance electrochemical performance.²²

1.1.3 Applications

The electrical conducting polymers were reported to have light weight, electrical conductivity, mechanical flexibility and low cost along with economical merits. The polyaniline was studied to show three oxidation states showing different colors that could be useful for energy and display applications.^{23,24} The advancement of mechanical integrity of the

polymer make it hero in textile engineering and science.²⁵ Another possible application is to apply the polymer layer on a conformal substrate for flexible electronic and energy devices.²⁶

Other attractive application fields of polyaniline are antistatic, charge dissipation or electrostatic dispersion (ESD) coating and blending, electromagnetic interference (EMI) shielding, anti-corrosion coatings, hole injection layer, transparent conductors, actuator, chemical vapor and solution sensors, paints and coatings, toxic metals recovery, catalysis, fuel cells and active electronic components such as non-volatile memory.²⁷⁻³⁰ At present, the main applications are printed circuit board manufacturing, anti-static coatings and anti-corrosion.

1.2 Purpose of the Study

There are several pathways that were developed to improve the solubility and electrical properties of the conjugated polymers for several decades. One of the main routes was to change molecular structure of polymers applying additional solubilizing side chain that can hinder charge transport in turn.³¹ Another approach is to modulate the molecular structure of dopants that induce high electrical conductivity and solubility.³² We would like to apply highly solubilizing dopants for maximizing electrical conductivity and solubility as means of processability enhancement. We aim to acquire superb polymer conductor layer from thin polymer films that used state-of-the art polymers on several substrates.

PANI exhibits high performance for the application in energy and organic electronic devices. For this application, it is critical to have appropriate highly conductive electrode. Chemical doping and post treatment on polyaniline were reported to induce electrical and optical properties. I am trying to achieve ultimately high electrical conductivity and conformal

properties from the polymer films after chemical doping and post treatment. It is a promising for achieving state-of-the art energy and organic electronic device performance via mobile era.

CHAPTER 2

LITERATURE REVIEW

This chapter is reviewing the certain concept of PANI, the synthesis mechanism and steps and how it works as an electron conductive polymer. And This chapter is reviewing the specific method used to increase the conductivity of PANI.

2.1 Polymerization

Polymerization refers to the macromolecule formation of monomer molecules through mutual connection, especially very large molecules with average molecular weight of 5000 or more to get new material, called polymers.^{72,73}

2.1.1 Oxidative Polymerization

2.1.1.1 Oxidative Polymerization of PANI

Chemical oxidative polymerization of aniline occurs acidic aqueous solution using antioxidant oxidation polymerization of aniline monomers. Oxidative polymerization method prepare of large quantities of polyaniline is the most common method to prepare of polyaniline. This kind of synthesis is mainly impacted by kinds and concentrations of acid reaction medium, the kinds and concentrations of oxidizing agent, monomer concentration and reaction temperature, reaction time and other factors. Protonic acid are the important factors influencing on the oxidation polymerization of aniline. The most common oxidants are hydrogen peroxide, dichromate, sulfate and ferric chloride.

2.1.1.2 Chain Mechanism of Aniline Polymerization

Oxidative polymerization is usually regarded as a condensation due to chain growth accompanied by the formation of low molecular products. The formation of the chain may take place in two ways. The first step is the free radical oxidation of the complex cation. In this step, the polymer growth process is classified as condensation because any length of the fragment may be recombined. The second method of chain growth is electrophilic substitution. For aniline, the aniline attacks the ortho position of phenyl ring proton of another aniline molecule. After the ring and nitrogen lose a proton, the monomer units bind each other and the chain becomes longer.

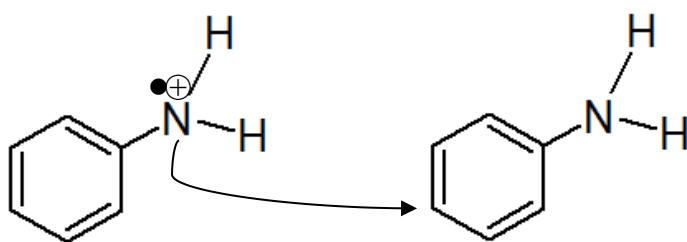


Figure 2.1 Electrophilic substitution reaction of aniline.

2.1.2 Emulsion Polymerization

Emulsion polymerization is referred as emulsifier is used under mechanical agitation or oscillation having monomer encapsulated in the emulsifier in the water. The emulsion polymerization reaction products including latex can be directly used and can also keep the rubber latex after washing and drying operations. Drawback of the polymerization is adding emulsifier and other affected products performance.

2.1.2.1 Emulsifiers

Emulsifier is a substance capable of improving the surface tension between the various constituent phases in the emulsion to form a uniform and stable dispersion or emulsion. The emulsifier is a surfactant that has both a hydrophilic group and a lipophilic group at the same time. It accumulates at the oil / water interface to reduce the interfacial tension and to reduce the energy required to form the emulsion, thereby increasing the energy of the emulsion.

2.1.2.2 Emulsion Polymerization of PANI

Emulsion polymerization in preparing polyaniline has the following advantages. 1. Water is used as the heat transfer medium; the product can be easily separated; 2. Macromolecular organic sulfonic acid as surface active agent can be combined or one step of the proton acid doping to improve the conductivity of polyaniline; 3. The yield of polyaniline produced by this method reaches more than 80% having the conductivity of polyaniline is greater than 1 s/cm; 4. Solubility in organic solvent is improved significantly.

2.1.3 Free Radical Polymerization

Free radical polymerization uses free radicals to growing the length of chain molecules. Addition polymerization, mostly by the alkene monomers containing unsaturated double bond as raw material forms macromolecules by opening the double bond of the monomer molecules and by repeating the addition reaction between the monomer and connecting the monomer. It is mainly used in alkene addition polymerization. The most common way to produce free radicals is via the thermal decomposition of initiation using heat, ultraviolet irradiation, high-energy irradiation, electrolysis and plasma methods.

Because the chemical polymerization of aniline is very fast, it is hard to track and to separate of intermediate. Electrochemical polymerization is relatively easier to control and to tracking.

2.2 Conducting Polymers

Conducting polymers, more accurately, is intrinsically Conductive polymer(ICP). It is a kind of electrical conductivity of the polymer also known as conductive plastics. The simplest example is polyacetylene. It is completely different material compare to the conductor which made with metal or carbon powder blended with other materials.^{33,34} Besides conducting polymers that are modulated structure, it is introduced by "doping" and contains a pair of anion (p - doped) or a pair of cationic (n - doped). So, the structural characteristics of conductive polymer is usually composed of a polymer chain and non-bonding of anion or cation. Such compounds can be metallic conductive or can be semiconductive.³⁵⁻³⁷ The biggest advantage of conducting polymers is their machinability. Usually it is thermoplastic conductive polymers, in other words, they are not thermoformable.³⁸ As well as insulating polymer, they are organic material.

2.2.1 Conductivity

Based on the electrical properties, materials are generally classified as insulators, semiconductors, conductors and superconductors.^{39,40} Figure 2.1 shows a material with conductivity less than 10^{-8} S/cm is regarded as an insulator; a material with conductivity between 10^{-8} S/cm and 10^3 S/cm is regarded as a semiconductor; a material with conductivity

larger than 10^3 S/cm is regarded as a conductor and a material with conductivity larger than 10^3 S/cm is regarded as a superconductor.

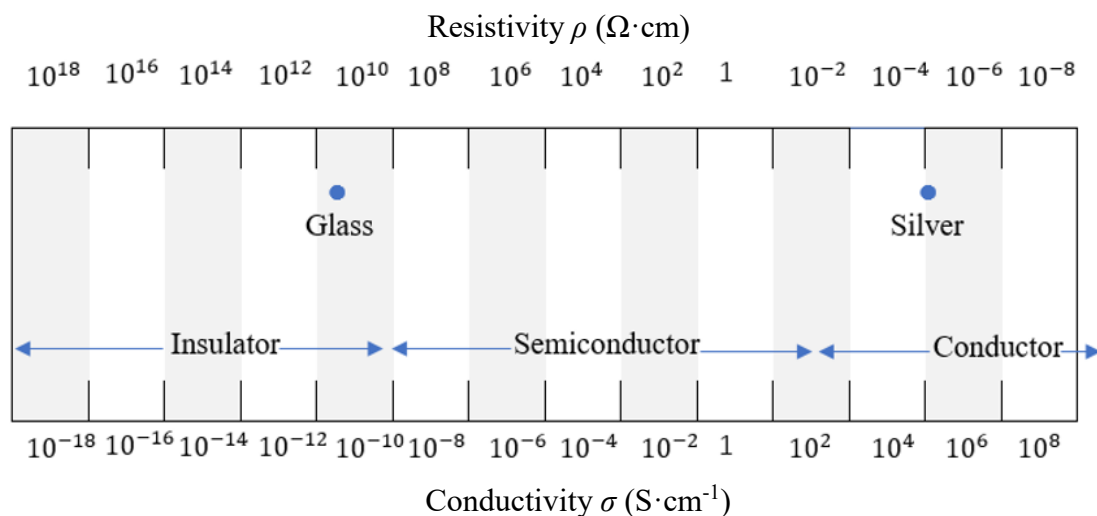


Figure 2.2 Classification of insulators, semiconductors, conductors.

It was generally believed that polymers and electronic conductivity were mutually exclusive and the inability of polymers to carry electricity was distinguished them from metals and semiconductors.⁴¹ As such, polymers were traditionally used as inert, insulating and structural materials in packaging, electrical insulations and textiles where their mechanical and electrically insulating properties were paramount.

The conductivity of the conducting polymers could change under room temperature, and the scope could be various from insulator, semiconductor to conductor.^{16,42} This is unmatched by any other materials until now. Because the electrical properties of conducting polymer cover such a wide range, it is versatile in a very wide range of applications. For example, a high conductivity of conducting polymer can be used for electricity conductor, magnetic shielding, anti-static, or molecular wires. The semiconducting properties of conducting polymer can also be used for photovoltaic electronics, like transistor, rectifier and light emitting diode (LED).²⁷⁻

2.2.2 Resistivity

The resistivity is used to represent characteristic quantities of resistance of various material. A substance made from resistance at room temperature and the ratio of the product of the cross-sectional area and the length is called the resistivity of the material. Resistivity and the length of the conductor, cross-sectional area and other factors, are used for assessing the electrical properties of conductor material itself. The resistivity is determined by the conductor material and is related to the temperature.

In a certain temperature, it can be expressed as:

$$\rho = \frac{Rs}{L} \quad (1)$$

Where ρ is resistivity, L is the length of the material, s is the area and R is resistance. The resistance of the material is proportional to the length of the size and material, namely in the material and at constant cross-sectional area, the longer the length, material more resistance: the materials and is inversely proportional to the cross-sectional area, namely the material and at constant length, cross-sectional area will impact on decreasing the resistance.

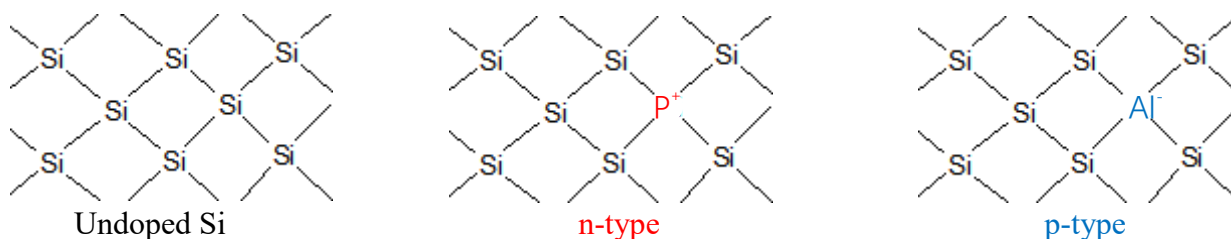
2.3 Doping

In semiconductor production, doping is a process that intentionally introduces impurities in purpose to make the semiconductor to modulate its electrical properties. Doping materials are known as extrinsic semiconductors. Doped semiconductors can achieve very high conductivity, which is closer to a conductor than the semiconductor itself.

2.3.1 Doping in Conducting Polymers

Doping in organic conjugated polymer is responsible for the great importance of science and technology through these materials since its discovery in 1977.⁴³ Doping is the concept of unique and a central theme, uniting all conductive polymers and distinguishes them from the other types of polymer. In doping process, insulating organic polymer or semiconducting polymer coats can be converted into electronic polymer showing metallic conductivity.^{12,44} Although the term “doping” might look familiar to inorganic semiconductors, the concept is much different.⁴⁵ Figure 2.2 shows a schematic diagram to explicit the difference between the mechanisms of doping in inorganic semiconductors and conjugated polymers.

Doping in Inorganic Semiconductor



Doping in Conjugated Polymer

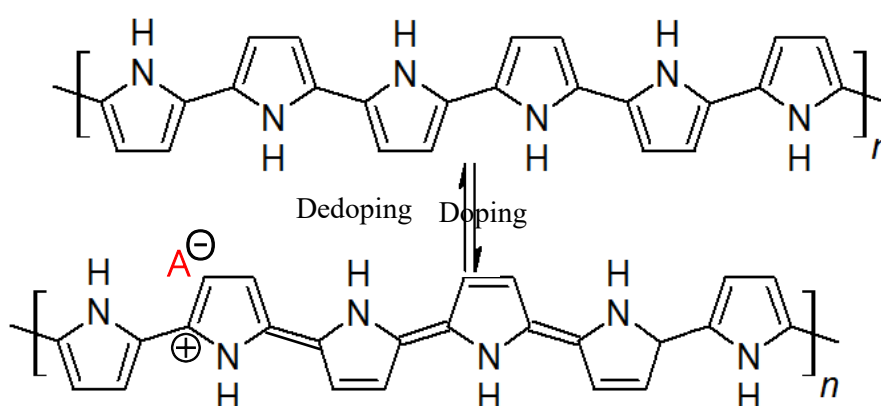


Figure. 2.3 Schematic diagram to explicit the difference between the mechanisms of doping

in inorganic semiconductors and conjugated polymers.

The physics in inorganic semiconductor physics doping process describes dopant kinds in a small amount of lattice in the main material leading to a change of the conductivity in the doped material rather than in the undoped one.⁴⁶ Where conjugated polymers in doping process is the nature of the charge transfer reaction leading to partial oxidation and reduction (or less frequently reduction) of the polymer. Unlike inorganic semiconductor, doping in conjugated polymers is a reversible process keeping original structure where almost no degradation of the polymer backbone can be achievable.^{15,47}

2.3.2 Dopant

Doping process is essentially a process of oxidation or reduction of conductive polymer that uses oxidizing or reducing agent in the doping process known as dopant.⁴⁸ Dopant, also known as the doping agent, is trace amount of impure elements inserted into the material (at very low concentration) to change the electronic or optical properties of the matrix material. Dopant having oxidation ability called p-type dopant is the electron acceptor; On the contrary, capable of reducing dopant called n-type dopant is electron donor.^{49,50}

2.4 Conjugated Polymer

In unsaturated compounds, there are three or more than three parallel p-orbital forming large π -bond each other, which can be characterized by a backbone chain of alternating double- and single-bonds in this system is called conjugated compounds.⁵¹ Figure 2.3 shows the examples of the conjugated compounds. Conjugated compounds by one or several structural

unit linked by covalent bond formation of high molecular weight compounds is the conjugated polymers.

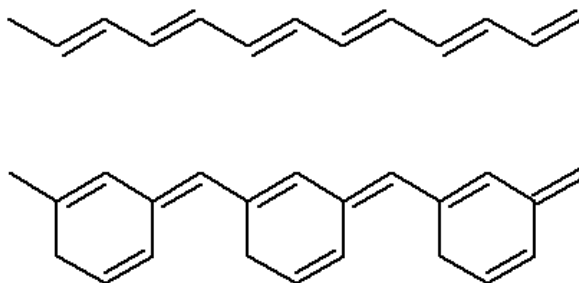


Figure. 2.4 Examples of the conjugated compounds.

2.4.1 Electron Mobility

Electron mobility is a kind of speed that how quick the electrons within the outer electric field under the action of liquid medium are accelerated and are migrated.⁵² Usually in solid state physics, it is used to describe the internal electronics, metal or semiconductor in electric field under the action of moving speed of physical quantities. The electron mobility (electron transfer rate under the unit field) is the force along the electric field on the direction on the electron. The mobility is usually less than the random thermal motion rate and its size is decided by blocking medium and can achieve a balance between field acceleration to determine.

In the semiconductor, a similar physical concept called hole transportation. People commonly used carrier mobility to refer to the semiconductor electrons and holes within the overall movement speed.⁵³

2.4.2 Band Gap

Band gap is the difference between the lowest point of the conduction band and the highest point of the valence band and is also known as energy gap. The greater the band gap, the harder the electrons are excited from the valence band to the conduction band, the lower the intrinsic carrier concentration, and the lower the conductivity, as showing in Figure 2.4.

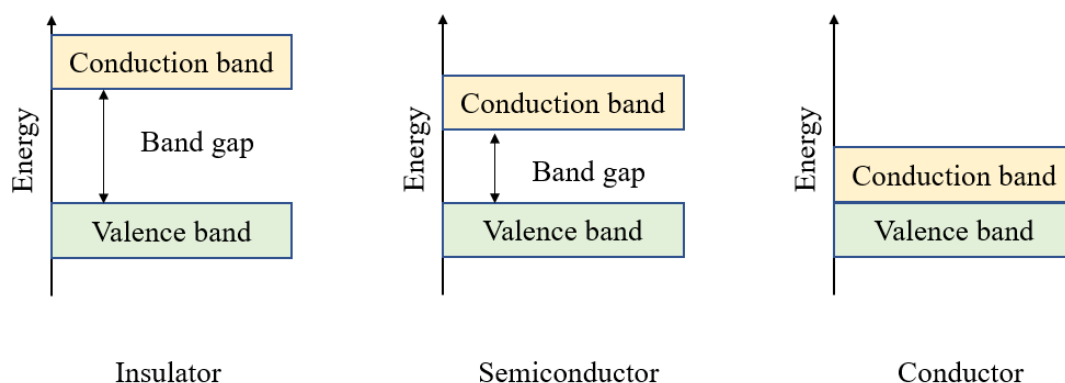


Figure 2.5 Energy band gaps in materials.

2.5 Polyaniline

Polyaniline (PANI) is a kind of macromolecular compounds having special optical property, electrical conductivity and electrochemical properties after doping.^{23,54} Figure 2.5 shows the molecular structure of PANI. Polyaniline has been widely research and application materials because of its easy and simple synthesis process and the characteristics of chemical and environmental stability.^{21,22}

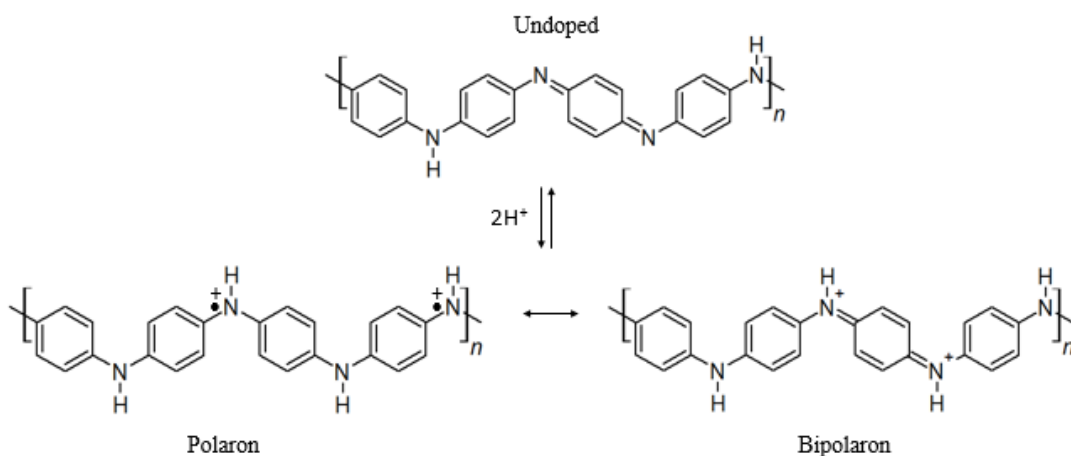


Figure 2.6 Molecular structure of Polyaniline.

Figure 2.6 shows the synthesis mechanism of PANI. This unique doping mechanism make the doping and *de*-doping of PANI completely reversible. The doping level is affected by factors including pH value and potential. According to the change of doping level, the color of PANI was observed to be changed. It also induces electrically discoloration according to electrochemical activity and features.^{21,55} Figure 2.7 shows the synthesis step of PANI.

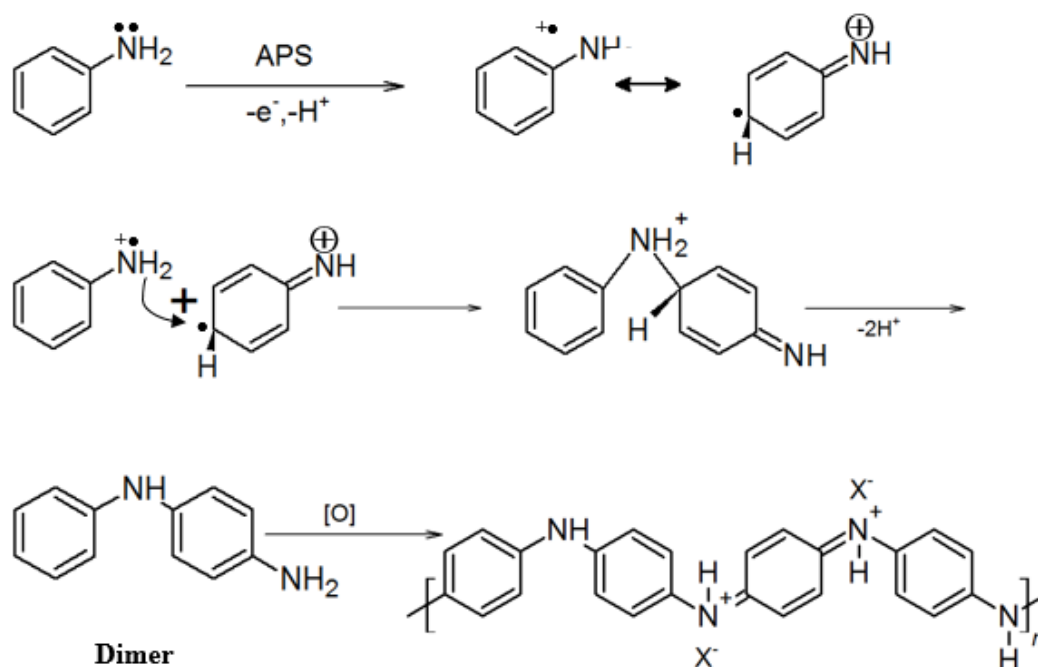


Figure 2.7 Polymerization mechanism.

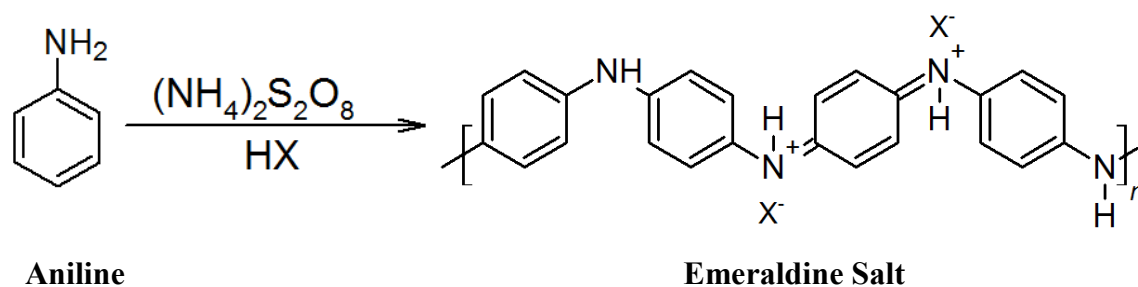


Figure 2.8 Polyaniline overall synthesis.

2.5.1 Doping in PANI

The structure of polyaniline doped with dopants is, mainly composed of polaron lattice and benzoquinone variant. The main part of doped polyaniline is imine nitrogen atoms.⁵⁶

Proton is a key atom to induce doping polyaniline by changing insulation state into a metal state key. Polyaniline is originally insulator and the protonic acid can dope the polymer or oxidation can make conductivity of polyaniline increase ten orders of magnitude. In the proton acid doping, electron number does not change.^{57,58}

2.5.2 Solubility of PANI

Because of the strong rigidity of the chain and the strong interaction between the chains makes the PANI have poor solubility, poor machinability and accordingly, limited application.⁵⁹ Today, improving the solubility and processability of polyaniline has become the topic concerned by the researcher. Polyaniline is known to be soluble in a very few solvents, including N - methyl pyrrolidone, dimethyl allyl urea, m-cresol and concentrated sulfuric acid.⁶⁰

2.5.3 Conductivity of PANI

The conductivity of polyaniline is greatly influenced by the pH and temperature. When the $\text{pH} > 4$, the conductivity has nothing to do with the pH showing the insulation properties; When $2 < \text{pH} < 4$, the electrical conductivity of the solution was represented to the increase rapidly showing its performance as for semiconductor; When $\text{pH} < 2$, metallic properties were represented the doping having more than 40% of doping level, along with good electrical conductivity. Studies have shown that the use of 12.0 mol/L of HCl, can dope polyaniline as much as 46.7% which means that the molecular chain on every two nitrogen atoms has less than a proton.^{61,62}

In a certain temperature range, the conductivity of polyaniline increases with the increase of temperature.^{61,63-64} Under a certain pH, with the potential rise, the conductivity increases gradually and then reach a to a saturation point. But when potential continue to rise, conductivity fell sharply and finally shows insulating characteristics. The change of scan potential change is reflected from the structural change of polyaniline. Illustrating a state of polyaniline performance, the highest oxidation state and minimum square one are the insulation state, while only half oxidation state can be shown in the middle of the electrical conductivity.

In addition, the sample of the high conductivity shows weak temperature dependence.⁶⁵ Polyaniline conductivity is not only related to the main chain structure but also and is related to substituent. Increasing the substituents on the benzene ring replaced the plane distortion angle to plane between the benzene rings, boosting delocalized electronic p orbital on the main chain, reducing the conductivity of polymer. In amino nitrogen atoms substituted aniline

derivatives on the conductivity and the length of the alkyl substituents, namely the longer the substituent, the lower corresponding molecular weight of the product, the greater the solubility in organic solvent, but the conductivity drops.⁶⁶ Aromatic dopants based polyaniline shows higher than alkyl derivatives based polymer.

2.5.4. Dopants

In this specific experiment, three different dopants were added to the pure PANI to increase the solubility and conductivity.

2.5.4.1 Primary Dopant

Dinonylnaphthalenesulfonic acid (DNNSA) referring as 4-Tolythiourea p-Methylphenylthiourea 4-Methylphenylthiourea is a kind of cationic surfactant to make a coating catalyst and can also be used as catalyst for the production amino paint cooling (closed, not enclosed) materials.^{67,68} Figure 2.8 shows the molecular structure of the DNNSA and DNNSA doped PANI (DNPA). As we can see from the structure, the DNNSA molecule contains two long alkyl groups. When it is attached to PANI, it reacts as a proton acid and is directly attached to the PANI cluster by ionic bond. In this case, the long alkyl group is left freely into the opposite space. To increase the solubility of pure PANI, DNNSA was added as primary dopant. The long alkyl chains in the DNNSA enlarge the space between the PANI clusters, which led to decrease the density of the polymer, and finally to increase the solubility of the polymer.

2.5.4.2 Secondary Dopants

To increase the conductivity of the polymer, two secondary dopants, *m*-cresol and thymol are separately added to the polymer.

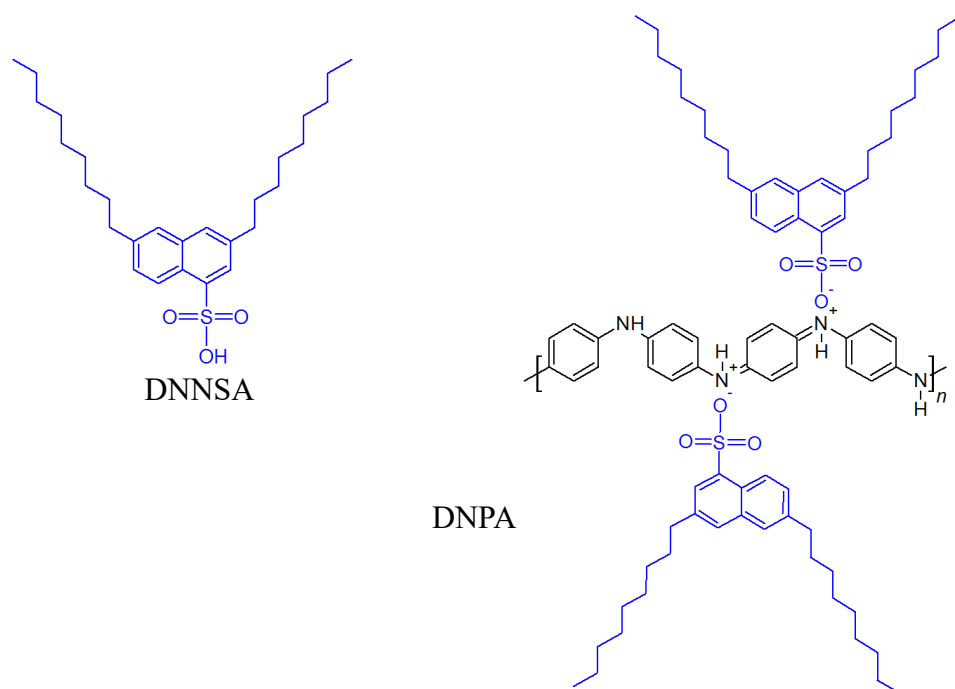


Figure 2.9 Structure of DNNSA and DNPA.

2.5.4.2.1 *m*-cresol

m-cresol is known to be one of the most effective dopant and solvent for PANI doping.^{69,70}

Figure 2.9 shows the structure of *m*-cresol and the DNPA doped with *m*-cresol (DNPAmc).

Please note that *m*-cresol molecules are small enough to spread to PANI cluster and can exchange a proton with polyaniline to increase the conductivity of the polymer. When 3-methylphenolate ions is stayed in PANI cluster can decrease the energy band gap for polaronic and bipolaronic structures were represented to decreasing.⁷¹

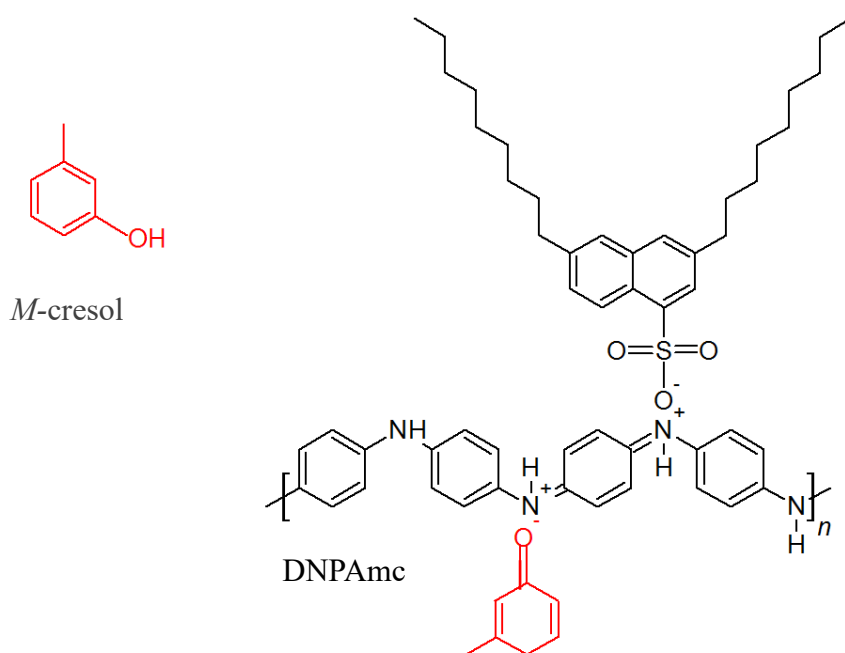


Figure 2.10 Structure of *m*-cresol and DNPAmc.

2.5.4.2.2 Thymol

Thymol, also known as 2-isopropyl-5-methylphenol is a natural monoterpene phenol derivative of cymene. Figure 2.10 shows the structure of thymol and the DNPA doped with thymol (DNPA_{tm}). We can tell from the structure that thymol has a similar chemical structure as *m*-cresol, but contains an extra isopropyl group at ortho position. It is still small enough to approach to PANI blustery. However, because of as the existing of the isopropyl group, there is a steric hindrance between the isopropyl group and PANI cluster. This makes a rotation of the thymol molecular causing out-of-plane geometry. In this case, DNPA_{tm} has a lower density then DNPA_{mc}, which is resulting in a lower conductivity.

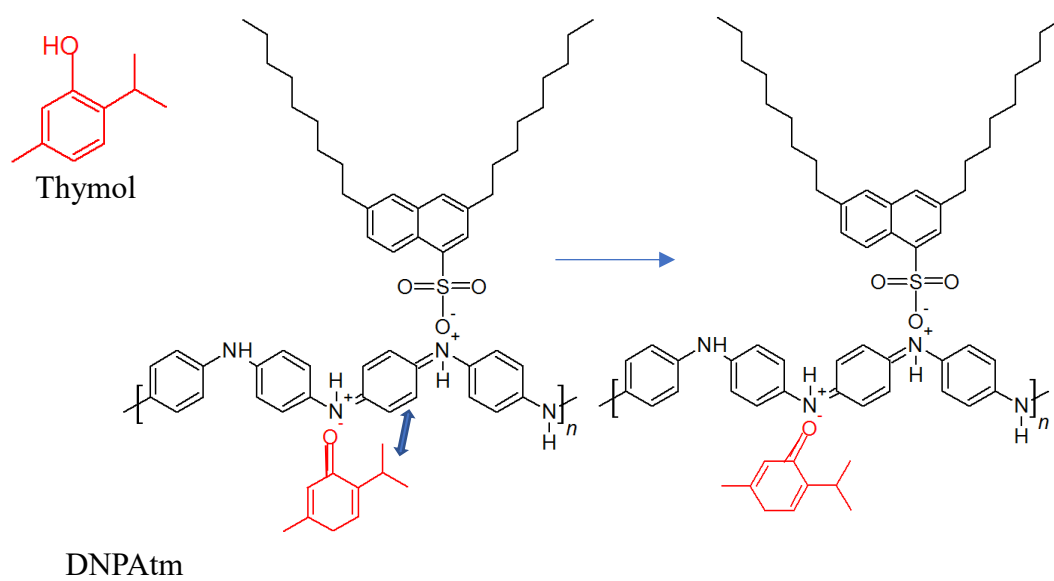


Figure 2.11 Structure of thymol and DNPAtm.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

Dinonylnaphthalene Sulfonic Acid (DNNSA) was used for synthesized DNPA and was obtained from King Industries. Aniline (99+%, ACS reagent) was purchased from Acros Organics. Ammonium Peroxydisulfate (Crystalline/Certified ACS) ((NH₄)₂S₂O₈) was purchased from Fisher Scientific. 2-Butoxyethanol (99%, CH₃(CH₂)₃OCH₂CH₂OH) and *o*-Xylene (99%, C₆H₄(CH₃)₂) was purchased from Acros Organics. Sulfuric Acid (certified ACS Plus, (H₂SO₄)) was purchased from Fisher Scientific. *m*-Cresol (99%, CH₃C₆H₄OH) and Thymol (99%, C₁₀H₁₄O) were used for solution doping and thin film doping and were purchased from Acros Organics. All reagents were used without further purification.

3.2 Methods

3.2.1 Synthesis of Polyaniline

Deionized water from a Barnstead NANOpure Ultrapure water system was used throughout this work to prepare the solutions.

0.0868 mol of DNNSA (as a 50% w/w solution in 2-butoxyethanol) was mixed with 0.0601 mol of aniline and 200 mL of water was used to form a milky white emulsion. The emulsion was chilled to 5°C, mechanically stirred. Separately ammonium peroxydisulfate (0.07212 mol in 40 mL of water) was also chilled to 5°C and was added dropwise to the mixture over a period of approximately 1 h. During this period the color of emulsion solution was

changed from white to amber. The reaction was allowed to run for 4 h under 4°C, overall reaction was run for 8h. During the reaction time, the emulsion was separated into a green 2-butoxyethanol phase and a colorless aqueous phase.⁷⁴

The organic phase was washed one time with 50 mL portions of water, leaving a dark green and highly concentrated polyaniline phase in 2-butoxyethanol. This concentrate was readily soluble in xylene.

0.01M Sulfuric Acid solution was prepared using 0.00571 mol of sulfuric acid and 30.24 mL of deionized water. The solution was added dropwise to the synthesized polymer solution. The organic phase was washed another two times with 50 mL portions of water. Adjust the polymer solution was adjusted to 15% using o-Xylene.

3.2.2 Coating Methods

3.2.2.1 Dip Coating

Dip-coating method is a construction method of coating with dipping. The operation is to merge the substrate totally immersed in the liquid of the polymer solution after waiting for all the parts with polymer solution is coated. This method is used for the same color coating on both sides of substrate at the same time. However, the thickness of top and bottom may not be uniform and solvent is easily evaporated. Figure 3.1 shows the dip coating method used in the experiment. Dip-coating method is often used in the production of thin film of sol-gel precursor research purposes and it is usually used in the application of thin film on the substrate of flat or cylindrical substrates.⁷⁵

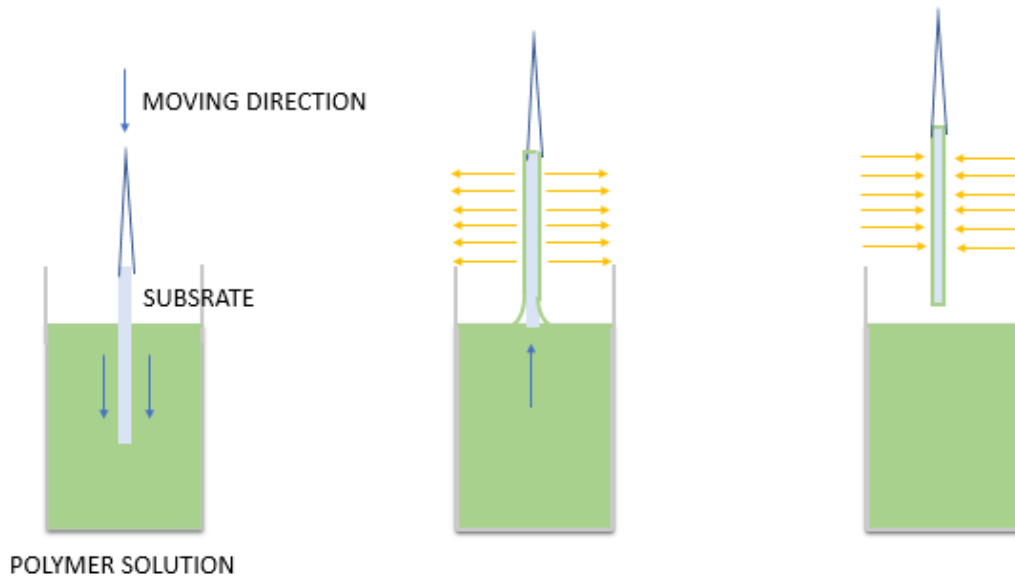


Figure 3.1 Thin film dip coating process.

3.2.2.2 Dr. Blade Coating

Dr. Blade coating, also known as the knife coating or a doctor blading, is the processing method of coating a large area film on rigid or flexible substrate.⁷⁶ Figure 3.2 shows the coating method used in the experiment. Dr. Blade coating requires to provide a constant pressure of wiping. In that case, the solution volume carried by roll plate is determined only by the net volume. To achieve homogeneously constant wipe, different materials and edge configuration are used.⁷⁷

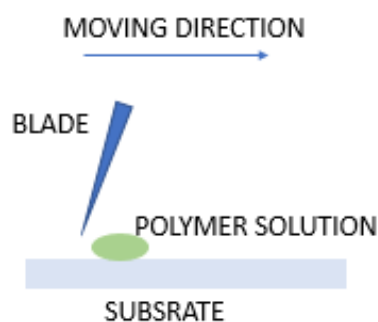


Figure 3.2 Thin film Dr. Blade coating process.

3.2.3 Doping Methods

3.2.3.1 Solution Doping

Solution doping is a doping method which dopes other substances into original solution. Doping is usually referring material to improve the performance of the targeted materials. This kind of method can make materials produce a specific electrical, magnetic and optical properties, making it has a specific value or purpose. Figure 3.3 shows the solution doping process used in the experiment.

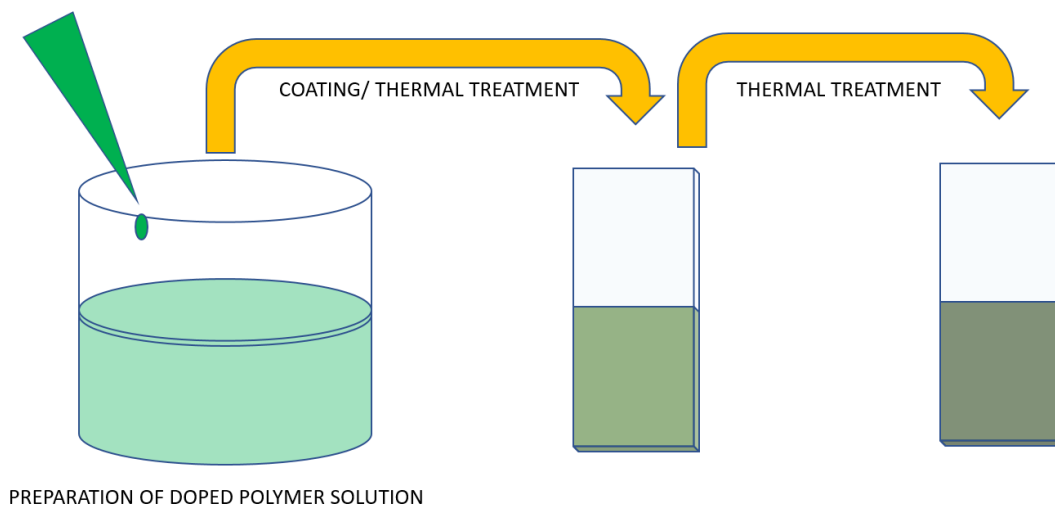


Figure 3.3 Solution doping process.

3.2.3.2 Film Doping

Film doping is a doping method which is a secondary doping after the thin film is already coated. The method is to merge the existing thin film into the doping solution to improve the performance of the targeted material further. To maintain the thin film from degradation in the doping solution, the solution concentration and the temperature should be controlled in a

certain range. Usually, the temperature need under both T_g of the polymer and the T_m of the doping solution. In this experiment, we keep at the room temperature. Figure 3.4 shows the film doping process used in the experiment.

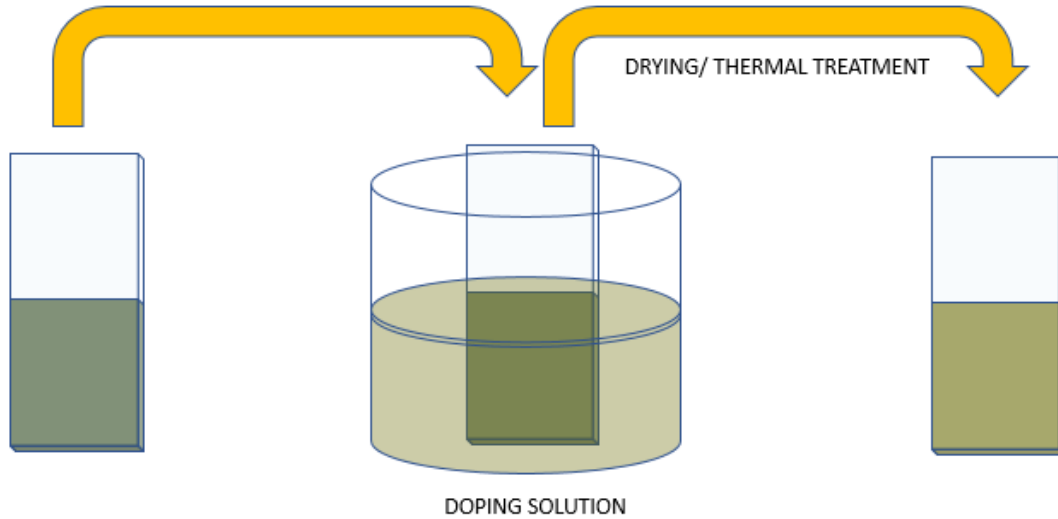


Figure 3.4 Thin film doping process.

3.3 Experimental

3.3.1 Surface Resistance Studies

Surface resistance of physical units is the ohm (Ω). Often, in practice, the surface resistance Ω/square ($\square$). It is important to understand the unit $\Omega/\square$ does mean.⁷⁹ Figure 3.5 shows an example of the size of a square which is used in the series of experiments, which was 1 cm $\times$ 1 cm in this experiment that is consider to be 1cm²-size square.

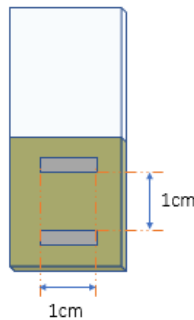


Figure 3.5 Electrical conductivity measurement.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Material Characterization

Fourier transform infrared (FTIR) spectroscopy was used to obtain the information of functional group of the polymer. Ultraviolet-visible (Uv-Vis) spectroscopy was used to obtain the optical property in the ultraviolet-visible spectral region.

4.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

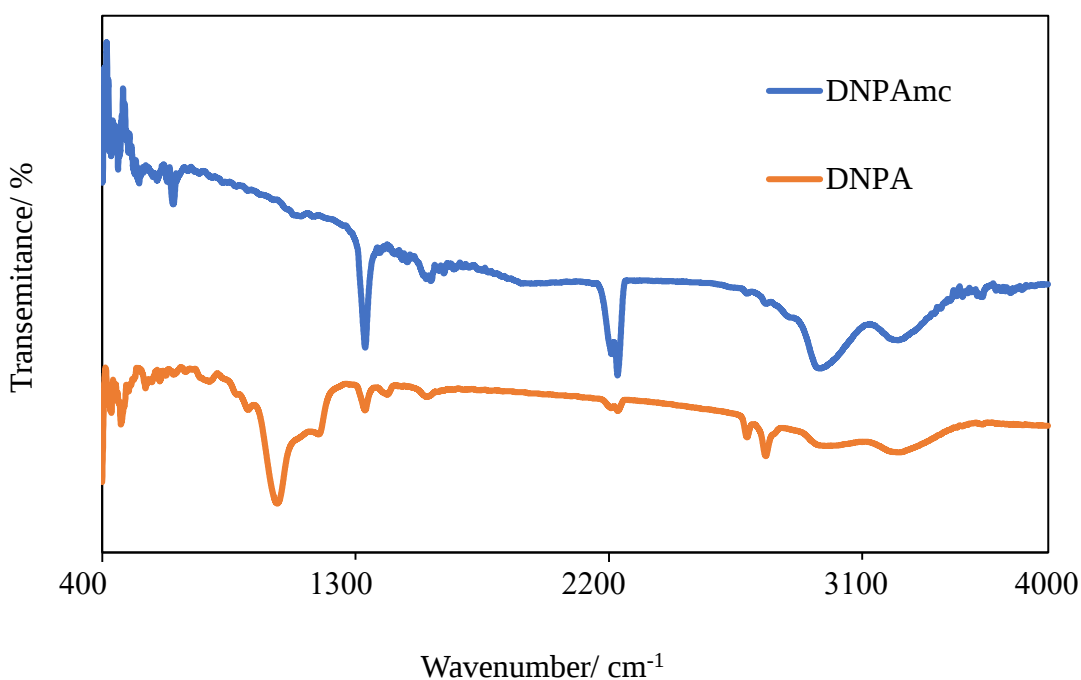


Figure 4.1 FTIR spectra of DNPA and DNPAmc.

Figure 4.1 shows the FTIR spectra of DNPA and DNPAmc composite. For DNPA, the bands at 2926 and 2856 cm⁻¹ correspond to C–H stretching vibration of DNNSA which is the doping agent of PANI. The bands at 1492 cm⁻¹ reflect stretching deformation of quinone and benzene rings, respectively. The band at 1401 cm⁻¹ corresponds to C–N stretching vibration of benzene

ring, while other bands about 1235 and 1072 cm^{-1} reflect aromatic C–H in plane bending and out-of-plane deformation of C–H in the 1,4-disubstituted benzene ring, respectively. Compared with DNPA, the DNPAmc composite is red-shifted obviously, resulting from direct interaction between the delocalized electrons in the m-cresol and the PANI chains.⁸¹

4.1.2 Ultraviolet-Visible (Uv-Vis) Spectroscopy

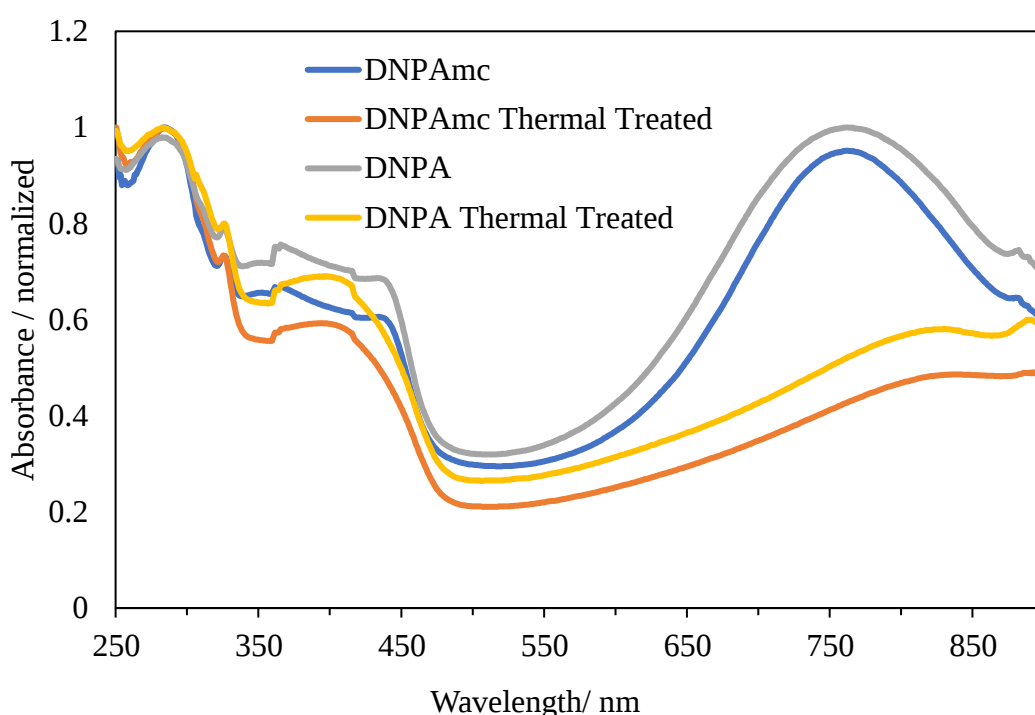


Figure 4.2 Normalized thin film UV–Vis spectra.

Three characteristic absorption peaks of the pure PANI appear at 373, 443, and 871 nm corresponding to $\pi-\pi^*$ transition of the benzenoid rings, polaron- π^* transition and π -polaron transition, respectively, indicating the resulting DNPA is in the doped state of DNPAmc.^{82,83}

As can be seen in DNPA which is the primary doped, thermal treatment does produce the decrease in the absorption in the disappearance of the band at ca. 750 nm (localized polarons)

which only shifts slightly to lower energies with temperature. The absorbance of DNPAmc is observed in all the temperature range as similar to DNPA, but little bit red shift. These results show that the thermal treatment produce a different conformational change, compared to the original samples and the peaks show that after thermal treatment, the random coil-like conformation is changed to a plain extended coil-like conformation.

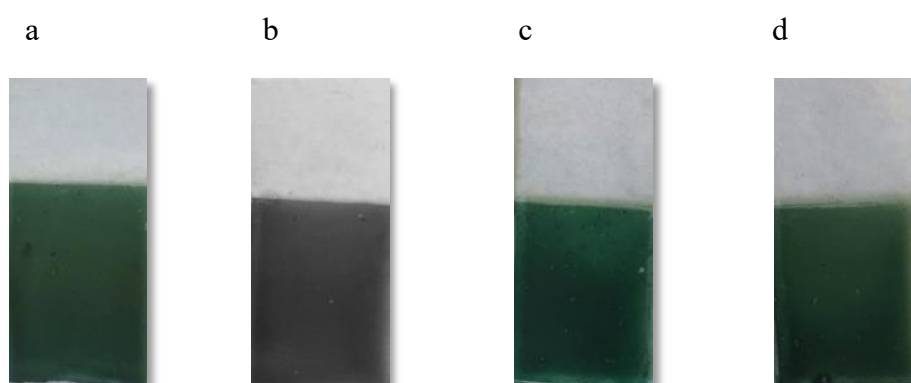
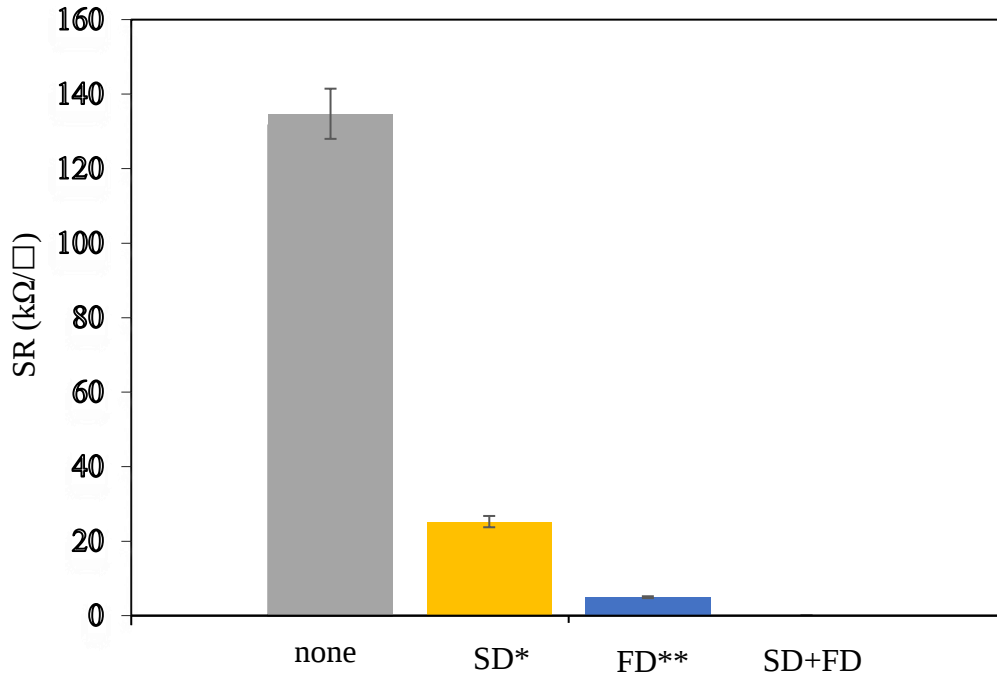


Figure 4.3 Glass plate thin film samples (fixed size) (a) DNPA, (b) DNPA thermal treated, (c) DNPAmc and (d) DNPAmc thermal treated.

Figure 4.3 shows all the DNPA and DNPAmc samples, both original and thermal treated ones are dark green color; but after thermal treatment, the samples become darker. It shows that there is no significant color change before and after thermal treatment, which could be proved by the normalized thin film UV–Vis spectra between 400-700nm which shows the absorbance of visible light. There is no much change between the DNPA and the doped sample of DNPAmc.

4.2 Surface Resistance

Figure 4.4 shows the surface resistance of DNPA using different secondary doping methods. The result of surface resistance ($\Omega/\square$) from high to low follows: none (134730) > solution doping (25250) > film doping (4960) > solution and film doping (60.3).



*SD, solution doping

**FD, film doping

Figure 4.4 Surface resistance of DNPA (grey), solution doped DNPA (yellow) film doped DNPA (blue) and solution and film doped DNPA (orange).

Here we used the same 5% dopant: 1. none doped as original pure thin film sample of DNPA; 2. Secondary doping method was solution doping 3. Secondary doping method was film doping; 4. Two combined methods of secondary doping were using including first solution doping and then film doping. The combined secondary doping method or the tertiary doping method were observed to shows a further lower surface resistance then single secondary doping. The best surface resistance was observed to show $60.3\Omega/\square$, which is a 3-orders of magnitude decrease of the original.

Figure 4.5 shows the surface resistance of DNPA using different thermal treatment method.

The result of surface resistance ($\Omega/\square$) from high to low follows: 15 min (123160) > 15 min×2 times (38150) > 30 min (25250). Here we used three different kinds of thermal treatment at the same temperature: 150 °C and the total thermal treatment of 15 to 30 minutes: 1. thermal treatment once of 30 minutes, 2. thermal treatment once of 15 minutes and 3. thermal treatment separately for two times, 15 minutes each time and totally of 30 minutes.

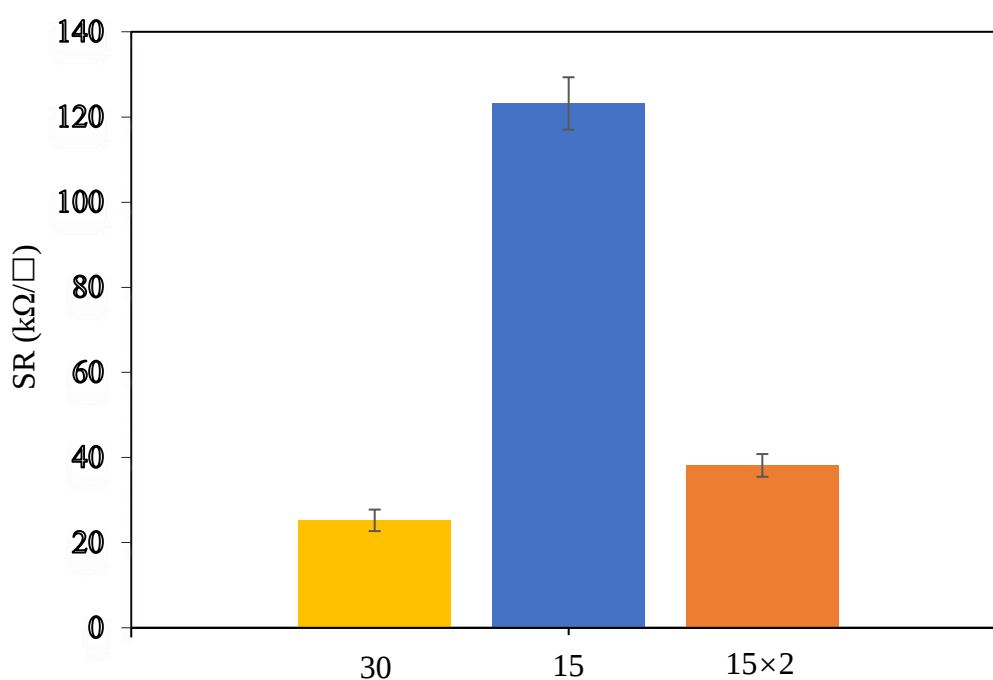


Figure 4.5 Surface resistance of DNPA with different thermal treatments, 30 min (yellow), 15min (blue) and two times of 15 min (orange).

The 30 minutes' treatments has a best result among these three treatment. Compared to the heating for 15 minutes, the cross-link will not well be extending during the 15 minutes' period, and the 30minutes is preferred. Compare to two times of 15 minutes heating, a continuous thermal treatment was found to lead the cross-link conformation more smoothly to extend.

*45-minute controlled thermal treatment is also tested as a similar series without showing a

good result.

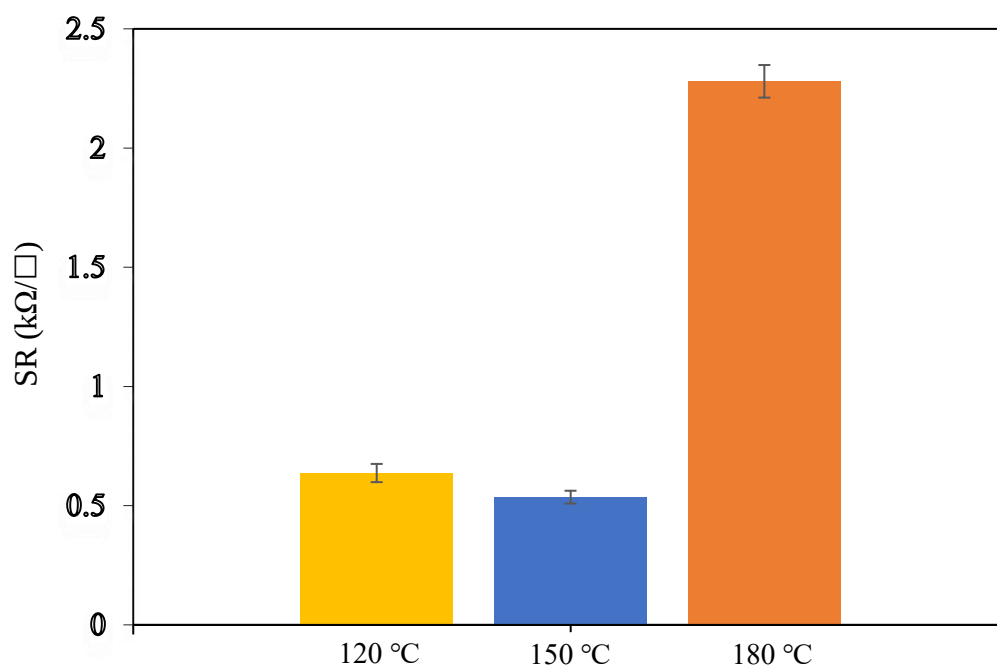


Figure 4.6 Surface resistance of DNPA with different thermal treatments, 120 °C (yellow), 150 °C (blue) and 180 °C (orange).

Figure 4.6 shows the surface resistance of different thermal treatment method. The result of surface resistance from ($\Omega/\square$) high to low follows: 180 °C (2280) > 120 °C (637) > 150 °C (536). Here we controlled three different kinds of thermal treatment at the same period: 15 minutes followed by another 15 minutes; and the total thermal treatment of totally 30 minutes: 1. thermal treatment at 120 °C, 2. thermal treatment at 150 °C and 3. thermal treatment at 180 °C. The treatment at 150 °C has a best result among these three treatment. Compared to 150 °C heating, under the thermal treatment at 120 °C cross-link will not well be extended, and the 150 °C was preferred. The 180 °C might be over the T_g of the polymer, and the structure of it might be impacted.

Figure 4.7 shows the surface resistance of DNPA used two different secondary doping dopants of solution doping. The result of surface resistance ($\Omega/\square$) from high to low follows: none (134730) > m-cresol (19029) > thymol (21010).

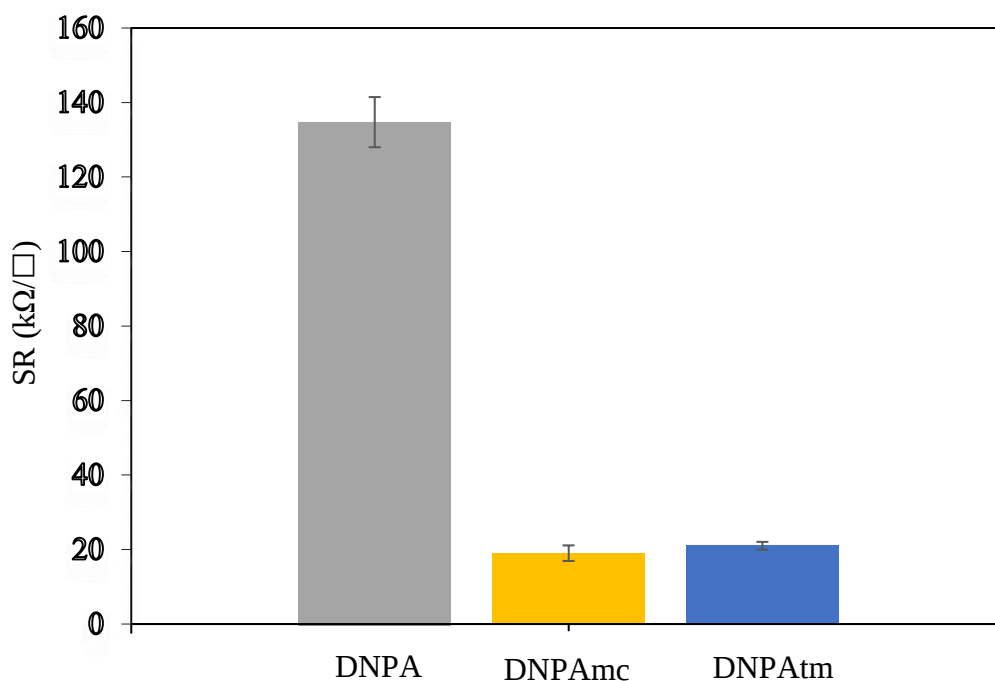


Figure 4.7 Surface resistance of DNPA with different solution doping, DNPA (grey) DNPAmc (yellow) and DNPAtm (blue).

Here we used the sample dopant of the same percentage (5%): 1. Original DNPA, 2. *m*-cresol doped DNPA (DNPAmc) and 3. Thymol doped DNPA (DNPAtm). The treatment at 150 °C was shown best result among these three treatment. Compared to DNPA, both DNPAmc and DNPAtm were observed to the electrical property with secondary doping. But the DNPAmc shows a better result than DNPAtm. As we mentioned in Chapter 2 that thymol contains an extra ortho-position isopropyl group compared to *m*-cresol, and the steric hindrance may break planer p-orbital creating the thymol group attached to DNPA cluster

rotate. This rotation will make a larger space of a single DNPA_{tm} chain than the DNPA_{mc} chain. It means the polymer system will have lower density than DNPA_{mc}, and this will lead the incensement of the surface resistance.

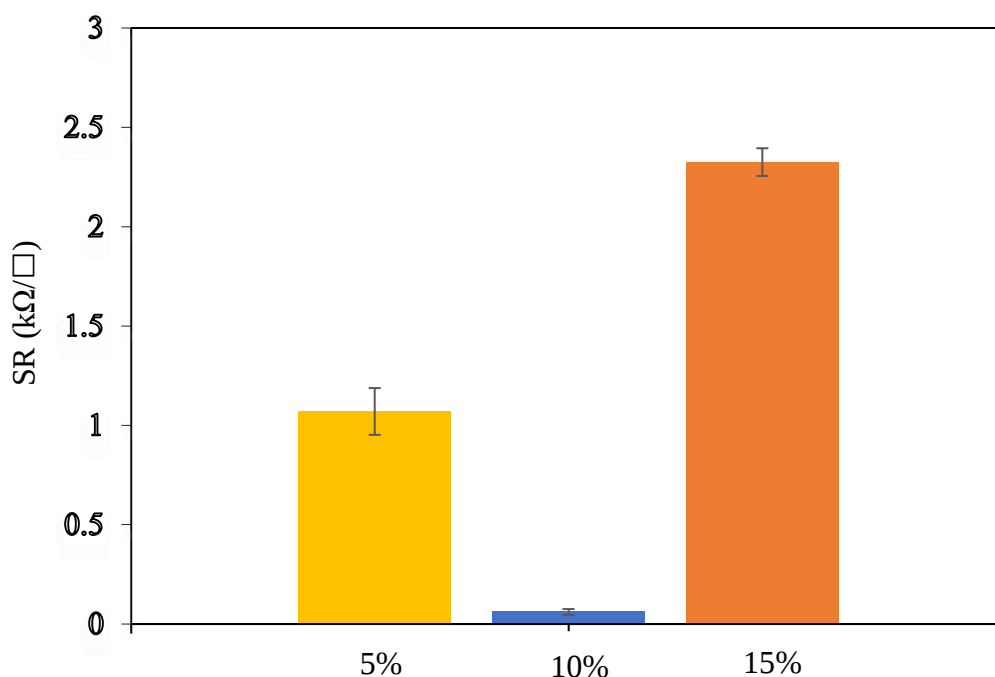


Figure 4.8 Surface resistance of *m*-cresol/ xylene solution film doped DNPA with different percentage, 5% (yellow), 10% (blue) and 15% (orange).

Figure 4.8 shows the surface resistance of DNPA using three different percentage of film doping solutions. The result of surface resistance ($\Omega/\square$) from high to low follows: 5% (1070) > 10% (60.3) > 15% (2325). Here we controlled the sample dopant and the same solution with various percentage of dopant concentration: 1. 5% *m*-cresol/ xylene solution, 2. 10% *m*-cresol/ xylene solution and 3. 15% *m*-cresol/ xylene solution. In the series of experiments, 5% was used to control of the same percentage as the solution doping. Then increase to 10%. When it was increased to 15%, the surface resistance dramatically increased, which means deceased

in conductivity. Under this percentage, the thin film is easy to dissolve in the solution and washed out. Separately, pure *m*-cresol, which means 100% *m*-cresol was also tested and but the result was not as good as the conjecture.

Surface resistance of DNPA was measured with different solution doping, DNPA with 5% *m*-cresol/ 2-butoxyethanol solution doping (grey) and DNPA with 5% *m*-cresol/ xylene solution doping (yellow).

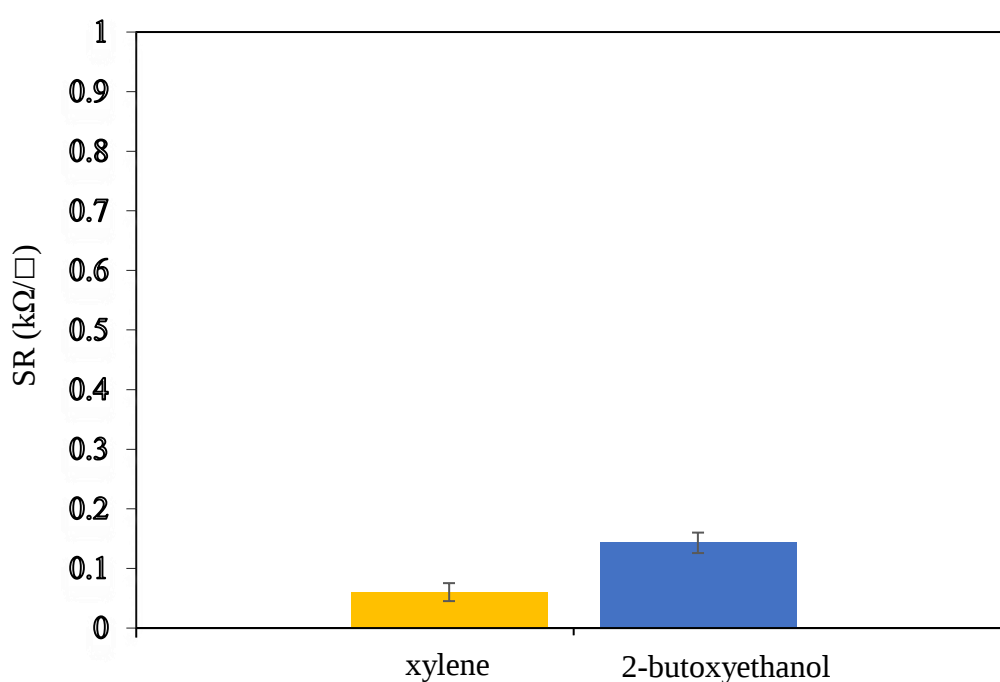
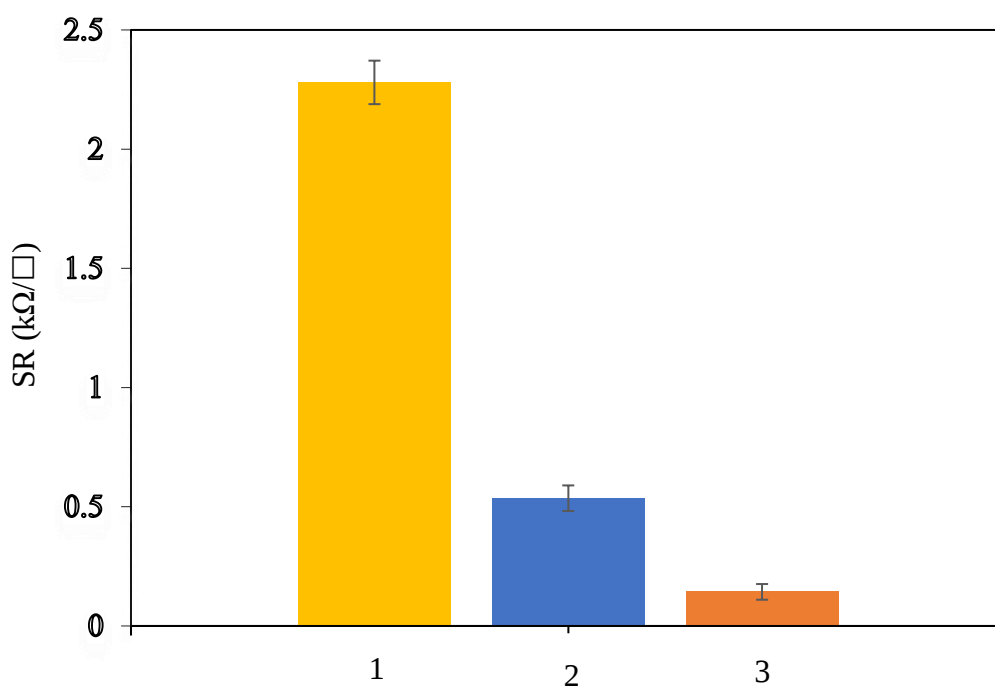


Figure 4.9 Surface resistance of *m*-cresol-based film doped DNPA with different solutions, xylene (yellow) and 2-butoxyethanol (blue).

Figure 4.9 shows the surface resistance of DNPA using two different secondary doping solution of solution doping. The result of surface resistance ($\Omega/\square$) is listed from high to low follows: 2-butoxyethanol (4070) > xylene (1275). Here we controlled the same dopant of the doping solution: 1. *m*-cresol/ 2-butoxyethanol solution and 2. *m*-cresol/ xylene solution. 2-

Butoxyethanol is the original solution contained in the primary doping DNNSA (50% dissolved in 2-butoxyethanol). Compared to 2-butoxyethanol, xylene got a lower surface resistance. It is because the 2-butoxyethanol contains a longer alkyl group than xylene (o-xylene), which improves the solubility instead of conductivity.

Figure 4.10 shows the surface resistance of three different coating methods. The result of surface resistance($\Omega/\square$) from high to low follows: 1 (2280) > 2 (536) > 3 (143). Here we used the same doping solution and same film doping methods: 1. Dip Coated, 2. Doctor Blade coating and Dip coating and 3. Doctor Blade Coating and 2 times of Dip Coatings. As the thickness of film was increased, the surface resistance was decreased, which means increase in the conductivity was increased.



1: Dip Coated;

2: Doctor Blade coating and Dip coating;

3: Doctor Blade Coating and 2 times of Dip Coatings.

Figure 4.10 Nomex[®] paper substrate, Surface resistance of different coating methods. 1 (yellow), 2 (blue) and 3 (orange).

Figure 4.11 shows the surface resistance of two different substrates. The result of surface resistance ($\Omega/\square$) from high to low follows: glass (60.3) > Nomex[®] (143). Here we used the same methods of making thin films: 1. The original (controller), 2. glass plate substrate and 3. Nomex[®] paper substrate.

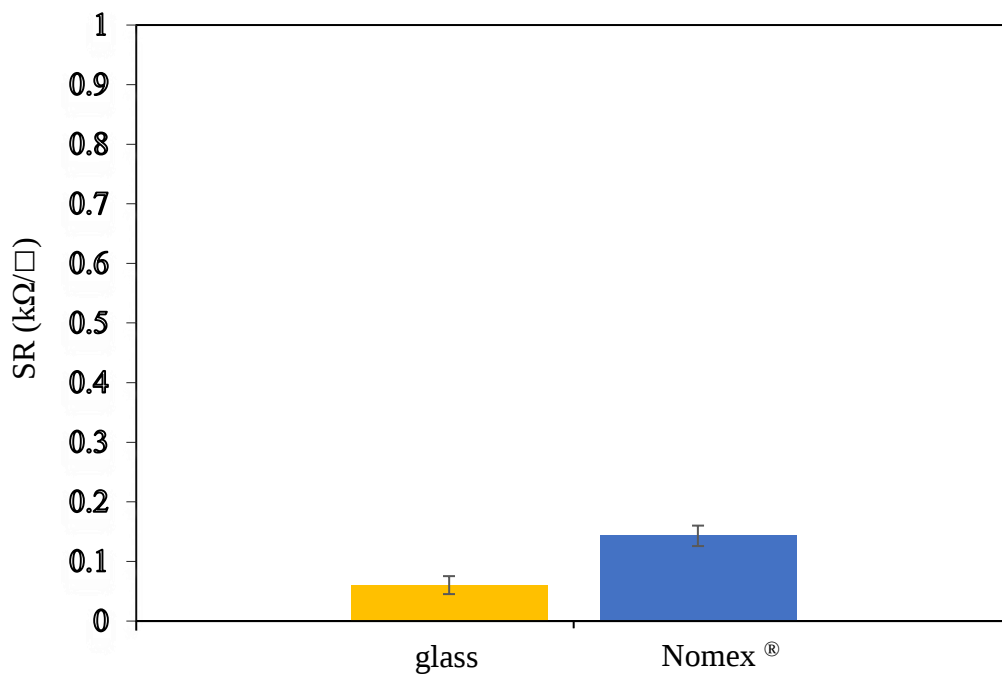


Figure 4.11 Surface resistance of DNPA with different substrates, glass plate substrate (yellow) and Nomex[®] paper substrate (blue).

Compared to the original works we got, there was not much difference between the glass plate substrate and the flexible Nomex[®] paper substrate, where further treated film had better results showing *ca.* 100 $\Omega/\square$.

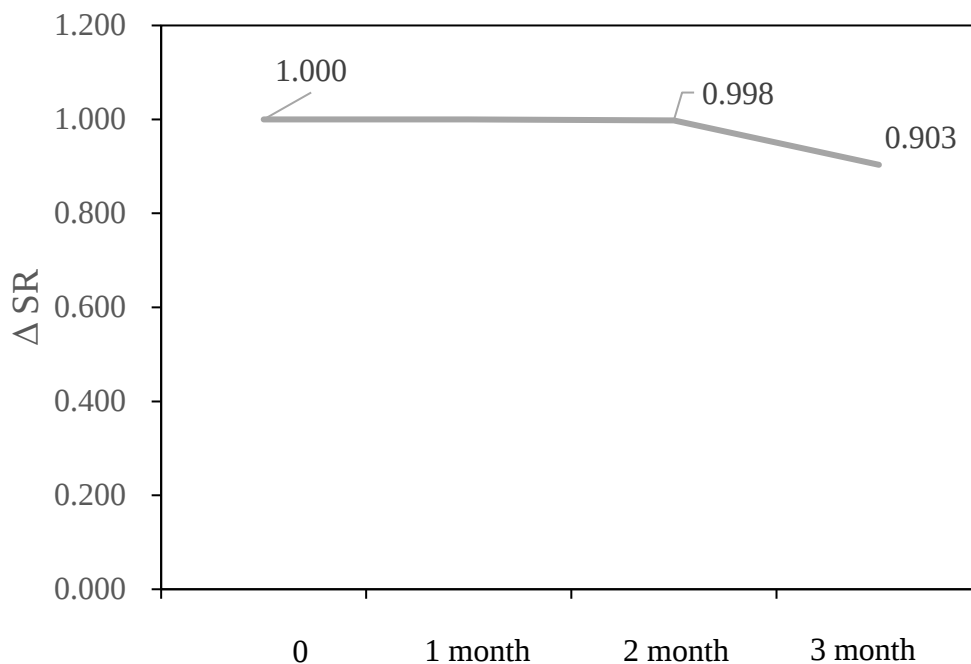


Figure 4.12 Aging test of the DNPAmc surface resistance during 3 months (kept in lab), glass plate substrate.

Figure 4.12 shows aging test results of the surface resistance of DNPA on glass plate substrate using DNPAmc during 3 months (kept in air). We monitored the surface resistance of the film when the film was made and applied the silver paint and then dried overnight and get the respect surface resistance after 1month to 3 months' period, and converted to the series of respect percentage.

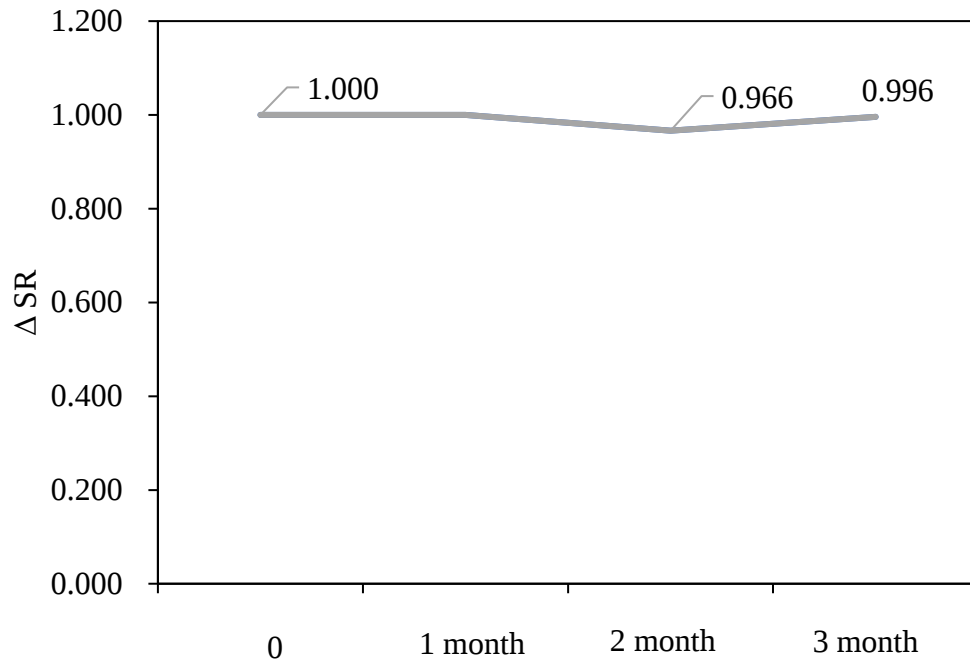


Figure 4.13 Aging test of the DNPAmc surface resistance during 3 months (kept in lab), glass plate substrate. Nomex® paper substrate.

Like Figure 4.12, Figure 4.13 shows aging test results of the surface resistance of DNPA coated on Nomex® paper substrate using DNPAmc during 3 months (kept in air). There was a little increased in electrical property of the third month. It might refer to a well compact of silver paste on the Nomex® paper substrate.

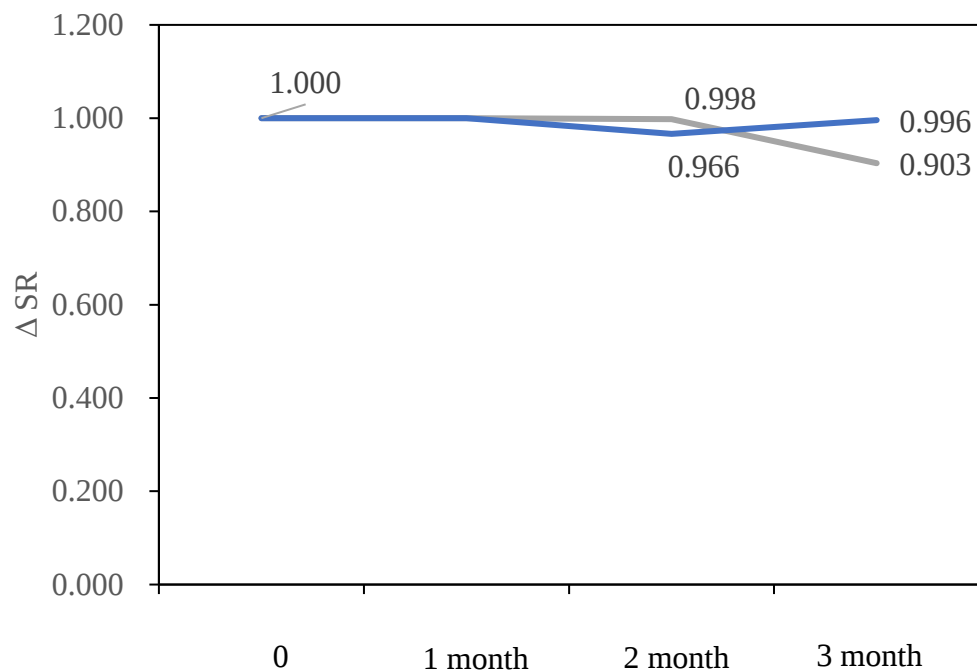


Figure 4.14 Aging test comparison glass plate substrate (grey) and Nomex® paper substrate (blue).

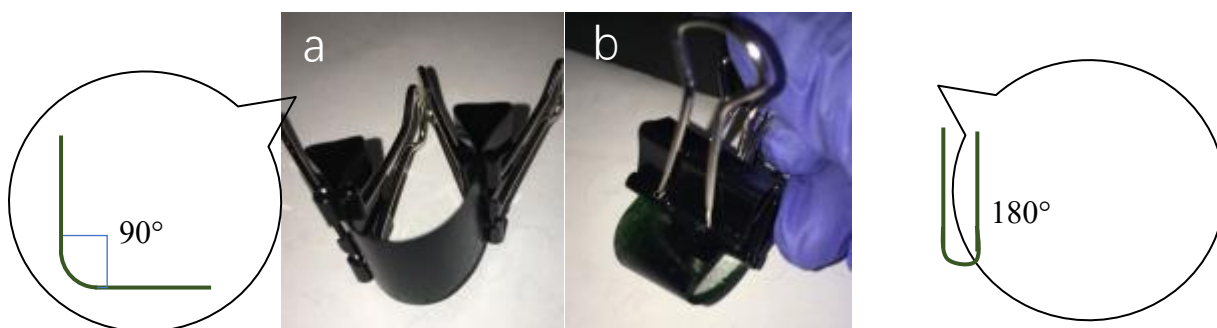


Figure 4.15 Flexible test for polymer thin film Nomex® paper substrate. (a) Bending for 90°; (a) Bending for 180°.

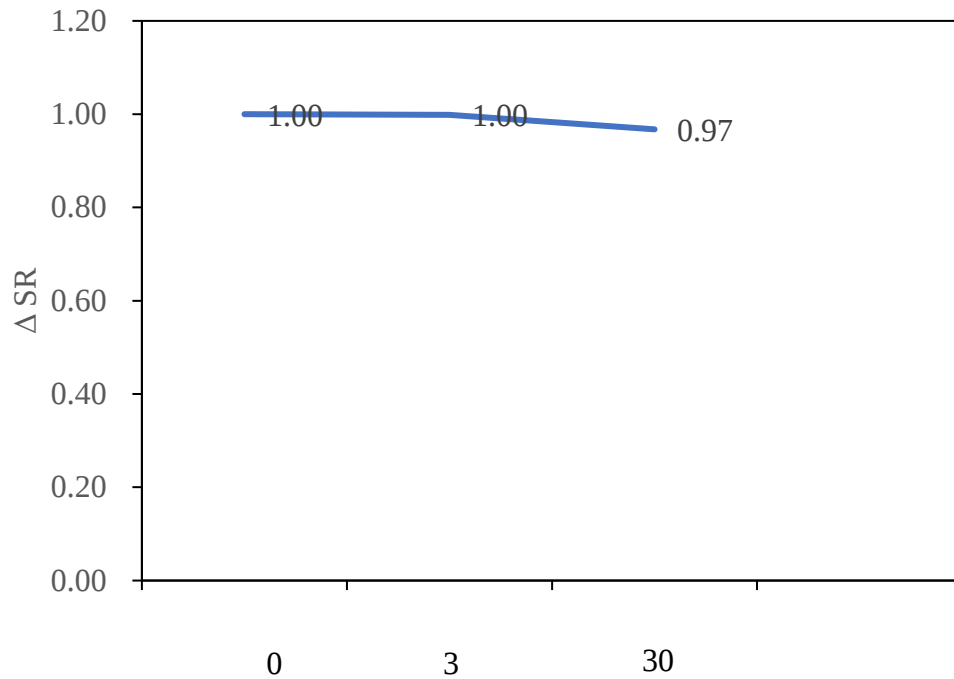


Figure 4.16 Flexible test for polymer thin film Nomex® paper substrate.

Figure 4.16 shows the percentage of original surface resistance, surface resistance after 3 times 180° bending, and surface resistance after 30 times 180° bending. There was no big change even after 30 times of 180° bending. Figure 4.15 shows the digital picture and the shape position that how the film was bended.

CHAPTER 5

CONCLUSION

5.1 Summary

Solution processable electrical conductive polymer was synthesized and characterized applying on a flexible aramid paper (NOMEX®, DuPont). The solution processable electrical conductive polymer was coated on solid substrate as a control and was observed to show enhancement in electrical property from *ca.* 1,000,000 $\Omega/\square$. to $\sim 100 \Omega/\square$. according to post-treatment conditions. Corresponding conformal polymer coats on NOMEX® were fabricated showing similar electrical property and were observed to show sustainable electrical property over 3 months proving excellent mechanical and electrical integrity. Comprehensive characterization and the test results are addressed in the thesis.

5.2 Future Work

The electrical conducting polymers were reported to have light weight, electrical conductivity, mechanical flexibility and low cost along with economical merits. The polyaniline was studied to show three oxidation states showing different colors that could be useful for energy and display applications. The advancement of mechanical integrity of the polymer make it hero in corresponding science. Another possible application is to apply the polymer layer on a conformal substrate for flexible electronic and the energy devices.

Other attractive application fields of polyaniline are antistatic, charge dissipation or electrostatic dispersion (ESD) coating and blending, electromagnetic interference (EMI)

shielding, anti-corrosion coatings, hole injection layer, transparent conductors, actuator, chemical vapor and solution sensors, paints and coatings, toxic metals recovery, catalysis, fuel cells and active electronic components such as non-volatile memory. At present, the main applications are printed circuit board manufacturing, anti-static coatings and anti-corrosion.

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