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DEVELOPMENT OF NANO-THIN FILMS OF CONDUCTIVE POLYMERS BY USING
POLY(VINYL ALCOHOL) AND SPIN-COATING FOR ORGANIC SOLAR CELL
APPLICATIONS

Mr. Nathavat Romyen



จุฬาลงกรณ์มหาวิทยาลัย
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A Dissertation Submitted in Partial Fulfillment of the Requirements
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CHAPTER I

INTRODUCTION

PART1 (PEDOT:PSS)

Among intrinsically conductive polymers (ICPs) nowadays, the poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is the most successful conjugated polymer, that is commercialized in worldwide markets since it was synthesized in the late 1980s [1]. It has been extensively applied in many fields of electronic device industries such as organic light emitting diodes (OLEDs) [2], organic photovoltaic devices (OPVs) [3], capacitors [4], and sensors [5]. This popularity is due to its several advantageous properties such as high conductivity [6], high stability in the p-doped form [7], good film-forming properties [8], and excellent transparency in the visible range [9]. However, several drawbacks of PEDOT:PSS, including high acidity, poor durability and very brittle film properties, UV light-induced degradation, and varying morphology [10], have limited the variety of its applications. The majority of research has focused on procedure in conductivity enhancement of PEDOT:PSS through three major methods [11]. The first was to mix PEDOT:PSS with organic solvents, e.g., dimethyl sulfoxide, *N,N*-dimethylformamine, and tetrahydrofuran. The screening effect plays a crucial role in improvement of charge transport properties due to the polar solvent between the PSS and the PEDOT polymer main chain [12]. The modification of PEDOT:PSS morphology by addition of a dopant was considered as the second method. Sorbitol, isopropanol, glycerol, and *N*-methylpyrrolidone are generally employed as the dopant to induce a conformational change leading to an

increase in the conductivity of PEDOT:PSS films [13-16]. Finally, the addition of a small amount of anionic surfactant, e.g., sodium dodecyl sulfate, could not only boost up the conductivity through a conformational change in the films by the replacement of PSS- as the counteranions to PEDOT, but also could improve the wettability of the film surface [17]. However, such methods described above could only improve the conductivity of PEDOT:PSS by several orders of magnitude, but they did not exhibit any other development of specific PEDOT:PSS properties, such as thermal, mechanical, and morphologic properties. These others important properties development were very rare to have report and usually were neglected despite of their crucial involvement beside the conductivity for advanced electronic applications. In fact, these advanced requirements for PEDOT:PSS could be simply achieved by mixing with other polymers as well known in the concept of polymer blending. It was a widely accepted route to effectively design polymers for specific properties. The beneficial polymer properties can be achieved by physical mixing of two or more polymers together, creating the polymer blends, which exhibit the desirable properties of each pure component in the final products. Indeed, insulating polymers with functional groups of OH, poly (ethylene glycol) (PEG) as an additive in a PEDOT:PSS system could impressively boost up the conductivity of PEDOT:PSS [18,19]. In the same way with poly(vinyl alcohol)(PVA), that also has OH functional groups in its molecule together with its many advantages such as wide commercial availability, excellent solubility in water with high transparency, good film formation, and good flexibility, could possibly improve conductivity of PEDOT:PSS [20]. Moreover, it is possible that a suitable amount of insulating PVA could not only induce the improvement to the conductivity of PEDOT:PSS but also reasonably

improved other properties of PEDOT:PSS because of the interactions between the functional groups of insulating polymers and PEDOT:PSS.

Thus, for the first part of this work, the effects of the integration of two effective strategies, the polymer blending and the addition of a dopant, on the improvement of PEDOT:PSS Nano-thin film properties were investigated. The PEDOT:PSS matrix was physically mixed with various amounts of PVA filler in accordance with the polymer-blending concept. The dopant, quinoxaline, was then added to precisely enhance the conductivity of PEDOT:PSS in accordance with the secondary dopant concept. The Nano-scale thin films were formed by means of the conventional spin-coating. As the conclusion, the introduction of appropriate amounts of both PVA and quinoxaline into PEDOT:PSS could be proven to simultaneously alter various PEDOT:PSS thin-film properties in a desirable way, especially its thermal, mechanical, and electrical properties together for usage in electronic fields as transparent conductive nano-thin films.

PART2 (PEDOT:SPI)

From the first of this work, we have known that PEDOT:PSS is a polyelectrolyte complex formed during polymerization reaction as a gel particle dispersed in water, consisted of conductive PEDOT (polycation) and insulating PSS (polyanion). The PEDOT joined the repeating units of the PSS via ionic interaction, which could not be separated by electrophoresis [21]. PSS segment in PEDOT:PSS did not contribute to charge transport directly, but it acted as a template to keep PEDOT in the dispersed state, that is the dissociated sulfonate groups of PSS balanced the charges of the

cationic PEDOT by forming a stable salt [22,23]. However, the integration of PSS into PEDOT resembled a main factor to diminish its conductivity due to the distortion of PEDOT chain in PEDOT:PSS chain [17]. In the polymerization step, excess PSS was non-stoichiometrically added to stabilize soluble particles in solution and provides film-forming properties. However, oxidizing agents for the polymerization of EDOT in water such as iron (III) nitrate and iron (III) chloride led to the precipitation of the PEDOT:PSS complex in the latest stages of the reaction [24]. This was due to multivalent cations such as Fe (III) formed a complex with PSS and reduced the stability of the PEDOT:PSS complex. Sulfonic acid groups of PSS could cause swelling films after baking process because of water absorption in air, resulting in change in film thickness and its mechanical property [25]. Furthermore, the strong acidity of PSS would oxidize the metal to form a thin, poorly defined and insulating AlO_x layer, when vacuum deposited Al contacts on PEDOT:PSS film [26,27]. However, the strong acidity in solution acted as effective catalyst for EDOT polymerization and also found that the highest conductivity was at pH value between 0 and 3 [28]. In the absence of acid, the oxidation of EDOT could result in keto-functionalized side products [29]. The thermal stability of PEDOT:PSS was stable up to 200 °C [30]; however, annealing beyond this temperature led to an obvious decrease in its conductivity [31]. To maintain the quality of PEDOT:PSS film, exposing to UV light in ambient air under high relative humidity were needed to be avoided. The wavelength of radiation below 320 nm [32], elevated temperature above 70 °C as well as high relative humidity in air would dramatically affect the degradation of film conductivity due to the oxidation of PEDOT [6,33]. The encapsulation of conducting film or the addition of stabilizing agents would reduce the increase of resistivity over time [32]. Due to

several problems of PEDOT:PSS including high acidity, easy to water uptake, UV light-induced degradation, and varying morphology, mainly coming from the PSS segment, therefore, there have been several studies focused on other materials to replace it [34,35].

Due to sulfonated poly(imide)s (SPIs) are well-known as high performance polymers, because of excellent properties such as thermal stabilities surpassing 400 °C, mechanical properties, solution processability and superior chemical resistance [36], therefore, the integration of sulfonated polyimide into the PEDOT (PEDOT:SPI) instead of the conventional PSS template (PEDOT:PSS) in order to effectively solve some of PEDOT:PSS drawbacks, especially the ability in keeping conductivity value at high temperature during annealing has been considered [37]. This conductive polymer had the ability in extension of the usage in area of high-temperature processing and application in electronic industries. For wide applications usage in an aqueous dispersion of conductive polymer, which could be formed into nano-scale thin films with good conductivity, high transparency, and excellent environmental stability, was required. Again, however, the lack of good dispersion of PEDOT:SPI in aqueous solution because of strong interaction between PEDOT:SPI particles, was the main issue to hinder its nano-scale thin film-forming. The problem of particle dispersion did not appear in PEDOT:PSS suspension. In addition, other important properties of PEDOT:SPI film such as good thermal, mechanical, and morphologic properties also needed for using in advanced conditions. To achieve these crucial properties, the concept of polymer blending which exhibits the desirable properties of each pure component in the final products had been considered. However, up to now, PEDOT:SPI has not been mixed with any other polymers including poly (vinyl

alcohol) (PVA) yet, which was a polymer having many advantages as confirmed by the first part. Thus, PVA had become a suitable polymer to modify the PEDOT:SPI for desirable properties achievement.

Therefore, in this part aimed to investigate the formation of synthesized PEDOT:SPI nano-scale thin films with the aid of an anionic surfactant and the conventional spin-coating process and also to study the effects of PVA in PVA/PEDOT:SPI blending on various properties enhancement of PEDOT:SPI in order to apply them as a conductive material for electronic device applications. In addition, the effects of different polyimide structures in PEDOT:SPI on their thin film properties were also investigated.

1.1 Objectives of the Research

PART1 (PEDOT:PSS)

- 1.1.1 To form nano-thin films of PEDOT:PSS on glass substrate by using conventional spin-coating process.
- 1.1.2 To improve physical properties of PEDOT:PSS thin films by mixing with an insulating polymer in accordance with the blending concept.
- 1.1.3 To precisely enhance the conductivity of PEDOT:PSS thin films by an additive in accordance with the secondary dopant concept.
- 1.1.4 To integrate the two effective strategies, the polymer blending and the addition of a dopant, for optimization of PEDOT:PSS thin film properties.

PART2 (PEDOT:SPI)

- 1.1.5 To form nano-thin films of PEDOT:SPIs on glass substrate by using conventional spin-coating process with the aid of an anionic surfactant.
- 1.1.6 To improve various properties of PEDOT:SPIs thin films by mixing with an insulating polymer in accordance with the blending concept.
- 1.1.7 To compare the impact of different chemical structures of sulfonated polyimide (SPI) on their PEDOT:SPIs thin film properties.
- 1.1.8 To optimize PEDOT:SPIs properties for electronic applications.

1.2 Scope of the Research

- 1.2.1 Poly (vinyl alcohol) (PVA) was an insulating polymer used for mixing with both PEDOT:PSS and PEDOT:SPIs at its different weight ratios (0.05, 0.08, 0.1, 0.3, 0.5, and 1 %wt) in the conducting mixtures.
- 1.2.2 Quinoxaline was a secondary dopant used for the conductivity enhancement of only PEDOT:PSS at its various weight ratios (0.05, 0.1, 0.3, 0.5, and 1 %wt) in the conducting mixtures.
- 1.2.3 Sodium dodecyl sulfate (SDS) was employed as anionic surfactant to promote good dispersion of only PEDOT:SPIs particles in aqueous solution at a fixed weight ratio between PEDOT:SPIs and SDS of 1:2
- 1.2.4 Synthesis two types of PEDOT:SPIs from different kinds of sulfonated polyimide structures, 4,4'-oxydiphthalic anhydride (O-DPDA) in case PEDOT:SPI1 or 4,4'-Hexafluoroisopropylideneoxydiphthalic anhydride (6FDA), in case PEDOT:SPI2.

CHAPTER II

THEROY

2.1 Conductive Polymers

Conductive polymers or intrinsically conducting polymers (ICPs) are organic polymers that can conduct electricity; they allow charges transfer along their polymer chain. Such organic compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their ability to process by dispersion in the suspension form. Conductive polymers can generally provide high electrical conductivity but do not exhibit similar mechanical properties to other polymers. The common nature of ICPs is the possession of alternating single and double bonds along the polymer chain, which offers the delocalization or mobility of charges along the polymer backbone. The conductivity is assigned to the delocalization of π -bonded electrons over the polymeric backbone, indicating the unusual electronic properties, such as low ionization potentials, low energy optical transitions and high electron affinities [38]. ICPs are classified as doped conjugated polymers and are fundamentally different from conducting polymer composites [39], redox polymers [40], and ionically conducting polymers such as polymer/salt electrolytes [41].

2.2 Conjugated Polymers

The electrical properties can be adjusted using the steps of organic synthesis and by advanced dispersion techniques. The result of such conductivity in the polymers is attributed from several processes. For traditional polymers such as polyethylenes,

their valence electrons are bound in sp^3 hybridized covalent bonds. Such "sigma-bonding electrons" have fairly low charges mobility and do not contribute to the electrical conductivity of the material. However, the situation is totally different in case of conjugated materials because they have backbones of contiguous sp^2 hybridized carbon centers. One valence electron on each center residing in a p_z orbital, which is orthogonal to the other three sigma-bonds, can combine with each other to form a molecule wide delocalized set of orbitals. The electrons in these delocalized orbitals become high mobility when the material is doped by oxidation, which removes some of these delocalized electrons. Therefore, the conjugated p -orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. Although the π -electrons in polyacetylene are delocalized along the chain, pristine polyacetylene is not a metal. Undoped conjugated polymers, semiconductors or insulators, can be > 2 eV of the energy gap, which is too great for thermally activated conduction. Thus, the polymers only show a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. However, electrical conductivity increases by doping at a very low level ($< 1\%$). Subsequent doping of the conducting polymers will lead to a saturation of the conductivity for different polymers. For example, the films of polyacetylene (PAC) tremendously increase their conductivity when they are exposed to iodine vapor, from a basic value at the lower end of the semiconducting range up to values comparable to metals. **Figure 2.1** represents these iodine dopant induced changes in a comparison with other materials. They encompass the enormous range of seventeen orders of magnitude.

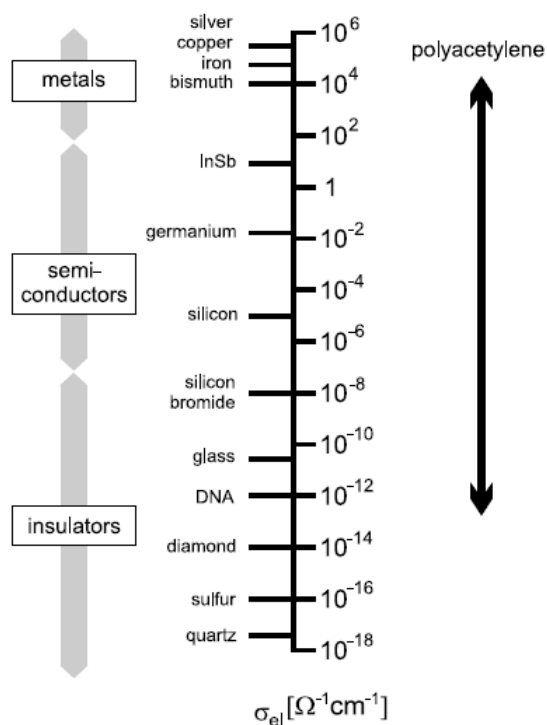
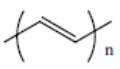
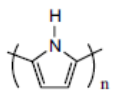
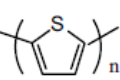
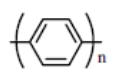
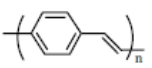
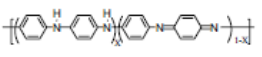


Figure 2.1 Range of conductivities covered by doped PAc in a comparison with other materials

The most concerned conducting polymers that have been researched over the past 30 years base on polythiophenes, polypyrroles, polyanilines, polyphenylenes, and poly (*p*-phenylene vinylene)s, as shown in **Table 2.1**. These structures of some conjugated polymers are in their neutral insulated form. To make them electronically conductive, mobile carriers are essentially introduced into the conjugated system by oxidation or reduction reactions and the insertion of counterions (called “doping”). Dedoped conjugated polymers are performed as semiconductors with band gaps ranging from 1 to several eV. During the doping process, an organic polymer having low conductivity, typically in the range of 10^{-10} to 10^{-5} S/cm, is modified to a polymer having higher conductivity in a metallic conducting regime ($1-10^4$ S/cm).

Table 2.1 Some conjugated conducting polymers

Polymer (date conductivity discovered)	Structure	••• # gap (eV)	Conductivity [#] (S/cm)
I. Polyacetylene and analogues			
Polyacetylene (1977)		1.5	$10^3 - 1.7 \times 10^5$
Polypyrrole (1979)		3.1	$10^2 - 7.5 \times 10^3$
Polythiophene (1981)		2.0	$10 - 10^3$
II. Polyphenylene and analogues			
Poly(paraphenylene) (1979)		3.0	$10^2 - 10^3$
Poly(p-phenylene vinylene) (1979)		2.5	$3 - 5 \times 10^3$
Polyaniline (1980)		3.2	30 - 200

[#] The range of conductivities listed is from that originally found to the highest values obtained to date (after Dai, 1999, copyright 1999 Marcel Dekker, Inc.)

The highest value reported to date has been achieved in iodine-doped polyacetylene and the predicted theoretical limit is about 2×10^7 , more than an order of magnitude higher than that of copper. Conductivity of other conjugated polymers is shown in Figure 2.2.

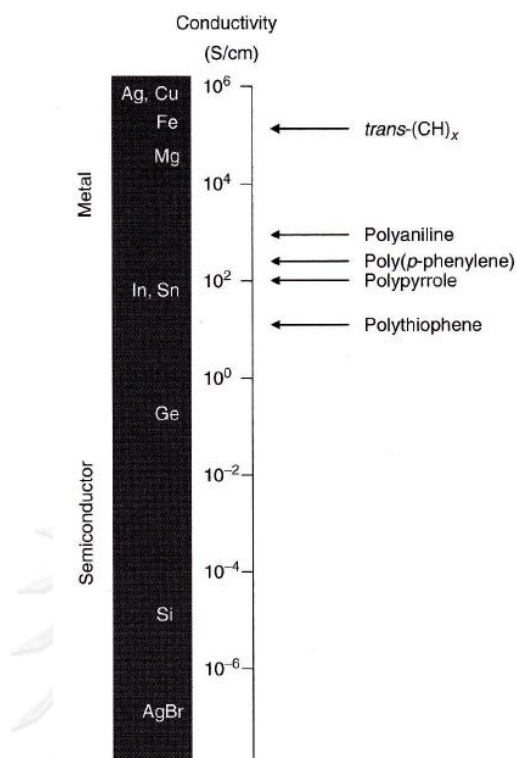


Figure 2.2 Conductivity of some metals and doped conjugated polymers

2.3 Band Theory [42]

According to band theory, the electrical properties of direct gap inorganic semiconductors are determined by their electronic structures, and the electrons move within discrete energy states called *bands*. By analogy, the bonding and anti-bonding π -orbitals of the sp^2 hybridized π -electron materials generate energy bands, which are fully occupied and empty. The highest occupied band is called the *valence band*, and the lowest unoccupied band is the *conduction band*. The energy difference between them is called the *band gap*. Electrons must have certain energy to occupy a given band and need extra energy to move from the valence band to the conduction band. Moreover, the bands should be partially filled in order to be

electrically conducting, as neither empty nor full bands can carry electricity. Owing to the presence of partially filled energy bands, metals have high conductivities (**Figure 2.3(a)**). However, the energy bands of insulators and semiconductors are either completely full or completely empty. For instance, most conventional polymers have full valence bands and empty conduction bands, which are separated from each other by a wide energy gap (**Figure 2.3(b)**). In contrast, conjugated polymers have narrower band gaps (**Figure 2.3(c)**) and doping can change their band structures by either taking electrons from the valence band (*p*-doping) or adding electrons to the conduction band (*n*-doping).

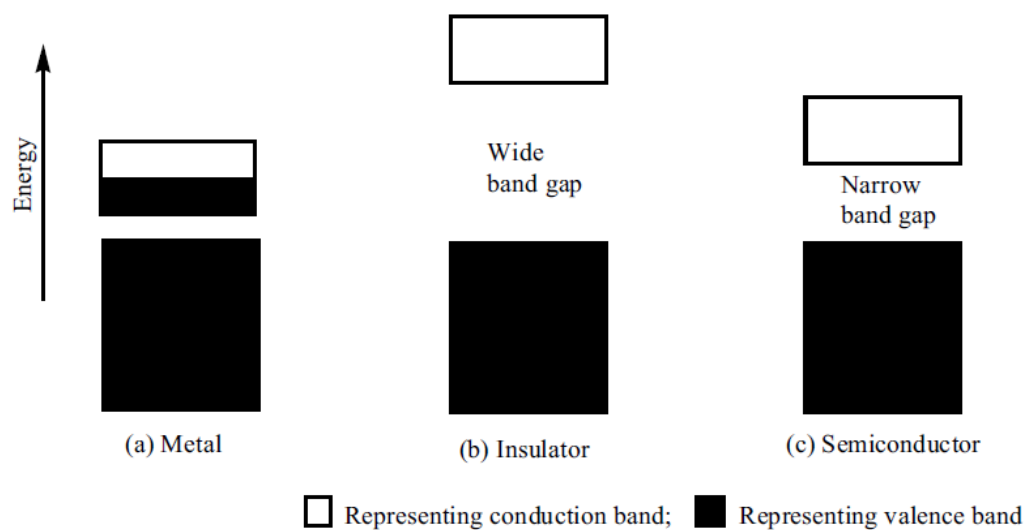


Figure 2.3 A schematic representation of energy gaps in (a) metal, (b) insulator, (c) semiconductor [42]

2.4 Background of PEDOT:PSS [43]

During the second half of the 1980s, scientists at the Bayer AG research laboratories developed a new polythiophene derivative, poly (3, 4 ethylenedioxythiophene) (PEDOT), having the backbone structure shown in **Figure 2.4**.

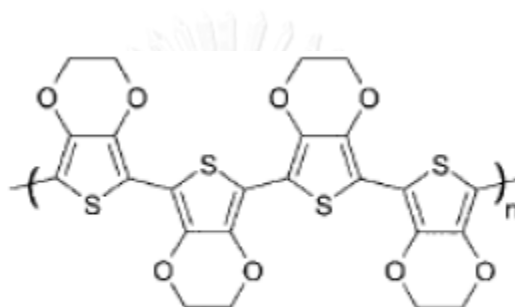


Figure 2.4 The molecular structure of PEDOT [44]

Conductive PEDOT is a derivative of polythiophene and is generally synthesized by electrochemical or chemical polymerization of ethylenedioxythiophene (EDOT). PEDOT doped with small anions are insoluble in any solvent. The solubility problem was subsequently circumvented by using a water-soluble polyelectrolyte, poly (styrene sulfonic acid) (PSS), as the charge-balancing dopant during polymerization to yield PEDOT: PSS. Thus, the polymer can be dispersed in aqueous solution. The PEDOT chains are attached to the PSS main chains through the Coulombic interaction. The excess PSS is responsible for the dispersion ability of PEDOT:PSS. **Figure 2.5** illustrates the schematic microscopic structure of a PEDOT:PSS film prepared from PEDOT:PSS aqueous solution. There is core/shell structure. The PEDOT:PSS core is surrounded by an insulating PSS-rich shell. The hydrophilic PSS chains form micelles with the hydrophobic PEDOT chains inside. This structure in water is conserved in the PEDOT:PSS films. The PEDOT:PSS films are composed of grains with diameters of

about 50 nm. The conductive PEDOT is rich in the core while the insulating PSS is rich in the shell of a grain. The shell has a thickness of about 5-10 nm. This insulator shell blocks the charge transport across the grains, which is considered as one of the reasons for the low conductivity of < 1 S/cm observed on PEDOT:PSS films prepared from the PEDOT:PSS aqueous solution. In addition, the PEDOT and PSS chains are bonded by the Coulombic attraction. There is a stress in the polymer chains owing to the mismatch between the PEDOT and PSS chains, so that the PEDOT chains adopt a coiled structure, which results into the localization of the positive charges (**Figure 2.6**). This is another reason account for the low conductivity of PEDOT:PSS. Therefore, approaches which lower the amount of PSS in the PEDOT:PSS film and/or reduce the stress in PEDOT:PSS can improve the conductivity of PEDOT:PSS.

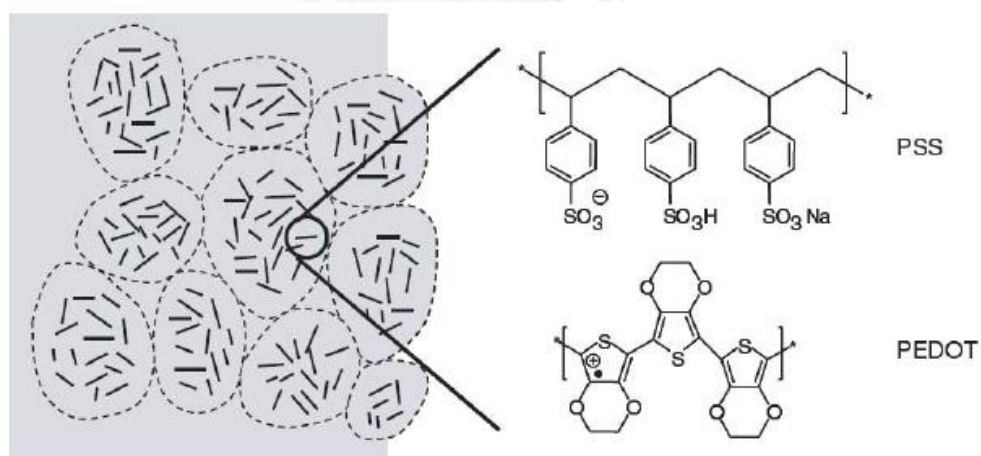


Figure 2.5 The schematic picture of the morphology of PEDOT:PSS and its chemical structure in a thin film of PEDOT:PSS particles [54]

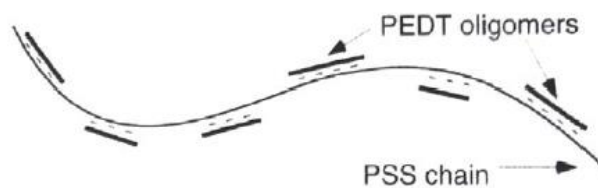


Figure 2.6 Schematic image of PEDOT:PSS chain: a long PSS chain with PEDOT oligomeric chains [55]

2.5 Synthesis of PEDOT:PSS [44]

Polystyrenesulfonic acid (PSS) was the first polyelectrolyte used for a PEC with PEDOT in 1990 and has remained the industrial standard ever since. PSS forms durable films and shows no absorption in the visible range of light, resulting in transparent films. The sulfonic acid group is strongly acidic and hence highly polar. PSS as a counterion for PEDOT is always used in excess. The molar ratio of thiophene groups to sulfonic acid groups in standard PEDOT:PSS dispersions is in the range of 1:1.9 to 1:15.2, which corresponds to a weight ratio range of 1:2.5 up to 1:20. Since only one charge is found for every three to four thiophene rings, the charge excess of PSS is between 6-fold and 46-fold. The solvent of choice for the synthesis of PEDOT:PSS complex is water. Water is inert with respect to most oxidation or reducing agents. It is highly polar and a good solvent for PSS. However, water is a poor solvent for the monomer EDOT. The EDOT solubility increases in the presence of PSS and temperature. An important parameter for the EDOT polymerization is the pH value. The presence of PSS leads to a low pH of less than 3. This is beneficial since acid acts as a catalyst for the reaction. In the absence of acid, the oxidation of EDOT can result in keto-functionalized side products. A range of oxidizing agents is available for the polymerization of EDOT in water. Iron (III) salts such as iron (III)

nitrate and iron (III) chloride can be used. However, the presence of stoichiometric amounts of iron (III) or iron (II) ions leads to the precipitation of the PEDOT:PSS complex. This is because multivalent cations such as Fe(III) form a complex with PSS and reduce the stability of the PEDOT:PSS complex. The most versatile oxidizing agents are peroxodisulfates. From a stoichiometric point of view, one equivalent of peroxodisulfate is needed for each thiophene unit for the oxidative polymerization, taking two electrons from each thiophene. Additional peroxodisulfate is consumed in the oxidation of the polymer chain resulting in a polycation. Approximately one positive charge is found for every three to four thiophene rings. For simplicity, the reaction depicted in **Figure 2.7** shows a PEDOT repeat unit with six thiophene rings and two positive charges. The exact chain length and the exact charge of the PEDOT chains have not been determined since these main chains cannot be totally obtained as a separated material without counterions.

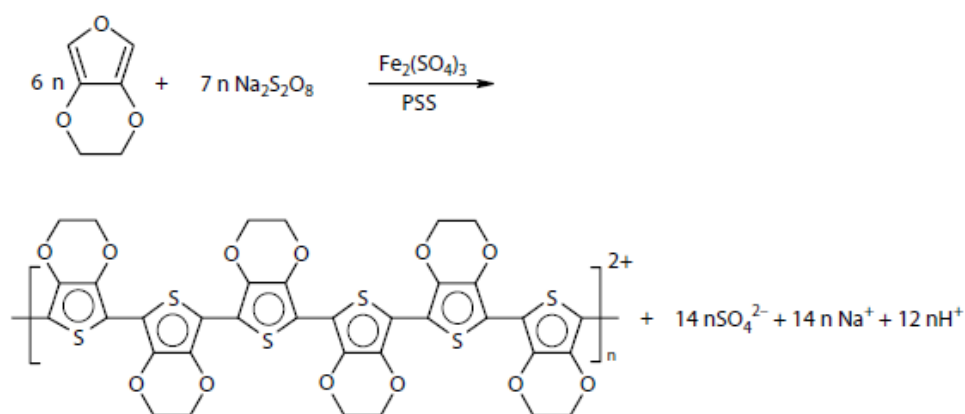


Figure 2.7 Reaction scheme for the PEDOT synthesis using sodium peroxodisulfate as an oxidant [44]

2.6 The Model of Charge Transport in PEDOT:PSS

Following the concept of charge transport in amorphous inorganic semiconductors, the conduction mechanism of conjugated polymers is commonly discussed in terms of charge hopping between adjacent sites. Segments of conjugated polymers are preferentially forming electronic active sites due to their ability of being easily oxidized and reduced. The frequency of charge transport between adjacent sites depends on its relative energetic position, the distance, and the relative orientation. The mechanisms of conductivity in PEDOT:PSS films have been made by studying the conductivity and magneto-resistance of PEDOT:PSS as a function of temperature and found that both parameters increase with temperature. The temperature dependence of conductivity was discussed using the model of variable range hopping (VRH). The VRH model can be expressed as:

$$R(T) = R_0 \exp \left[\left(\frac{T_0}{T} \right)^\alpha \right]$$

Where σ_0 is the conducting prefactor, T_0 is the characteristic temperature dependent on the pH and α is an exponent that is related to the transport process. This temperature dependence is characteristic of strongly disordered, inhomogeneous systems. The temperature variation of the conductivity $\log [\sigma(T)]$ is plotted as a function of the $-\alpha$ power of the temperature, $T^{-\alpha}$ and the appropriate value which straightens out the curve is considered to provide information about the conducting mechanism. A value close to $\frac{1}{4}$ is attributed to variable range hopping and a value close $\frac{1}{2}$ is generally attributed to the presence of a Coulomb gap, either in the homogenous system of localized interacting electrons or in the form of a charging

energy in a granular metal-like system. The charge transport mechanism in the case of PEDOT: PSS can be generally explained within the framework of the charging-energy limited tunneling model, originally proposed for highly disordered conducting polymers. In this model, conduction is supposed to proceed from tunneling between small conducting grains separated by insulating barriers. This model is an extension of Sheng's model of granular metals; it focuses on the disorder present in the polymer and the polaronic ground state characteristic in many conducting polymers. According to this model, the conducting clusters are highly doped 'polaronic islands' generated by heterogeneities in the doping distribution. The dopant centers act as bridges between neighboring chains and therefore improve the charge carrier transport.

2.7 Morphology and Anisotropy of PEDOT: PSS

Very little is known about the molecular structure and the surface and bulk morphology of PEDOT: PSS. The structure and morphology of thin films are not necessarily the same as that of bulk material. For PEDOT, thin spin-cast and bulk solution-cast films show very different kinds of orientation, although they have the same basic crystalline structure. Grazing-incidence X-ray diffraction studies have shown that the dopant ions, form distinct planes, which alternate with stacks or lamellae of polymer chains, as shown in **Figure 2.8**. The material is very anisotropic, with the planes of the dopants and of the stacks of polymer chains parallel to the substrate. It is in a paracrystalline state, with small size of the individual paracrystalline regions. This model corroborates well with the strong optical anisotropy observed. Despite the observed anisotropy in the optical response,

possible anisotropies in the conductivity were systematically addressed, only until recently. Multimodal AFM studies carried out to map the local charge transfer properties in correlation to the molecular superstructure of the polymer blend show that efficient charge injection occurs in regions where the lamellar edges are exposed to the probe. Charge mobility's are considerably higher along the polymer lamellae, as compared to normal mobilities for PEDOT. In regions where the AFM tip has access to orbital that belong to a lamellar edge, efficient charge transport occurs. Therefore, high currents are observed. On the contrary, when the AFM tip is scanning on top of intact lamellae, the high inter-sheet barrier, limits the transport. The interlamellar distance is estimated to be 3nm.



Figure 2.8 The lamellar structure of PEDOT: PSS blend

These studies suggest that the charge transport perpendicular to the substrate is dominated by space charge effects, in striking contrast to the hopping transport observed parallel to the substrate. Recent studies combine scanning probe microscopy with macroscopic temperature dependent conductivity measurements to build a full 3 Dimensional morphological model that explains the observed anisotropic conductivity of spin coated PEDOT: PSS thin films. The vertical conductivity that is perpendicular to the substrate can be up to three orders of magnitude lower than the lateral conductivity in the plane of the film. Surface

Tunneling Microscopy shows that the PEDOT: PSS films have a granular morphology, with a typical grain size of about 10-25nm. The low surface roughness of approximately 1.75 nm implies that the grains actually have the shape of flattened balls, or pancake-like structures. The transformation of spherical particles in solution to pancakes in thin films is most likely the result of spin casting procedure, during which the evaporating water causes the thickness to shrink while the film remains continuous in the lateral direction.



CHAPTER III

LITERATURE REVIEWS

3.1 PART1 (PEDOT:PSS)

O.P. Dimitriev *et al.* 2011[45] provided a better understanding of the effect of PSS on the intramolecular conductivity of PEDOT chains in the PEDOT:PSS complex, as shown in **Figure 3.1**.

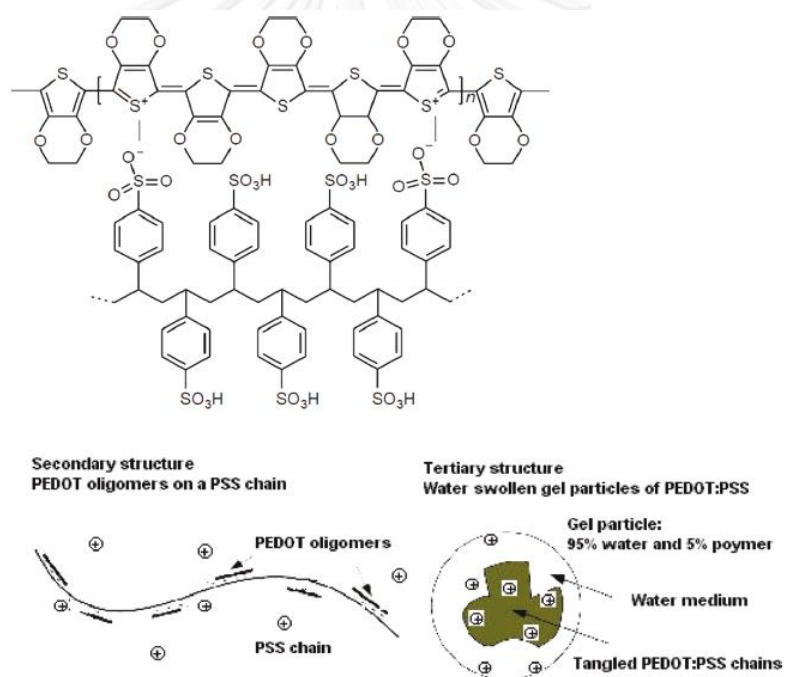


Figure 3.1 Hierarchy of the PEDOT:PSS complex structures: primary (at the top), secondary, and tertiary. Protons in the lower chart are shown by the positive circles [47]

The amount of dissociated protons from the PSS chains controlled interaction between PEDOT and PSS counterparts in the complex. The association of protons with the PSS coil weakened the electrostatic interaction between PSS and PEDOT and

led to a smaller distortion of the planar PEDOT structures which favored better intramolecular conductivity in the PEDOT molecule. The approaches which reduced the stress in PEDOT:PSS could enhance the conductivity of PEDOT:PSS.

A.R. Hopkins *et al.* 2000 [46] blended PEDOT:PSS with poly(ethylene oxide) (PEO) or poly(vinyl alcohol) (PVA) matrix. These mixtures exhibited the rising in conductivity, smoothly and rapidly, from the insulated state to conductive state with increasing conducting PEDOT:PSS content, as shown in **Figure 3.2**. However, there was no significant difference in the conductivity of the both polymers was found. They also found that PEO could induce the creation of the agglomeration of PEDOT:PSS as shown in **Figure 3.3**.

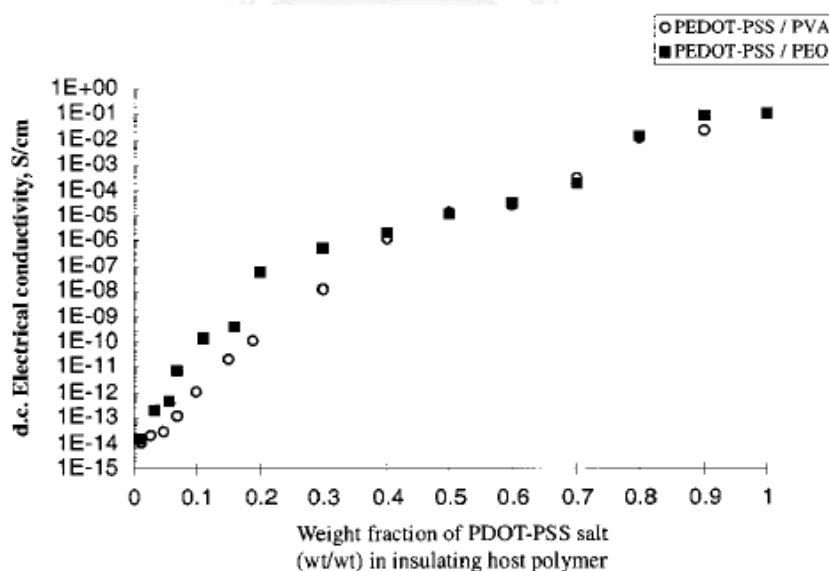


Figure 3.2 Conductivity as a function of PEDOT-PSS salt loading fraction in host PVA and PEO. Blend concentration range of 0-1 (wt/wt) [46]

C.-H. Chen *et al.* 2009 [47] blended PEDOT:PSS with polyvinyl Alcohol (PVA), leading to increase tensile strength, durability and flexibility. The mixtures were prepared and spin coated to form thin conductive films. The film conductivities increased proportionally with increasing PEDOT:PSS content, as shown in **Figure 3.4**. The thermal stability of PEDOT:PSS could be improved by the addition of PVA because the OH group of PVA could bond by strong covalent bonds with the SO_3^- groups of PSS. In addition, both of the substrates provided similar conductivities at all weight fractions of the additive.

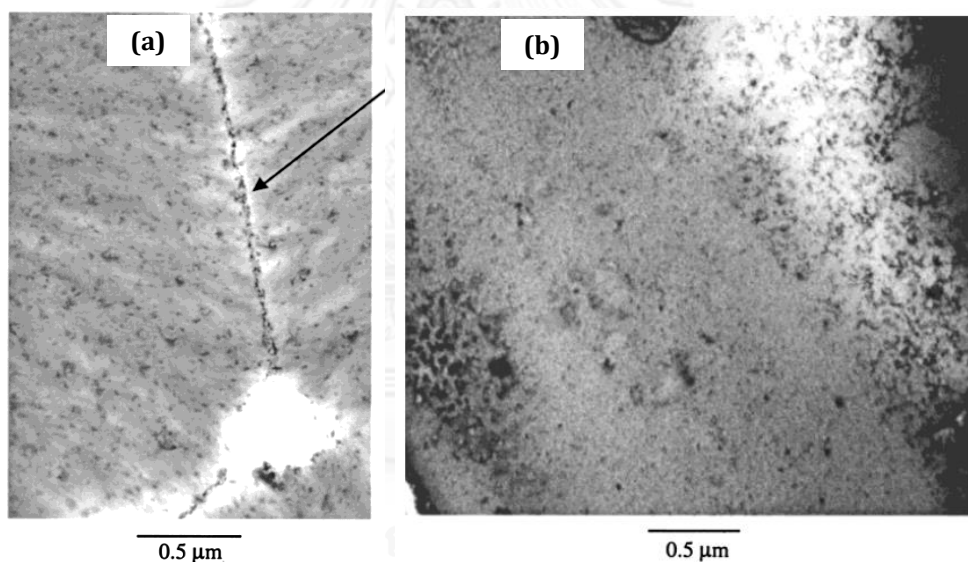


Figure 3.3 TEM micrograph of 2% (wt/wt) PEDOT-PSS/polymer matrix for (a) PEO and (b) PVA, the arrow shows agglomeration of PEDOT:PSS in PEO matrix [47]

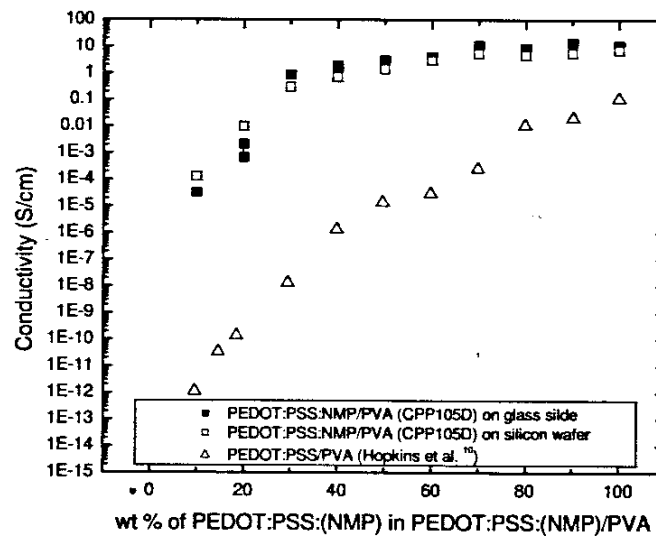


Figure 3.4 Conductivity as a function of wt% of PEDOT:PSS:NMP in a blend of PEDOT:PSS:NMP/PVA on both substrates and corresponding conductivity measurement of Hopkins and Reynolds [46] for PEDOT:PSS/PVA

C.-h. Chen *et al.* 2011 [48] described the mechanical characterization of PEDOT:PSS/Polyvinyl Alcohol (PVA) blends produced by casting with uniaxial tensile tests, as shown in **Figure 3.5**. Mixing PEDOT:PSS with other polymers was a promising route to reach a good trade-off between electrical and mechanical properties. The mechanical properties as a function of the weight fraction of the components were shown in **Table 3.1**. The Young's modulus monotonically increased with PEDOT:PSS content, reached 1.63 GPa at 50%. To determine the optimal PEDOT:PSS/PVA blend for electro-mechanical applications based on free standing films, a PEDOT:PSS content between 30% and 40% presented a reasonable trade-off between electrical and mechanical properties. This research confirmed the blending between PVA and PEDOT:PSS for electro-mechanical improvement needed principally to be optimized.

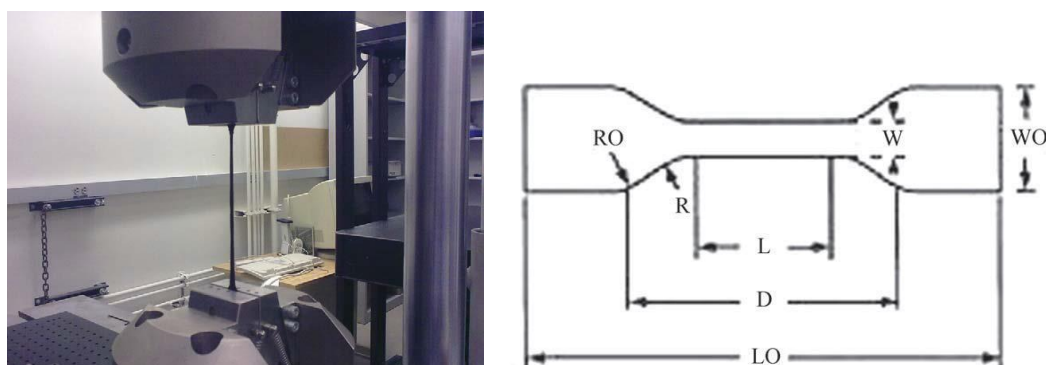


Figure 3.5 Uniaxial tensile test setup; dimensions of ASTM D638 type IV specimen (W: 6 mm, L: 33 mm, WO: 19 mm, LO: 114 mm, D: 64 mm, R: 14 mm, RO: 25 mm) [48]

Table 3.1 Mechanical properties of PVA from the present and previous studies, pure PEDOT:PSS from previous studies and the highest weight percentage of the present study [48]

Material	Specimen	Young's modulus	Tensile strength	Breaking elongation
PVA	Thin film	49.5 ± 3.2 MPa	12.5 ± 0.8 MPa	265.1 ± 6.3%
PVA	Cast film	68.5 MPa	22.5 MPa	N/A
PVA	Cast film	41.3 MPa	41.3 ± 3.3 MPa	111.0 ± 2.2%
PEDOT:PSS	Pipetted film	2.8 ± 0.5 GPa (23% rH)	53.2 ± 9.5 MPa (23% rH)	N/A
		1.9 ± 0.02 GPa (40% rH)	33.7 ± 10 MPa (40% rH)	
		0.9 ± 0.2 GPa (55% rH)	22.2 ± 4 MPa (55% rH)	
PEDOT:PSS	Cast film	1.8 ± 0.2 GPa	42.8 ± 9.2 MPa	N/A
PEDOT:PSS	Fiber	1.1 ± 0.3 GPa	17.2 ± 5.1 MPa	4.3 ± 2.3%
PEDOT:PSS/PVA	Cast film	1.632 GPa (50% PEDOT:PSS)	78.1 ± 9.3 MPa (50% PEDOT:PSS)	56.2 ± 2.0% (50% PEDOT:PSS)

T. Hino *et al.* 2006 [49] prepared conductive composites in the presence of several water soluble polymers [alginate (AA), poly(acrylic acid) (PAA), and poly(vinyl alcohol) (PVA)] and/or anionic surfactants [dodecylbenzenesulfonic acid (DBSA) and sodium dodecylsulfate (SDS)]. As a result, PANI prepared in the presence of SDS (PANI/SDS) generally showed extremely poor film-forming property due to its low solubility/miscibility and processability. In the other hand, the addition of PVA in PANI/SDS could significantly improve film-forming property, as shown in **Figure 3.6**. Moreover, the conductivities of the composites synthesized with SDS tended to be better than those of the similar composites prepared with DBSA or without anionic

surfactants. In particular, the composite prepared by using PVA and SDS to aniline monomer exhibited the highest conductivity.

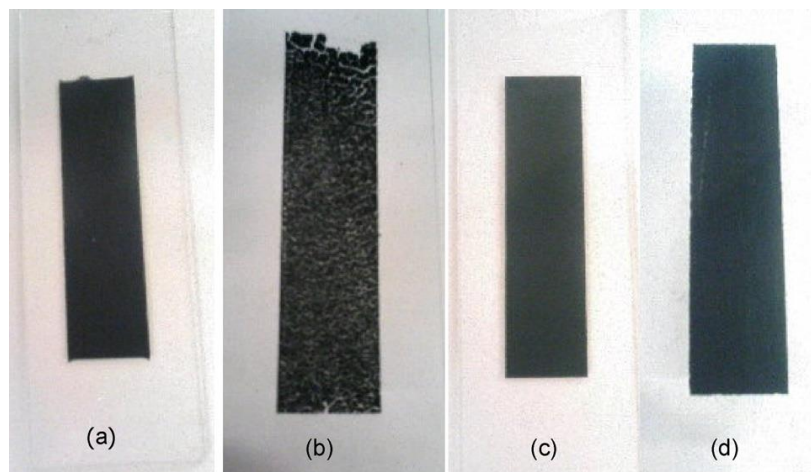


Figure 3.6 Photographs of the composite films, (a) PANI/AA/SDS, (b) PANI/PAA/SDS, (c) PANI/PVA-L/SDS, and (d) PANI/PVA-H/SDS [51]

3.2 PART2 (PEDOT:SPI)

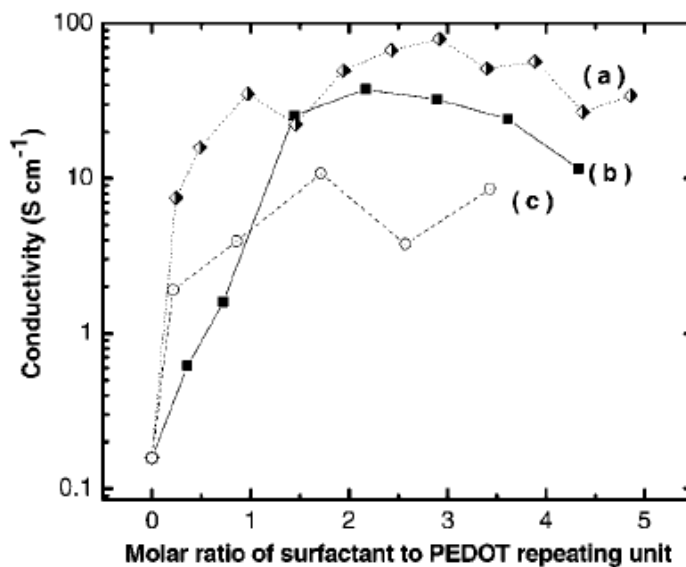


Figure 3.7 The conductivities of the PEDOT:PSS(surfactant) films. The additives are (a) SDS, (b) TsONa, and (c) (DBSA) [17]

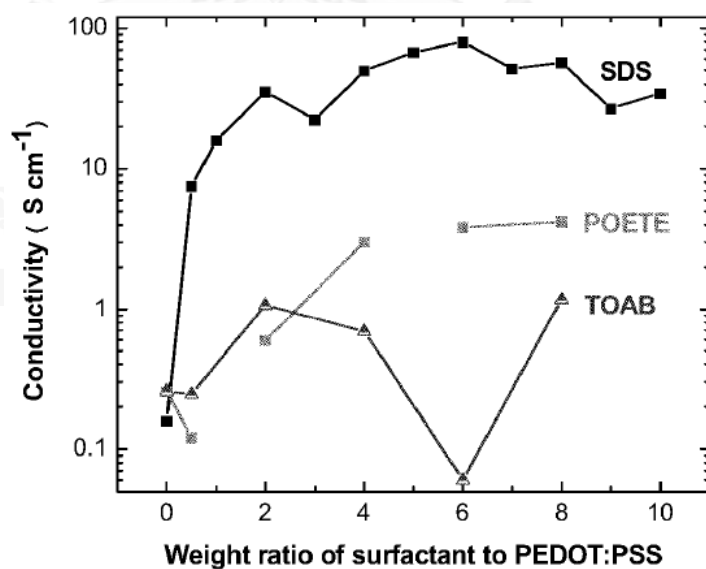


Figure 3.8 Variations of the conductivity of PEDOT:PSS with the weight ratio of added surfactants to PEDOT:PSS [50]

From literature reviews [17,50], it was found that the addition of anionic SDS surfactant into PEDOT:PSS aqueous solution could provide the highest film conductivity when compared to other surfactants as shown in **Figure 3.7 and 3.8** below. This suggests that SDS surfactant was the first priority to be selected for the modification of conducting polymers, especially in term of efficient conductivity enhancement.

S. Bongkoch *et al.* 2010 [7] developed the polymerization of EDOT with sulfonated poly(amic acid) (SPAA). After imidization, PEDOT:poly(imide) (PEDOT-SPI) with 10-fold conductivity enhancement was obtained. This material was highly thermally stable as compared to PEDOT:PSS. Annealing of films at 300 °C for 10 min caused the immeasurable conductivity of PEDOT:PSS micron-films while those of PEDOT-SPAA increased 6-fold, as shown in **Table 3.2**. The experimental results imply that thermal stability at quite high temperature of PEDOT:SP was better than conventional PEDOT:PSS.

Table 3.2 Conductivities of PEDOT-PSS and PEDOT-SPAA at various temperatures [7]

Processing temperature		PEDOT-PSS	PEDOT-SPAA
20 °C	Conductivity (S/cm)	3.15×10^{-4}	1.12×10^{-4}
	Std. Dev.	4.03×10^{-5}	8.69×10^{-6}
180 °C (90 min)	Conductivity (S/cm)	2.65×10^{-4}	2.96×10^{-4}
	Std. Dev.	3.32×10^{-5}	5.49×10^{-6}
300 °C (10 min)	Conductivity (S/cm)	$<1 \times 10^{-5}$	6.06×10^{-4}
	Std. Dev.	$<1 \times 10^{-5}$	4.84×10^{-5}

And two years later, 2012 [39], they improved the novel method to synthesize PEDOT:SPI without meeting the precedent step of PEDOT:SPAA preparation. This procedure could reduce the reaction time and also enhanced the conductivity and

thermal property of final product (PEDOT:SPI) when compared to the conventional method as shown in **Table 3.3** and **Figure 3.9** respectively.

Table 3.3 Conductivities of PEDOT–SPAA and PEDOT–SPI (upon annealing, PEDOT–SPAA partially imidizes to PEDOT–SPI) [39]

ProcessingTemp. (°C)	PEDOT-SPAA ^a	PEDOT-SPI ^b
25 °C	Conductivity (S/cm)Std dev. $2.04 \times 10^{-4} 3.42 \times 10^{-5}$	$4.0 \times 10^{-3} 1.18 \times 10^{-3}$
180 °C (10 min)	Conductivity (S/cm)Std dev. $5.83 \times 10^{-3} 1.18 \times 10^{-3}$	$1.99 \times 10^{-1} 1.03 \times 10^{-3}$
300 °C (10 min)	Conductivity (S/cm)Std dev. $6.47 \times 10^{-4} 3.73 \times 10^{-5}$	$2.44 \times 10^{-4} 5.50 \times 10^{-3}$

^a Ref. [9].

^b Cured at 70 °C/1 h+150 °C/1 h+250 °C/1 h.

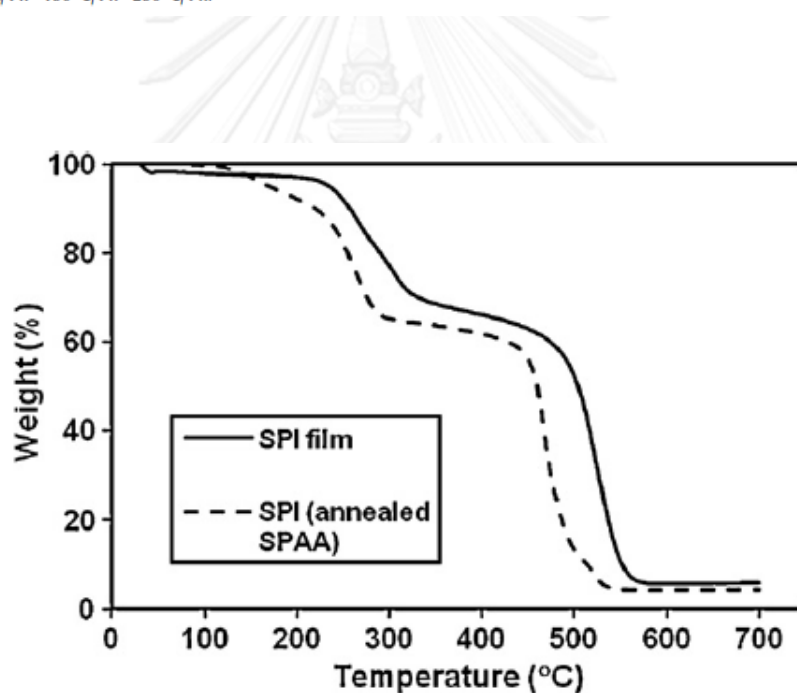


Figure 3.9 TGA results of SPI film and SPI (annealed SPAA) template [39]

B. Fan *et al.* 2008 [17] significantly enhanced the conductivity of PEDOT:PSS film by adding anionic surfactant into the PEDOT:PSS aqueous solution. Conductivity enhancement by a factor of 500 was observed. The conductivity enhancement was attributed to the effect of the anionic surfactant on the conformation of the conductive PEDOT chains. The PEDOT chain had to follow the structure of the PSS

chain in water, giving rise to the distortion structure of the PEDOT chain. The anionic surfactant replaced PSS as the counteranions to PEDOT in water, so that the distortion structure of the PEDOT chain disappeared as shown in **Figure 3.10**. This conformational changes in the PEDOT chain resulted in the significant enhancement in the conductivity of the PEDOT:PSS films.

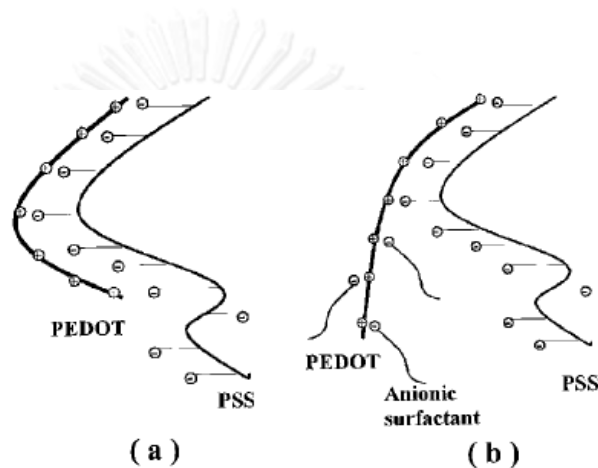


Figure 3.10 Schematic structures of a PEDOT segment and a PSS segment in water (a) without and (b) with adding anionic surfactant [17]

Y. Xia *et al.* 2010 [51] The conductivity of PEDOT:PSS films could be significantly enhanced to be close to 100 S cm^{-1} through a treatment with aqueous solution of zwitterions. The mechanism for the conduction enhancement was attributed to the zwitterion-induced charge screening, as shown in **Figure 3.11**. The zwitterions effectively screen the coulombic attraction between the PEDOT and PSS chains, resulting in PSSH loss from the PEDOT:PSS film and the conformational changes of PEDOT chains. The zwitterion-treated PEDOT:PSS films had a low ion diffusion due to the bulky size and the two opposite charges in the same molecule of the zwitterion. They are more suitable to replace ITO as the anode of PVs than PEDOT:PSS film

treated with normal salts. Photovoltaic efficiency as high as 2.48% was achieved on the P3HT:PCBM PVs with zwitterion-treated PEDOT:PSS films as the anode.

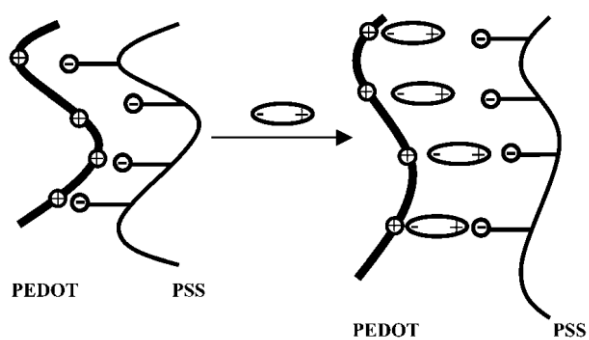


Figure 3.11 Schematic structures of a PEDOT:PSS before and after zwitterions treatment [5]

CHAPTER IV

EXPERIMENT

The experimental procedures of this work were classified into two main parts: PEDOT:PSS and PEDOT:SPI. For PEDOT:PSS, the effects of PVA and a secondary dopant on various properties of conducting PEDOT:PSS nano-films were investigated. In the same way, SDS surfactant and PVA were effectively combined to improve conductive PEDOT:SPI films. The different kinds of PEDOT:SPI were also used for comparison of an intrinsic characteristic of each molecular structure. The entire experiments can be divided into four parts as follows,

- (i) Materials and Chemicals
- (ii) PEDOT:PSS films
- (iii) PEDOT:SPI films
- (iv) Characterization techniques

The details of each part are explained as follows;

4.1 Materials and Chemicals

Chemical Name	Abbrev.	Company
1. 4,4'-oxydiphthalic anhydride	O-DPDA	Sigma-Aldrich
2. 4,4'-Hexafluoroisopropylideneoxydiphthalic anhydride	6FDA	TCI America
3. Triethylamine	Et3N	Fisher BioReagents
4. m-cresol	-	Acros Organics
5. 3,4-ethylenedioxythiophene	EDOT	Sigma-Aldrich
6. Ion-exchange resin (DOWEX 50WX8 50-100 mesh)	-	Acros Organics

Chemical Name	Abbrev.	Company
7. Iron (III) p-toluene sulfonate hexahydrate	-	Sigma-Aldrich
8. poly(styrene sulfonic acid) (18 wt.% in water)	PSS	Sigma-Aldrich
9. Surfynol® 2502 surfactant	S-2502	Air Products, Inc.
10. Quinoxaline	-	Sigma-Aldrich
11. Poly(vinyl Alcohol) MW = 146,000-186,000	PVA	Sigma-Aldrich
12. Sodium dodecyl sulfate	SDS	MP Biomedicals

4.2 PART I (PEDOT:PSS films)

4.2.1 Preparation of PEDOT:PSS aqueous suspension

The 300 mL of de-ionized (DI) water was added to a 500-mL one-neck flask. After that, the 0.3195 g (2.25 mmol) of EDOT and 4.356 g of 18 wt.% PSSA aqueous solution were added respectively, and then left the mixture for 1 h to make a good dispersion. To start the reaction, 1.626 g of iron (III) p-toluene sulfonatehexahydrate (2.40 mmol) was added and stirred vigorously for 3 days at room temperature, leading to a dark blue dispersion which signified to a complete reaction. During the oxidative polymerization, the mixture flask should be covered by Al foil to prevent the contact with surrounding light.

4.2.2 The fabrication of PEDOT:PSS Nano-thin films on glass substrates

The dark blue PEDOT:PSS dispersed in aqueous solutions were centrifuged at 3,000 rpm for 15 min to separate agglomerated particles from the suspension. The supernatant was subsequently sonicated for 3 h and then transferred into a rotary

evaporator at 40 °C for partial water evaporation to obtain a high concentration and good dispersion of PEDOT:PSS in aqueous solution. After that, Surfynol was added to the highly-concentrated PEDOT:PSS aqueous suspensions at a ratio of PEDOT:PSS to Surfynol equal to 5mL:1 μ L in order to reduce their surface tension. Various amounts of PVA were then added to the PEDOT:PSS aqueous suspensions to obtain 0.05-1.0 wt.% of PVA, resulting in the film thicknesses ranging from 80 to 130 nm. The PVA/PEDOT:PSS with different PVA weight fractions were deposited on dried, clean glass substrates by means of spin-coating at a fixed spin speed of 4,000 rpm for 60 s to obtain thin films on the Nano-scale. Glass slides were sonicated in soap water, DI water, acetone, and IPA for 15min in each solvent sequentially before using as substrates. The Nano-scale thin films were thermally treated on a hotplate at 70 °C for 1 h and then kept in a dark desiccator or glove box for future characterization.

4.2.3 Preparation of PEDOT:PSS doped with quinoxaline

The appropriate weight fraction of PVA in PVA/PEDOT:PSS mixture that provided the highest conductivity was chosen as the starting point to dope with quinoxaline. Various wt. % of quinoxaline, 0.05-1.0, were mixed with PVA/PEDOT:PSS by ultrasonication for 2 h and then stirred overnight. The mixtures were dropped on a clean glass substrate to spin-coat at a fixed spin speed of 4,000 rpm for 60 s, thus thin films on the Nano-scale in the range of 100 -300 nm were obtained. The Nano-scale thin films were thermally treated on a hotplate at 70 °C for 1 h and then kept in a dark desiccators or glove box for future characterization.

4.3 PART II (PEDOT:SPI films)

4.3.1 Preparation of PEDOT:SPI aqueous suspensions

4.3.1.1 Preparation of sulfonated polyimide (SPI) films

3.5 g (9.71 mmol) of 4,4'-ODADS prepared according to the previously published procedure [16], 50 mL of m-cresol, and 1.96 g (19.42 mmol) of triethylamine was added to a 100 mL three-neck flask with a nitrogen inlet and outlet. After 4,4'-ODADS was completely dissolved, 3.01 g (9.71 mmol) of O-DPDA (for SPI1) or 4.32 g (9.71 mmol) of 6FDA (for SPI2) was added and the solution was stirred under a nitrogen atmosphere at room temperature for 72 h. When the reactions were completed, the poly (amic acid) solution was casted onto glass dishes and was thermally treated at 70 °C, and 150 °C for 1 h each, and 250 °C for another 1.5 h in a temperature controlled oven. After the thermal curing, the sulfonated polyimide (SPI) films in salt form were obtained.

4.3.1.2 Ion exchange of sulfonated polyimide films

The SPI film in salt form (3.015 g of SPI1 or 3.458 g of SPI2) was dissolved in 300 mL of DI water at 80 °C. After the solution was cool down, it was changed to SPI in acid form by reaction with an ion exchange resin of strong acid type DOWEX 50WX8 (cation exchange). The SPI in salt form was stirred in DI water with 4.21 g of the ion exchange resin for 3 h to convert it to the free acid form (H^+). It was then centrifuged to separate the ion exchange resin to obtain the polyimide acid form solution as templates for conducting polymer polymerizations.

4.3.1.3 Polymerization of PEDOT:SPI

The typical procedures for preparing PEDOT-SPI dispersion are described as follows. 0.3195 g (2.25 mmol) of EDOT was added to the sulfonated polyimide solutions. The suspensions were continuously stirred for 2 h, and then 1.626 g (2.4 mmol) of iron (III) p-toluene sulfonate hexahydrate was added for polymerizations. The reaction was stirred vigorously for 5 days at room temperature leading to a dark blue dispersion for PEDOT-SPI. During the oxidative polymerization, the mixture flask should be covered by Al foil to prevent it from light.

4.3.2 The fabrication of PEDOT:SPI Nano-scale thin films on glass substrates

The dark blue PEDOT:SPI dispersed in aqueous solutions were centrifuged at 500 rpm for 3 min in order to separate agglomerated particles from the suspension. After that, the supernatant was added by SDS surfactant, the ratio of PEDOT:SPI to surfactant is 1:2 by weight, and subsequently sonicated for 3 h and then transferred into a rotary evaporator at 40 °C for partial water evaporation to obtain a high concentration and good dispersion of PEDOT:SPI in aqueous solution. Surfynol was added to the highly-concentrated PEDOT:SPI aqueous suspensions at the ratio of PEDOT: SPI to Surfynol was 5mL:1 μ L in order to reduce its surface tension and increase film smoothness. Various amounts of PVA were then added to the PEDOT:SPI aqueous suspensions to obtain 0.05-1.0 wt.% of PVA.

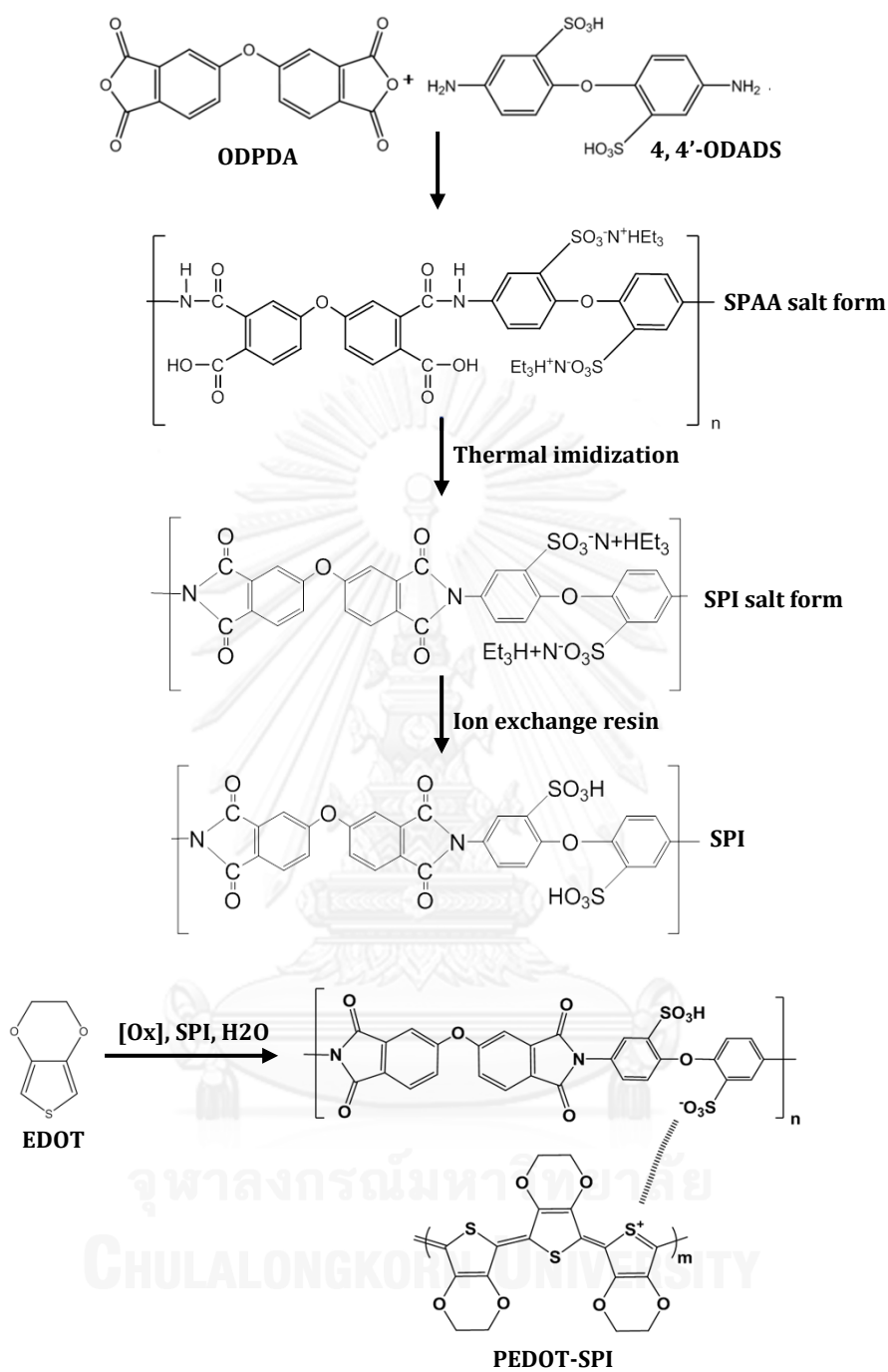


Figure 4.1 The synthesis procedure of PEDOT:SPI1 suspension

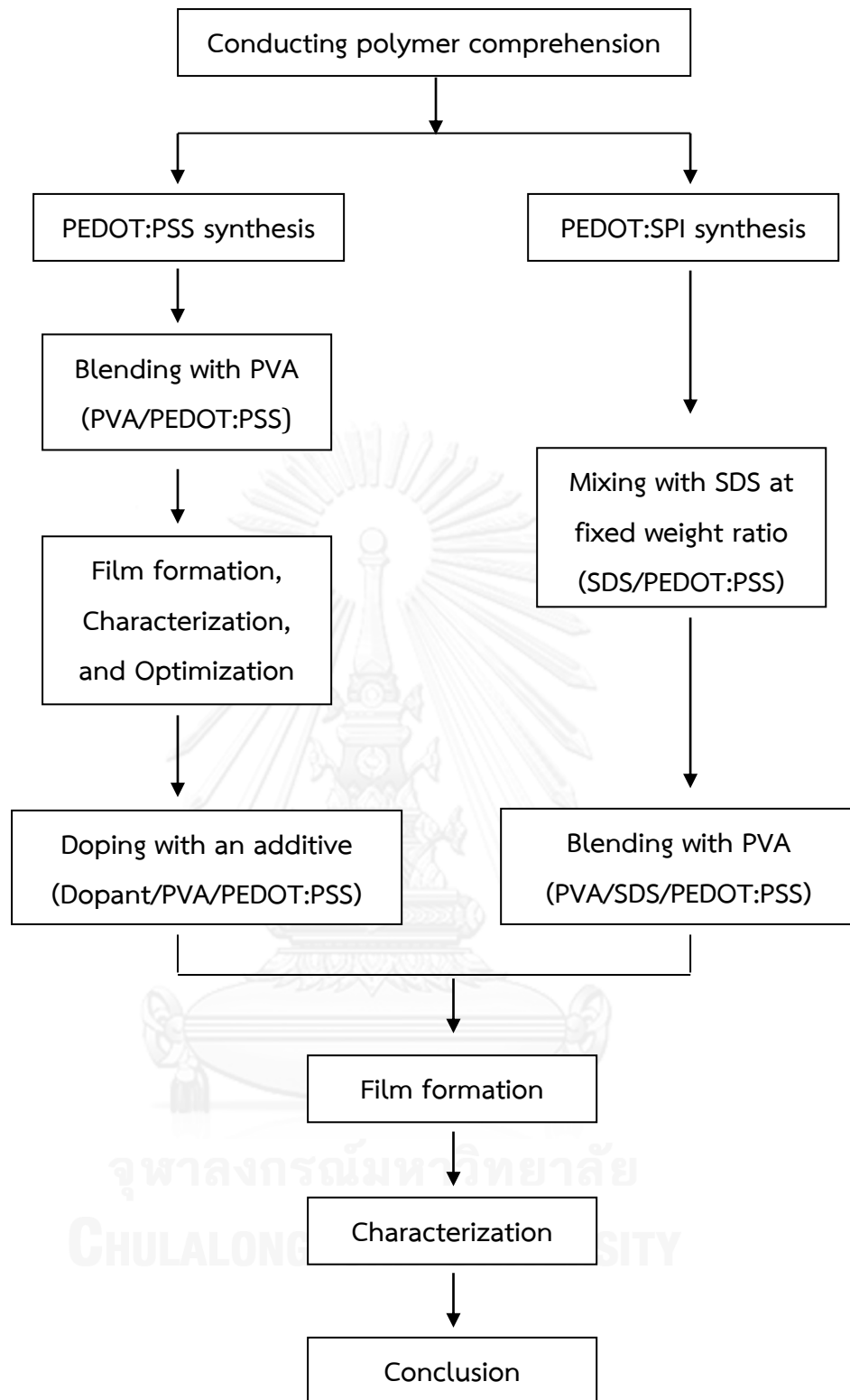


Figure 4.2 The research methodology of this work

The PVA/PEDOT:SPI with different PVA weight fractions were deposited on dried, clean glass substrates by means of spin-coating at a fixed spin speed of 4,000 rpm for 60 s, resulting in film thicknesses ranging from 80 to 340 nm. Glass slides were sonicated in soap water, DI water, acetone and IPA for 15 min in each solvent sequentially before used as substrates. The thin films were thermally treated on a hotplate at 70 °C for 1 h and then kept in a dark desiccator or glove box for characterization.

4.4 Characterization techniques

4.4.1 Conductivity

Conductivities were measured using a four-line collinear array utilizing a Keithley Instruments 224 constant current source and a 2700 Multimeter. The polymer thin films coated on glass substrates by spin-coating were placed on four Cu-coated leads, 0.25 cm apart from each other, on the surface across the entire width of the polymer. The current was applied across the outer leads and voltage was measured across the inner leads.

4.4.2 Thermal property

The conducting polymer suspensions were dropped-cast on glass slides and dried at room temperature in a hood for 24 h. After that, the specimens were scraped and baked at 80 °C for 1 h before analysis. Thermo gravimetric Analysis (TGA) was performed by a Perkin–Elmer TGA 7 series analysis system with a heating rate of 20 °C/min, under air and a flow rate of 60 mL/min.

4.4.3 Optical property

The Transmittance values of conducting thin films coated on glass slides were conducted by Varian Cary 5000 UV-VIS-NIR Spectrophotometer. The reference (blank) for comparison is air.

4.4.4 Wettability

The contact angles of conducting thin films were measured by Rame Hart Model 100 Goniometer at 25 °C to determine the static contact angle of a liquid droplet on a solid surface (with 0° being defined as absolute wetting and 180° as completely non-wetting). A droplet of DI water was about 20 µL. The results of contact angle values were reported at 15 s after dropping.

4.4.5 Film thicknesses

Film thicknesses of thin films were measured by a Dektak 150 Surface Profilometer. All specimens were scraped off by a tip of needle and baked at 70 °C for a while before used.

4.4.6 Macroscopic thin film image

The images of Polymer film surface were assessed by Nikon Metaphor metallurgical microscopes, with magnification ranges from 25X to 1000X.

4.4.7 Dimension of conductive Particles

The images of agglomerated and single PEDOT:PSS particle were taken using JEOL 2010 Fas and Philips EM420 transmission electron microscope (TEM). TEM image was obtained from dry sample of dropping of PEDOT:PSS solution on grids and then evaporating to remove liquid solvent.

4.4.8 Thin film topography

JEOL JSM-6400 scanning electron microscopy (SEM) was used for observation of film topography by coating thin films with gold particles by sputtering device.

4.4.9 Thin film morphology

AFM images of conductive thin films were performed using scanning probe microscope (Veeco Model MMAFMLN, 1959EX, operated in tapping mode). All specimens were coated on $1.5 \times 1.5 \text{ cm}^2$ thin glass slide by spin coating

CHAPTER V

RESULTS AND DISCUSSION

5.1 PART1 (PEDOT:PSS)

The almost all previous studies strongly focused on how to improve the conductivity of PEDOT:PSS by doping with organic solvents, secondary dopants, and surfactants. It is due to the PEDOT:PSS have been widely applied in many electronic fields. However, beside conductivity, these doping agents did not show any significant devolvement in others properties of PEDOT:PSS. Thus, the investigation of improvements in their others properties such as mechanical, thermal and contact angles are very rare to find and usually be neglected despite of the importance of those properties, which were crucial in combination with the conductivity for further advanced applications. These advanced properties of PEDOT:PSS could be simply achieved by mixing with other polymers in order to obtain the desired properties. However, almost all of researchers always believe that the addition of insulation polymers into conductive polymers surely diminishes their conductivity. Therefore, PEDOT:PSS have not been mixed with insulating polymers as a domain phase. Generally, we have found that PEDOT:PSS are often used for addition into insulating polymers as a filler for the conductivity improvement [4,5]. In this work, however, we perversely found that the suitable amounts of the insulating polymer (PVA) could reasonably improve the conductivity of PEDOT:PSS together with their mechanical and thermal properties, and contact angles, to open up another aspect of scientific comprehension. The correlation between various PEDOT:PSS and PVA amounts are

also presented here. All in all, the blending of PEDOT:PSS with PVA, as well as the addition of a dopant becomes one of effective routes to simultaneously improve various properties of PEDOT:PSS for advanced applications such as spin coating applicable and to give significant information for further development in the area of conductive polymers.

5.1.1 PEDOT:PSS dispersion

PEDOT:PSS is dark blue particles which are suspended in aqueous solution, as shown in **Figure 5.1**. It is generally synthesized by oxidative polymerization of EDOT monomer and oxidizing agent. Its dark blue color originated when the transfiguration from EDOT to PEDOT occurred. PEDOT is a semi-conductive polymer for electronic applications. The function of PSS is to balance the positive charges of PEDOT to form PEDOT:PSS via ionic interaction. It is also utilized to keep PEDOT in dispersion state for film-forming application on any substrates.



Figure 5.1 PEDOT:PSS aqueous suspension

5.1.2 The formation of PVA/PEDOT:PSS thin films

After PEDOT:PSS synthesis completed, it was mixed with various amounts of PVA in accordance with blending concept to improve PEDOT:PSS properties. After that the mixtures were spun-coating at a fixed speed rate of 4,000 rpm to form conductive thin films on glass substrates. The specimens were shown in **Figure 5.2** below. From visual observation, the thin films were more opaque with increasing PVA amounts. This was due to the difficulty of light transmission that went across thicker films. However, all samples were still clear and transparent. After characterization, all numerical experimental results were shown in **Table 5.1**.



Figure 5.2 (a) PEDOT:PSS thin films on glass slides with various wt.% PVA, (b) 0.05, (c) 0.08, (d) 0.3, (e) 0.5, (f) 0.8, and (g) 1.0

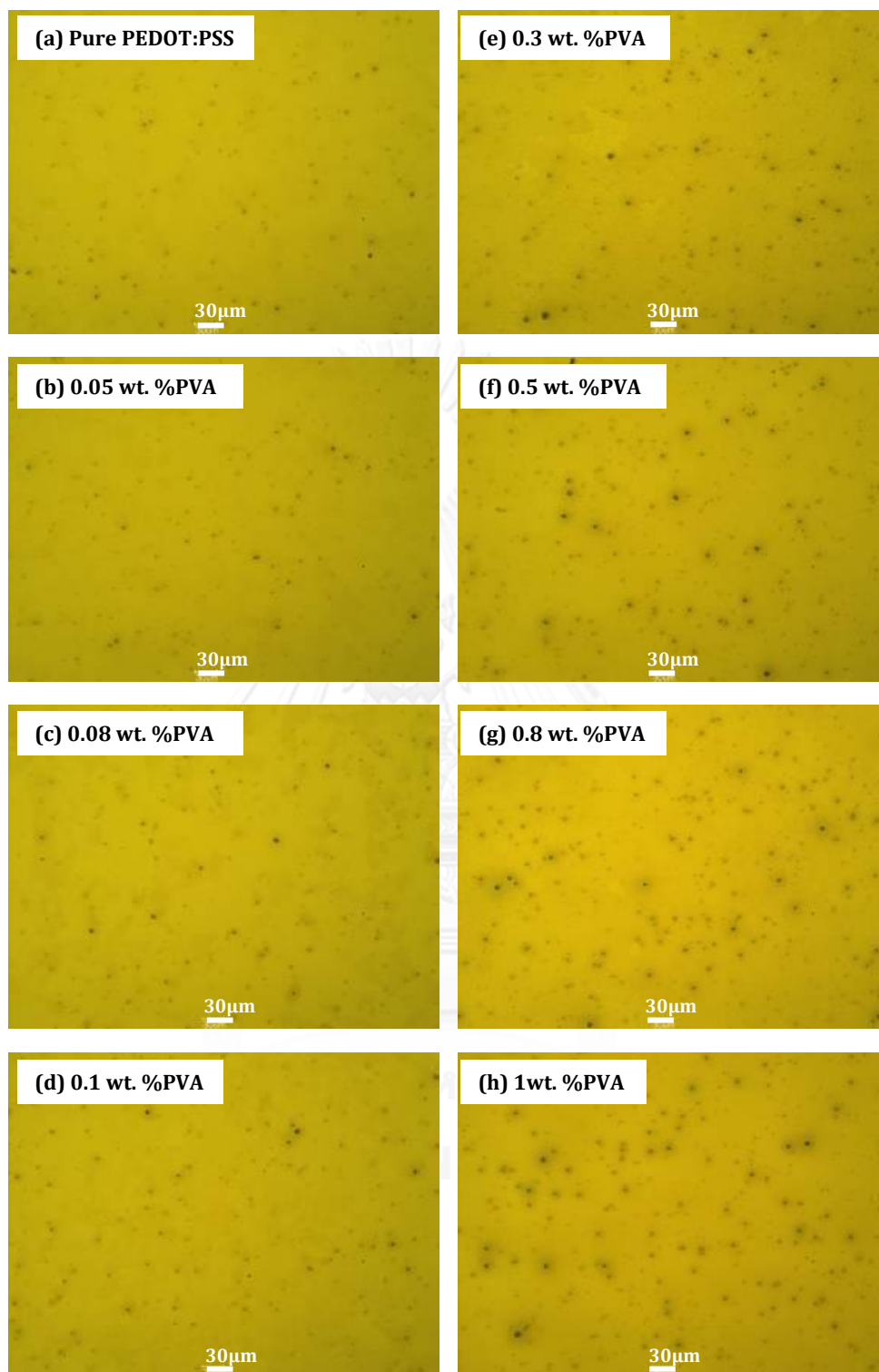


Figure 5.3 Optical microscopic images of PVA/PEDOT:PSS thin films with various weight fractions of PVA (The dark spot is agglomerated PEDOT:PSS)

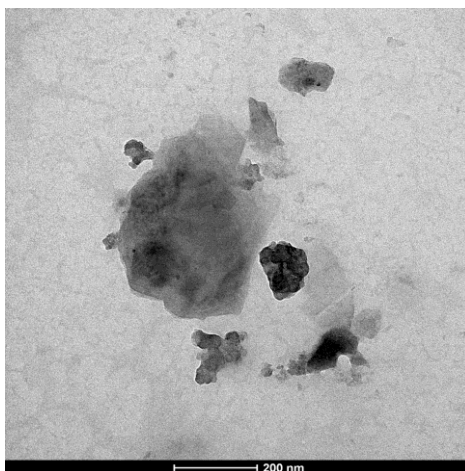


Figure 5.4 TEM image of PEDOT:PSS agglomeration and its single particles

Table 5.1 Various properties of PEDOT:PSS thin films with different wt.% PVA

Samples	Film thickness (nm)	Transmittance at 550nm. (%T)	Contact Angle (°)	Resistance (k Ω)	Conductivity (S/cm)	Solution viscosity (cP)
(1) Glass slide	-	91.73	26.5	-	-	-
(2) pure PEDOT:PSS	80	89.86	15.0	195.91	0.641	1.68
(3) 0.05wt.% PVA	91.2	89.35	7.6	107.02	1.030	1.74
(4) 0.08wt.% PVA	94.4	89.31	8.8	89.55	1.180	1.79
(5) 0.1wt.% PVA	103.3	89.03	12.2	122.54	0.801	1.82
(6) 0.3wt.% PVA	112.4	88.96	16.5	412.20	0.216	2.34
(7) 0.5wt.% PVA	118.6	86.22	19.8	415.33	0.204	2.74
(8) 0.8wt.% PVA	127.0	83.39	22.0	1539.20	0.052	3.37
(9) 1.0wt.% PVA	130.0	82.94	20.0	1646.77	0.047	3.86

The thin film surfaces of all specimens were shown in Figure 5.3. The dark spots were the agglomerated PEDOT:PSS. The agglomeration increased with increasing PVA amounts, leading to more surface roughness. This might imply to the lack of perfection in single dispersion of PEDOT:PSS particle. PEDOT:PSS agglomeration and

its individual particles were in the range of sizes of 320 and 70 nm, respectively, and were clearly verified by TEM image as shown in **Figure 5.4**.

5.1.3 The relationship between conductivities and contact angles of PEDOT:PSS thin films

The conductivity of thin films is another important property to reveal the ability of charge transfer along conductive mediums. In the area of electronic application, this property has been firstly taken to consideration. In addition, the wettability between PEDOT:PSS layer and other layers in electronic devices should be compatible as well, which can express in contact angle values of conductive thin films. These two properties should properly harmonize for efficient applications. From **Figure 5.5**, the tendency of the conductivity was initially increased with increasing PVA amounts and it reached the highest value at 0.08 wt. %PVA. This was possibly due to the new rearrangement of PEDOT:PSS morphology. That is, an insulating PVA acts as a binder to improve the connection network between the PEDOT:PSS polymer chains, leading to better conductivities [18]. This result proven that the addition of a proper insulating polymer amount has a strong potential for improving the conductivity of conductive polymers matrix. However, it depends on the intrinsic properties of both the additive and the matrix. After the concentration of PVA exceeded 0.08 wt.%, the reduction of conductivity was obtained. This was because of the more influence of insulator behavior of PVA when we added too much PVA into PEDOT:PSS suspension. Furthermore, the OH groups of PVA can possibly interact with the SO_3^- groups of PSS by the strong covalent bonds in between, which reduced some of the negative charge of the conducting polymers. Thus, more PVA amounts in the mixture implied

that more SO_3^- groups of PSS would be bonded with OH groups of PVA, and finally decreased in the number of conductive SO_3^- groups resulting in ultimately decrease of the conductivity of the blended polymers.

The initial point of increasing contact angle values with increasing PVA amounts was observed at 0.08 wt.%PVA. When PVA gradually increased from the 0.08 to 1.0 wt.%, the conductivities continuously decreased in this range. The lower contact angle implied to better wettability and adhesiveness properties of the conductive film surface. These properties were essential for actual usability when PEDOT:PSS films were applied to make electrical contact with other materials. As concluded from this relationship between conductivities and contact angle values, the optimal condition of PEDOT:PSS for its both conductivity and contact angle was fulfilled at 0.08 wt.%PVA.

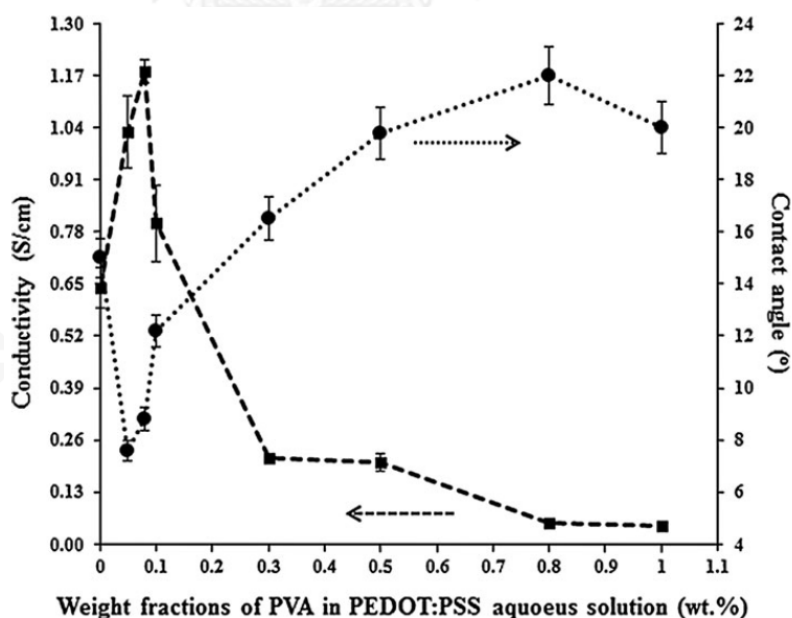


Figure 5.5 Relationship between conductivities (dashed line) and contact angle values (dotted line) of PEDOT:PSS thin films with various weight fractions of PVA

Moreover, as the results of increasing in contact angle values with increasing PVA weight fractions, the higher polymer viscosities were encountered because of the higher PVA amounts in aqueous suspension, leading to more PEDOT:PSS agglomeration in the films, **Figure 5.3(a-h)**. These rough films resulted in an increase in contact angle values of PEDOT:PSS films. In fact, PVA is a hydrophilic polymer, so the contact angle values should be normally decreased when increasing the PVA amount. However, the opposite phenomena were observed, which might result from the stronger influence of the polymer film roughness than the influences from hydrophilicity of the filler, PVA, on contact angle. In addition, the advantages to adding more PVA in PEDOT:PSS were to solve the problems of poor durability and brittleness of PEDOT:PSS films, which directly resulted in poor mechanical properties of the films. These problems were not only successively disappeared with increasing PVA amounts, but also the addition of PVA would improve film-forming properties at the same time. From visual observation, the defects on film surfaces originated from scratching with the tip of needle were gradually diminished with increasing PVA amounts because of the more interactions between the OH groups of PVA and the SO₃⁻ groups of PSS, leading to the improvement of PEDOT:PSS mechanical properties. Scratch test was an indirect way to effectively investigate the mechanical properties of PEDOT:PSS because the PEDOT:PSS can not be made in the form of free-standing films with the micro-scale sizes.

5.1.4 The relationship between thicknesses and transmittance values of PEDOT:PSS thin films

Transparency throughout the visible spectrum is one of the important film properties in certain application. The film should allow as much sunlight as possible to pass through it for efficiency in application as transparent electronic materials, e.g., electrodes and hole transporting layer of organic solar cells. **Figure 5.6** shows the transmission of visible light at 550 nm through PEDOT:PSS thin films with various amounts of insulating PVA. The transmittances were decreased with increasing PVA weight fractions because the increase of the amount of PVA in polymer suspension, the polymer viscosities were also higher, leading to thicker films during spin-coating at a fixed spin rate. As the consequences, the thicker polymer films caused the decrease in transmittance values. However, all specimens still showed the high transmittance values of more than 80%. The whole UV-VIS spectrum of pure PEDOT:PSS and with various weight fractions of PVA can be shown in **Figure 5.7**. The level of transparency of PEDOT:PSS blended with various wt.% PVA are in the order as follows; 0 (pure PEDOT:PSS) > 0.05 > 0.08 > 0.1 > 0.3 > 0.5 > 0.8 > 1.0 wt.% PVA. The relationship between conductivities, contact angles, film thicknesses, and transmittances of PEDOT:PSS films versus various amounts of insulating PVA would be extremely useful for choosing a suitable mixture to achieve specific PEDOT:PSS properties as designed.

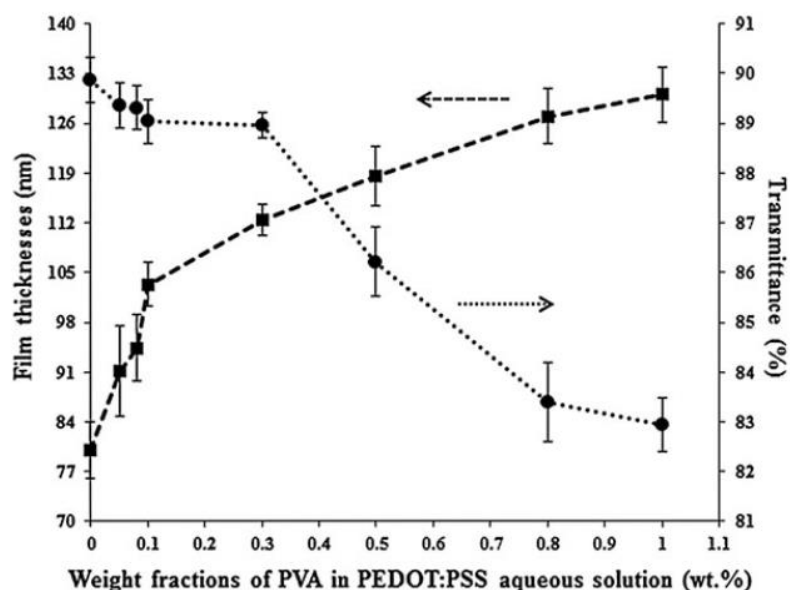


Figure 5.6 Relationship between thicknesses (dashed line) and transmittance values (dotted line) of PEDOT:PSS thin films with various weight fractions of PVA

The variation of PEDOT:PSS structure changed because of the influence of PVA amounts, can be shown in **Figure 5.8**. SEM topography of each specimen clearly provided the different feature of PEDOT:PSS dispersion when added more PVA amounts. There were two types of appearance in the films, the PEDOT:PSS cluster as islands in a sea of the free area. As, the PEDOT:PSS clusters were smaller, their conductive network were more well developed in order to cover free area more, when added more PVA amounts, as shown in **Figure 5.8 (a-h)**. This may be the key factor to the properties change in many films produced. However, PVA is an insulating polymer; it should be suitably adjusted to optimize all of its properties. In addition, SEM topography also supported the result from the optical microscopy, namely, the created PEDOT:PSS network were linked together to form a large agglomeration of PEDOT:PSS sizes leading to the decreased in free areas. For this

reason, the big dark spots were observed easily when increasing PVA amounts, as seen in **Figure 5.3**.

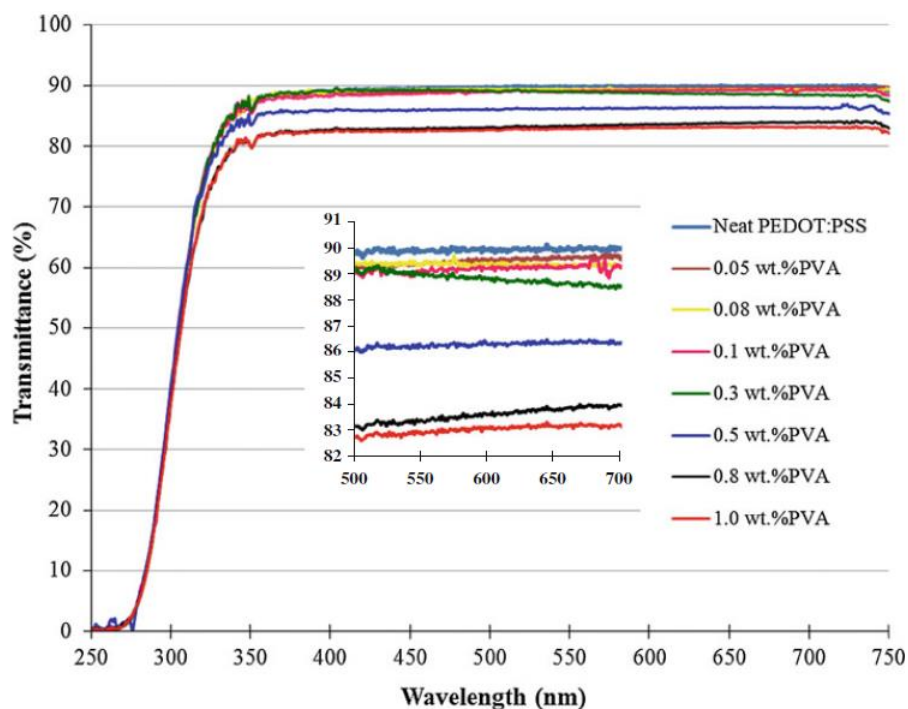


Figure 5.7 UV-Vis spectrum of PVA/PEDOT:PSS thin films with various weight fractions of PVA. The inset is a magnification of 500-700 nm

5.1.5 Thermal properties of PEDOT:PSS thin films

The effect of PVA on the thermal stability of conducting polymers was another interesting significant property to investigate. This property is related to the thermal degradation when the films are exposed to high temperature operation. The good thermal properties are required for extending the useful life of electronic devices, comprised of PEDOT:PSS.

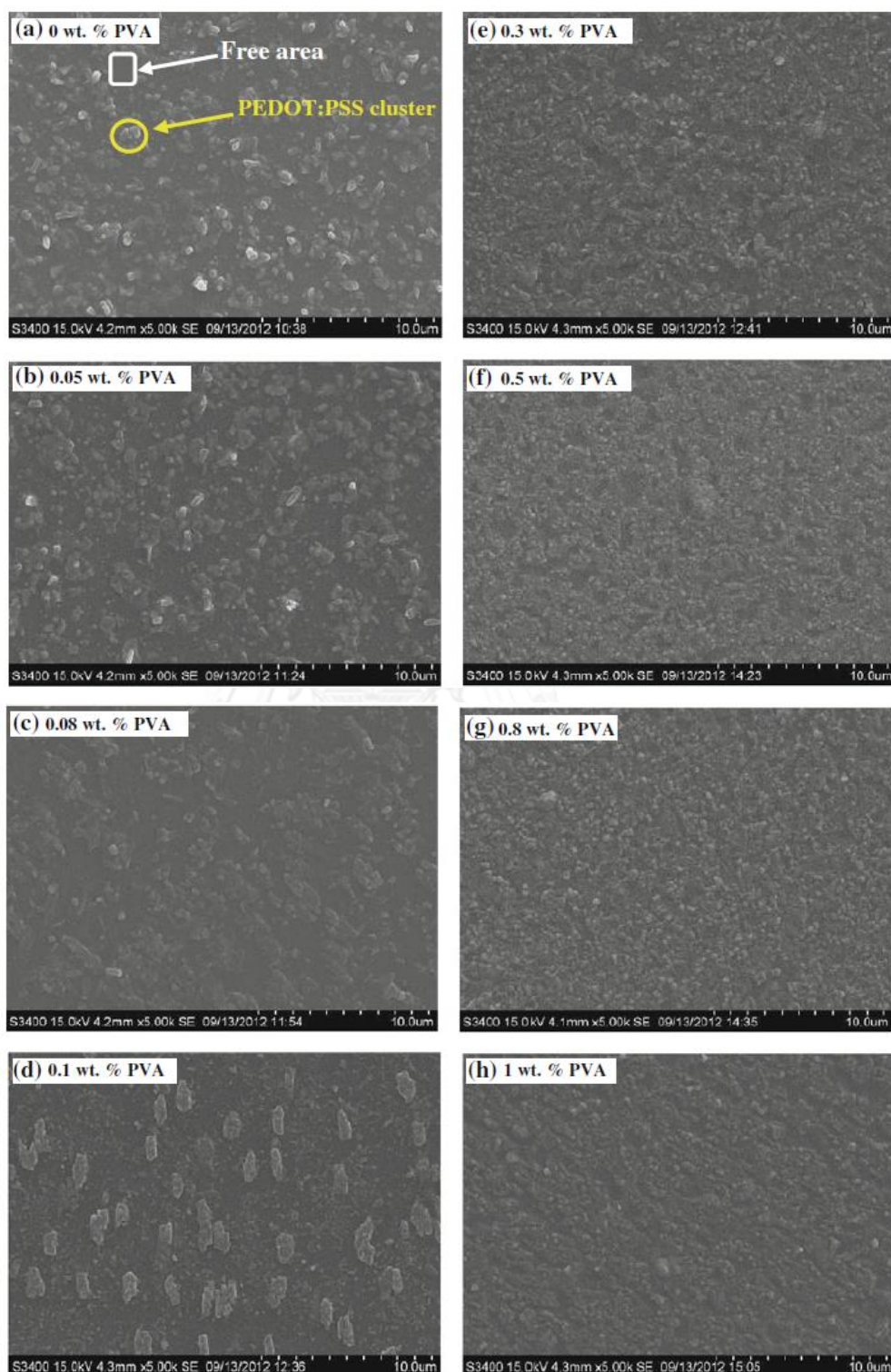


Figure 5.8 SEM images of PVA/PEDOT:PSS thin films with various weight fractions of PVA

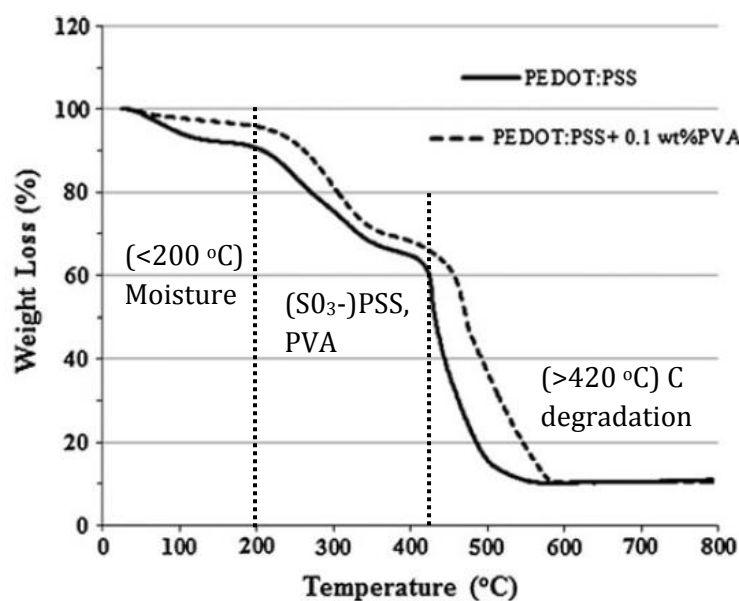


Figure 5.9 TGA results of PEDOT:PSS thin film (solid line) and with 0.1 wt% PVA (dashed line)

Figure 5.9 shows that the thermal stability of PEDOT:PSS could be reasonably improved by the addition of PVA. The thermal stability of PVA/PEDOT:PSS was better than that of pure PEDOT:PSS. Namely, Td5 and Td10 for PVA/PEDOT:PSS were 216.05 and 261.44 °C, whereas values for pure PEDOT:PSS were 90.76 and 207.88 °C, respectively. Due to the ability of the OH group of PVA to bond by strong covalent bonds with the SO_3^- groups of PSS, therefore, a higher PVA concentration in the mixture would result in stronger thermal properties of the films. For pure PEDOT:PSS, significant weight loss taking place at temperature below 200 °C, because of the contained moisture, while the fragment of PSS sulfonate group degradation occurred approximately at 230 °C. Moreover, PVA degradation temperature is in the range of 270-280 °C, slightly more than PSS sulfonate group degradation. Thus, the addition of PVA could slightly improve the thermal resistivity of the blend. At higher

temperatures above 420 °C, the other fragments due to carbon oxidation degradation were observed. In the same way, PEDOT:PSS blended with PVA provided more stability in the fragment of PSS sulfonate group (about 250 °C) and the carbon oxidation (about above 450 °C) than that of pure PEDOT:PSS. This result also supported evidence that the presence of insulating PVA in PEDOT:PSS could effectively improve the thermal properties of PEDOT:PSS.

5.16 Interaction between PEDOT:PSS and PVA

The nature of interactions between PVA (OH) and PSS (SO_3^-) via Covalent bonding (or sometimes H-bonding) requires FTIR evidence.

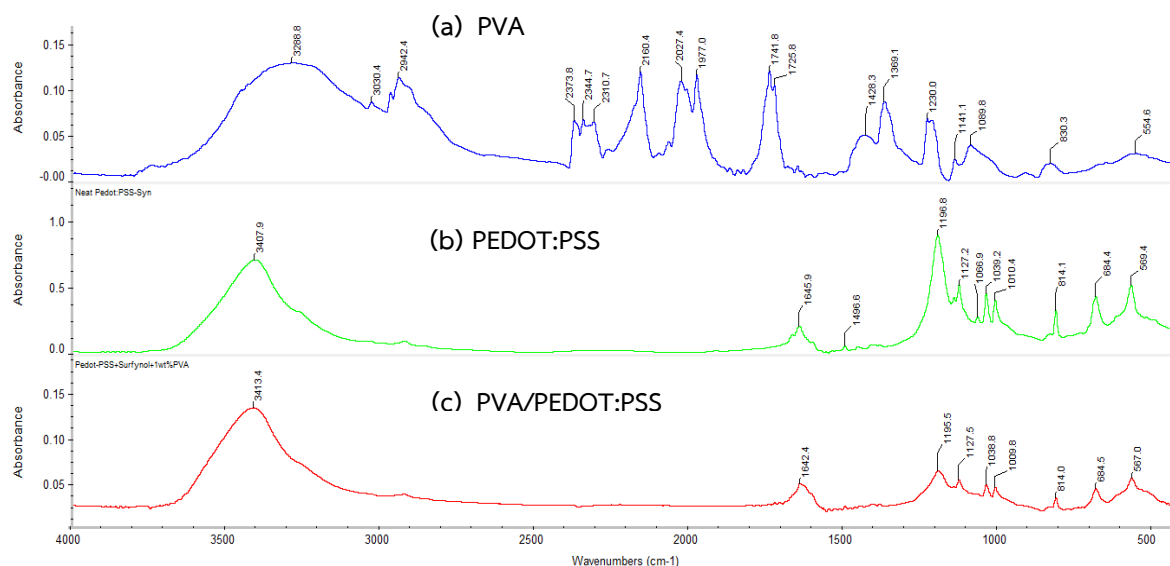


Figure 5.10 FT-IR patterns of (a) pure PVA, (b) pure PEDOT:PSS, and (c) 1wt.% PVA/PEDOT:PSS

The interaction between OH groups of PVA and SO_3 groups of PSS normally takes place at $3580\text{-}3480\text{ cm}^{-1}$. However, characteristic peaks of pure PEDOT:PSS also appeared at the same range as the bonding peaks, as shown in **Figure 5.10(b)**. Thus, it was impossible to precisely observe the appearing peaks of the bonding because of peaks overlapping. However, the peak shifts to higher wavenumber of PVA/PEDOT:PSS (3413.4 cm^{-1}), comparable to pure PEDOT:PSS (3407.9 cm^{-1}), might be because of the influence of the interaction and this could be the only evidence of the existence of the bonding between PVA and PSS as can observe by FTIR. Moreover, the very low amounts of PVA added into PEDOT:PSS not only cause the smaller emerging of the bonding, but also result in the absence of all PVA peaks characteristic peak, as shown in **Figure 5.10 (c)**. The very strong signal of PEDOT:PSS is the main reasons to make the unobservable PVA characteristic peaks patterns in the PVA/PEDOT:PSS mixtures.

5.1.7 Conductivities and contact angle of PEDOT:PSS with a secondary dopant

The mechanical and thermal properties of PEDOT:PSS were successfully improved by the addition of suitable amounts of insulating PVA in accordance with the concept of polymer blending. The optimal condition to balance between the conductivity and contact angle was achieved at 0.08 wt.%PVA in PVA/PEDOT:PSS thin films. As this initial point, the further investigations of the specific effect of adding a secondary dopant on conductivity enhancement according to the concept of doping agent were conducted. The conductivity gradually increased with increasing amounts of quinoxaline, the doping agent, and reached the highest value at 0.5 wt. %

quinoxaline, as shown in **Figure 5.11**. The screening effect might be the driving force for the conformational change of PEDOT chains due to the interactions between the polar solvent, the PSS and the PEDOT polymer main chain, leading to the improvement in charge transport properties of PEDOT:PSS and the better conductivity was finally achieved. After the concentration exceeded 0.5 wt.%, the conductivity of doped films sharply decreased to lower than that of the undoped film. Intrinsic insulating behavior of quinoxaline might become more substantial dominated at higher concentration, so causing this phenomenon. In other words, the excessive amounts of insulating doping agent remaining in the film could disperse around and form a surrounding network enclosing the conductive PEDOT:PSS particles, which eventually obstructed charge hopping between adjacent sites, thus, considerable deteriorating the conductivity was observed.

The variation in contact angle arising from the change in the amount of quinoxaline was also investigated. The contact angles had a tendency of slightly reduction from 23 to 16.5 degree when more doping agents were added. The decrease in contact angles might be ascribed as a significant increment of the polar force of the surface free energy due to the possession of pyrazine groups in quinoxaline structure. This polar group would increase with increasing quinoxaline concentration, leading to more hydrophilicity of the films. Thus, contact angle values of the doped films would decrease with increasing quinoxaline concentration. However, they were still higher than the starting point (8.8 degree) of nascent PVA/PEDOT-PSS. The highest conductivity (2.75 S/cm) was achieved when PEDOT:PSS was added with 0.08 wt.% PVA and 0.5 wt.% quinoxaline while the other properties

were not significantly altered. The produced films were still maintained in good conditions comparing with nascent PVA/PEDOT:PSS films.

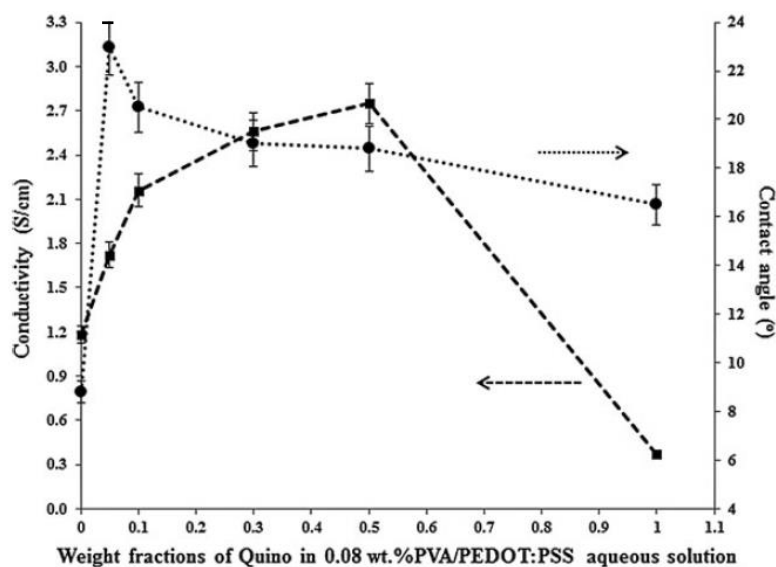


Figure 5.11 Dependence of conductivities (dashed line) and contact angle values (dotted line) of 0.08 wt.% PVA/PEDOT:PSS thin films with various weight fractions of the dopant, quinoxaline

5.1.8 Summary of PART1

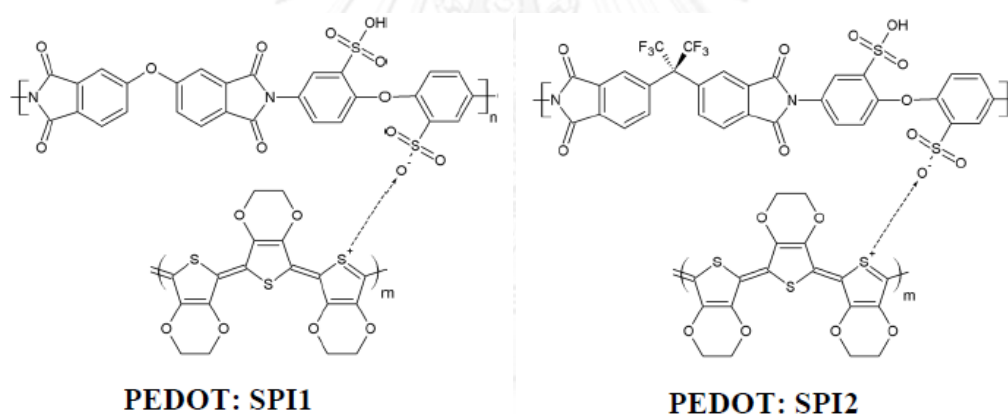
The integration of the useful concept of polymer blending and doping agent to improve various properties of PEDOT:PSS thin films including conductivity, wettability, and thermal and mechanical properties were proposed. Using the polymer blending concept, it was found that the appropriate amount of PVA (0.08 wt.%), an insulating filler, has a superior potential to improve the conductivity of PEDOT:PSS, due to a binder actions to improve the connection network between PEDOT:PSS chains, leading to a maximum conductivity of 1.18 S/cm. It also provided a good contact

angle of 8.8° at the same wt.% of PVA. The film transmission decreased with increasing PVA amounts; however, all specimens still showed excellent transmittance values of more than 80 %. The thermal stability and the resistance to scratched abrasion of the conductive films were improved by strong covalent bonds between SO_3^- groups of PSS and OH groups of PVA. The doping agent of quinoxaline significantly enhanced the conductivity of PEDOT:PSS. The highest conductivity (2.75 S/cm) was achieved when 0.5 wt.% quinoxaline was added into 0.08 wt.% PVA/PEDOT:PSS while the other properties remained unchanged. The relationship of conductivities, contact angles, film thicknesses, and transmittances of PEDOT:PSS films were the basis information for choosing a suitable condition to achieve specific PEDOT:PSS properties. All in all, the blending of PEDOT:PSS with PVA as well as the addition of a dopant became one of effective routes to simultaneously improve various properties of PEDOT:PSS for nano-thin film and also provided significant information for further development in the area of conducting polymers for electronic applications.

5.2 PART2 (PEDOT:SPI)

The main issue of this part is the precipitation of PEDOT:SPI particles in aqueous solution which are unable to form a conductive thin film. Although a repeating unit of SPI is much bigger than that of PSS, the amount of SO_3^- groups in SPI chain are less than that of PSS chain resulting in poor suspension of PEDOT:SPI. Furthermore, the interaction nature between SPI molecules is also stronger than that of PSS, finally leading to an agglomeration into big particles. For the sake of aforementioned reasons, the SDS surfactant was necessarily used in fairly high amount in order to stabilize the PEDOT:SPI in aqueous solution. From our experiment, the weight ratios of PEDOT:SPI to SDS surfactant varied from 1:0.5 to 1:5. It was found that the weight ratio of 1:2 is the initial point of complete stabilization of the PEDOT:SPI particles without precipitating into a bottom vial. If the SDS amount exceeded this point, the leftover SDS would be clearly observed at a bottom vial. Moreover, residual surfactant could not only lead to rough conductive film but also diminished the film conductivity because they penetrate between PEDOT:SPI particles obstructing the charge transfer. In addition, since majority of the published works have widely exercised the commercial PEDOT:PSS for their experiments, they did not face any problem concerning the particle dispersion. Hence it is noted that they often used only small amount of additives for PEDOT:PSS modification. In the case of PEDOT:PSS, large amounts of the SDS surfactant resulted in the precipitation of PEDOT:PSS which was totally different from PEDOT:SPI, which in fact could lead to the prevention of PEDOT:SPI from the precipitation. Thus, SDS surfactant and the weight ratio of 1:2 became the optimum condition for this work. All in all, SDS surfactant was mainly used to stabilize the conductive particles and to enhance the

film wettability. It also had a side benefit to provide better film conductivity when compare to other surfactants [17,53]. Moreover, surfynol could benefit by reducing the formation of bubble in PEDOT:SPI during preparation step and making a more smooth film than using SDS alone as well; however, its small amount as used did not have the significant effect on the film conductivity. Both the SDS and Surfnol additives still totally remained in a fully processed thin film because the thin film was thermally cured at low temperature ($70\text{ }^{\circ}\text{C}$) that was lower than the melting point of SDS ($206\text{ }^{\circ}\text{C}$) and boiling point of Surfnol ($367\text{ }^{\circ}\text{C}$). In addition, PVA was aimed to form nano-conductive thin films and to improve various conductive PEDOT:SPI film properties in order to apply them for electronic areas.



Scheme 5.1 Representation of the molecular structures of PEDOT:SPI1 and PEDOT:SPI2

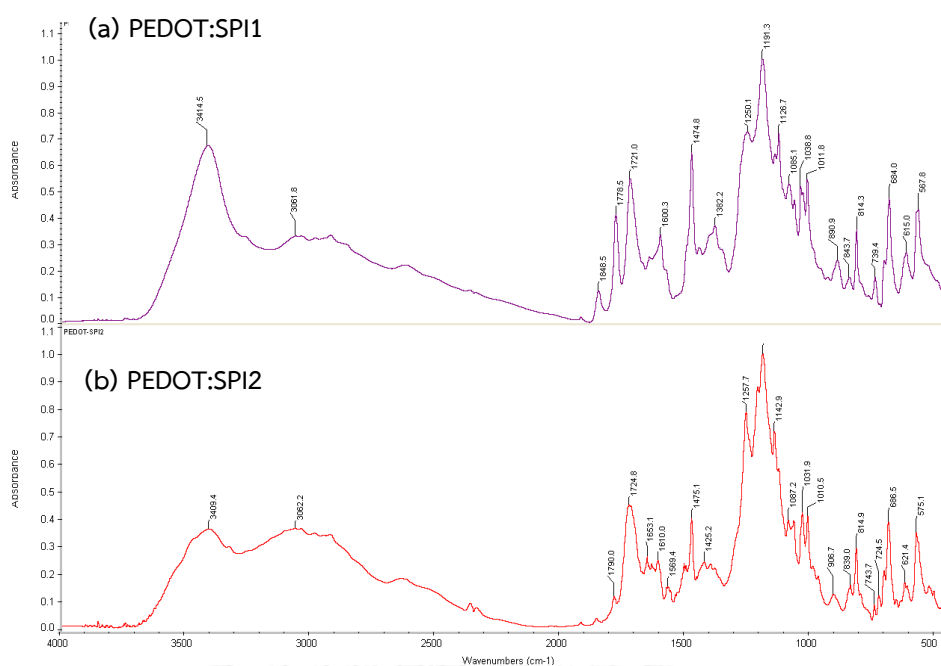


Figure 5.12 FT-IR patterns of (a) pure PEDOT:SPI1 and (b) pure PEDOT:SPI2

The chemical structures of both PEDOT:SPI1 and PEDOT:SPI2 were shown in **scheme 5.1**. The difference between PEDOT:SPI1 and PEDOT:SPI2 system was their molecular structures. SPI1 had ether group (-O-), but SPI2 has CF_3 group in its own polyimide structure. This difference possibly was the key point to make PEDOT:SPI2 to have many properties better than that of PEDOT:SPI1. The FT-IR patterns for the both were identical as shown in **Figure 5.12**. The CF_3 group in PEDOT:SPI2 might be obscured by other molecules leading to the similarity of the both FT-IR patterns.

5.2.1 Dispersion state of PEDOT:SPI

In this work, the role of the SDS surfactant was to improve the dispersion stability of PEDOT:SPI particles after finishing the completed polymerization step. Otherwise, they had a tendency to agglomerate into large particles in a short time leading to, finally, being unable to form the conductive films on glass substrates by spin-coating. This was due to the weak electrostatic repulsion between sulfonated polyimide molecules. TEM image showed individual particles of each PEDOT:SPI at about 70 nm, as shown in **Figure 5.13**. Without SDS surfactant; however, their unstable dispersion in water was observed. And it was found that the suitable ratio of PEDOT:SPI to SDS surfactant to prevent the precipitation of PEDOT:SPI was 1:2 by weight. The good dispersion stability of PEDOT:SPI in water with SDS surfactant was achieved even after 2 months, as shown in **Figure 5.14**. This phenomenon totally differed from the addition of SDS into PEDOT:PSS as published in [17]. The less stable solution was occurred, within just 1 week after adding SDS surfactant into PEDOT:PSS aqueous solution. This evidence clearly indicated that the mechanism of the interaction between SDS surfactant and PEDOT:PSS was absolutely different from that of PEDOT:SPI. In case of PEDOT:PSS, the SDS surfactant acted as the counteranions to PEDOT resulting in the conformational changes and eventually led to the precipitation of PEDOT:PSS particles. In case of PEDOT:SPI, it might be due to the electrostatic repulsion between PEDOT:SPI particles stemming from the enclosure of PEDOT:SPI with SDS surfactant.

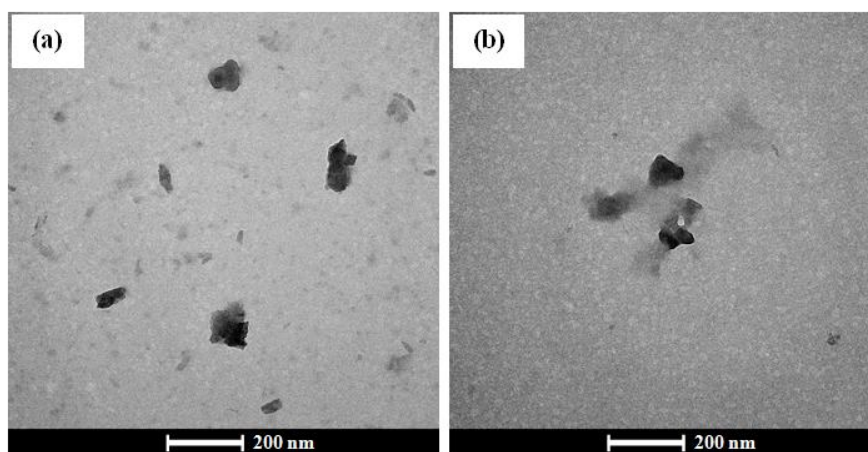


Figure 5.13 TEM images of (a) PEDOT:SPI1 and (b) PEDOT:SPI2 particles

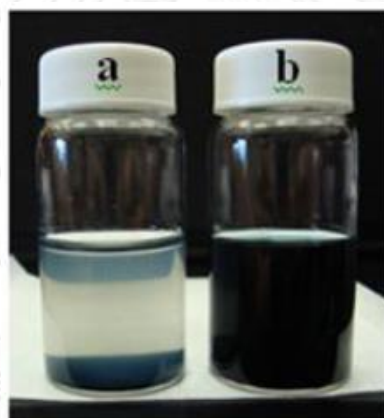


Figure 5.14 Dispersion of PEDOT:SPI in an aqueous solution (a) without SDS and (b) with SDS, after 2 months

5.2.2 Film conductivities

From **Figure 5.15**, the research found that in case of PEDOT:SPI2 the conductivity gradually increased from the beginning point (0.038 S/cm) and reached its highest value at 0.08 wt.% PVA (0.134 S/cm) because of the new rearrangement of PVA morphology. When PVA was added to PEDOT:SPI, the OH groups of PVA might be

bonded by strong covalent bond with the SO_3^- of SPI. This possibly leads to the interactions among PEDOT:SPI chains in which PVA maybe acts as a connector in linking the PEDOT:SPI chains together to improve the connection network between the polymer chains. This phenomenon could reduce the distance (gap) between the PEDOT:SPI chain and as a result PEDOT chains came in proximity of each other as well. Therefore, the charge transport from PEDOT chain to another one was better which eventually attributed to the increment in film conductivity. The change in film morphology because of PVA was shown by AFM in **Figure 5.16**. The PEDOT:SPI (without PVA) cluster were separately dispersed throughout the film as shown in **Figure 5.16a** whereas the connection of the PEDOT:SPI particles to form a conductive bridge after adding PVA could be observed in **Figure 5.16b**. This morphology changes might imply the role of PVA to the conductivity enhancement, regardless of the difference of domain in Micron scale found in Microscope pictures. After the concentration of PVA exceeded this optimum point, the conductivity continuously decreased because of an insulator behavior of PVA having more influence when more PVA was added into the polymer suspension. Furthermore, since the OH group of PVA could bond by strong covalent bonds with the SO_3^- groups of SPI which reduced some of the negative charge of the conducting polymers, more PVA concentration in the mixture meant more SO_3^- groups of SPI would be bonded with OH groups of PVA, which ultimately degraded the conductivity of the blended polymers due to the decrease in the number of conductive SO_3^- groups [49]. However, the conductivity of PEDOT:SPI1 incessantly decreased with increasing more PVA and then increased again after 0.3 wt.% PVA. This occurrence differed from PEDOT:SPI2 due to the difference in their polyimide

molecules. Comparison between PEDOT:SPI1 and 2, from the previous work [52] it was claimed that after heat treatment, the chain alignment in the conductive films would change due to the differences in rigidity of the polyimide, leading to modified morphologies, which causes the observed conductivity enhancement. That is, the rigid structure can still remain the straightness of its polymer main chain, which finally promotes electron transfer along the straight chain easier than the distorted one. For this reason the conductivities of PEDOT:SPI2 films were better than those of PEDOT:SPI1 because of their more rigid molecular structure. In all experiments, the interaction between SPIs and PVA, naturally insulated by the property of PVA additive, and the rigidity of polymer backbone had become the main influences on the changes in conductivity of conductive PEDOT:SPI films.

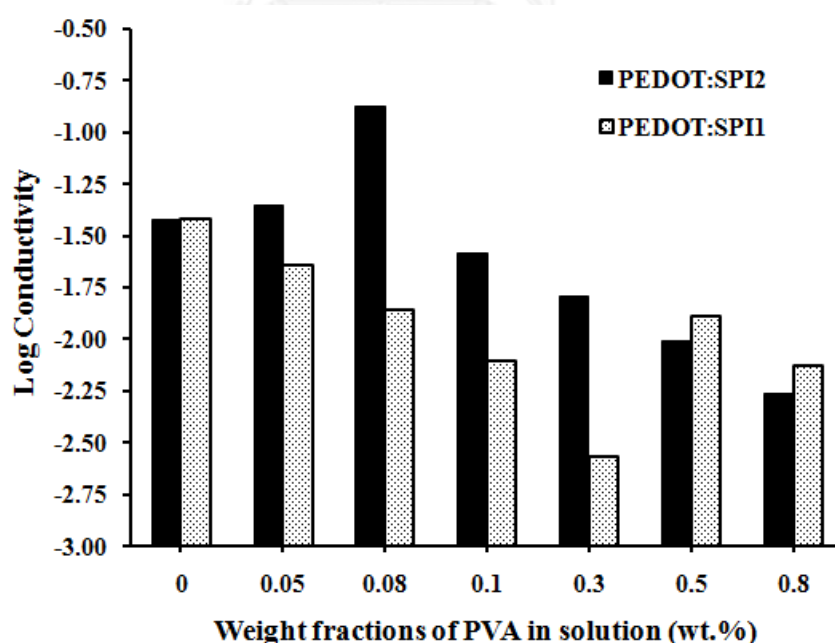


Figure 5.15 Variation of the conductivity of PEDOT:SPI1 and PEDOT:SPI2 with various weight fractions of PVA

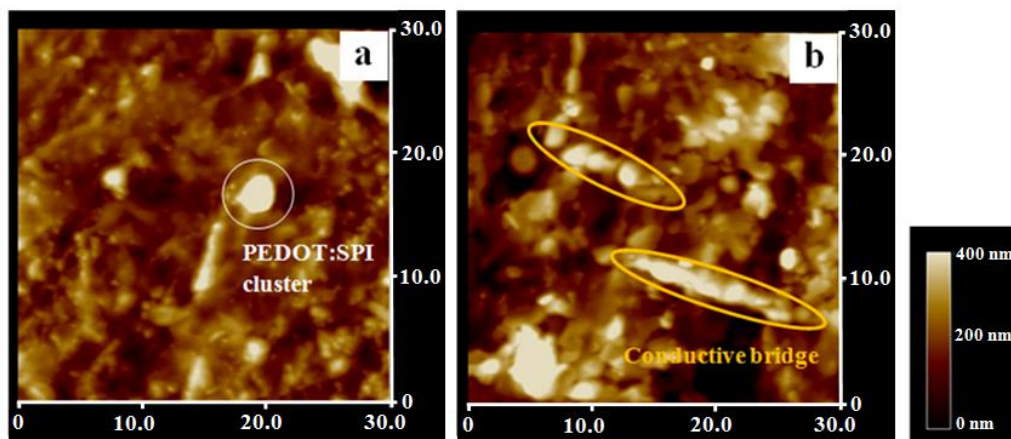


Figure 5.16 AFM images of (a) SDS/PEDOT:SPI2 and (b) 0.3 wt.% PVA/SDS/ PEDOT:SPI2 film, the unit of scale bar (x-y axis) is micron (μm). The height (z axis) is nanometer (nm) unit

5.2.3 Transparency properties

Transparency throughout the visible spectrum is one of the required properties for application as a transparent conductive film. From **Figure 5.17**, It was clearly seen that pure PEDOT:SPI and with various weight fractions of PVA provided high transmittance values in the whole visible spectrum. In addition, the cut-off wavelength of all samples was about 280 nm, indicating that they were transparent film. Although all PVA/PEDOT:SPI2 spectra were close each other, the significant difference in each transmittance value was found as shown in the magnification. **Figure 5.18** shows the transmission of visible light of PEDOT:SPI thin films with various amounts of PVA at 550 nm. The transmittance values decreased with increasing PVA weight fractions because when the amount of PVA in polymer suspension increased, the polymer viscosities were higher as well, leading to thicker films during spin-coating at fixed spin rate as shown in **Figure 5.19**. Therefore, the

thicker polymer films caused the decrease in transmittance values. The film of PEDOT:SPI2 was quite thicker than that of PEDOT:SPI1 but its transmittance values still remained higher than those of PEDOT:SPI1, which demonstrated that the transparency of PEDOT:SPI2 films was better than PEDOT:SPI1 due to CF_3 groups in polyimide molecules of PEDOT:SPI2 gave higher intrinsic transparent properties than ether groups of PEDOT:SPI1. The bulky CF_3 group in polyimide was effective in decreasing charge transfer complex (CTC) formation between polymer chains through steric hindrance [53]. The reduction of CTC formation eventually led to the improvement in transparency property of polyimide. Since the CF_3 is more bulky than the ether, PEDOT:SPI2 provided better transparent conductive films than those of PEDOT:SPI1 because of less charge transfers. However, all specimens still showed fairly high transparency values of more than 85%. It was contributed from the good dispersion of small PEDOT:SPI particles in aqueous solution by aiding of SDS surfactant. For comparison, Film thickness and transmittance values of each pure specimen can be shown in **Table 5.2**.

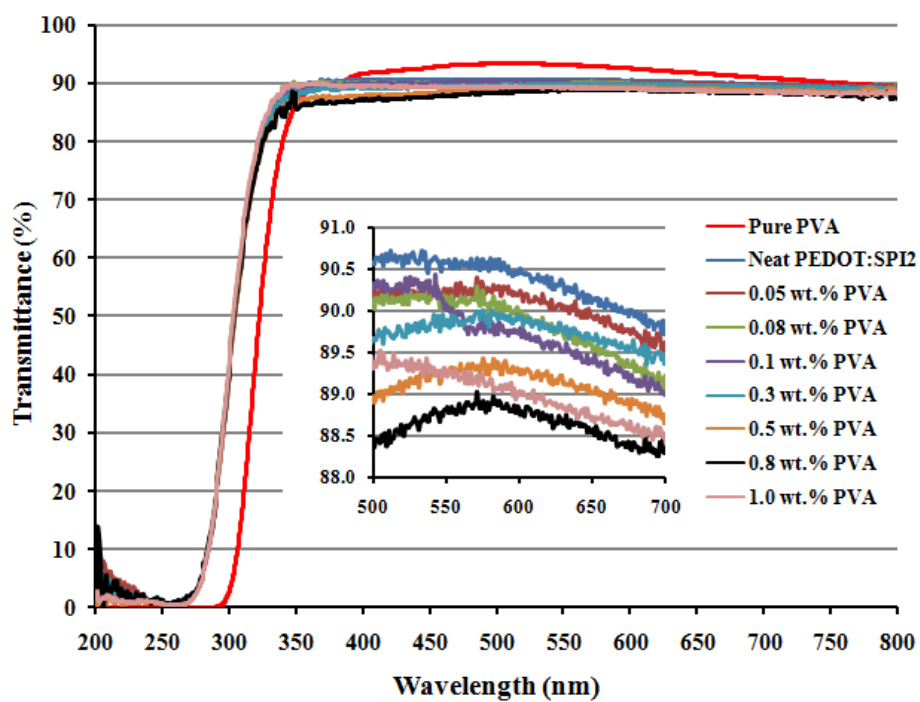


Figure 5.17 UV-Vis spectrum of pure PVA and PVA/PEDOT:SPI2 thin films with various weight fractions of PVA. The inset is a magnification of 500–700 nm which does not include the pure PVA (red line)

Table 5.2 Film thickness and transmittance values of each pure specimen

Samples	Film thickness (nm)	Transmittance at 550 nm (%)
Pure PVA	91.2	93.37
Neat PEDOT:SPI1	84.6	90.55
Neat PEDOT:SPI2	89.8	90.63

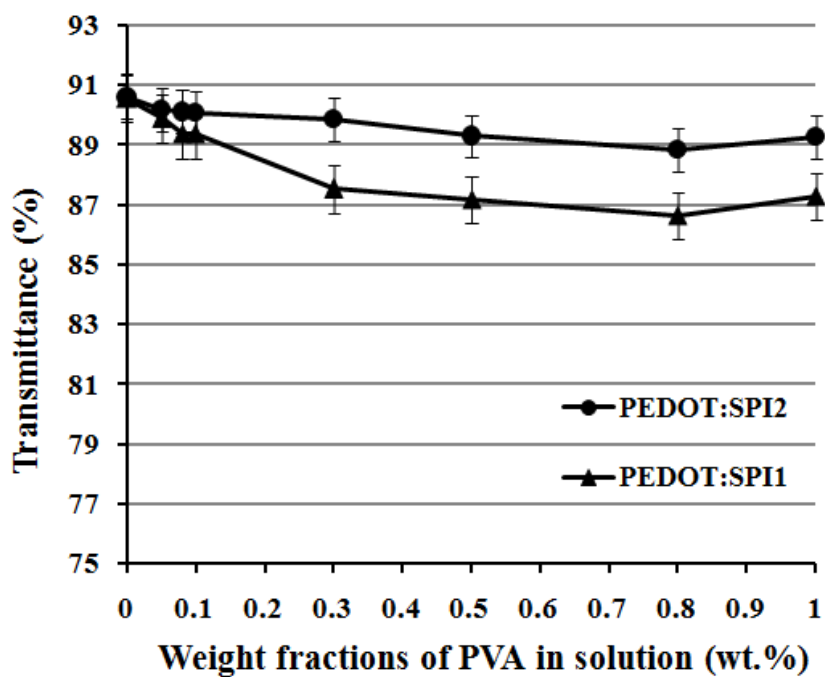


Figure 5.18 The transmittance of PEDOT:SPI1 and PEDOT:SPI2 thin films with various weight fractions of PVA at 550 nm

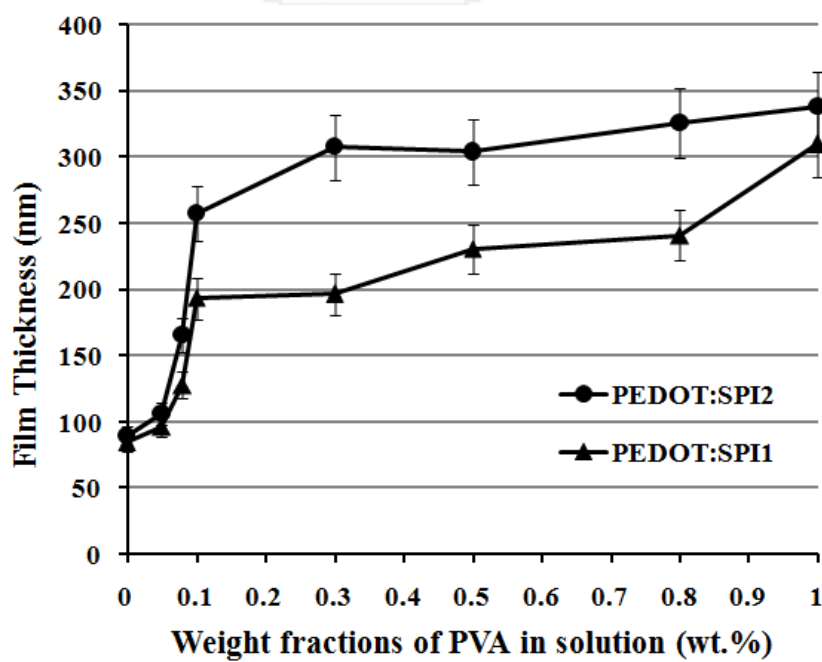


Figure 5.19 The film thickness of PEDOT:SPIs thin films with various weight fractions of PVA

5.2.4 Contact angle of PEDOT:SPI thin films

The hydrophilicity, adhesiveness and wettability of PEDOT:SPI film were one of the important properties that needed to be studied through the investigation of contact angle. **Figure 5.20** shows the effects of various amounts of PVA on the contact angle of conducting polymer films. We found that contact angle values gradually decreased from the original point to 1.0 wt. % PVA with increasing PVA weight fractions. The very low contact angle values at the original point of each film were due to the influence of anionic SDS surfactant remaining in the films. This could be implied that PEDOT:SPI/SDS film surface had an exceptional wettability properties when they were contacted with other materials. After incessant adding of PVA, lower contact angle values were obtained. To comprehend this occurrence, it should be related to the optical microscopic images, as shown in **Figure 5.21**. Film roughness with PEDOT:SPI agglomeration decreased with increasing PVA weight fraction, thus leading to lower contact angle values and smoother films.

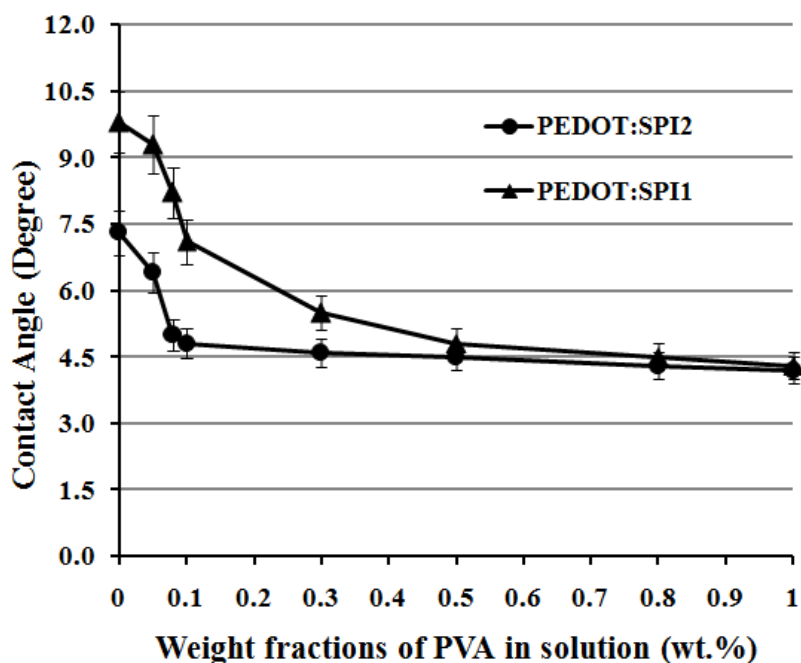


Figure 5.20 The Contact angle of PEDOT:SPI1 and PEDOT:SPI2 thin films with various weight fractions of PVA

It was noticed that, these results obtained from the optical microscopic did not conflict to the AFM images because the AFM analysis demonstrates the transformation in the molecular scale, which cannot be observed by the optical microscopic which is an instrument showing the overall image of the film in micro scale. Since the OH groups of PVA could interact with salt complexes formed upon polymerization, more decrease in salt complexes with adding more amounts of PVA was obtained. The decrease in salt complexes not only resulted in more stable PEDOT:SPI particles in aqueous solution, but also boost up electrostatic repulsion between PEDOT:SPI particles, thus, leading to the reduction of particle agglomeration during film formation.

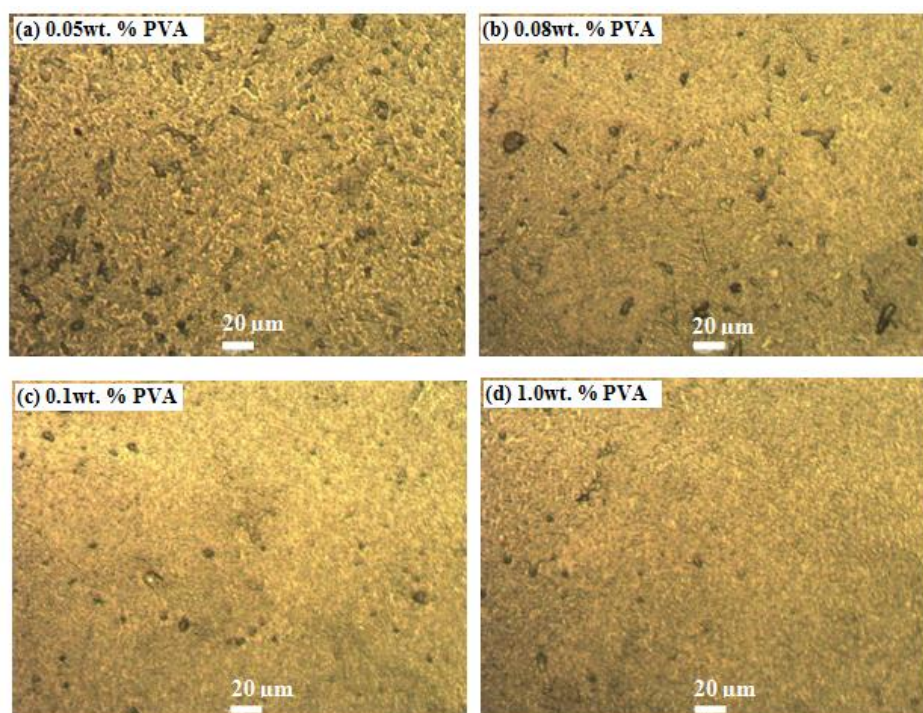


Figure 5.21 Optical microscopic images of PEDOT:SPI2 thin films with various weight fractions of PVA

In addition, the hydrophilicity of conductive films would increase with amount of PVA, OH groups. Therefore, hydrophilic PVA was the main driving force to change the hydrophilicity of such conductive films and also resolved the particle agglomeration, resulting in more clear PEDOT:SPI films when increasing the amount of PVA. The better conducting films with lower surface energy, lower contact angle values, were found in PEDOT:SPI2 due to higher polarity in polyimide molecule of PEDOT:SPI2 than that of PEDOT:SPI1. That was, the polarity nature of CF_3 groups in SPI2 was higher than ether groups in SPI1. Although SPIs were formed with PEDOT to make conductive films, PEDOT:SPI2 films had still provided higher hydrophilicity than that of PEDOT:SPI1 films. Therefore, the wettability of PEDOT:SPI2 was better.

5.2.5 Thermal stability of PEDOT:SPI thin films

The effect of PVA on the thermal stability of conducting polymers was the other interesting properties, needed to be under further investigation. This property was related to the thermal degradation when the films are exposed to a severe condition. High thermal stability of conducting polymers was required to extend the useful life of electronic devices. From TGA, it demonstrated that the thermal stability of PEDOT:SPI was affected by additives as shown in **Figure 5.22**. The presence of SDS surfactant in PEDOT:SPI films could cause the weight loss at a temperature below 250 °C while pure PEDOT:SPI was quite stable at this temperature range. This weight loss was due to the decomposition of SDS related to its thermal stability. However, the presence of PVA in PEDOT:SPI/SDS/PVA films could reasonably improve their thermal stability because of interactions between the OH group of PVA and the SO₃⁻ groups of SPI. When PVA was added to PEDOT:SPI, the OH group of PVA could bond by strong covalent bonds with the SO₃⁻ groups of SPI. Therefore, a higher PVA concentration in the mixture would result in stronger mechanical and thermal properties of films. It was noticed that after adding PVA into pure PEDOT:SPIs, the thermal stability of PVA/PEDOT:SPIs was significantly better when compared to the pure PEDOT:SPI though pure PVA had its thermal stability less than that of pure PEDOT:SPI. Td 5% and Td 10% of PVA were 201 and 246 °C, respectively. In addition, the thermal stability of PEDOT:SPI2 was slightly better than that of PEDOT:SPI1 as its molecular structure exhibited a more rigidity. Namely, Td5% and Td10% for PEDOT:SPI2 were 234.07 and 267.38 °C whereas values for PEDOT:SPI1 were 215.47, 261.19 °C, respectively.

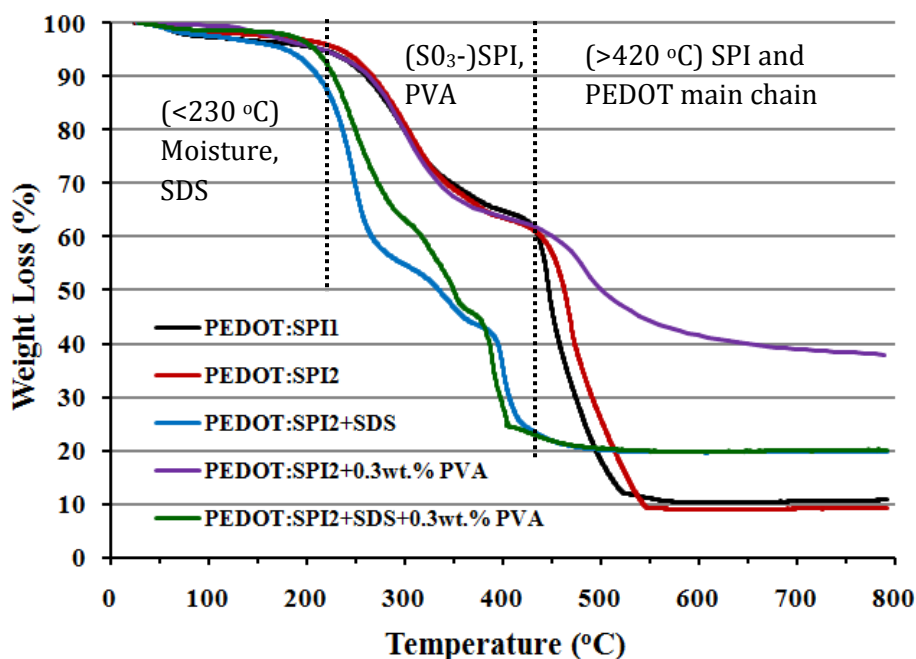


Figure 5.22 Thermal stability of pure PEDOT:SPI1 and pure PEDOT:SPI2 with SDS and 0.3 wt.% PVA

From the previous work [52] SPI1 and SPI2 were used as a template of various conducting polymers for thermal stability comparison. It was claimed that the more rigid of the initial template were able to achieve higher thermal stability. For this reason, the results showed that all conducting polymers/SPI2 were absolutely better thermal stability than that of conducting polymers/SPI1. In the same way with this work, PEDOT:SPI2 had higher thermal stability than that of PEDOT:SPI1 because CF₃ groups in polyimide molecules of PEDOT:SPI2 provided more intrinsic rigidity properties than ether groups in PEDOT:SPI1. For comparison, the thermal decomposition (Td) at 5% and 10% weight loss of each specimen can be shown in Table 5.3.

Table 5.3 The thermal decomposition (Td) at 5% and 10% weight loss

Samples	SPI1 (° C)		SPI2 (° C)	
	Td 5%	Td 10%	Td 5%	Td 10%
Neat PEDOT:SPI	215.5	261.2	234.1	267.4
PEDOT:SPI+0.3wt.% PVA	219.0	275.0	220.0	270.0
PEDOT:SPI+SDS+0.3wt.% PVA	193.1	216.9	208.9	227.6
PEDOT:SPI+SDS	197.3	216.6	179.2	212.1

*Td 5% and Td 10% of pure PVA are 201 and 246 ° C, respectively.

5.2.6 Summary of PART2

In this research, we could form the conducting PEDOT:SPI nano-scale thin films with various excellent properties by using an anionic surfactant, PVA and a conventional spin-coating process. SDS surfactant was utilized to improve the dispersion stability of PEDOT:SPI in water due to electrostatic repulsion between PEDOT:SPI particles, leading to the high transparent PEDOT:SPI films. All of the obtained films showed high transmission of more than 85% because of a good dispersion of PEDOT:SPI particles in aqueous solution by aiding of SDS surfactant. Vary low contact angle values of the films ($10^\circ <$) were mainly due to the hydrophilicity of the surfactant and they would decrease with increasing PVA. The highest conductivity, 0.134 S/cm, was achieved at 0.08 wt. % of PVA in conductive PEDOT:SPI2/SDS/PVA thin film due to better connection network of the conducting polymer chain. In addition, PVA also improved the thermal stability of films because of interactions between the OH groups of PVA and the SO_3^- groups of SPI, as verified by TGA analysis. The

competition in various film properties between PEDOT:SPI1 and PEDOT:SPI2 depended on their intrinsic molecular properties. All in all, the combination of SDS and PVA into PEDOT:SPI had potential to effectively modify the conductive PEDOT:SPI films to have various good properties at the same time for applying them as a conductive material in the area of electronic fields.



CHAPTER VI

CONCLUSIONS & RECOMMENDATIONS

6.1 Conclusions

6.1.1 PARTI (PEDOT:PSS)

1. Conductive PEDOT:PSS thin film could be successfully formed on glass substrates by means of the conventional spin-coating process together with adding PVA, leading to conductive films thicknesses in nano-scale.
2. According to blending concept, several PEDOT:PSS properties were significantly improved by adding an insulating PVA such as the thermal stability and mechanical properties. Although the film transmission decreased with increasing PVA amounts, all specimens still showed excellent transmittance values of more than 80 %. At the appropriate amount of PVA (0.08 wt.%), it could improve the connection network between PEDOT:PSS chains leading to a maximum conductivity of 1.18 S/cm, and also could provide a good contact angle of 8.8° at this point.
3. According to doping concept, the highest conductivity (2.75 S/cm) was achieved when 0.5 wt.% quinoxaline was added into 0.08 wt.% PVA/PEDOT:PSS while the other properties changed insignificantly.
4. The integration of the two effective strategies, the polymer blending and the addition of a dopant, exhibited the broad PEDOT:PSS thin film properties which are suitable for specific applications in electronic devices.

6.1.2 PARTII (PEDOT:SPI)

1. Conductive PEDOT:SPI thin film could be successfully formed on glass substrates with the aid of an anionic SDS surfactant, PVA and a conventional spin-coating process, leading to conductive films thicknesses in nano-scale.
2. The function of SDS surfactant was to improve the dispersion stability of PEDOT:SPI aqueous solution. In the same way, PVA was utilized to improve various properties of PEDOT:SPIs thin films in accordance with the blending concept.
3. All properties of conductive PEDOT:SPI2 were better than those of PEDOT:SPI1 because of their intrinsic molecular property of CF_3 group in SPI2.
4. The integration of PVA into PEDOT:SPIs exhibited various their thin film properties, needed to suitably optimize for specific applications in electronic devices.

6.2 Recommendations

1. The band gap for both of the before and after modifying PEDOT:PSS and PEDOT:SPI should be investigated for better understanding their electro-chemical properties.
2. The molar ratios between PEDOT and PSS (or SPIs) should be appropriately varied for optimization the dispersion stability of the suspensions.
3. Other secondary doping agents should be explored for efficient enhancing the conductivity of PEDOT:PSS system.
4. Other surfactants having high thermal stability should be examined to improve thermal property of conducting PEDOT:SPIs thin films.

5. The effects of high speed mixing on the reduction of conductive particle agglomeration and other conductive film properties should be observed.



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APPENDIX

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APPENDIX A

PEDOT:SPI CHARACTERIZATION

Table A.1 Various properties of PEDOT:SPI1

Samples	Film thickness (nm)	Transmittance at 550nm. (%T)	Contact Angle (°)	Resistance (kΩ)	Conductivity (S/cm)
(1) Pedot:SPI1	84.6	90.55	9.8	3221.5	0.038
(2) 0.05wt.% PVA	96.2	89.87	9.3	4754.3	0.023
(3) 0.08wt.% PVA	127.7	89.35	8.2	5510.0	0.014
(4) 0.1wt.% PVA	193.3	89.35	7.1	6657.0	0.0078
(5) 0.3wt.% PVA	196.7	87.51	5.5	18770.0	0.0027
(6) 0.5wt.% PVA	230.8	87.15	4.8	3438.5	0.0130
(7) 0.8wt.% PVA	241.1	86.63	4.5	5632.0	0.0074
(8) 0.1wt.% PVA	309.6	87.25	4.3	N/A	N/A

Table A.2 Various properties of PEDOT:SPI2

Samples	Film thickness (nm)	Transmittance at 550nm. (%T)	Contact Angle (°)	Resistance (kΩ)	Conductivity (S/cm)
(1) Pedot:SPI2	89.8	90.63	7.3	2992.0	0.038
(2) 0.05wt.% PVA	106.4	89.88	6.4	2152.1	0.044
(3) 0.08wt.% PVA	165.7	90.09	5.0	449.1	0.134
(4) 0.1wt.% PVA	257.2	90.30	4.6	1475.6	0.026
(5) 0.3wt.% PVA	307.9	90.07	4.6	2031.0	0.016
(6) 0.5wt.% PVA	304.1	90.38	4.5	3438.5	0.0098
(7) 0.8wt.% PVA	326.1	88.82	4.3	5632.0	0.0055
(8) 0.1wt.% PVA	337.9	91.12	4.1	N/A	N/A

APPENDIX B

FT-IR CHARACTERIZATION

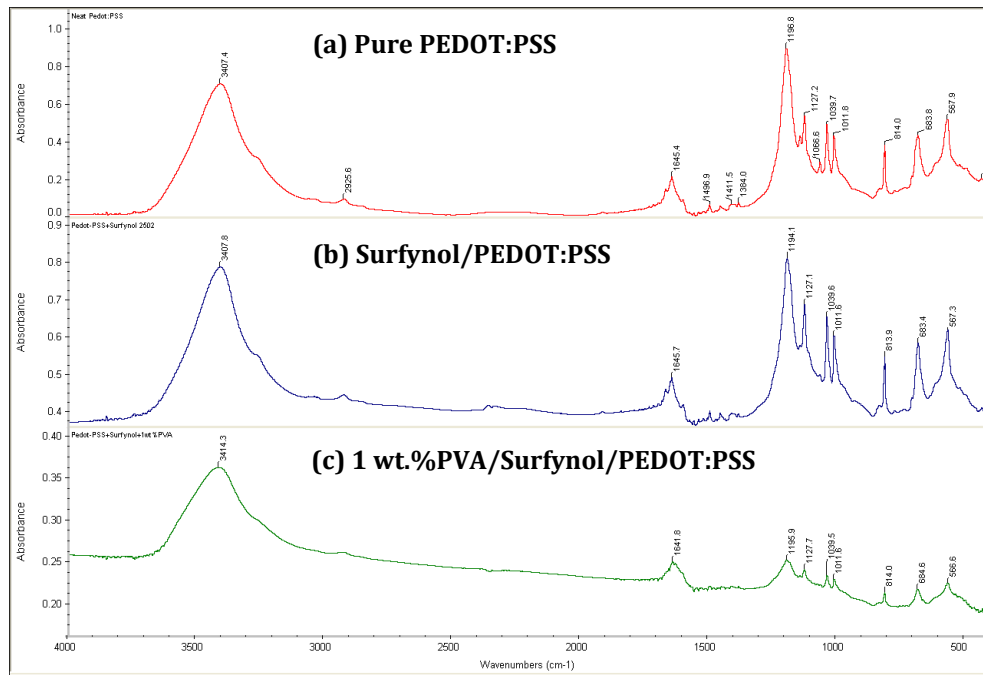


Figure B-1 Comparison of FT-IR of PEDOT:PSS

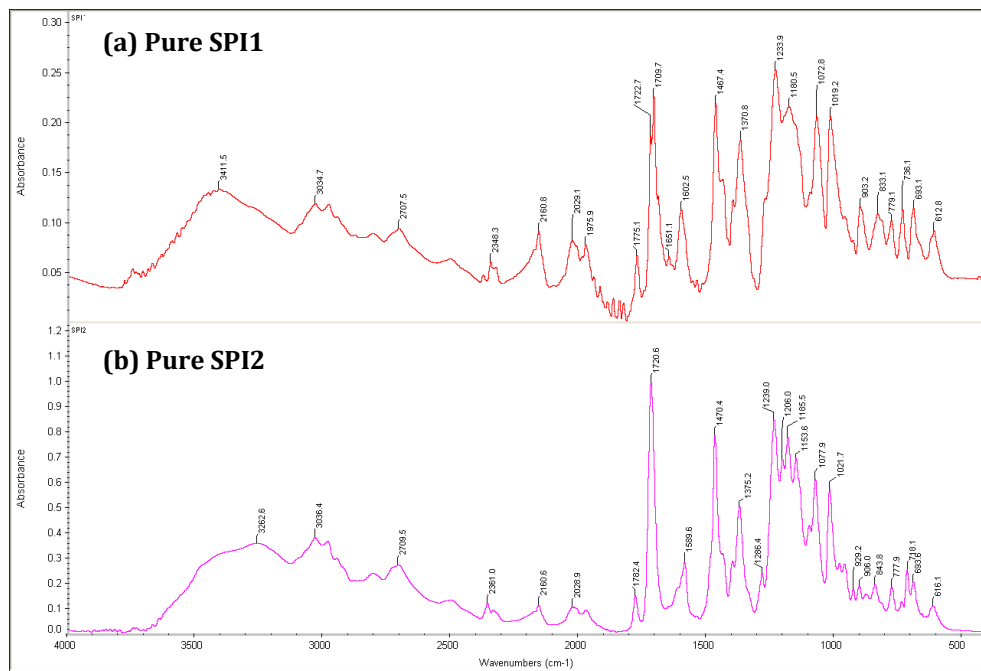


Figure B-2 FT-IR of pure SPI1 and SPI2

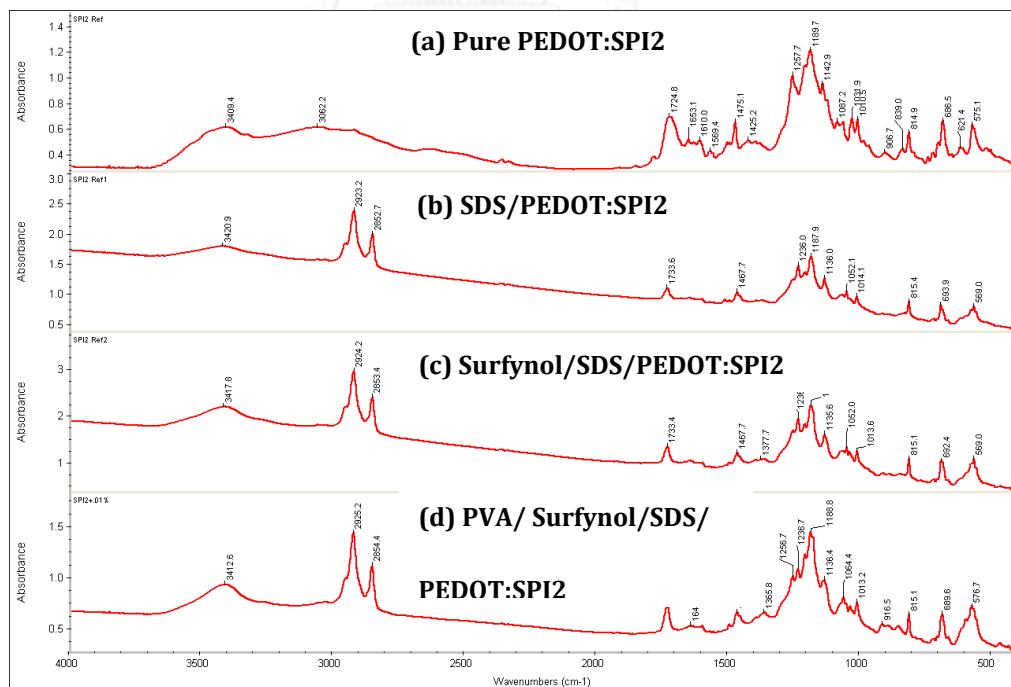


Figure B-3 Comparison of FT-IR of PEDOT:SPI2

APPENDIX C

CONDUCTIVITY CALCULATION

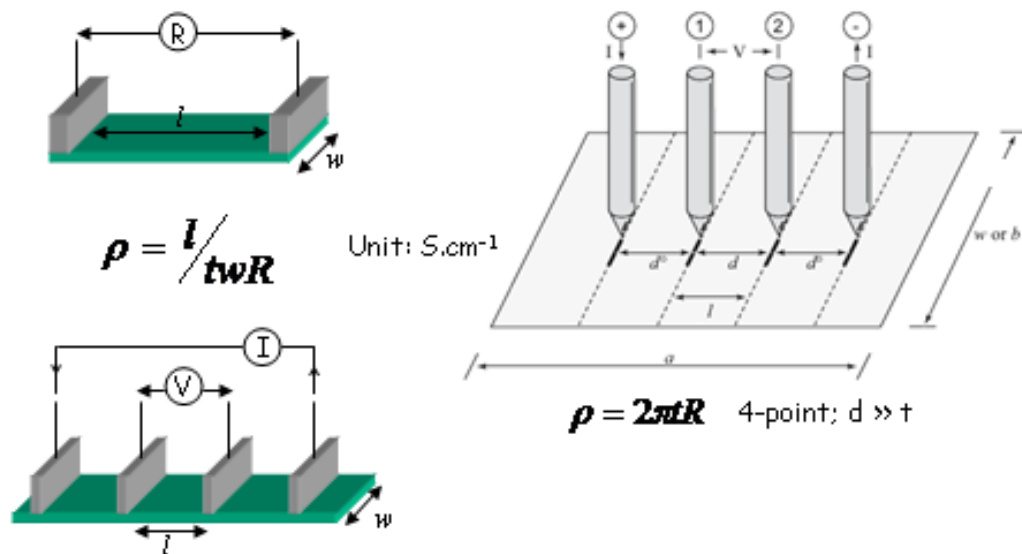


Figure C-1 Conductivity measurement

Definition

Conductivity is calculated from the equation of $\sigma = l/twR$ (S/cm) where l is the distance between gold or platinum wires, t is the thickness of the film, and w is the width of the film. Resistance is calculated from the equation of $R = V/I$ (Ω) where V is the voltage measured and I is the current applied.

APPENDIX D

LIST OF PUBLICATIONS

Articles

1. N. Romyen, S. Thongyai, P. Prasertthdam, G.A. Sotzing, Enhancement of poly(3,4-ethylenedioxy thiophene)/poly(styrenesulfonate) properties by poly(vinyl alcohol) and doping agent as conductive nano-thin film for electronic application, **J. Mater. Sci: Materials in Electronics**, 24 (2013) 2897-2905.
2. N. Romyen, S. Thongyai, P. Prasertthdam, G.A. Sotzing, Modification of novel conductive PEDOT:sulfonated polyimide Nano-thin films by anionic surfactant and poly(vinyl alcohol) for Electronic Applications, **Journal of Electronic Materials**, 42 (2013) 3471-3480.

Conference contributions

1. N. Romyen, S. Thongyai, P. Prasertthdam, G.A. Sotzing, "The Effects of Poly(vinyl alcohol) and Anionic Surfactant on Properties Improvement of Novel Conductive Poly(3,4-ethylenedioxythiophene):Sulfonated Polyimide (PEDOT:SPI) Nano-Thin Films", **The 9th SPSJ International Polymer Conference(IPC2012)** "Progress and Future of Polymer Science and Technology" December 11-14, 2012, Kobe, JAPAN

VITA

Mr. Nathavat Romyen was born on August 12, 1985 in Phrae, Thailand. He received the Bachelor's Degree in Chemical Engineering from Department of Chemical Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi in April 2007. He received the Degree of Master of Engineering in Chemical Engineering at the Department of Chemical Engineering, Chulalongkorn University in 2009. After the M.Eng graduation, he has received a scholarship from The Royal Golden Jubilee Ph.D. Program to study the Doctoral Degree of Engineering in Chemical Engineering at Chulalongkorn University in June 2010. He had spent one-year research at Institute of Materials Science and the Polymer program, University of Connecticut, USA during his Ph.D. program.





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