



공학박사 학위논문

# Development of smart electrode using PEDOT:PSS

# PEDOT:PSS를 이용한 스마트 전극 개발

2023 년 8 월

서울대학교 대학원

재료공학부

명 준 호

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이 논문을 공학박사 학위논문으로 제출함

2023 년 6 월

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## 명 준 호

명준호의 공학박사 학위논문을 인준함

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## Abstract

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is one of the most widely used conjugated polymers due to its intrinsic mechanical, electrical, and optical properties, making it a popular candidate for electrodes in electronics. A new method for synthesizing conductive PEDOT:PSS-based composites is proposed, and PEDOT:PSS electrodes with various functionalities(stretchable, transparent, and shape memory) are developed.

A novel method for fabricating conductive PEDOT:PSS composites has been suggested to overcome the limitation of existing synthesis methods. Previously, an acid catalyst or a strong oxidant was required to induce oxidative polymerization of the monomer, EDOT (3,4-Ethylenedioxythiophene). However, the PEDOT:PSS-AgNP(silver nanoparticle) nanocomposite was developed through an in-situ synthesis without an acid catalyst via a spontaneous redox reaction between silver precursor and EDOT. Firstly, the effect of solvents on the reaction was investigated, and high-quality PEDOT:PSS-AgNP nanocomposites were found to be formed in the organic solvent; acetonitrile. Secondly, the influence of polymer additives such as PSS ions and PVP was examined. The addition of PSS ions led to the formation of PEDOT:PSS, and inclusion of a small amount of PVP enabled the production of a nanocomposite with smaller-sized and well-distributed AgNPs without the need for acid catalyst. Finally, the mechanism for synthesis process is also proposed.

To impart stretchability to PEDOT:PSS, a composite was fabricated by combining it with elastomer PDMS (polydimethylsiloxane) to overcome its intrinsic brittleness.

The presence of a polymer component in immiscible blends of polymers causes phase separation, resulting in different polymer morphologies that range from dispersed spherical particles to a continuous matrix phase, depending on the weight ratio of the polymers. Firstly, the surface energy of the component was calculated using the geometric mean method to analyze its affinity with the substrate. The PEDOT:PSS and PDMS in the coated layer vertically phase separate, forming a bilayer structure owing to their different affinities to the poly(ethylene terephthalate) (PET) substrate. Secondly, the morphology of bottom layer was analyzed and mechanism was proposed. Bar-coating a solution of PEDOT:PSS blended with a high fraction of PDMS and a surfactant results in a continuous PEDOT:PSS matrix distributed with spherical PDMS islands. When cured at 100 °C, water and other volatiles in the PEDOT:PSS phase in the bottom layer evaporate, generating spaces that are subsequently filled with PDMS from the phase-separated top layer. Finally, the electrical, optical and mechanical properties were measured.

A new technique for creating a shape memory composite film of PEDOT;PSS by using an air plasma-treated substrate. Firstly, surface modification of a commercial polypropylene(PP) substrate was achieved using air-plasma treatment. The surface energy of a commercially available PP substrate was increased and water contact angle was decreased through air plasma treatment. Plasma treatment increases the surface energy of the PP substrate, enabling PEDOT:PSS with high surface energy to accumulate at the substrate/film interface, which transforms the bottom layer of the composite film into a continuous matrix of PEDOT:PSS and isolated islands of epoxy. Secondly, the mechanism of bottom layer formation was proposed. Upon thermal curing, the size of the epoxy islands increases due to water evaporation from the PEDOT:PSS aqueous solution and crosslinking of the epoxy resin. Finally, shape memory characteristics were measured.

Keywords: PEDOT:PSS, spontaneous redox reaction, phase separation, stretchable, shape memory

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## **Chapter 1. Introduction**

#### **1.1. PEDOT:PSS**

#### **1.1.1 Structure**

Electronically conducting polymers (ECPs) are a recent category of conducting polymers (CPs) that exhibit high intrinsic conductivity and feature a  $\pi$ -conjugated structure. These materials possess properties similar to those of metals or semiconductors in terms of electrical, electronic, magnetic, and optical behavior, while still maintaining the favorable mechanical properties and processing advantages associated with traditional organic polymers[1-3]. Among them, Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) is the most widely used conjugated conducting polymer consisting of a blend of a conjugated polymer, PEDOT, and a polyelectrolyte, PSS. The complex structure of PEDOT:PSS arises from the association of two polyelectrolytes. In solution, the commonly accepted model for the structure involves small segment of PEDOT in close contact with bundles of PSS[4]. As shown in Figure 1-1, the primary structure of the polymer consists of a specific sequence of partially cationic ethylenedioxythiophene and anionic styrenesulfonic acid monomer units. This sequence results in the formation of a polyion complex through electrostatic interactions, which gives rise to a secondary structure. When dispersed in water, the secondary structure assembles into a colloidal gel particle, which represents the tertiary structure of the polymer[5].





#### 1.1.2 Synthesis of PEDOT:PSS

The most common method for synthesizing PEDOT is chemical polymerization, which has undergone continuous development and is now the main method for preparing PEDOT and its derivatives. The oxidative polymerization of PEDOT can be broken down into two steps[6]: oxidation of the EDOT monomer to form cationic radicals, followed by free radical dimerization. The resulting dimer undergoes deprotonation to become an active neutral dimer that can then react in the following oxidation process for chain growth. The neutral PEDOT is doped by oxidants, and the anions of the oxidants act as counter ions to stabilize the charged PEDOT. While oxidants are typically used in the chemical polymerization process, PEDOT can also be prepared without an oxidant by acid-assisted polycondensation or selfpolymerization of EDOT. The most widely used method for chemical polymerization of EDOT is oxidative chemical polymerization using with iron(III)-chloride as oxidant. Several metal ions, such as cerium (IV)[7], manganese (IV)[8], and copper (II)[9], have been utilized as oxidants in the synthesis of PEDOT. These metal ions can facilitate the polymerization of EDOT monomers and promote the formation of the conducting polymer. The use of different metal ions as oxidants in PEDOT synthesis can lead to variations in the properties of the resulting polymer, such as its conductivity and morphology. For instance, cerium (IV) has been found to produce PEDOT with a high molecular weight and high conductivity [7], while copper (II) has been shown to produce PEDOT with a low molecular weight and low conductivity[9]. These variations in properties can be attributed to differences in the

oxidation potential of the metal ions and their ability to initiate the polymerization reaction.

Electrochemical polymerization has become a popular method for creating polymer materials with exceptional mechanical, electrical, and optical properties [10-13]. PEDOT:PSS can be mainly obtained by the electrochemical polymerization [14-16]. In a typical electropolymerization experiment, a three-electrode cell configuration is used where a counter electrode, a reference electrode, and a working electrode are employed. The EDOT monomer is dissolved in an electrolyte solution and subjected to electrochemical oxidation, resulting in a doped PEDOT film attached to the conductive working electrode surface. Anions from the electrolyte solution stabilize the charged form of the polymer during this process. However, the main limitation of this approach is the requirement for a conductive substrate such as Au, ITO, or glassy carbon to deposit the film onto. This prerequisite restricts the versatility of the method to substrates with conductive surfaces [17, 18]. The electropolymerization technique offers various advantages. Firstly, it eliminates the need for binders to improve adhesion as the PEDOT film is directly obtained on the conductive substrate. Moreover, the films produced using this technique are often more stable than those generated through other methods. This intimate electrical connection between the polymer film and the target electrode is especially crucial for bioelectronics applications. Furthermore, it is easy to control the thickness and morphology of the film using this method. The ability to synthesize copolymers is another significant advantage, especially when considering the polymerization of substituted EDOT-like

monomers to produce a bio-functionalized surface. Additionally, the electrochemical approach enables easy adjustment of the properties of the electro-polymerized PEDOT film. This is due to various factors such as the electrochemical method and its parameters, the nature of the working electrode, the composition of the electrolyte, and the type and ratio of dopants, which significantly influence the physicochemical and electrochemical characteristics of the resulting polymer.

Vapor-phase polymerization (VPP) is a widely used in-situ synthesis technique, where the reactants undergo polymerization in a gaseous state. The VPP method involves a three-step process. First, a solvent containing an oxidant and/or additive is deposited on a substrate using a solution processing technique[19]. Next, the coated substrate is exposed to EDOT monomer vapor in a closed chamber to initiate polymerization. Finally, the deposited film is washed to eliminate any remaining oxidant and adsorbed monomer [20]. There is ongoing debate regarding the mechanism of PEDOT film formation, which involves an oxidation reaction at the interface between oxidants and monomers in the gas phase. Some suggest that the process may occur "bottom-up" as the oxidant mixture diffuses upward, while others propose a "top-down" mechanism as the monomer diffuses downward. However, further research is needed to clarify this speculation [21].

#### **1.1.3 Properties of PEDOT:PSS**

PEDOT is a highly useful material for industrial applications due to several key properties. It exhibits a high and stable conductivity, as well as optical transparency when used as a conductor or semiconductor. Additionally, PEDOT can be rapidly switched between conducting and insulating states, and boasts superior chemical and environmental stability. These unique properties have made PEDOT a highly desirable material for use in various industries [22-24]. Compared to other conjugated polymers such as PANi and PTh, PEDOT is relatively environmentally friendly and has lower toxity[23]. PEDOT is a highly promising ECPs material that has emerged as a desirable alternative to previously discovered materials such as PPy, PANi, and PTh. With its high conductivity and transparency, PEDOT is ideal for use as a transparent and/or conductive electrode in a wide range of emerging applications in deformable electronics and optoelectronics. In addition, PEDOT exhibits good biocompatibility, low toxicity, and structural stability, making it an attractive material for use in the medical field. PEDOT has potential applications in the detection of biologically important molecules[25], including living neural cells, neural communication, chronic neural stimulation, drug-releasing vehicles, clinical diagnosis, and medical sensing applications. Furthermore, the excellent electrochemical and aqueous stability of PEDOT, along with its low impedance, make it suitable for use in various sensors, fuel cells, and capacitors [1, 22, 23, 26].

#### **1.2. Conductive PEDOT:PSS based nanocomposites**

There have been several endeavors to fabricate nanocomposites comprising metal nanoparticles (NPs) and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). Ventosa and colleagues put forward a novel one-pot synthesis approach for producing PEDOT:PSS-AuNPs nanocomposites in water-based mediums[27].

Ventosa et al. conducted an investigation on the impact of composition, monomer ratio, and metal precursor on the size of the nanocomposites in their study. On the other hand, Wang et al. attempted an in-situ synthesis method to create PEDOT:PSS@AgNPs nanocomposites in their research[28]. In their study, Ventosa et al. found that the pH value of the acidic solution plays a crucial role in determining the morphology of the PEDOT:PSS@AgNP nanocomposites. They also proposed a mechanism involving reduction and polymerization. Meanwhile, Wang et al.'s insitu synthesis method is effective for creating nanocomposites; however, it requires the removal of the reducing agent to obtain high-quality PEDOT:PSS.

In various other studies, noble metals have been employed as the oxidizing agent for EDOT polymerization. Balamurugan et al. developed a different approach, where they synthesized PEDOT-silver nanograin (AgNG) composites using an electrochemical method. In this method, AgNG served as the oxidizing agent for EDOT polymerization, enabling the formation of PEDOT-AgNG without the need for a separate reducing agent or stabilizer[29].

#### **1.3. Stretchable and transparent PEDOT:PSS based composites**

Stretchable electronics, capable of accommodating significant mechanical deformations, are seen as the future technology for bio-electronic applications. These innovations aim to overcome the limitations posed by conventional rigid and flexible electronics in this field. [30-32] In the realm of bio-electronics, various applications, such as stretchable displays[33, 34], wearable smart devices[35, 36], implantable devices[37, 38], and human motion sensors[39-42], demand stretchable components capable of enduring mechanical strain exceeding 30%. These components need to withstand the dynamic movements of the human body, including bending, curling, twisting, and stretching, without experiencing any degradation in their performance.[43] Transparent stretchable electrodes have been garnering significant interest as essential elements within stretchable electronics, catering to diverse applications. [44] Indium tin oxide (ITO) is one of the most widely used conductive materials in transparent electrodes owing to its high optical transparency (>90% in the visible-light range) and low sheet resistance (10  $\Omega$ ·sq-1 on glass).[45]

Despite their advantages, indium tin oxide (ITO) electrodes face significant limitations in further stretchable electronic applications. The intrinsic ceramic structure of ITO leads to mechanical brittleness and lack of flexibility, which hinders their effectiveness in stretchable electronic devices.[46] Therefore, various materials, such as carbon nanotubes,[47, 48] graphene,[49, 50] metal nanowire,[51-54] metal mesh,[55-57] and conductive polymers,[58, 59] have been actively studied.

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is one of

the most widely used conductive polymers owing to its mechanical flexibility,[60] excellent optical/electrical properties,[61, 62] low cost, easy processability,[23, 63, 64] thermal and chemical stability,[65, 66] biocompatibility, and non-toxicity.[67-69] PEDOT:PSS has been a subject of extensive research in both academic and industrial realms due to its diverse applications in organic light-emitting diodes (LEDs),[70] organic solar cells,[71] energy-storage devices,[72] and sensors.[73, 74] However, it comes with inherent mechanical limitations in stretchable electronics. The fracture strain of as-cast PEDOT:PSS films is only 2–6%,[75] which falls short of meeting the 30% strain requirement for stretchable electronics To address the mechanical brittleness of PEDOT:PSS, various studies have primarily focused on two main approaches: methods based on homogeneous dispersion and techniques involving heterogeneous assembly. These efforts aim to improve the mechanical properties of PEDOT:PSS and enable its successful integration into stretchable electronic devices.[76]

The homogeneous dispersion approach is a chemical strategy in which several additives are uniformly blended into a PEDOT:PSS solution. Plasticizers or ionic liquids, such as xylitol,[77] Zonyl,[78] Triton X-100,[79] and *d*-sorbitol[68] can improve the stretchability of PEDOT:PSS films by reducing the interactions between the PEDOT:PSS molecular chains and increasing the free volume. In addition, blending PEDOT:PSS with soft polymers such as poly(ethylene glycol), poly(ethylene oxide), poly(vinyl alcohol), and water-borne poly(urethane) can enhance the stretchability of PEDOT:PSS films. The advantage of this homogeneous

dispersion approach is its easy processability; it requires only one blending process. However, there are limitations to the types of additives, because additives should also be water-soluble to be uniformly blended with water-soluble PEDOT:PSS. Furthermore, because most additives are insulating in nature, the PEDOT:PSS concentration can only be decreased to a limited extent owing to the percolationdependent conductivity.[80] Otherwise, the connectivity between conductive domains is hindered, resulting in reduced conductivity.[81] In addition, increasing the PEDOT:PSS loading causes poor mechanical properties and optical transparency.[68, 77]

The heterogeneous assembly approach is a mechanical strategy for forming a bilayer structure of PEDOT:PSS on stretchable substrates such as poly(dimethyl siloxane) (PDMS)[82-85] or styrene ethylene butylene styrene (SEBS).[86] Therefore, by utilizing a water-insoluble elastomer as a stretchable substrate and controlling the thickness of the deposited PEDOT:PSS layer, a heterogeneous assembly approach can achieve satisfactory electromechanical stability as well as optical transparency.[83-85, 87, 88] However, owing to the intrinsic mechanical brittleness of PEDOT:PSS, the cracking of PEDOT:PSS films supported on elastomers is inevitable upon stretching, resulting in a permanent loss of conductivity.[82-84] To minimize crack formation in the deposited PEDOT:PSS layer, the substrate is prestrained before deposition,[60, 85, 87] the encapsulation process is performed after deposition,[85, 89, 90] or the PEDOT:PSS layer is deposited in special geometric patterns, such as serpentine or wavy patterns, using laser-cutting or

screen-printing techniques.[91, 92] Furthermore, because some substrates, such as PDMS and SEBS, are hydrophobic, it is necessary to improve the wettability of the substrate surface before PEDOT:PSS deposition for uniform adhesion between the PEDOT:PSS layer and substrate.[82] Thus, an additional process, such as UV/O3,[84, 93, 94] oxygen plasma,[82, 95] or acid treatment,[82] is required. In summary, the heterogeneous assembly approach can provide both satisfactory electromechanical stability and optical transparency but requires complex and multiple pre-deposition processes that may limit its industrial application.

#### 1.4. Shape memory PEDOT:PSS based composites

Shape-memory polymers (SMPs) are categorized as smart materials capable of recovering their original, macroscopic shape from a predefined, temporary shape when exposed to external stimuli, including temperature, humidity, light, or electricity.[96]. Thermally activated shape-memory polymers (SMPs) undergo shape changes in the vicinity of their transition temperature (Tg). The shape memory effect can be triggered by deforming the material above the Tg and subsequently cooling it below the Tg while keeping the constraints in place. These materials find applications in various fields, including biomedical applications, drug delivery systems, and flexible electronics, due to their thermoresponsive properties and ability to revert to their original shape under specific temperature conditions. [97-99].

Several studies have explored the combination of PEDOT:PSS with epoxy resin to improve the electrical conductivity and water stability of PEDOT:PSS films. In these attempts, epoxy resin was added to the PEDOT:PSS matrix at weight ratios of up to 5wt%, with the majority of the film still comprising PEDOT:PSS. However, despite these modifications, the resulting films did not exhibit shape memory characteristics. The focus of these efforts was primarily on enhancing electrical conductivity and water stability, rather than achieving shape memory properties in the PEDOT:PSSepoxy resin composite films. [100, 101]. Methanol-facilitated PEDOT: PSS was used for conductive filler for epoxy resin[102], 60wt% of silver microflake were used for dominant conductive pathway in epoxy matrix, small amounts about 1wt% of PEDOT:PSS connect the unlinked conductive pathway of silver microflake. The barcoating method was chosen as a suitable technique for fabricating large-area thin films on substrates. This method was preferred due to its simplicity and compatibility with roll-to-roll processes, enabling the deposition of large-area active layers for electronics on substrates in a continuous manner. [103-105]. When creating a thin film using a polymer blend, phase separation can take place to achieve thermodynamic stability. This occurs when the two components of the polymer blend are not compatible thermodynamically. During the process of solvent evaporation or curing reaction (crosslinking), vertical phase separation happens within the film, leading to the formation of distinct domains of each component.[106]. The substrate plays an important role in the vertically phase separation process, especially in surface energy. The vertical phase separation into two layers in thin film occurred by

using a substrate with a higher surface energy than two components of the polymer blend [107-109].

#### **1.5. Research objectives**

PEDOT:PSS is a highly versatile material that has gained widespread usage among conjugated polymers, finding numerous applications across various field. In particular, it has been widely adopted in the electronics industry, where the demand for electrodes with diverse functionalities is rapidly increasing. As a result, there is a growing need for the development of novel PEDOT:PSS-based electrodes that can offer enhanced performance and advanced functionalities to meet the evolving demands of modern electronics.

In chapter 2, a novel approach for producing PEDOT:PSS-AgNP composites. Unlike conventional methods that required the use of acid catalyst or oxidant, this method offers solution that eliminates this requirement. For this, the study analyzes the quality and yield of PEDOT:PSS-AgNP composites formation depending on the solvent and polymer additive used. Additionally, the mechanism of composite formation during the process is elucidated. Finally, we fabricated fiber containing PEDOT:PSS-AgNP nanocomposite through electrospinning and UV irradiation.

In chapter 3, a new approach was proposed for developing transparent and stretchable electrodes using PEDOT:PSS. Vertical phase separation was induced by utilizing the difference in surface energy between the components of the polymer

blend. The morphological, electrical and optical characterization of composite film was measured. Finally, the utilization of the composite film as a stretchable and transparent electrode was demonstrated.

In chapter 4, a new method was suggested for developing shape memory electrodes using PEDOT:PSS. The substrate was chemically modified using air plasma treatment. Vertical phase separation was induced using the plasma treated substrate. The morphological characterizations were analyzed, and the formation mechanism was elucidated. Finally, the shape memory and electrical properties were analyzed.

# Chapter 2. Conductive PEDOT:PSS based nanocomposite electrode

Metal and metal-alloy nanoparticles (NPs) are widely used in electronics, optics, sensors, and catalytic applications due to their unique electric, magnetic, optical and chemical properties [110-112]. Especially, noble metal NPs have received much attention for potential optoelectronics applications, due to their strong absorbance under visible light irradiation as a result of surface plasmon effects[113]. Among the noble metals, silver (Ag) is relatively inexpensive compared with gold, platinum, and palladium, and also offers enhanced electrical and optical properties[114]. As such, there has been extensive research into the synthesis of AgNPs.

Methods for synthesizing AgNPs can be classified into three categories. The first is chemical reduction of the Ag precursor. This method uses a strong reducing agent, such as sodium borohydride, hydrazine, or NaBH<sub>4</sub> [115-118]. The yield of AgNPs under chemical reduction is relatively high; however, additional treatments are required to remove byproducts. The second approach is to apply heat or light irradiation, via gamma rays or ultraviolet light, to reduce the AgNPs. Polymeric additives are used to initiate photoactivation of the Ag (I) ion with this method [119-121]. Finally, the third method employs conducting polymers to reduce AgNPs for metal–polymer composite synthesis. Metal-conducting polymer composites show great potential for use in multifunctional nanocomposite applications, due to their intrinsic conductivity and favorable optical properties[122, 123].

There have been numerous attempts to synthesize nanocomposites consisting of metal NPs and PEDOT:PSS. Ventosa *et al.* proposed a one-pot synthesis method for creating PEDOT:PSS-AuNPs nanocomposites in aqueous mediums[27]; they focused on the effects of composition, the ratio of monomers and the metal precursor on the size of the nanocomposites. Wang *et al.* attempted in-situ synthesis of PEDOT:PSS@AgNPs nanocomposites[28]; they determined that the pH value of the acidic solution affects the morphology of the PEDOT:PSS@AgNP nanocomposites and proposed a mechanism for reduction and polymerization. The method of Wang et al. is effective for nanocomposite fabrication; however, the reducing agent must be removed after the reaction to obtain high-quality PEDOT:PSS. In several studies, noble metals have been used as the oxidizing agent for EDOT polymerization. Balamurugan *et al.* synthesized PEDOT-silver nanograin (AgNG) composites using an electrochemical method; here, AgNG was used as the oxidizing agent for EDOT polymerization to create PEDOT-AgNG, without the need for a reducing agent or stabilizer[29].

The chapter presents a new method for producing high-quality PEDOT:PSS-AgNP nanocomposites using organic solvents without acidic catalysts or strong reducing agent. The study investigates the effects of different solvents on the chemical and structural characteristics of the products and uses various analyses to evaluate the quality and stability of the synthesized nanocomposites. Polymer additives and reducing agents are also introduced to enhance the polymerization and stability of AgNPs. A mechanism for synthesis method is proposed based on the findings.

Finally, we used the synthesized PEDOT:PSS-AgNP nanocomposites to produce conductive fibers through electrospinning and UV reduction methods-

#### 2.1 Preparation of PEDOT:PSS-AgNP nanocomposites

#### 2.1.1 Materials

EDOT (97% purity; Sigma-Aldrich, St. Louis, MO, USA), silver nitrate (AgNO<sub>3</sub>) (99%, DaeJung Chemicals & Metals, Seoul, Republic of Korea), Na-PSS (Sigma-Aldrich), and PVP (M<sub>w</sub>: 1,300,000; Sigma-Aldrich) were used as received to synthesize PEDOT:PSS-AgNP nanocomposites. Nitric acid (70%; Sigma-Aldrich), acetonitrile (anhydrous; Sigma-Aldrich), and distilled water were used as solvent to evaluate quality of PEDOT:PSS-AgNP nanocomposites.

#### 2.1.2 In-situ synthesis of PEDOT:PSS-AgNP nanocomposites

Balamurugan's process[124] was modified in this study to synthesize PEDOT:PSS-AgNP composites. We used 0.1 M nitric acid, distilled water, and acetonitrile as a solvent, respectively. AgNO<sub>3</sub>, EDOT, and Na-PSS were added to the solutions; the weight ratio was 18:3:2 in 20 mL of each sample. The weight of the AgNO<sub>3</sub> was 0.17 g. The reaction proceeded by stirring at 50°C. The pH was not controlled during polymerization in order to consider the effect of acid catalyst when using 0.1M nitric acid.

To investigate the effect of PSS<sup>-</sup> ions and PVP on the morphology of the PEDOT:PSS-AgNP nanocomposite, samples with and without PSS<sup>-</sup> ions and PVP were also prepared. The compositions and weight ratios of the solutions are listed in **Table 2-1**.

Table 2-1Composition of samples for synthesizing PEDOT:PSS-AgNPnanocomposites

Weight ratio of component				
Solvent	AgNO <sub>3</sub>	EDOT	Na-PSS	PVP
Nitric acid	18	3	2	
Distilled water	18	3	2	
Acetonitrile	18	3	2	
Acetonitrile	18	3		
Acetonitrile	18	3	2	3

#### 2.1.3 Electrospinning of PEDOT:PSS-AgNP nanocompsites

In total, 405 mg of PVP was dissolved in 5 g of acetonitrile at room temperature for 2 h; 2.43 g of AgNO<sub>3</sub> 0.5g of PEDOT:PSS-AgNP nancomposites were added to the solution and stirred for 1 h. Before electrospinning was performed, the solution was vigorously stirred with a centrifugal mixer (ARE-310, THINKY) for 10 min. The flow rate of the solution was 0.4 mL/h, tip-to-collector distance was 15 cm, and applied voltage was 18 kV. Free-standing nanofibers were collected on a tailored collector to maintain their structure and minimize damage. The collector rotated at 50 rpm (21 cm/sec). The silver precursor nanofibers were reduced to silver by

irradiation for 3 h with a UV curing machine (RX-H1000R, Raynics, Republic of Korea); the distance between the sample and the lamp was 10 cm.

#### 2.2 Characterization of PEDOT:PSS-AgNP nanocomposites

XRD (D8 ADVANCE; Bruker, Billerica, MA, USA) and FT-IR (Nicolet 6700; Thermo Fisher Scientific, Waltham, MA, USA) analyses were carried out to identify the crystalline structures and verify the change in chemical bonds after EDOT polymerization. FT-IR analysis was conducted using KBr disks. Thermogravimetric analysis (TGA; Discovery; TA Instruments, New Castle, DE, USA) was employed to measure the ratio of the products at a heating rate of 10°C/min up to 700°C in air. High-resolution transmission electron microscopy (HR-TEM; JEM-2100F; JEOL, Tokyo, Japan) was used to examine structural changes in the composites. The electrical conductivity of PEDOT:PSS-AgNP nanocomposites were measured by Veeco FPP-5000 four-point probe equipment. To identify the chemical interactions among the AgNPs, PEDOT:PSS, and PVP, the surface of the constituents was analyzed using XPS (Axis-His; Kratos Analytical Ltd., Manchester, UK).

#### **2.3 In-situ synthesis of PEDOT-AgNP nanocomposites**

#### **2.3.1 Effect of solvent**

Figure 2-1(a) displays the X-ray diffraction (XRD) patterns of PEDOT-AgNP nanocomposites prepared using various solvents. The nanocomposites were synthesized using EDOT monomer and AgNO<sub>3</sub>. The XRD curves showed distinct peaks at 20 angles of  $37.8^\circ$ ,  $43.8^\circ$ ,  $64.2^\circ$ , and  $77.2^\circ$ , which corresponded to the (111), (200), (220), and (311) crystallographic planes of the standard cubic phase of silver, respectively, as reported in previous studies.[125]. The observed XRD pattern was exclusively present in the samples prepared using acetonitrile as the solvent, whereas no such pattern was observed in the samples synthesized using distilled water or nitric acid. In acidic conditions, the analysis showed the presence of Ag precursor and Ag oxides rather than pure Ag. The formation of AgNPs during solution mixing from AgNO<sub>3</sub> can be attributed to a coordination-reduction mechanism. [126]. Based on the aforementioned results, it can be inferred that the coordination-reduction mechanism was successful in facilitating the formation of AgNPs in solution reactions without the involvement of acid catalysts. Note that Moraes et al. synthesized PEDOT-metal nanocomposites using noble metal NPs as an oxidizing agent for polymerization[122]; they first fabricated the metal NPs using a reducing agent and then added an EDOT monomer for polymerization. In contrast, our study aimed for in-situ synthesis of PEDOT-AgNP nanocomposites, accompanying the spontaneous reduction of Ag and oxidation of EDOT.
The FT-IR analysis, as shown in **Fig. 2-1(b)**, demonstrated that the polymerization of PEDOT occurred independently of the solvent used. The oxidative polymerization of EDOT into PEDOT is known to involve the formation of radical cations, which then undergo deprotonation and coupling reactions.[127]. Previous studies have attributed the peak at approximately 1,300 cm<sup>-1</sup> in the spectra to the C-C and C=C stretching modes of the quinoidal structure of the thiophene rings [124]. In addition, the band at 1,082 cm<sup>-1</sup> has been associated with the stretching modes of the ethylenedioxy group[128], while the peaks at 977 cm<sup>-1</sup>, 804 cm<sup>-1</sup>, and 731 cm<sup>-1</sup> are due to the stretching vibration of the C-S bond in the thiophene ring [124]. Interestingly, the strong C-H bending mode of EDOT at 890 cm<sup>-1</sup>(See **Figure 2-2**) disappeared, which can be attributed to the formation of PEDOT chains with  $\alpha$ , $\alpha$ '-coupling[129]. Overall, the FT-IR analysis indicated that the polymerization of radical cations followed by deprotonation and coupling reactions.



**Figure 2-1** Characterization of synthesized PEDOT-AgNP nanocomposites according to solvent, (a) XRD analysis and (b) FT-IR

The results suggest that the formation of PEDOT was not affected by the presence of Ag ions in solution[130]. Therefore, it can be inferred that the polymerization process of EDOT was possible in any type of solvent. However, the quality of the AgNPs produced was found to be dependent on the solvent used, with acetonitrile yielding AgNPs of superior quality. Taking this into consideration, we employed acetonitrile as the solvent for the synthesis of our PEDOT-AgNP nanocomposites and focused on investigating the influence of additives (PSS<sup>-</sup> ions and PVP) on their formation.



**Figure 2-2** FT-IR analysis of 3,4-ethylenedioxythiophene(EDOT)

## 2.4 In situ-synthesis of PEDOT:PSS-AgNP nanocomposites

## 2.4.1 Effect of PSS ion on PEDOT:PSS-AgNP formation

The role of PSS- ions in the polymerization of EDOT in the presence of Ag ion clusters acting as oxidizing agents was studied in this research. PSS<sup>-</sup> ions function as counter ions to maintain charge neutrality and increase the solubility of EDOT in solution, resulting in increased production of PEDOT:PSS. To assess the impact of PSS<sup>-</sup> ions on the formation of PEDOT:PSS-AgNP nanocomposites, a slightly basic solution was prepared using acetonitrile as the solvent. The study involved comparing the FT-IR, XRD, and TGA curves of PEDOT:PSS-AgNP nanocomposites synthesized with and without PSS- ions. The XRD patterns in **Fig. 2-3(a)** showed that the diffraction pattern of AgNPs changed with noise, indicating that the polymerization occurred at the surface of AgNPs due to the stabilization effect of PSS- ions. However, the XRD results suggested that the AgNPs remained of high quality, irrespective of the presence of PSS<sup>-</sup> ions. The disappearance of the peak at 890 cm<sup>-1</sup> after PEDOT:PSS polymerization (**Fig. 2-3(b**)) indicated that  $\alpha, \alpha'$ -coupling occurred. [129].

According to the TGA analysis results presented in **Fig. 2-3**, the nanocomposites obtained from the in-situ synthesis of PEDOT:PSS-AgNPs only showed the presence of Ag crystals at 700°C, indicating that the PEDOT:PSS component of the nanocomposites decomposed completely. The TGA curve of pure PEDOT:PSS (shown in blue in **Fig. 2-3**) exhibited an abrupt weight loss near 450°C, which is the characteristic temperature for the decomposition of PEDOT:PSS. In comparison, the

TGA curve of the nanocomposites obtained with the addition of PSS- ions (shown in red in **Fig. 2-3**) displayed a much larger weight loss ranging from 10.9% to 35.5% over the temperature range of 450–700°C, implying that a greater amount of PEDOT:PSS was polymerized in the presence of PSS- ions.

These findings suggest that the addition of PSS<sup>-</sup> ions resulted in a higher degree of polymerization of PEDOT:PSS, which took place at the surface of AgNPs due to the stabilization effect of the PSS<sup>-</sup> ions. The results also imply that the presence of PSS<sup>-</sup> ions did not compromise the quality of the AgNPs formed in the in-situ synthesis process. Furthermore, these observations suggest that the use of slightly basic conditions and the addition of PSS<sup>-</sup> ions can be considered as effective strategies for the formation of PEDOT:PSS-AgNP nanocomposites with improved properties.





**Figure 2-3** Characterization of nanocomposites synthesized in acetonitrile as solvent with or without PSS- ion (a) FT-IR analysis, (b) XRD analysis, and (c) TGA analysis.

#### 2.4.2 Effect of PVP additives on PEDOT:PSS-AgNP formation

Next, PVP was added to the solution, to increase the reaction site rate and thus enhance the formation of Ag ion clusters, as follows. PVP is generally used as a capping agent to increase the stability of metal NPs[131]. PVP has been shown to interact with metal ions, such as Ag ions, through a coordination mechanism, resulting in the formation of a coordinative complex in solution[132]. In this complex, the nitrogen and oxygen atoms of the PVP donate their electrons to the sp orbitals of the Ag ion, leading to the formation of a coordinative bond [132]. This coordinative bond makes it easier to reduce the Ag ion, as it receives more electrons from the electronic clouds around the PVP chains. The reduced Ag ion then serves as a nucleation site for the formation of AgNPs. [126]. PVP was added to the solution to increase the reaction site rate and thus enhance the formation of Ag ion clusters. PVP was also used as a capping agent to increase the stability of the AgNPs. The enhanced stability of the AgNPs could be attributed to the strong interaction between PVP and Ag ions. Therefore, the effect of PVP on the formation of PEDOT:PSS-AgNP nanocomposites was investigated in this study, and the FT-IR, XRD, and TGA curves of PEDOT:PSS-AgNP nanocomposites prepared with and without PVP were compared.

The XRD and FT-IR results in **Fig. 2-4** are similar to the previous ones. The formation of AgNPs and PEDOT:PSS was verified. The broad peak in the XRD pattern at 20–35° indicated PEDOT:PSS formation (**Fig. 2-4(a**)) [28]. FT-IR results showed that the peaks at 1,306 and 799 cm<sup>-1</sup> assigned to AgNO<sub>3</sub> disappeared completely with PVP addition (**Fig. 2-4(b**))[133]. This means that all of the Ag precursor was reduced to AgNPs. The amount of synthesized PEDOT:PSS increased with the number of AgNPs. TGA analysis showed that weight loss between 450°C and 700°C increased from 35.5% to 38.8% with PVP addition, mainly due to PEDOT:PSS decomposition. The yield of PEDOT:PSS contained in PEDOT:PSS-AgNP nanocomposite is a mixture of silver

nanoparticles and PEDOT:PSS, it was not routine to accurately measure the amount of PEDOT:PSS formed by polymerization of EDOT by silver ions. Instead, we calculated the yield of polymerization indirectly based on the yield of PEDOT:PSS-AgNP nanocomposites. The yield of PEDOT:PSS-AgNP nanocomposite fabricated in acetonitrile was 32.7%. Since final amount of AgNP in PEDOT:PSS-AgNP nanocomposites was 41.8% based on TGA results, it can be deduced that the amount of PEDOT:PSS was 58.2%.





**Figure 2-4** Characterization of nanocomposites synthesized in acetonitrile as solvent with or without PVP. (a) XRD analysis, (b) FT-IR analysis, and (c, d) TGA analysis.

The morphologies of PEDOT:PSS-AgNP nanocomposites in acetonitrile as a solvent were investigated using TEM. Figure 2-5 shows TEM images of PEDOT:PSS-AgNP nanocomposites prepared without PVP (Fig. 2-5(a) and (c)) and with PVP (Fig.2-5(b) and (d)). Both nanocomposites were synthesized at a pH value higher than 7; therefore, their morphologies seem to follow the synthesis mechanism proposed by Wang et al.[28]. The morphology of the PEDOT:PSS-AgNP nanocomposites was affected by the presence of PVP during the synthesis process. When PVP was added, all of the Ag precursors were reduced to AgNPs, resulting in smaller and more evenly distributed individual AgNPs with a polycrystalline structure (Fig. 2-5(b) and (d)). On the other hand, when PVP was not used, the AgNPs had a single-crystalline structure. PVP acted as both a reducing agent and capping agent, creating this difference in morphology. The presence of a PVP protection layer prevented the agglomeration of small AgNPs, but a high concentration of PVP resulted in a thick layer at the surface of AgNPs, hindering electron transfer between Ag ions and their surroundings due to the steric effect of PVP.[131, 134]. It should be noted that the crystal structure of AgNPs can be influenced by the ratio of PVP in solution[135]. In our study, the ratio of AgNO<sub>3</sub> and PVP was set at 6:1, which is considered to be a low enough concentration to prevent agglomeration during the synthesis of PEDOT:PSS-AgNP nanocomposites. This suggests that the morphology and crystal structure of the resulting nanocomposites can be controlled by adjusting the concentration of PVP in the synthesis process.



(b)





**Figure 2-5** TEM images of PEDOT:PSS-AgNP nanocomposites; (a, b) without PVP and (c, d) with PVP.

PVP disperses perfectly in acetonitrile up to about 15 wt%. Specifically, when reduction occurs between silver ions (AgNO<sub>3</sub>) and acetonitrile, metal ligand coordination forms part of the polymer main chain around the silver nanoparticles, acting as a capping agent[136]. This leads to the formation of silver nanoparticles of a consistent size, surrounded by the polymer. As a result, the consistent size of the silver nanoparticles helps facilitate the reduction of silver ions that acetonitrile cannot directly participate in. Therefore, the size of the silver nanoparticles is maintained to a certain extent. To investigate the chemical interaction of elements at the surface of PEDOT:PSS-AgNP nanocomposites, XPS analysis was conducted. Figure 2-6 shows the binding energy of Ag3d region of PEDOT:PSS-AgNP nanocomposites prepared with and without PVP. The Ag3d region was fitted with each Ag(Ag3d<sub>3/2</sub>, Ag3d<sub>5/2</sub>) doublet, and the ratio between was maintained at 2:3, with a peak energy separation of 6.0eV. The peak-fitted Ag3d core-line spectrum shows two strong signals due to  $Ag3d_{5/2}(368.1 \sim 368.3)$  and  $Ag3d_{3/2}(374.1 \sim 374.3)$  electrons. Each signal is adequately peak-fitted with only one component, clearly showing that only one silver species is present. Regardless of the presence of PVP, the formation of silver nanoparticles was observed. However, as shown in **Figure 2-5**, the addition of PVP resulted in smaller silver nanoparticles, which led to a 0.20eV decrease in the binding energy of Ag3d<sub>5/2</sub> compared to the case without PVP.[137]



**Figure 2-6** XPS analysis of PEDOT:PSS-AgNP nanocomposites with and without PVP.

**Figure 2-7** shows the binding energy of the S2p region of PEDOT:PSS-AgNP nanocomposites prepared with and without PVP. The S2p region was fitted with each S (S2p<sub>1/2</sub>,S2p<sub>3/2</sub>) doublet, and the ratio between them was maintained at 1:2, with a peak energy separation of 1.18 eV. The S2p<sub>1/2</sub> and S2p<sub>3/2</sub> doublets indicating neutral S were observed at 162.9–165.2 eV, and a highly oxidized SO<sub>4</sub><sup>2-</sup> band was located at 167.7–169.0 eV, as the main components of PEDOT:PSS[138, 139]. The appearance of these peaks indicates that PEDOT:PSS was polymerized successfully, regardless of the existence of PVP. However, the peak around 160 eV, which

represents the S atom interacting with AgNP[140], was not observed in the typical PEDOT:PSS spectrum. The shift in the binding energy of the S2p band in the XPS spectrum of PEDOT:PSS-AgNP nanocomposites was also noteworthy. The addition of PVP resulted in a reduction of the binding energy by 0.14 eV compared to that of the nanocomposites synthesized without PVP. This shift can be attributed to the interaction between the S atom in PEDOT and the surface of AgNPs, which is facilitated by the presence of PVP. AgNPs formed with the help of PVP had a slightly negative charge, which enhanced the delocalization of electrons between S+ in EDOT and the PVP-(Ag)<sub>n</sub><sup>-</sup> surface. This interaction may have led to a change in the electronic state of the S atom, resulting in the observed shift in the binding energy of the S2p band.[141, 142].

In summary, the addition of PVP increased the nucleation of AgNPs and resulted in a reduction of the binding energy of S-Ag bonding. Consequently, the ratio of S-Ag bonding on the surface of PEDOT:PSS-AgNP nanocomposites increased from 25% to 33%, indicating that a significant portion of PEDOT:PSS was synthesized at the surface of the AgNPs. It should be noted that a higher ratio of PVP:AgNO<sub>3</sub> (5:1) prevents the polymerization of PEDOT:PSS at the surface of AgNPs due to the thick PVP protective layer, as reported in a previous study.[131]. However, in our case, the ratio was much lower (1:6) than that reported in the previous study; thus, the PVP layer did not affect PEDOT:PSS polymerization at the surface of AgNPs.



**Figure 2-7** XPS analysis of PEDOT:PSS-AgNP nanocomposites with and without PVP. (a) XPS S2p core-line spectra without PVP and (b) XPS S2p core-line spectra with PVP sample.

The electrical conductivity of PEDOT:PSS-AgNP nanocomposites fabricated by adding all polymer additive(PSS<sup>-</sup> ion and PVP) in acetonitrile was measured using a four-point probe equipment. The Veeco FPP-5000 PEDOT:PSS-AgNP nanocomposite films were prepared by dip coating method and dried in vacuum oven at 80°C. The electrical conductivity of PEDOT:PSS-AgNP nanocomposites were measured to be 0.303S/cm. According to Wang[28]'s report, PEDOT:PSS-AgNP nanocomposites in this study has higher electrical conductivity than that of PEDOT:PSS-AgNP nanocomposites fabricated by traditional method (0.02S/cm) and Balamurugan's method (0.22S/cm). The measured conductivity is lower than that fabricated by Wang's method. Please note that we didn't add other agent to improve the electrical conductivity of our nanocomposites because we focused on the fabrication and mechanism of PEDOT:PSS-AgNP nanocomposites by adding polymer additive in organic solvent.

# 2.5 Mechanism of PEDOT:PSS-AgNP formation

Based on our observations and Wang's proposed mechanism[28], we suggest a synthesis mechanism for the PEDOT:PSS-AgNP nanocomposites under basic conditions when PSS<sup>-</sup> ions and PVP are used as additives (**Fig. 2-8**). PSS<sup>-</sup> ions also act as counter-ions and a stabilizer[28]. PSS<sup>-</sup>ions are distributed between AgNPs, maintaining the charge neutrality and stabilizing the polymerization of EDOT, thereby resulting in the synthesis of a mixed form of PEDOT:PSS and AgNPs nanocomposites (**Fig. 2-8(a)**). When PVP is added, the difference arises from the

nucleation and growth of AgNPs. PVP forms coordination-complexes with Ag ions, helping reduce Ag ions. Here, depending on the ratio of PVP and the Ag precursor, the capping ability of PVP is determined. For low ratios, PVP promotes the nucleation of smaller AgNPs from ion complexes and the distribution of AgNPs. The ion complex is formed from the aggregation of Ag ions to element Ag. Via the PVP chain, the nearby ion complex can show a slightly negative charge to form  $(Ag)_n^-$ [143]. Due to the negative charge of the ion complex, the binding energy of S-(Ag)<sub>n</sub><sup>-</sup> is reduced; this enhances the distribution of electrons between S<sup>+</sup> in EDOT, thereby promoting the polymerization of EDOT at the surface of AgNPs. Here, the ion complex and small AgNPs agglomerate locally, forming polycrystalline AgNPs with PVP.



**Figure 2-8** Schematic illustration of synthesis mechanism of PEDOT:PSS-AgNP nanocomposites according to additives. (a) Without PVP and (b) with PVP.

**2.6 Application of PEDOT:PSS-AgNP to electrospun microfiber** Electrospinning was utilized to produce fibers containing PEDOT:PSS-AgNP composites. The method used for producing silver nanofibers was adopted from previous research in our laboratory[54]. The surface morphology of fibers containing PEDOT:PSS-AgNP composite over time under UV irradiation is presented in **Figure 2-9**. It can be observed from the surface of the pristine fiber (0 min) that PEDOT:PSS-AgNP composite can be distributed on the surface of the fiber through the electrospinning process. As the UV exposure time increases to 30 minutes, very small silver nanoparticles are formed due to reduction on the microfiber containing PEDOT:PSS-AgNP composite, but there is no significant connection between the silver nanoparticles. After 1hour of UV irradiation, the size of the silver nanoparticles increases, and connections between them are formed, resulting in the formation of conductive pathway. Furthermore, it is observed that the PEDOT:PSS-AgNP composite remains stable and does not undergo any significant changes due to UV irradiation.

Through **Figure 2-10**, the reduction of silver was confirmed as a function of UV exposure time using UV-Vis spectroscopy. The UV-Vis spectrum showed a maximum absorbance at 270 nm, which is attributed to the formation of large, stabilized clusters of silver ranging in size from 2-8 nm[144]. The formation of silver nanoparticles on the fiber surface was detected after 30minutes of UV exposure and beyond. **Figure 2-11** illustrates the measurement of sheet resistance as a function of UV irradiation. Silver nanoparticles began to form after 30 minutes of UV exposure,

but no conductivity was observed due to the lack of interparticle connections. However, after 60 minutes of UV exposure, the silver nanoparticles began to connect with each other, leading to the formation of conductivity. After 180 minutes of UV exposure, the resulting sheet resistance was approximately 160 ohms/sq.



**Figure 2-9** Surface morphology of fiber containing PEDOT:PSS-AgNP nanocomposite according to UV irradiation time.



**Figure 2-10** UV-vis spectroscopy of fiber containing PEDOT:PSS-AgNP nanocmoposites to confirm silver reduction according to UV irradiation time.



**Figure 2-11** Sheet resistance of fiber containing PEDOT:PSS-AgNP nanocmoposites to confirm silver reduction according to UV irradiation time

# 2.7 Summary

In this chapter, PEDOT:PSS-AgNP nanocomposites were fabricated through spontaneous redox reaction between silver precursor and EDOT in organic solvent. We verified that the quality of AgNPs depends on the solvent, and the quality is better when the solvent is acetonitrile. We also verified that PSS- plays a role as a stabilizer and counter-ion in the EDOT polymerization process, similar to an acidic solution. In addition, we defined the role of polymer additive influencing and presented mechanisms to increase the yield of nanocomposites through the addition of PVP. PVP (e.g., PVP:AgNO3 = 1:6) facilitated PEDOT:PSS-AgNP synthesis by increasing the number of nucleation Ag ion clusters. This resulted in a large number of well-dispersed AgNPs during the EDOT polymerization process. PVP stabilized the Ag ion clusters and reduced the binding energy between the Ag ion clusters and sulfur in the neighboring EDOT, resulting in enhanced EDOT polymerization at the surface of AgNPs. Based on these observations and our analysis results, we propose a synthesis mechanism for the PEDOT:PSS-AgNP nanocomposite in an organic solvent.

# Chapter 3. Stretchable and transparent PEDOT:PSS-based composite film electrode

Stretchable electronics capable of accommodating large mechanical deformations are considered the next-generation technology for bio-electronic applications, which are currently limited by conventional rigid and flexible electronics. [30-32] For bioelectronics, including stretchable displays, [33, 34] wearable smart devices, [35, 36] implantable devices, [37, 38] and human motion sensors, [39-42] the stretchable components should be able to withstand mechanical strain (>30%) generated by dynamic human motions (bending, curling, twisting, and stretching) without performance deterioration.[43] Recently, transparent stretchable electrodes have received considerable attention as key components of stretchable electronics for various applications.[44] Indium tin oxide (ITO) is one of the most widely used conductive materials in transparent electrodes owing to its high optical transparency (>90% in the visible-light range) and low sheet resistance (10  $\Omega$ ·sq-1 on glass).[45] However, the mechanical brittleness and lack of flexibility owing to the intrinsic ceramic structure are major limitations of ITO for further stretchable electronic applications.[46] Therefore, various materials, such as carbon nanotubes,[47, 48] graphene, [49, 50] metal nanowire, [51-54] metal mesh, [55-57] and conductive polymers, [58, 59] have been actively studied.

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is one of the most widely used conductive polymers owing to its mechanical flexibility,[60] excellent optical/electrical properties,[61, 62] low cost, easy processability,[23, 63,

64] thermal and chemical stability,[65, 66] biocompatibility, and non-toxicity.[67-69] PEDOT:PSS has been actively investigated in both academic and industrial fields for various applications in organic light-emitting diodes (LEDs),[70] organic solar cells,[71] energy-storage devices,[72] and sensors.[73, 74] However, PEDOT:PSS has certain inherent mechanical limitations in stretchable electronics. The fracture strain of as-cast PEDOT:PSS films is only 2–6%,[75] which is insufficient considering the 30% strain requirement of stretchable electronics. To overcome the mechanical brittleness of PEDOT:PSS, various studies have been focused mainly in two major directions: approaches based on homogeneous dispersion and heterogeneous assembly.[76]

The homogeneous dispersion approach is a chemical strategy in which several additives are uniformly blended into a PEDOT:PSS solution. Plasticizers or ionic liquids, such as xylitol,[77] Zonyl,[78] Triton X-100,[79] and *d*-sorbitol[68] can improve the stretchability of PEDOT:PSS films by reducing the interactions between the PEDOT:PSS molecular chains and increasing the free volume. In addition, blending PEDOT:PSS with soft polymers such as poly(ethylene glycol), poly(ethylene oxide), poly(vinyl alcohol), and water-borne poly(urethane) can enhance the stretchability of PEDOT:PSS films. The advantage of this homogeneous dispersion approach is its easy processability; it requires only one blending process. However, there are limitations to the types of additives, because additives should also be water-soluble to be uniformly blended with water-soluble PEDOT:PSS Furthermore, because most additives are insulating in nature, the PEDOT:PSS

concentration can only be decreased to a limited extent owing to the percolationdependent conductivity.[80] Otherwise, the connectivity between conductive domains is hindered, resulting in reduced conductivity.[81] In addition, increasing the PEDOT:PSS loading causes poor mechanical properties and optical transparency.[68, 77]

The heterogeneous assembly approach is a mechanical strategy for forming a bilayer structure of PEDOT:PSS on stretchable substrates such as poly(dimethyl siloxane) (PDMS)[82-85] or styrene ethylene butylene styrene (SEBS).[86] Therefore, by utilizing a water-insoluble elastomer as a stretchable substrate and controlling the thickness of the deposited PEDOT:PSS layer, a heterogeneous assembly approach achieve satisfactory electromechanical stability as well as optical can transparency.[83-85, 87, 88] However, owing to the intrinsic mechanical brittleness of PEDOT:PSS, the cracking of PEDOT:PSS films supported on elastomers is inevitable upon stretching, resulting in a permanent loss of conductivity.[82-84] To minimize crack formation in the deposited PEDOT:PSS layer, the substrate is prestrained before deposition, [60, 85, 87] the encapsulation process is performed after deposition, [85, 89, 90] or the PEDOT: PSS layer is deposited in special geometric patterns, such as serpentine or wavy patterns, using laser-cutting or screen-printing techniques.[91, 92] Furthermore, because some substrates, such as PDMS and SEBS, are hydrophobic, it is necessary to improve the wettability of the substrate surface before PEDOT:PSS deposition for uniform adhesion between the PEDOT:PSS layer and substrate.[82] Thus, an additional process, such as

UV/O3,[84, 93, 94] oxygen plasma,[82, 95] or acid treatment,[82] is required. In summary, the heterogeneous assembly approach can provide both satisfactory electromechanical stability and optical transparency but requires complex and multiple pre-deposition processes that may limit its industrial application.

This chapter aimed to develop a new method for producing stretchable and transparent electrode that combine the advantage of two existing approaches: simple processing and good electrochemical stability and optical transparency. First, PEDOT:PSS and precured PDMS were homogenously mixed with the aid of a surfactant, and then the mixture was bar-coated on a substrate. By inducing phase separation between hydrophilic PEDOT:PSS and hydrophobic PDMS based on their different affinities to the substrate, a highly stretchable, conductive, and transparent film was created with an extreme bilayer structure. When a blend with a large PDMS fraction was used, a thick top layer predominantly consisting of PDMS, which is responsible for stretchability and transparency, and a thin bottom layer rich in PEDOT:PSS, which is responsible for conductivity, were formed on the substrate. The continuous PEDOT:PSS matrix ensures excellent conductivity (66.17  $\Omega \cdot sq^{-1}$ ), while the PDMS islands provide high stretchability. The electrical conductivity of the new electrodes varies negligibly when stretched at 50% strain and is even maintained up to 150% strain. The electrodes exhibit high transparency (~90% at 550 nm) and electromechanical stability over 1000 cycles of 30% stretch/release tests.

## **3.1 Preparation of PEDOT:PSS/PDMS composite film**

#### **3.1.1 Materials**

PDMS (Sylgard 184) and a curing agent were purchased from Dow Corning. The PEDOT:PSS aqueous solution (Clevios PH1000) was purchased from Heraeus. Ethylene glycol (EG, 99 wt%) and Triton X-100 were purchased from Sigma– Aldrich. The PET film substrate was purchased from Hansol Paper Co. Ltd. (Seoul, Korea). The Teflon film was purchased from DuPont. All the materials were used as received.

### **3.1.2 Fabrication of the PEDOT:PSS/PDMS composite film**

To prepare the polymer blends, a PEDOT:PSS solution was mixed with PDMS, a curing agent, Triton X-100, and EG. Based on the PEDOT:PSS aqueous solution, the weight fractions of Triton X-100 and EG were fixed at 10 and 7 wt%, respectively. The weight ratios between PDMS and PEDOT:PSS aqueous solution were varied as 2:1, 5:1, 10:1, 15:1. The amount of the curing agent was fixed at 10 wt% of PDMS. The mixtures were stirred at 2000 rpm for 20 min to obtain homogeneous suspensions. Then, the blend was poured onto an PET film, and a 100–120  $\mu$ m thick film was fabricated using an bar coater. The coated film was maintained at room temperature for 1 h for phase separation of PDMS and PEDOT:PSS, and then cured at 100 °C for 1 h in a vacuum oven. After cooling to room temperature over 1 h, the film was cut into 1×2 cm<sup>2</sup> specimens and the PET substrate was peeled off for morphological, mechanical, and electrical characterizations.

# **3.2 Characterization of PEDOT:PSS/PDMS composite film**

Morphological characterization was conducted by field-emission SEM (SUPRA 55VP, Carl Zeiss, Germany), (AURIGA, Carl Zeiss, Germany), and optical microscopy (BX51, Olympus, Japan). The static water contact of the PET film was measured using a contact-angle measurement system (Smart Drop). Electrical characterization was conducted at room temperature by applying Ag pastes to each corner of the 3×3cm2 samples to create electrical contacts with a diameter of approximately 1mm and the electrical properties were measured using a four-point resistance probe (RM3544, Hioki, Japan). Image analysis was conducted using ImageJ software. Mechanical characterization was conducted using a universal testing machine (Quasar 5, Galdabini, Italy). For electromechanical characterization, the PDMS/PEDOT:PSS film was fixed on the universal testing machine and the resistance change upon deformation was measured using an electrometer (6517 B, Keithley, USA). Optical transmission measurements were conducted using a UV-vis spectrophotometer (V770, Jasco, Japan)

# **3.3 Morphology of PEDOT:PSS/PDMS composite film**

### **3.3.1** Formation of bilayer structure

When two immiscible polymers are mixed together, the resulting solution will typically undergo phase separation. The resulting morphologies can range from isolated spherical shapes to a continuous matrix, depending on the relative contents of the two polymers [145-147]. For example, a polymer with a low weight ratio in

the solution adopts an isolated particle structure. In the absence of a surfactant, the hydrophobic PDMS and hydrophilic PEDOT:PSS were expected to be immiscible, resulting in the segregation and distribution of PEDOT:PSS (with a low-weight-ratio component of about 0.5wt% of PDMS excluding water) in the form of spherical particles on the surface of the bar-coated film, as shown in **Figure 3-1(a) and (b)**. This type of structure is likely to have low electrical conductivity.



(b)





**Figure 3-1** Surface morphology of the PDMS/PEDOT:PSS composite film with a PDMS to PEDOT:PSS weight ratio of 2:1. (a) Scanning electron microscopy (SEM) and (b) optical images of the film without any surfactant, showing PEDOT:PSS islands distributed in the PDMS matrix. (c) SEM and (d) optical images of the film with the surfactant, showing PDMS islands distributed in the PEDOT:PSS matrix.



Figure 3-2 Chemical structure of (a) PEDOT:PSS (b) PDMS and (c) Triton X-100

To enhance the miscibility of hydrophobic PDMS with hydrophilic PEDOT:PSS, an amphiphilic surfactant (Triton X-100) with a hydrophilic head and hydrophobic tail was added to the blend. [148]. The hydrophilic end of Triton X-100 is attached to PEDOT:PSS, while the hydrophobic end is attached to PDMS, enabling the two immiscible polymers to achieve complete miscibility (as illustrated in **Figure 3-2**). When Triton X-100 was added, PEDOT:PSS did not form isolated spherical particles as observed before (**Figure 3-1(c) and (d)**). Instead, a thin layer of PEDOT:PSS was formed on the bottom side of the composite film (a cross-sectional SEM image of the composite film according to the weight ratio of PDMS and PEDOT:PSS in the solution is shown in **Figure 3-3**). The thickness of the resulting film increased from 100 to 125 µm as the weight ratio of PDMS to PEDOT:PSS decreased. This increase in thickness was due to the loss of volume resulting from the evaporation of water in the PEDOT:PSS layer during the curing process. Across all weight ratios, the composite films displayed a clearly defined bilayer structure, with a thick top layer that was primarily composed of PDMS and a bottom layer that was mainly composed

of PEDOT:PSS. As the weight fraction of PEDOT:PSS in the coating solution decreased, the thickness of the bottom layer that was rich in PEDOT:PSS decreased.


10μm

**(b)** 



(d)



**Figure 3-3** Cross-sectional SEM images of PDMS/PEDOT:PSS composite films with PDMS to PEDOT:PSS weight ratios of (a) 2:1, (b) 5:1, (c) 10:1, and (d) 15:1. A surfactant was added to the solutions.





**Figure 3-4** Measured contact angles of distilled water on two substrates: (a) PET film and (b) Teflon film.

To investigate the driving force of the phase separation of the polymer solution that leads to the formation of the bilayer structure, the surface energies of the two different substrates, hydrophilic PET and hydrophobic Teflon film, were indirectly measured using water contact angles. The contact angles of distilled water droplets on PET and Teflon films were measured as 55.1° and 97.8°, respectively, as depicted

in **Figure 3-4.** Because the contact angle tends to decrease as the surface energy of the substrate increases [149], it is clear that the PET film substrate has a higher surface energy than the Teflon substrate. Next, the contact angles of distilled water and diiodomethane drops were measured to calculate the surface energies of PEDOT:PSS and PDMS,[150, 151] according to the geometric mean method based on the following equation:

$$((1 + \cos\theta)\sigma_l = 2\{(\sigma_l^D \sigma_s^D)^{1/2} + (\sigma_l^P \sigma_s^P)^{1/2}\}$$

Where,  $\theta$  is the contact angle of the test liquid on a solid surface and  $\sigma_l$  and  $\sigma_s$  are the surface energies of the test liquid and solid surface, respectively.  $\sigma^D$  and  $\sigma^P$ are the dispersive and polar interaction surface energies, respectively.

The calculated surface energy of PEDOT:PSS was found to be 74.9  $mJ \cdot m^{-2}$ , which is significantly higher than that of PDMS (16.5  $mJ \cdot m^{-2}$ ) (**Table 3-1**). This result indicates that PEDOT:PSS has a greater tendency to migrate to a substrate with a higher surface energy.[152] The difference in surface energy between the two polymers appears to be a key factor in the phase separation that leads to the formation of the bilayer structure.

 Table 3-1
 Surface energies of PEDOT:PSS and PDMS

Sample	H <sub>2</sub> O(°)	CH <sub>2</sub> I <sub>2</sub> (°)	$\sigma^{D}$	$\sigma^{P}$	$\sigma_{total}$
PEDOT:PSS	23.1 <sup>a)</sup>	23.8 <sup>a)</sup>	46.6	28.3	74.9
PDMS	116 <sup>b)</sup>	72.6 <sup>b)</sup>	16.5	0.04	16.5

a: [149]; b: [150, 151]

The mechanism of how the bilayer structure of the PDMS/ PEDOT:PSS composite film is formed based on the substrate is presented in **Figure 3-5**. In the case of using a PET film with a high surface energy as the substrate, the polymer solution tends to form a bilayer structure with a PEDOT:PSS-rich bottom layer due to the migration of PEDOT:PSS with a higher surface energy to the surface of the PET film. On the other hand, when a Teflon film with a low surface energy is used, the low surface energy PDMS tends to migrate to the air and the Teflon film surface, resulting in a trilayer structure where the higher surface energy PEDOT:PSS is trapped in the middle layer. In summary, phase separation occurs according to the difference in the surface energies of immiscible PEDOT:PSS and PDMS, and a PEDOT:PSS-rich bottom layer is formed on the PET surface. On PET, an intriguing morphology of the PEDOT:PSS-rich bottom layer was observed; PDMS islands (stretchable) were distributed in a continuous PEDOT:PSS matrix (conductive), which led to the stretchable and conductive nature of the composite film.



**Figure 3-5** Optical cross-sectional images of free-standing PDMS/PEDOT:PSS composite films with a PDMS to PEDOT:PSS weight ratio of 5:1 prepared using (a) PET and (b) Teflon substrates, and (c) a schematic illustrating the phase separation of the polymer solution and resulting layered structure formation according to the substrate.

**3.3.2 Formation of continuous PEDOT:PSS matrix - PDMS island structure** Next, we investigated the morphologies of the top and bottom layers of the PDMS/PEDOT:PSS composite film prepared with a PDMS to PEDOT:PSS weight ratio of 2:1. It is noteworthy that the top layer of the PDMS/PEDOT:PSS composite film, which was prepared using a weight ratio of 2:1, exhibited the presence of only PDMS (as depicted in **Figure 3-6(a) and (b)**), while the bottom layer displayed a mixture of PDMS and PEDOT:PSS (as shown in **Figure 3-6(c), (d), and (e)**). By analyzing the elemental mapping images provided in **Figure 3-6(d) and (e)**, it was found that PDMS was uniformly distributed in the form of spherical particles within a continuous matrix of PEDOT:PSS in the bottom thin layer. Moreover, the morphological variations between the PDMS/PEDOT:PSS composite films were investigated as per the weight ratio of PDMS to PEDOT:PSS in the solution, namely 2:1, 5:1, 10:1, and 15:1.





(d)



(e)



(c)



**Figure 3-6** Morphology of the PDMS/PEDOT:PSS composite film with a PDMS to PEDOT:PSS weight ratio of 2:1. (a) SEM images and (b) elemental silicon mapping image of the top layer and (c) SEM images and (d) and (e) elemental silicon and sulfur mapping images of the bottom layer, respectively. (f) and (g) Optical surface morphology of PDMS/PEDOT:PSS films without and with a dwell time (3 days) before curing.

**Figure 3-7** shows that in the bottom layer, PDMS existed in the form of spherical particles surrounded by PEDOT:PSS, regardless of the weight ratio; that is, PDMS islands were distributed in a PEDOT:PSS continuous matrix. In the previous section, we discussed the formation of a bilayer structure of the PDMS/PEDOT:PSS solution. However, the formation of PDMS islands in the continuous PEDOT:PSS matrix was not explained. First, we investigated the effect of the phase separation behavior on this structure by standing the solution for 3 days before curing to prolong the phase separation process. **Figure 3-6 (f) and (g)** show the same PDMS islands distributed in the PEDOT:PSS matrix, regardless of the dwell time, suggesting that the phase separation behavior did not influence the formation of the observed segregated structure.

Therefore, we speculate that the curing reaction is responsible for the formation of PDMS islands in the PEDOT:PSS thin layer. The surface morphologies of the PEDOT:PSS-rich bottom layer in the PDMS/PEDOT:PSS composite films showed that larger PDMS islands were formed in the 2:1 case compared to the other cases, as depicted in **Figure 3-7**. To investigate the size distribution of the PDMS islands in the 2:1 and 5:1 cases, we performed image analyses. The results showed that the 2:1 case had a larger average diameter of PDMS islands ( $8.48 \pm 5.16 \mu m$ ) compared to the 5:1 case ( $1.93 \pm 1.69 \mu m$ ) (**Figure 3-8 (a)**), as well as the other cases (**Figure 3-9**). The thickness fraction of the PEDOT:PSS- rich layer in the composite film was significantly reduced from 47.2 to 4.5% for 2:1 and 5:1 cases, respectively ((**Figure 3-8(b**)). The reduced thickness fractions can be attributed to the reduced weight

fraction of PEDOT:PSS. Interestingly, the size of the PDMS particles decreased, whereas their number increased as the PEDOT:PSS content decreased. This can be attributed to the mechanism of PDMS particle formation involving the evaporation of water, a good solvent of PEDOT:PSS. During the curing process at 100 °C after the bar-coating of the polymer mixture, the water in the bottom PEDOT:PSS-rich layer evaporated, leaving voids in this layer; these voids were subsequently filled with PDMS as the curing process proceeded. As the thickness of the PEDOT:PSSrich laver decreased because of the reduced weight fraction of PEDOT:PSS in the coating solution, the amount and evaporation time of water also decreased, resulting in a decreased size of the pores and thus that of the PDMS islands. The increased number of smaller PDMS particles for blends with a low weight fraction of PEDOT:PSS can also be explained by the thickness of the bottom layer. When the bottom PEDOT:PSS-rich layer is thin, water molecules evaporate before they coalesce into larger drops compared to the high PEDOT:PSS fraction case. Accordingly, we propose a mechanism for the formation of PDMS islands in a PEDOT:PSS continuous matrix, as illustrated in Figure 7(c). Note that the fraction of PDMS islands increased because of the increased number of smaller particles, that is, the areal fraction of PEDOT:PSS decreased as the PEDOT:PSS content decreased (see Figure 3-12(a) for the detailed areal fraction). These morphological changes in the PDMS/PEDOT:PSS composite films are important factors that determine their mechanical, electrical, and optical properties.



(b)





**Figure 3-7** Surface morphology of the PEDOT:PSS-rich bottom layer in the PDMS/PEDOT:PSS composite film according to the PDMS to PEDOT:PSS weight ratio in the solution: (a) 2:1, (b) 5:1, (c) 10:1, and (d) 15:1. Note that isolated spherical shapes in the images represent PDMS particles dispersed in a PEDOT:PSS continuous matrix.



#### (c)

#### i) Thick PEDOT:PSS-rich layer



**Figure 3-8** Characterization of PDMS islands in the bottom layer of the PDMS/PEDOT:PSS composite film: (a) PDMS island diameter distribution, (b) correlation between the thickness of the PEDOT:PSS-rich layer and island diameter, (c) schematic illustrating the formation and size difference of the PDMS islands in the bottom layer of the PDMS/PEDOT:PSS composite film.



**Figure 3-9** Diameter distribution and average diameter of PDMS islands in the bottom layer of the PDMS/PEDOT:PSS composite film according to the polymer weight ratios: (a) 10:1 and (b) 15:1.

The morphological change of the PDMS/PEDOT:PSS composite film upon stretching was investigated with a focus on the thin bottom layer. To conduct this investigation, nominal strains of 0%, 25%, 50%, and 75% were applied to the composite film prepared at a weight ratio of 5:1. The results revealed that both the spherical PDMS particles and the surrounding PEDOT:PSS matrix in the segregated structure elongated in the stretching direction without apparent interfacial failure. This observation suggests that the adhesion between the PDMS particles and PEDOT:PSS matrix was strong enough to prevent delamination at the interface during stretching. This strong adhesion is attributed to the improved interaction of the hydrophobic PDMS with hydrophilic PEDOT:PSS mediated by Triton X-100. [79] Figure 3-10 (b) displays the elemental mapping image of the PDMS/PEDOT:PSS composite film with a weight ratio of 5:1 at 50% strain. The image provides clear evidence that the PDMS particles elongated and transformed into elliptical shapes while stretching through the PEDOT:PSS matrix. It is noteworthy that the interface between PDMS and PEDOT:PSS remained intact without any delamination during stretching, indicating excellent adhesion between the two phases. This is an important aspect for maintaining the transparency of the film during stretching, as voids or delamination could lead to light scattering and reduced transparency.

In summary, on the bottom side of the PDMS/PEDOT:PSS composite film, PEDOT:PSS was continuously connected as a segregated structure, which was maintained even when stretched, at any weight fraction (**Figure 3-11**). Therefore, it

can be deduced that the properties of PEDOT:PSS, for example, its electrical conductivity, can be maintained even under a large strain because PDMS particles accommodate the applied strain (see **Figure 3-10(c)** for a schematic explanation of this stretching behavior). Such a composite film can be used as a bilayered structure because the top PDMS layer provides mechanical resilience and integrity without significantly influencing the optical characteristics of the film. Because the top layer is not electrically conductive, only the bottom layer (PDMS islands distributed in the continuous PEDOT:PSS matrix) can be used for through-thickness or both top- and bottom-electrode applications. The stretchable, transparent, and conductive properties of the bilayered PDMS/PEDOT:PSS composite films are discussed in the following sections.

### **(a)**



**(b)** 





**Figure 3-10** (a) Optical microscopy images of the PDMS/PEDOT:PSS composite film with a PDMS to PEDOT:PSS weight ratio of 5:1 under different strain values. (b) SEM and elemental mapping images of the PDMS/PEDOT:PSS composite film (PDMS to PEDOT:PSS weight ratio of 5:1) under 50% strain. (c) Schematic illustration of the deformation behavior of the PDMS/PEDOT:PSS composite film. The white arrows in (a) and (b) represent the elongation direction.

### **(a)**

(c)

20µm

0% strain

50% strain





**Figure 3-11** Optical microscopy images of PDMS/PEDOT:PSS composite films with different polymer weight ratios at rest and under 50% strain. (a) 2:1 (b) 5:1 (c) 10:1 and (d) 15:1.

# 3.4 Electro-mechanical and optical properties of PEDOT:PSS/PDMS composite film

The change in the sheet resistance of the PDMS/PEDOT:PSS composite film was measured using the four-point van der Pauw method for different weight ratios and sample sizes of 3×3cm<sup>2</sup> (Figure 3-12(a)). The areal fraction of the PEDOT:PSS matrix in the bottom layer of the composite was also characterized according to the PDMS and PEDOT: PSS ratio using image analysis (see Figure 3-7 and 3-8). The sheet resistance increased as the PEDOT:PSS content decreased; for example, the sheet resistances were 66.17, 115.98, 322.90, and 382.39  $\Omega \cdot sq^{-1}$  for the 2:1, 5:1, 10:1, and 15:1 cases, respectively, owing to the formation mechanism of the PDMS islands explained in Section 3.2.2 (the number of smaller PDMS particles and their areal fraction increased as the PEDOT:PSS content decreased). In the 2:1 and 5:1 cases, for which the areal fraction of the PEDOT:PSS matrix was larger than 0.5, the sheet resistance was relatively low (~100  $\Omega \cdot sq^{-1}$ ). However, for the 10:1 and 15:1 ratios with lower areal fractions of the conductive PEDOT:PSS matrix, the resistance significantly increased compared to the previous two ratios. As the ratio of PEDOT:PSS in the solution decreased, the PEDOT:PSS-rich layer became thinner, and the sheet resistance tended to increase; it was however still low at approximately 400  $\Omega \cdot sq^{-1}$ .

**Figure 3-12(b)** shows the relative sheet resistance changes  $(R/R_0, \text{ where } R_0 \text{ and } R$  are the sheet resistances before and after deformation, respectively) of

PDMS/PEDOT:PSS composite films upon stretching up to 150% strain. Note that the elongation strain at break was 161.6, 173.2, 186.9, and 194.4% for the 2:1, 5:1, 10:1, and 15:1 cases, respectively (not shown). This can be explained by the reduced areal fraction of PEDOT:PSS in the bottom layer. Because PEDOT:PSS is brittle, the reduced areal fraction of PEDOT:PSS in the segregated structure (and also increased smaller PDMS particles and their fraction) resulted in a larger deformability of the PDMS/PEDOT:PSS composite films with a lower PEDOT:PSS content.







**Figure3-12** Electrical and optical properties of PDMS/PEDOT:PSS composite films. (a) Sheet resistance according to the weight ratio of PDMS and PEDOT:PSS, (b) relative sheet resistance change according to the strain, (c) and (d) changes in the relative sheet resistance of PDMS/PEDOT:PSS composite films with PDMS to PEDOT:PSS weight ratios of 5:1 and 15:1, respectively, during a cycle test with 30% strain, and (e) transmittance according to the weight ratio of PDMS and PEDOT:PSS, and (f) appearances of 2:1 and 15:1 cases.



**Figure3-13** Optical microscopy image showing the breakage of the segregated structures of PEDOT:PSS in the PDMS/PEDOT:PSS composite film under 150% strain

Nonetheless, regardless of the PDMS to PEDOT:PSS ratio, the PDMS/PEDOT:PSS composite film exhibited a breakage strain of >150%. The  $R/R_0$  values of the PDMS/PEDOT:PSS composite films increased with increasing strain. As shown in **Figure 3-10**, the spherical PDMS islands deformed into elliptical shapes in the loading direction, between which PEDOT:PSS networks also deformed but to a smaller extent because PDMS accommodates the majority of strain. The shape of the PEDOT:PSS network changed with a small deformation that was sufficient to accommodate the deformation of the PDMS particles. Accordingly, the conductive

paths decreased owing to the elongated PDMS particles, resulting in an increased sheet resistance. The  $R/R_0$  values of the PDMS/PEDOT:PSS composite films with 2:1, 5:1, 10:1, and 15:1 weight ratios of the polymer components stretched by 150% were 20.5, 10.8, 12.7, and 13.8, respectively. The significant increase in the  $R/R_0$  value can be explained by the breakage of the segregated PEDOT:PSS structure at such a high strain (see **Figure 3-13**) and the elongation of PDMS particles. Relatively large particles of PDMS in the 2:1 case induced more dimensional changes as the strain increased, leading to higher  $R/R_0$  values than those of the other ratio cases, and its sheet resistance at 150% strain was 657.8  $\Omega \cdot \text{sq}^{-1}$ . For the other ratio cases, the relative resistance changes were similar, presumably due to their similar morphologies, i.e., similar sizes of the PDMS particles. Note that when the strain was within 30%, the maximum strain that can be applied by human motions,<sup>[43]</sup> a low change in sheet resistance of 1.5–2.5 was observed, implying that the electrical stability of the PDMS/PEDOT:PSS composite film would be sufficient under mechanical deformations induced by body motions.

Next, the durability of the PDMS/PEDOT:PSS composite film was investigated by subjecting it to 1000 stretch/release cycles. A strain of 30% was applied to 5:1 and 15:1 ratio cases (**Figure 3-12 (c) and (d)**). During the first stretching cycle at 30% strain, the resistance increased by ~10% because the percolation density of the segregated PEDOT:PSS network decreased. The resistance increase was maintained within 30% during the 1000 cycles of the test. This result clearly indicates that the durability of the PDMS/PEDOT:PSS composite film is sufficient for its application

in other stretchable electronics such as health-monitoring devices,[153] organic LED devices,[154] and transparent electrodes.[87] We speculate that the conductive pathway of the PDMS/PEDOT:PSS composite film could be maintained well under cyclic testing because of the continuous segregated network of PEDOT:PSS. The results indicate its high application potential in stretchable electronics.

The optical characteristics of the PDMS/PEDOT:PSS composite films were investigated by measuring their visible-light transmittance (**Figure 3-12 (e)**). The transparency of the PDMS/PEDOT:PSS composite film at 550 nm increased from 79.1% (2:1 ratio) to 89.6% (15:1 ratio), approaching that of pristine PDMS (95%). This is because the areal fraction of PDMS in the bottom layer increased as the PDMS ratio in the solution increased. In the case of the 2:1 ratio, although the PDMS particle size was the largest, the overall PDMS areal fraction was the lowest owing to the small number of PDMS particles, resulting in decreased optical transparency. However, as the ratio of PEDOT:PSS decreased, the number of PDMS particles increased and their size decreased, resulting in increased areal fraction of PDMS and improved optical transparency of the composite film. The transparency of the PDMS/PEDOT:PSS composite films was evaluated by placing the films on a university symbol (see **Figure 3-12(f)**) to demonstrate that the PDMS/PEDOT:PSS composite film can be used in applications requiring transparency.

Finally, we demonstrate the transparency of the PDMS/PEDOT:PSS composite films in the stretched state and their electrical conductivities using a circuit of the film and LED in series. As shown in **Figure 3-14**, the LED was normally lit when no external force was applied to the transparent PDMS/PEDOT:PSS composite film owing to its conductivity. When the strain was increased to 50%, the brightness of the LED changed slightly. At 150% strain, the brightness decreased significantly owing to decreased conductivity. Overall, this visual demonstration confirms that the PDMS/PEDOT:PSS composite films developed in this study can be directly integrated into stretchable electronics as transparent and stretchable electrodes.



**Figure 3-14** Demonstration of the electrical conductivity and transparency of the PDMS/PEDOT:PSS composite film in the stretched state using a circuit fabricated in series using the film and a light-emitting diode. (see a light at right below middle). As the strain increased, the transparency and brightness of LED did not change significantly until 50% strain.

#### 3.5 Summary

In this chapter, we developed highly stretchable, transparent, and electrically conductive PDMS/PEDOT:PSS composite films with an intriguing morphology (spherical PDMS islands distributed in a PEDOT:PSS continuous matrix) using the phase separation behavior of PDMS and PEDOT:PSS according to their affinity to the substrate and a subsequent curing process. PDMS particles and a continuous PEDOT:PSS network (matrix) were responsible for the stretchability and electrical conductivity, respectively. The size and number of PDMS particles in the PEDOT:PSS matrix were controlled by varying the PDMS to PEDOT:PSS weight ratio. As the PEDOT:PSS content decreased in the solution of precured PDMS and PEDOT:PSS, the size of the PDMS particles in the composite film decreased, but their number increased, resulting in an increase in the areal fraction of PDMS with respect to PEDOT:PSS. These changes can be explained by the evaporation of water molecules (a good solvent of PEDOT:PSS) from the bottom PEDOT:PSS-rich layer, pore generation where the water was present, and filling of the pores with PDMS during the curing process. The electrical conductivity and optical transparency of the PDMS/PEDOT:PSS composite films along with their breaking strains (and stretchability) can be attributed to their morphological features, such as the size, and areal fraction of the PDMS particles. The fabricated number. PDMS/PEDOT:PSS composite films exhibited a low sheet resistance of ~66  $\Omega \cdot sq^{-1}$ , visible transmittance of 85%, and a relative sheet resistance change  $(R/R_0)$  of 10 upon stretching with up to 150% strain, demonstrating their excellent electrical,

mechanical, and optical properties.

## Chapter 4. Shape memory PEDOT:PSS-based composite film

Shape-memory polymers(SMPs) are a type of smart materials that can restore a macroscopic (permanent) shape from a programmed(temporary) shape in response to external stimuli such as temperature, humidity, light and electricity[96]. Thermally activated SMPs change shape near their transition temperature (Tg). The shape memory phenomenon can be initiated by deforming the material above the Tg and then cooling it below the Tg while maintaining the constraints. Thermoresponsive SMPs are used in various field such as biomedical applications, drug delivery and flexible electronics [97-99].

There are several attempts to use PEDOT:PSS combined with epoxy resin. Epoxy resin was used for maintaining the electrical conductivity and enhancing the water stability of PEDOT:PSS film, but the weight ratio of epoxy resin was up to 5wt%, most of the film was consisted with PEDOT:PSS, and there were no shape memory characteristic[100, 101]. Methanol-facilitated PEDOT:PSS was used for conductive filler for epoxy resin[102], 60wt% of silver microflake were used for dominant conductive pathway in epoxy matrix, small amounts about 1wt% of PEDOT:PSS connect the unlinked conductive pathway of silver microflake.

The bar-coating method is candidate for fabricating large- area thin films on substrates because of its simplicity and compatibility with roll-to-roll process for large area active layer deposition over large areas for electronics [103-105]. The thin film fabricated with polymer blend, phase separation can be occurred to be thermodynamically stable. The two components of the polymer blend are thermodynamically incompatible, vertical phase separation occurs through solvent evaporation or curing reaction (crosslinking)[106]. The substrate plays an important role in the vertically phase separation process, especially in surface energy. The vertical phase separation into two layers in thin film occurred by using a substrate with a higher surface energy than two components of the polymer blend [107-109].

Polypropylene(PP) is one of the most used substrate for fabricating thin film through bar coating method. Because of its strong hydrophobic nature, it has low surface energy. Various techniques can be applied to surface modification such as chemical, flame and plasma treatment[155]. Among various method, plasma treatment is great method for inducing hydrophilic modification of polymer substrate and increasing the surface energy[156, 157]. In the plasma reactor, gas molecules such as air, oxygen and nitrogen are activated by collisions with electrons, cations and metastable species, and then attacks the polymer surface[158]. Through the low pressure air plasma treatment process, the polar functional group of the PP film is generated, the water contact angle of the PP film is decreased, and the surface energy is increased[159, 160].

In this chapter, we developed a shape memory PEDOT:PSS composite film through substrate modification. First, we modified the PP substrate surface through air plasma treatment. The hydrophilic group was formed on the surface on the intrinsic hydrophobic PP substrate through air plasma treatment, and the surface energy was increased. Well dispersed polymer blend of epoxy resin and PEDOT:PSS was bar-
coated on the plasma treated PP substrate. Plasma treatment increases PP substrate surface energy, forming a continuous matrix of PEDOT:PSS as the dominant component in the bottom layer. Through observations of morphology at various thermal curing times, epoxy islands are formed via nucleation and growth during the dwelling time, and their size increases rapidly upon the onset of water evaporation during thermal curing. The addition of PEDOT:PSS did not affect the shape memory characteristics of PEDOT:PSS/epoxy composite film. Finally, PEDOT:PSS/epoxy composite film maintained electrical conductivity under shape memory performance.

# 4.1 Preparation of PEDOT:PSS/epoxy composite film 4.1.1 Materials

Epoxy resin (EpoFix®; Struer, Denmark) and diamine curing agent (Jeffamine D-230; Huntsman, USA) was prepared for fabricating shape memory polymer composite. The PEDOT:PSS aqueous solution (Clevios PH1000) was purchased from Heraeus. Triton X-100 and Diiodomethane(CH<sub>2</sub>I<sub>2</sub>) were purchased from Sigma–Aldrich. The PP film substrate was purchased from Hansol Paper Co. Ltd. (Seoul, Korea).

#### **4.1.2** Plasma treatment of PP substrate

Surface treatment of commercially Polypropylene (PP) film was performed with a commercially plasma treatment system(GENIA Tech). As shown in Figure 4-1, two

stainless parallel plates with a diameter of 15cm inside the chamber, were coupled with radio frequency at a distance of 5cm. The frequency of the power source was 13.56MHz and maximum power was 50W. The working pressure was adjusted to 0.1Torr and air plasma treatment time of sample varied from 0, 1, 3, and 5mniutes.



Figure 4-1 Schematic illustration of plasma treatment

#### 4.1.3 Fabrication of PEDOT:PSS/epoxy composite film

To prepare the polymer blends, a PEDOT:PSS solution was mixed with epoxy resin, a curing agent and Triton X-100. Based on the PEDOT:PSS aqueous solution, the weight fractions of Triton X-100 was fixed at 10wt%. Due to amphiphilic properties coming from hydrophilic head and hydrophobic end of Triton X-100[161], the miscibility of hydrophilic PEDOT:PSS aqueous solution with the almost hydrophobic epoxy resin was increased(Li, Wu et al. 2019). The weight ratios between epoxy resin and PEDOT:PSS aqueous solution were varied as 1:1, 2:1, and 3:1. The amount of the curing agent was fixed at 28.2 wt% of epoxy resin. The mixtures were stirred at 2000 rpm for 15 minutes to obtain homogeneous suspensions. Then, the blend was poured onto an untreated, 1min, 3min, and 5min air plasma treated PP substrate, and film was fabricated using an bar coater(RDS-75 bar coater). The coated film was maintained at room temperature for 30minutes for phase separation of epoxy resin and PEDOT:PSS, and then cured at 110 °C for 1 h in a vacuum oven.

# 4.2 Characterization of PEDOT:PSS/epoxy composite film

FT-IR (Nicolet 6700; Thermo Fisher Scientific, Waltham, MA, USA) analyses was carried out to identify the surface modification of plasma-treated PP substrate. The surface energy was calculated by measuring dynamic contact angle by sessile-drop method. Surface energy of plasma treated PP film was calculated from contact angle of distilled water and Diiodomethane droplets through dynamic contact angle measurement vehicle (DSA100, KRÜSS GmbH, Germany). Morphological characterizations of bottom layer of shape memory PEDOT:PSS composite film was conducted by field- emission scanning electron microscopy (JSM-7600F, JEOL, USA), (AURIGA, Carl Zeiss, Germany), and optical microscopy (BX51, Olympus, Japan). Image analysis was conducted using Image J software. Electrical characterization was measured using a four-point resistance probe (RM3544, Hioki, Japan). The thermomechanical behavior of the PEDOT:PSS/epoxy composite film was conducted by dynamic mechanical analyzer (DMA Q800, TA Instruments, USA).

## **4.3 Surface modification through air plasma treatment**

To investigate the chemical modification of the surface of polypropylene (PP) film using air plasma treatment, FT-IR analysis was conducted as shown in **Figure 4-2**. FT-IR spectra were obtained for the PP film samples that were subjected to air plasma treatment for 0 min, 1 min, 3 min, and 5 min. The FT-IR spectrum of the untreated PP film showed four major peaks in the range of 3000-2800 cm<sup>-1</sup>, which are typical of aliphatic hydrocarbons. [162]. The spectra bands at 2948 and 2865cm<sup>-1</sup> were assigned to CH<sub>3</sub> asymmetric and symmetric stretching modes respectively, while the spectra bands of 2917 and 2838 cm<sup>-1</sup> were associated with the CH<sub>2</sub> asymmetric and symmetric stretching vibration modes respectively[163]. The absorption peak at 1730cm<sup>-1</sup> appears due to the presence of carbonyl(C=O) groups in aldehydes, carboxylic acid and ketones. The most prominent difference between before and after air plasma treatment can be seen in the region 3750-3250cm<sup>-1</sup>. A broad peak between 3750 and 3250cm<sup>-1</sup> appears after plasma treatment, which can be assigned to OH stretching mode[164]. By using plasma treatment, we increased the hydrophilic groups such as carbonyl groups and –OH on the surface of the PP film through plasma treatment.



Figure 4-2 FT-IR analysis of plasma treated PP film

To verify the hydrophilic nature of the plasma-treated PP film, contact angle measurements were carried out. The contact angle measurement is a reliable technique that determines the surface energy and wettability of the polymer surface. The changes in the surface energy of the plasma-treated PP film were assessed using contact-angle measurements. The surface energy of the plasma-treated PP films was calculated using the geometric mean method based on the contact angle of distilled water and diiodomethane ( $CH_2I_2$ ) droplets, as per the following equation.

$$((1+\cos\theta)\gamma_l = 2\{(\gamma_l^D\gamma_s^D)^{1/2} + (\gamma_l^P\gamma_s^P)^{1/2}\}$$

Where,  $\theta$  is the contact angle of the test liquid on a solid surface, and  $\gamma_l$  and  $\gamma_s$  are the surface energies of the test liquid and the solid surface, respectively.  $\gamma^D$  and  $\gamma^P$ are the dispersive surface and polar interaction surface energy, respectively. The standard values of test liquid are shown in **Table 4-1** [165].

Liquid	σ <sup>D</sup>	σ <sup>P</sup>	$\sigma_{ m total}$
H <sub>2</sub> O	21.8	51	72.8
CH <sub>2</sub> I <sub>2</sub>	50.8	0	50.8

Table 4-1 Surface energy of standard liquids

**Figure 4-3(a)** and **(b)** depict the contact angle measurements of distilled water on air-plasma treated PP films. Prior to treatment, the PP film was found to be hydrophobic with a water contact angle of  $106.3\pm3.4^{\circ}$ , which exceeded  $90^{\circ}$ .

Following plasma treatment, the water contact angle decreased to 44.2±1.7°, 35.1±2.2° and 33.6±0.9° after 1, 3 and 5 minutes of treatment, respectively. This suggests that the surface energy of the PP film was altered by the introduction of hydrophilic groups, thereby increasing the hydrophilic nature of the PP surface. Contact angle measurements are a reliable method to assess the wettability and surface energy of a polymer surface, and the results here indicate the success of air plasma treatment in enhancing the hydrophilic characteristics of the PP film. As the water contact angle decreases, the surface energy of the substrate tends to increase[149]. The dispersive, polar, and total surface energy of the air-plasma treated PP film were determined using the previously mentioned equation, and the results are presented in Figure 4-3(c). The untreated PP substrate had a very low polar surface energy of only 0.01  $mJ \cdot m^{-2}$ , indicating a highly hydrophobic surface. However, air plasma treatment resulted in a rapid increase in the polar surface energy of the PP film. As the treatment time increased, the polar surface energy and total surface energy of the PP film also increased. These results demonstrate that air plasma treatment is an effective method for increasing the hydrophilicity and surface energy of PP film.

# **(a)**





**Figure 4-3** Characterization of air-plasma treated PP substrate (a,b) Contacnt angle(D.I. water) (c) Surface energy

The surface energy of the diamine-cured epoxy based shape memory polymer and PEDOT:PSS was calculated using the contact angle of distilled water and diiodomethane droplet and the equation mentioned above to confirm the morphological characterization due to the difference in surface energy between the substrate and polymer blend. The contact angle of epoxy based shape memory polymer and PEDOT:PSS and the calculated surface energy are shown in **Table 4-2**.

Sample	D.I. water(°)	CH <sub>2</sub> I <sub>2</sub> (°)	Dispersive	Polar	Total
Epoxy resin	84.6	43.5	37.8	2.4	40.2
PEDOT:PSS <sup>[166]</sup>	23.1	23.8	46.6	28.3	74.9

Table 4-2 Contact angle and surface energy of components of polymer blend

## 4.4 Morphology of PEDOT:PSS/epoxy composite film

#### 4.4.1 Effect of plasma treated PP substrate

A solution composed of two immiscible polymer phases separates into different types of structures, from isolated spherical islands to continuous matrices, depending on the relative content of the two polymers [146, 147, 167] When a polymer blend is applied to a substrate that has higher surface energy than either of its components, the component with higher surface energy will be drawn towards the substrate interface because the substrate's high surface energy attracts it, causing it to spread out and adhere to the substrate. On the other hand, the component with lower surface energy will tend to accumulate at the air/film interface instead, where the surface energy is lower. This is because the low surface energy component is less attracted to the high-energy substrate and more attracted to the low-energy air/film interface. [107-109]. To investigate how air plasma treatment affects the morphology of the substrate/film interface layer, we used PP substrates treated with plasma for varying duration. **Figure 4-4** depicts the morphology of the substrate/film interface layer(bottom layer) of PEDOT:PSS/epoxy composite films with a weight ratio of

1:2 of PEDOT:PSS and epoxy when plasma-treated substrates were used. The weight ratio of PEDOT:PSS to epoxy resin, without water, is 1:153.8, leading to PEDOT:PSS existing in island form in the overall composite film. As expected, when an untreated PP substrate is used, PEDOT:PSS is dispersed throughout the substrate/film interface (bottom layer) of the composite film, as illustrated in **Figure 4-4(a)**.

However, when a plasma-treated PP substrate was used, the morphology of the bottom layer undergoes a significant changed. We observed that the epoxy domains distributed as island shapes within the continuous PEDOT:PSS matrix, and we confirmed that the continuous matrix was PEDOT:PSS by performing EDS mapping of S atoms. Although the untreated PP film (29.6  $mJ \cdot m^{-2}$ ) has a lower surface energy than that of epoxy resin ( $40.2mJ \cdot m^{-2}$ ) and PEDOT:PSS ( $74.9 mJ \cdot m^{-2}$ ), plasma treatment for 1,3 and 5 minutes respectively increased the surface energy to 60.9, 61.8, and 64.4  $mJ \cdot m^{-2}$ , creating a surface energy between epoxy resin and PEDOT:PSS. This enabled the high surface energy PEDOT:PSS to accumulate around the substrate with relatively high energy compared to the air/film interface. Consequently, the morphology of the composite film was visibly altered due to the plasma treatment.



**Figure 4-4** Surface morphology of the substrate/film interface(bottom layer) in the composite film with PEDOT:PSS to epoxy weight ratio of 1:2 according to airplasma treatment time (left) SEM images (right) elemental sulfur mapping images (a) 0min (b) 1min (c) 3min (d) 5min (scale bar: 100um)

We examined the influence of plasma treatment on the bottom layer's morphology in a composite film by scrutinizing its vertical cross-sectional morphology. SEM images of the cross-section of a composite film with a 1:2 weight ratio of PEDOT:PSS and epoxy were acquired at two different plasma treatment times, 0 and 5 minutes, as depicted in Figure 4-5(a). Although there was no significant visual difference, a thorough investigation of the sulfur element EDS line mapping from the substrate/film interface to the film/air interface revealed substantial differences. To ensure reliability, the average value of 10 EDS lines for each cross-section image was obtained. In Figure 4-5(b), we examined the changes in sulfur content normalized by film thickness. When a PP substrate without plasma treatment was used, sulfur was evenly distributed in most thicknesses. However, when a PP film treated with 5 minutes of plasma treatment was used as the substrate, the sulfur content sharply increased at around 18.4% of the total thickness. This suggests that plasma treatment increased the surface energy, leading to the accumulation of PEDOT:PSS around the substrate, resulting in its dominance at the substrate/film interface. Our results indicate that plasma treatment can be a powerful technique for controlling the morphology of composite films, with PEDOT:PSS forming a continuous matrix and a small amount of epoxy domains existing as isolated islands, as depicted in Figure 4-4.



**Figure 4-5** Cross-sectional morphology of composite film according to plasma treatment time (a) (up) 0min (down) 5min (b) EDS line mapping of S atom (scale bar: 10um)

To elucidate the mechanism behind the formation of the bottom layer morphology, we conducted observations of morphology at various thermal curing times. A dwelling time of 30 minutes was designated as the point at which accumulation of PEDOT:PSS takes place due to differences in substrate surface energy, with subsequent times defined as 0 minutes. After undergoing vertical phase separation, PEDOT:PSS becomes dominant at the substrate/film interface, whereas epoxy domains exist in the form of islands through nucleation and growth even prior to thermal curing (see **Figure 4-6**). During the process of thermal curing at 110°C, water evaporation from the PEDOT:PSS aqueous solution occurs simultaneously with crosslinking of the epoxy resin. It is noteworthy that no other spherical domains, except for the existing epoxy islands, are formed during thermal curing, and the size of the pre-existing epoxy domains increases. This implies that water evaporates from the phase-separated epoxy domain that has not yet cured.

**Figure 4-7** shows the numerical data for the size of the epoxy domains as a function of thermal curing time. To ensure reliability, fifteen sites with phase-separated epoxy island's diameters of both over and under 200  $\mu$ m were chosen, and the diameter of the epoxy islands was measured over time. The results show that the size of the epoxy islands increases sharply at the onset of water evaporation at one minute for all sites, regardless of their initial diameter. The average diameter of epoxy islands with diameters over 200  $\mu$ m increased by approximately 26.2% from 303.9±65.7  $\mu$ m at 0 minutes to 383.5±62.7  $\mu$ m, while the average diameter of those with diameters under

200  $\mu$ m increased by approximately 41.9% from 120.5±21.1  $\mu$ m to 171.1±19.0  $\mu$ m. However, after one minute, the size of the epoxy islands increased by only 7.3% and 19.8%, respectively, and then saturated until complete curing. In conclusion, plasma treatment increases the surface energy of the PP substrate, making the PEDOT:PSS dominant in the bottom layer, which forms a continuous matrix. Furthermore, the size of the initially created epoxy domains increases during the thermal curing process. As a result, changes in the substrate's surface energy can lead to the formation of a sea-island structure with a component having a low weight ratio forming a continuous matrix.



**Figure 4-6** Development of continuous PEDOT:PSS matrix/ epoxy island morphology according to thermal curing time in the composite film with PEDOT:PSS to epoxy weight ratio of 1:2 (scale bar: 100um)



**Figure 4-7** Epoxy island size according to thermal curing time in the composite film with PEDOT:PSS to epoxy weight ratio of 1:2 (a) Diameter bigger than 200um (b) Diameter smaller than 200um (scale bar: 100um)

# 4.4.2 Effect of weight ratio

The morphological difference between the PEDOT:PSS/epoxy composite films were investigated according to the weight ratio of PEDOT:PSS to epoxy resin in the solution(1:1, 1:2, 1:3 and 1:4). **Figure 4-8** illustrates the morphology of the bottom layer according to the weight ratio of PEDOT:PSS to epoxy resin. When the weight ratio of epoxy is 4 or higher, it can be observed that PEDOT:PSS exists in isolated particle form.



1:1

1:2

1:3

Figure 4-8 Surface morphology inversion of bottom layer in the composite film according to PEDOT:PSS to epoxy in the solution (scale bar: 100um)

However, the weight ratio is up to 1:3, a sea-island structure is formed regardless of the ratio, with epoxy existing in the form of spherical islands surrounded by PEDOT:PSS, which forms a continuous matrix. EDS mapping for S atoms confirmed that the continuous matrix is composed of PEDOT:PSS as shown in **Figure 4-9**. The diameters of epoxy islands according to the weight ratios are shown in **Figure 4-10**. As shown in **Figure 4-10**, the average diameter increases with increasing epoxy weight ratio, with values of 141.8±49.2um, 157.7±38.2um, and 236.1±63.1um for weight ratios of 1:1, 1:2, and 1:3, respectively. In summary, as the ratio of epoxy increases up to 3, the proportion of epoxy in the bottom layer increases, resulting in an increase in the diameter of epoxy islands. Eventually, when the ratio of epoxy becomes 4 or more, the continuous matrix in the bottom layer undergoes inversion from PEDOT:PSS to epoxy.



**Figure 4-9** Surface morphology of the bottom layer in the composite film according to epoxy to PEDOT:PSS weight ratio in the solution(left) Optical image (middle) SEM image (right) sulfur mapping image: (a) 1:1 (b) 2:1 (c) 3:1 (scale bar: 100um)



**Figure 4-10** Characterization of epoxy island diameter according to weight ratio (a) size distribution of epoxy island (b) comparison

# 4.5 Shape memory PEDOT:PSS/epoxy composite film

The thermomechanical behavior of the PEDOT:PSS/epoxy composite films using air- plasma treated PP substrate was measured using a dynamic mechanical analyzer (DMA). The dimensions of the test specimens were  $10 \times 5 \times 0.1 \text{ mm}^3$  (length  $\times$  width  $\times$  thickness). Figure 4-11 (a) shows the storage modulus of the pure epoxy-based shape memory polymer film and the PEDOT:PSS/epoxy composite film. The storage modulus of PEDOT:PSS varied between 1.0 and 7.5GPa between 250 and - 150°C[168], which was over 3 times higher than the pure epoxy-based shape memory polymer film (Fig. 4-11(a) black line; 355.8MPa). It was clearly observed that the storage modulus of PEDOT:PSS/epoxy composite film was higher than that

of pure epoxy shape memory film. The storage modulus of composite film with a plasma treatment time of 1, 3, and 5minutes was 1391.4, 1498.5, and 1600.5 MPa respectively, which was enhanced by around 420.7% compared to pure epoxy-based shape memory film. Due to intrinsically high storage modulus of PEDOT:PSS, the storage modulus increased with the addition of 33% of PEDOT:PSS aqueous solution.

The  $T_g$  values were identified by tan  $\delta$  peak which was the peak point and shown in **Figure 4-11(b)**. The pure epoxy-based shape memory polymer without PEDOT:PSS has  $T_g$  at 71.67 °C, which is similar to previous results at our laboratory[169]. The

PEDOT:PSS aqueous solution used is composed of 98.7% by weight of water. When water is mixed with epoxy resin, interactions occur between the resin and water molecules, allowing water to act as a plasticizer within the resin system. This results in a change in the molecular structure of the resin and a lowering of the glass transition temperature. In the case of an PEDOT:PSS/epoxy composite film[170-172]. However, as can be seen in **Figure 4-6**, most of the water evaporates in just 1minute at 110°C during the thermal curing process, and the interaction between water and epoxy resin during the dwelling time causes the glass transition to decrease slightly depending on the plasma treatment time of 1,3, and 5minutes, with values of 64.3, 69.8, and 65.1, respectively, compared to the pure epoxy-based shape memory film.



Figure 4-11 Thermomechanical characterization of PEDOT:PSS-epoxy composite film according to plasma treatment time (a) Storage modulus (b) tan  $\delta$ 

In order to verify the shape memory effect of PEDOT:PSS/epoxy composite film,

a model system is schematically shown in **Fig. 4-12(a)**. Here the PEDOT:PSS/epoxy composite film is first heated at high temperature above  $T_g$  (75°C) and deformed as bending specimen. Then, deformations of film was maintained and cooled down to room temperature. Upon re-heating to high temperature at 75°C, film recover its original shape. The real image of shape memory effect of PEDOT:PSS/epoxy composite film is shown in **Figure 4-12(b)**. We heated the composite film at 75°C in hot oven. Then we bended the PEDOT:PSS/epoxy composite 180° and cooled down to room temperature to fix the intermediate state. Finally film recovered its original shape like film when heating up to 75°C. The shape fixity and recovery ratio was calculated using the following equations.

$$R_{f}(\%) = (\theta_{0} - \theta_{int2}) / (\theta_{o} - \theta_{int1}) * 100$$
$$R_{r}(\%) = (\theta_{recov} - \theta_{int2}) / (\theta_{o} - \theta_{int1}) * 100$$

Here,  $\theta_{recov}$ ,  $\theta_{int1}$ ,  $\theta_{int2}$  and  $\theta_o$  denote the bending angles of composite shape at recovery, intermediate 1, intermediate 2 state and original state.

The resistance PEDOT:PSS/epoxy composite film at original, intermediate and recovery state was listed in **Table 4-3**. The relative resistance ratio,  $R/R_0$  was measured in the original, intermediated and recovery states to confirm that the electrical conductivity was maintained when the shape memory characteristics are

present (**Fig. 4-13**). Regardless of the air plasma treatment time, the electrical conductivity was maintained as  $R/R_0$  ratio was under 1.2 at intermediate 180° bending state and under 1.1 at recovery state. As a result, the PEDOT:PSS/epoxy composite film has electrical conductivity due to the accumulation of PEDOT:PSS on the bottom layer and also has shape memory characteristics, and has electrical conductivity even when it shows shape memory characteristics.



**Figure 4-12** Shape memory effect of PEDOT:PSS composite film (a) Schematic illustration of shape memory behavior (b) Real image of shape memory effect



Figure 4-13 Relative resistance change according to shape memory state

Table 4-3 Electrical and shape memory characterization according to plasma treatment time

	Original	Intermediate	Recovery	$R_{\mathrm{f}}$	R <sub>r</sub>
1min	1.61±0.23	1.88±0.20	1.78±0.21	98.7%	92.9%
3min	1.34±0.07	1.53±0.07	1.46±0.09	98.7%	93.0%
5min	1.33±0.14	1.52±0.13	1.44±0.15	98.9%	93.1%

## 4.6 Summary

In this chapter, we developed PEDOT:PSS/epoxy shape memory composite film through air plasma treated PP substrate. The air plasma treatment was used to modify the surface chemistry of PP film, resulting in an increase in hydrophilic groups and surface energy. Contact angle measurements confirmed the increase in hydrophilicity, with a decrease in water contact angle and an increase in polar surface energy. By subjecting the PP substrate to plasma treatment, the surface energy is increased, allowing for the accumulation of high surface energy PEDOT:PSS at the bottom layer. This results in the formation of a continuous matrix of PEDOT:PSS and isolated epoxy islands at the bottom layer of the composite film. Upon thermal curing, the size of the epoxy islands increases as the water evaporates from the PEDOT:PSS solution and the epoxy resin crosslinks. The addition of PEDOT:PSS enhances the storage modulus and reduces the glass transition temperature (Tg), but does not affect the shape memory effect of the composite film. The resulting PEDOT:PSS/epoxy composite film exhibits excellent shape memory performance, with high fixity and recovery ratios, while maintaining its electrical conductivity.

# **Chapter 5. Conclusions**

This study aimed to fabricate PEDOT:PSS based electrode using novel method of polymerization of PEDOT:PSS and develop transparent, stretchable and shape memory electrodes for deformable electronics using them. A series of research was carried out to achieve goals, from which the following conclusions were reached.

A novel method of in- situ synthesis of conductive PEDOT:PSS-AgNP nanocomposites through spontaneous redox reaction without acid catalyst. Two criteria was proposed to enhance the quality of PEDOT:PSS AgNP nanocomposites. High-quality PEDOT:PSS-AgNP nanocomposites were found to be formed in the organic solvent; acetonitrile. By adding a small quantity of PVP, it was possible to create a nanocomposite consisting a smaller and more evenly distributed AgNPs, without the requirement of an acid catalyst. Next, the formation of PEDOT:PSS-AgNP nanocomposite with or without PVP was proposed. Finally, the fiber containing PEDOT:PSS-AgNP was fabricated through electrospinning and UV irradiation, having good electrical conductivity.

A simple method for fabricating stretchable and transparent PEDOT:PSS based composite film was designed. We investigated the effect of affinity to substrate of polymer blend compositions. A dramatic vertical phase separation between PEDOT:PSS and PDMS according to surface energies difference. The morphologies of bottom layer was analyzed. Although PEDOT:PSS has lower weight fraction, continuous PEDOT:PSS matrix distributed with spherical PDMS islands. Regardless of the weight ratio used, the morphology of the bottom layer remains relatively similar. Next, the mechanism of morphology of bottom layer was proposed. Upon curing at 100°C, any water or volatile substances in the PEDOT:PSS phase of the lower layer evaporate, creating gaps which are then filled with PDMS from the phase-separated top layer. Finally, the fabricated PDMS/PEDOT:PSS composite films exhibited a low sheet resistance of ~66  $\Omega$ ·sq<sup>-1</sup>, visible transmittance of 85%, and a relative sheet resistance change (R/R<sub>0</sub>) of 10 upon stretching with up to 150% strain, demonstrating their excellent electrical, mechanical, and optical properties.

Shape memory composite film was fabricated using PEDOT:PSS and an epoxy resin shape memory polymer. The shape memory PEDOT:PSS composite was fabricated through air plasma treatment, simple polymer blending, and bar coating techniques. Vertical phase separation was induced through air plasma-treated PP substrate, and the morphology of bottom layer was similar to that of above section, and a conductive pathway was formed. The addition of PEDOT:PSS to the composite film increases the storage modulus and lowers the glass transition temperature (Tg), but does not have an impact on the shape memory effect of the film. As a result, the PEDOT:PSS/epoxy composite film maintains its electrical conductivity and displays exceptional shape memory characteristics, with high fixity and recovery ratios.

# Reference

- Chandrasekhar, P., Conducting polymers, fundamentals and applications: a practical approach. 2013: Springer Science & Business Media.
- 2. Skotheim, T.A. and J. Reynolds, *Conjugated polymers: theory, synthesis, properties, and characterization.* 2006: CRC press.
- 3. Skotheim, T.A., *Handbook of conducting polymers*. 1997: CRC press.
- 4. Rivnay, J., et al., *Structural control of mixed ionic and electronic transport in conducting polymers.* Nature communications, 2016. **7**(1): p. 11287.
- 5. Horii, T., et al., *Correlation between the hierarchical structure and electrical conductivity of PEDOT/PSS.* Polymer Journal, 2015. **47**(10): p. 695-699.
- Ha, Y.H., et al., *Towards a transparent, highly conductive poly (3, 4-ethylenedioxythiophene)*. Advanced Functional Materials, 2004. **14**(6): p. 615-622.
- 7. Corradi, R. and S. Armes, *Chemical synthesis of poly (3, 4-ethylenedioxythiophene).* Synthetic metals, 1997. **84**(1-3): p. 453-454.
- Hupe, J., G. Wolf, and F. Jonas, *DMS-E--a recognised principle with a novel basis. Through-hole contacting of printed circuit boards using conductive polymers.* Galvanotechnik(Germany), 1995. 86(10): p. 3404-3411.
- 9. Im, S.G., et al., Conformal coverage of poly (3, 4-ethylenedioxythiophene) films with tunable nanoporosity via oxidative chemical vapor deposition. ACS nano, 2008. 2(9): p. 1959-1967.
- 10. Cosnier, S. and A. Karyakin, *Electropolymerization: concepts, materials and applications*. 2011: John Wiley & Sons.
- Imisides, M.D., et al., *The use of electropolymerization to produce new* sensing surfaces: a review emphasizing electrode position of heteroaromatic compounds. Electroanalysis, 1991. 3(9): p. 879-889.
- 12. Tanaka, K., et al., *A study of the electropolymerization of thiophene.* Synthetic metals, 1988. **24**(3): p. 203-215.
- 13. Sarac, A.S., *Electropolymerization*. Encyclopedia of Polymer Science and Technology, 2002.
- 14. Benoudjit, A., M.M. Bader, and W.W.A.W. Salim, *Study of electropolymerized PEDOT: PSS transducers for application as*

*electrochemical sensors in aqueous media.* Sensing and bio-sensing research, 2018. **17**: p. 18-24.

- 15. Zajdel, T.J., et al., *PEDOT: PSS-based multilayer bacterial-composite films for bioelectronics.* Scientific reports, 2018. **8**(1): p. 15293.
- 16. Andreoli, E., et al., *PPy: PSS as alternative to PEDOT: PSS in organic photovoltaics.* Synthetic Metals, 2013. **185**: p. 71-78.
- Zotti, G., et al., *Electrochemical and XPS studies toward the role of monomeric and polymeric sulfonate counterions in the synthesis, composition, and properties of poly (3, 4-ethylenedioxythiophene).* Macromolecules, 2003. **36**(9): p. 3337-3344.
- Pettersson, L.A., et al., Spectroscopic ellipsometry studies of the optical properties of doped poly (3, 4-ethylenedioxythiophene): an anisotropic metal. Thin Solid Films, 1998. 313: p. 356-361.
- Bhattacharyya, D., et al., Vapor phase oxidative synthesis of conjugated polymers and applications. Journal of Polymer Science Part B: Polymer Physics, 2012. 50(19): p. 1329-1351.
- 20. Brooke, R., et al., *Recent advances in the synthesis of conducting polymers from the vapour phase.* Progress in Materials Science, 2017. **86**: p. 127-146.
- Jiang, Y., T. Liu, and Y. Zhou, *Recent advances of synthesis, properties, film fabrication methods, modifications of poly (3, 4-ethylenedioxythiophene), and applications in solution-processed photovoltaics.* Advanced Functional Materials, 2020. **30**(51): p. 2006213.
- 22. Elschner, A., et al., *PEDOT: principles and applications of an intrinsically conductive polymer*. 2010: CRC press.
- Groenendaal, L., et al., *Poly (3, 4-ethylenedioxythiophene) and its derivatives: past, present, and future.* Advanced materials, 2000. **12**(7): p. 481-494.
- Groenendaal, L., et al., *Electrochemistry of poly (3, 4-alkylenedioxythiophene) derivatives.* Advanced Materials, 2003. **15**(11): p. 855-879.
- 25. Rozlosnik, N., New directions in medical biosensors employing poly (3, 4-

*ethylenedioxy thiophene) derivative-based electrodes.* Analytical and bioanalytical chemistry, 2009. **395**: p. 637-645.

- Groenendaal, L., G. Zotti, and P. Aubert, *Way bright, SM, and Reynolds, JR.* Adv. Mater, 2003. 15: p. 855.
- 27. Ventosa, E., et al., One-pot synthesis of gold/poly(3,4ethylendioxythiophene) nanocomposite. Journal of Nanoparticle Research, 2012. 14(1): p. 661.
- 28. Wang, Y., et al., *In situ synthesis of PEDOT:PSS@AgNPs nanocomposites.* Synthetic Metals, 2017. **230**: p. 1-6.
- 29. Balamurugan, A., S.M.J.E.A.I.J.D.t.F. Chen, and P.A.o. Electroanalysis, *Silver nanograins incorporated PEDOT modified electrode for electrocatalytic sensing of hydrogen peroxide.* 2009. **21**(12): p. 1419-1423.
- 30. Kim, D.H., et al., *Epidermal electronics.* Science, 2011. **333**(6044): p. 838-43.
- 31. Kaltenbrunner, M., et al., *An ultra-lightweight design for imperceptible plastic electronics.* Nature, 2013. **499**(7459): p. 458-63.
- 32. Xu, S., et al., *Soft microfluidic assemblies of sensors, circuits, and radios for the skin.* Science, 2014. **344**(6179): p. 70-4.
- Sekitani, T., et al., *Stretchable active-matrix organic light-emitting diode display using printable elastic conductors.* Nature materials, 2009. 8(6): p. 494-499.
- 34. Li, S., et al., A stretchable multicolor display and touch interface using photopatterning and transfer printing. Advanced Materials, 2016. 28(44):
   p. 9770-9775.
- Yokota, T., et al., *Ultraflexible organic photonic skin.* Science advances, 2016. 2(4): p. e1501856.
- Choi, M.K., et al., *Extremely vivid, highly transparent, and ultrathin quantum dot light-emitting diodes.* Advanced Materials, 2018. **30**(1): p. 1703279.
- Lee, W., et al., *Nonthrombogenic, stretchable, active multielectrode array* for electroanatomical mapping. Science advances, 2018. **4**(10): p. eaau2426.

- 38. Park, S., et al., *Self-powered ultra-flexible electronics via nano-gratingpatterned organic photovoltaics.* Nature, 2018. **561**(7724): p. 516-521.
- Webb, R.C., et al., Ultrathin conformal devices for precise and continuous thermal characterization of human skin. Nature materials, 2013. 12(10): p. 938-944.
- 40. Kim, J., et al., *Stretchable silicon nanoribbon electronics for skin prosthesis.* Nature communications, 2014. **5**(1): p. 1-11.
- Jeong, J.W., et al., *Epidermal Electronics: Materials and Optimized Designs* for Human-Machine Interfaces Via Epidermal Electronics (Adv. Mater. 47/2013). Advanced Materials, 2013. 25(47): p. 6776-6776.
- 42. Gao, W., et al., *Fully integrated wearable sensor arrays for multiplexed in situ perspiration analysis.* Nature, 2016. **529**(7587): p. 509-514.
- 43. Kim, D.H., et al., *Flexible and Stretchable Electronics for Biointegrated Devices.* Annual Review of Biomedical Engineering, Vol 14, 2012. **14**: p. 113-128.
- 44. Trung, T.Q. and N.E. Lee, *Materials and devices for transparent stretchable electronics.* Journal of Materials Chemistry C, 2017. **5**(9): p. 2202-2222.
- 45. Ye, S., et al., *Metal nanowire networks: the next generation of transparent conductors.* Adv Mater, 2014. **26**(39): p. 6670-87.
- 46. Hecht, D.S., L. Hu, and G. Irvin, *Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures.*Advanced materials, 2011. 23(13): p. 1482-1513.
- 47. Zhang, J., et al., *Stretchable transparent electrode arrays for simultaneous electrical and optical interrogation of neural circuits in vivo.* Nano letters, 2018. 18(5): p. 2903-2911.
- 48. Zhang, Y., et al., *Polymer-embedded carbon nanotube ribbons for stretchable conductors.* Advanced Materials, 2010. **22**(28): p. 3027-3031.
- 49. Kim, K.S., et al., *Large-scale pattern growth of graphene films for stretchable transparent electrodes.* nature, 2009. **457**(7230): p. 706-710.
- 50. Liu, N., et al., *Ultratransparent and stretchable graphene electrodes.* Science advances, 2017. **3**(9): p. e1700159.
- 51. Sannicolo, T., et al., Metallic nanowire-based transparent electrodes for

*next generation flexible devices: a review.* Small, 2016. **12**(44): p. 6052-6075.

- Huang, Q. and Y. Zhu, *Gravure printing of water-based silver nanowire ink* on plastic substrate for flexible electronics. Scientific reports, 2018. 8(1): p. 1-10.
- Lee, C.-J., et al., *Crack-induced Ag nanowire networks for transparent, stretchable, and highly sensitive strain sensors.* Scientific Reports, 2017.
   7(1): p. 1-8.
- 54. Yoon, J., et al., Fabrication of a Highly Stretchable, Wrinkle-Free Electrode with Switchable Transparency Using a Free-Standing Silver Nanofiber Network and Shape Memory Polymer Substrate. Macromolecular Rapid Communications, 2020. 41(13): p. 2000129.
- 55. Zhang, C., et al., *Stretchable transparent electrodes with solutionprocessed regular metal mesh for an electroluminescent light-emitting film.* ACS applied materials & interfaces, 2018. **10**(24): p. 21009-21017.
- 56. Guo, C.F., et al., *Highly stretchable and transparent nanomesh electrodes made by grain boundary lithography.* Nature communications, 2014. 5(1):
   p. 1-8.
- 57. Jang, H.Y., et al., *Fabrication of metallic nanomesh: Pt nano-mesh as a proof of concept for stretchable and transparent electrodes.* Chemistry of Materials, 2013. **25**(17): p. 3535-3538.
- Zhou, X., et al., A sensitive, stretchable and transparent strain sensor with sandwiched structures of PDMS/PEDOT: PSS/PDMS. Journal of Nanoelectronics and Optoelectronics, 2018. 13(11): p. 1651-1655.
- 59. Yuan, W., et al. *New electrode materials for dielectric elastomer actuators.* in *Electroactive Polymer Actuators and Devices (EAPAD) 2007.* 2007. SPIE.
- Lipomi, D.J., et al., *Electronic properties of transparent conductive films of PEDOT: PSS on stretchable substrates.* Chemistry of Materials, 2012. 24(2): p. 373-382.
- 61. Ouyang, J., "Secondary doping" methods to significantly enhance the conductivity of PEDOT: PSS for its application as transparent electrode of optoelectronic devices. Displays, 2013. **34**(5): p. 423-436.
- Sun, K., et al., *Transparent conductive oxide-free perovskite solar cells with PEDOT: PSS as transparent electrode.* ACS applied materials & interfaces, 2015. 7(28): p. 15314-15320.
- 63. Yu, Z., et al., *PEDOT: PSS films with metallic conductivity through a treatment with common organic solutions of organic salts and their application as a transparent electrode of polymer solar cells.* ACS applied materials & interfaces, 2016. **8**(18): p. 11629-11638.
- 64. Zhang, X., et al., *Highly conductive PEDOT: PSS transparent electrode prepared by a post-spin-rinsing method for efficient ITO-free polymer solar cells.* Solar Energy Materials and Solar Cells, 2016. **144**: p. 143-149.
- Sun, K., et al., *Review on application of PEDOTs and PEDOT: PSS in energy conversion and storage devices.* Journal of Materials Science: Materials in Electronics, 2015. 26(7): p. 4438-4462.
- Marzocchi, M., et al., *Physical and electrochemical properties of PEDOT: PSS as a tool for controlling cell growth.* ACS applied materials & interfaces, 2015. 7(32): p. 17993-18003.
- Isaksson, J., et al., *Electronic control of Ca2+ signalling in neuronal cells using an organic electronic ion pump.* Nature materials, 2007. 6(9): p. 673-679.
- He, H., et al., *Biocompatible conductive polymers with high conductivity* and high stretchability. ACS applied materials & interfaces, 2019. **11**(29): p. 26185-26193.
- 69. Fan, Z., et al., *Significantly enhanced thermoelectric properties of PEDOT: PSS films through sequential post-treatments with common acids and bases.* Advanced Energy Materials, 2017. **7**(8): p. 1602116.
- Liu, S.H., et al., *Efficient ITO-free organic light-emitting devices with dual-functional PSS-rich PEDOT: PSS electrode by enhancing carrier balance.* Journal of Materials Chemistry C, 2019. **7**(18): p. 5426-5432.
- 71. Zhou, W., et al., *High conductivity PEDOT: PSS thin films affording improved open circuit voltages in PEDOT: PSS-Si heterojunction solar cells.* Materials Letters, 2021: p. 131466.
- 72. Cheng, T., et al., Inkjet-printed flexible, transparent and aesthetic energy

*storage devices based on PEDOT: PSS/Ag grid electrodes.* Journal of Materials Chemistry A, 2016. **4**(36): p. 13754-13763.

- Wen, Y. and J. Xu, Scientific importance of water-processable PEDOT–PSS and preparation, challenge and new application in sensors of its film electrode: a review. Journal of Polymer Science Part A: Polymer Chemistry, 2017. 55(7): p. 1121-1150.
- 74. Kayser, L.V. and D.J. Lipomi, *Stretchable conductive polymers and composites based on PEDOT and PEDOT: PSS.* Advanced Materials, 2019.
   31(10): p. 1806133.
- 75. Lang, U., N. Naujoks, and J. Dual, *Mechanical characterization of PEDOT: PSS thin films.* Synthetic Metals, 2009. **159**(5-6): p. 473-479.
- Kim, D.C., et al., Material-based approaches for the fabrication of stretchable electronics. Advanced Materials, 2020. 32(15): p. 1902743.
- Li, Y., R. Tanigawa, and H. Okuzaki, *Soft and flexible PEDOT/PSS films for applications to soft actuators.* Smart materials and structures, 2014. 23(7):
   p. 074010.
- 78. Savagatrup, S., et al., *Plasticization of PEDOT: PSS by common additives* for mechanically robust organic solar cells and wearable sensors. Advanced Functional Materials, 2015. 25(3): p. 427-436.
- 79. Oh, J.Y., et al., *Conducting polymer dough for deformable electronics.* Advanced Materials, 2016. **28**(22): p. 4455-4461.
- Pang, H., et al., *Conductive polymer composites with segregated structures*. Progress in Polymer Science, 2014. **39**(11): p. 1908-1933.
- Li, P., et al., *Transparent soft robots for effective camouflage.* Advanced Functional Materials, 2019. 29(37): p. 1901908.
- Lipomi, D.J., et al., *Electronic Properties of Transparent Conductive Films of PEDOT:PSS on Stretchable Substrates.* Chemistry of Materials, 2012.
   24(2): p. 373-382.
- Bauzon, E., et al., Stretchable and transparent conductive PEDOT: PSSbased electrodes for organic photovoltaics and strain sensors applications. Advanced Functional Materials, 2020. 30(28): p. 2001251.
- 84. Teo, M.Y., et al., *Highly stretchable and highly conductive PEDOT: PSS/ionic*

*liquid composite transparent electrodes for solution-processed stretchable electronics.* ACS applied materials & interfaces, 2017. **9**(1): p. 819-826.

- Wen, Z., et al., A wrinkled PEDOT: PSS film based stretchable and transparent triboelectric nanogenerator for wearable energy harvesters and active motion sensors. Advanced Functional Materials, 2018. 28(37): p. 1803684.
- Kraft, U., et al., *Ink development and printing of conducting polymers for intrinsically stretchable interconnects and circuits.* Advanced Electronic Materials, 2020. 6(1): p. 1900681.
- Vosgueritchian, M., D.J. Lipomi, and Z. Bao, *Highly conductive and transparent PEDOT: PSS films with a fluorosurfactant for stretchable and flexible transparent electrodes.* Advanced functional materials, 2012. 22(2): p. 421-428.
- Lo, L.-W., et al., An inkjet-printed PEDOT: PSS-based stretchable conductor for wearable health monitoring device applications. ACS Applied Materials & Interfaces, 2021. 13(18): p. 21693-21702.
- Sawyer, E.J., et al., *Large increase in stretchability of organic electronic materials by encapsulation*. Extreme Mechanics Letters, 2016. 8: p. 78-87.
- 90. Fan, X., et al., *Highly sensitive, durable and stretchable plastic strain sensors using sandwich structures of PEDOT: PSS and an elastomer.* Materials Chemistry Frontiers, 2018. 2(2): p. 355-361.
- 91. Won, Y., et al., *Biocompatible, Transparent, and High-Areal-Coverage Kirigami PEDOT: PSS Electrodes for Electrooculography-Derived Human– Machine Interactions.* ACS sensors, 2021. **6**(3): p. 967-975.
- 92. Bandodkar, A.J., et al., *All-Printed Stretchable Electrochemical Devices.* Advanced Materials, 2015. **27**(19): p. 3060-3065.
- Lee, J.H., et al., *Highly conductive, stretchable, and transparent PEDOT: PSS electrodes fabricated with triblock copolymer additives and acid treatment.* ACS applied materials & interfaces, 2018. **10**(33): p. 28027-28035.
- 94. Wang, Y., et al., *A highly stretchable, transparent, and conductive polymer.*

Science advances, 2017. 3(3): p. e1602076.

- 95. Takei, A., et al., *Stretchable and durable Parylene/PEDOT: PSS/Parylene multi-layer induced by plastic deformation for stretchable device using functionalized PDMS.* AIP Advances, 2020. **10**(2): p. 025205.
- 96. Liu, C., H. Qin, and P. Mather, *Review of progress in shape-memory polymers.* Journal of materials chemistry, 2007. **17**(16): p. 1543-1558.
- 97. Xu, J. and J. Song, *Thermal responsive shape memory polymers for biomedical applications.* Biomed. Eng. Front. Chall, 2011: p. 125-142.
- Baniasadi, M., et al., Crack self-healing of thermo-responsive shape memory polymers with application to control valves, filtration, and drug delivery capsule. European Journal of Mechanics-A/Solids, 2021. 85: p. 104093.
- 99. Zarek, M., et al., *3D printing of shape memory polymers for flexible electronic devices.* Advanced Materials, 2016. **28**(22): p. 4449-4454.
- 100. Park, M.U., S.M. Lee, and D.-w. Chung, *Model system of cross-linked PEDOT: PSS adaptable to an application for an electrode with enhanced water stability.* Synthetic Metals, 2019. **258**: p. 116195.
- 101. Solazzo, M., et al., PEDOT: PSS interfaces stabilised using a PEGylated crosslinker yield improved conductivity and biocompatibility. Journal of Materials Chemistry B, 2019. 7(31): p. 4811-4820.
- 102. Si, P., et al., PEDOT: PSS nano-gels for highly electrically conductive silver/epoxy composite adhesives. Journal of Materials Science: Materials in Electronics, 2018. 29(3): p. 1837-1846.
- Bucella, S.G., et al., *Macroscopic and high-throughput printing of aligned nanostructured polymer semiconductors for MHz large-area electronics.* Nature communications, 2015. 6(1): p. 1-10.
- 104. Fang, R.H., et al., *Cell membrane coating nanotechnology.* Advanced Materials, 2018. **30**(23): p. 1706759.
- 105. Nketia-Yawson, B., et al., *Bar-coated high-performance organic thin-film transistors based on ultrathin PDFDT polymer with molecular weight independence.* Organic Electronics, 2016. **29**: p. 88-93.
- 106. Verkholantsev, V., *Nonhomogeneous-in-layer coatings.* Progress in organic

coatings, 1985. 13(2): p. 71-96.

- 107. Wang, X., et al., Self-stratified semiconductor/dielectric polymer blends: Vertical phase separation for facile fabrication of organic transistors. Journal of Materials Chemistry C, 2013. 1(25): p. 3989-3998.
- Karagiannidis, P., et al., Evolution of vertical phase separation in P3HT: PCBM thin films induced by thermal annealing. Materials Chemistry and Physics, 2011. 129(3): p. 1207-1213.
- Pavlopoulou, E., et al., *Phase separation-driven stratification in conventional and inverted P3HT: PCBM organic solar cells.* Organic electronics, 2013. 14(5): p. 1249-1254.
- 110. You, H., et al., *Synthesis of colloidal metal and metal alloy nanoparticles for electrochemical energy applications.* 2013. **42**(7): p. 2880-2904.
- 111. Evanoff Jr, D.D. and G. Chumanov, *Synthesis and optical properties of silver nanoparticles and arrays.* ChemPhysChem, 2005. **6**(7): p. 1221-1231.
- 112. Morones, J.R., et al., *The bactericidal effect of silver nanoparticles.* Nanotechnology, 2005. **16**(10): p. 2346.
- 113. Kapoor, S., *Preparation, characterization, and surface modification of silver particles.* Langmuir, 1998. **14**(5): p. 1021-1025.
- 114. Wen, Y. and J.J.J.O.P.S.P.A.P.C. Xu, Scientific Importance of Water-Processable PEDOT–PSS and Preparation, Challenge and New Application in Sensors of Its Film Electrode: A Review. 2017. 55(7): p. 1121-1150.
- 115. Wang, W., S. Efrima, and O. Regev, *Directing Oleate Stabilized Nanosized Silver Colloids into Organic Phases.* Langmuir, 1998. **14**(3): p. 602-610.
- 116. Taleb, A., C. Petit, and M. Pileni, Synthesis of highly monodisperse silver nanoparticles from AOT reverse micelles: a way to 2D and 3D selforganization. Chemistry of Materials, 1997. 9(4): p. 950-959.
- 117. Jana, N.R. and X. Peng, *Single-phase and gram-scale routes toward nearly monodisperse Au and other noble metal nanocrystals.* Journal of the American Chemical Society, 2003. **125**(47): p. 14280-14281.
- Song, K.C., et al., *Preparation of colloidal silver nanoparticles by chemical reduction method.* Korean Journal of Chemical Engineering, 2009. 26(1):
   p. 153-155.

- Yanagihara, N., Y. Tanaka, and H. Okamoto, *Formation of silver nanoparticles in poly (methyl methacrylate) by UV irradiation.* Chemistry letters, 2001. **30**(8): p. 796-797.
- 120. Adegboyega, N.F., et al., *UV light induces Ag nanoparticle formation: roles of natural organic matter, iron, and oxygen.* Environmental Chemistry Letters, 2016. **14**(3): p. 353-357.
- Rehan, M., et al., *Towards multifunctional cellulosic fabric: UV photo*reduction and in-situ synthesis of silver nanoparticles into cellulose fabrics. International journal of biological macromolecules, 2017. **98**: p. 877-886.
- Moraes, B.R., N.S. Campos, and C.M.J.V.S. Izumi, *Surface-enhanced Raman scattering of EDOT and PEDOT on silver and gold nanoparticles*. 2018. 96: p. 137-142.
- 123. Xu, P., et al., *Multifunctional polymer–metal nanocomposites via direct chemical reduction by conjugated polymers.* 2014. **43**(5): p. 1349-1360.
- 124. Balamurugan, A., K.-C. Ho, and S.-M. Chen, *One-pot synthesis of highly stable silver nanoparticles-conducting polymer nanocomposite and its catalytic application.* Synthetic Metals, 2009. **159**(23-24): p. 2544-2549.
- Deivaraj, T., et al., Solvent-induced shape evolution of PVP protected spherical silver nanoparticles into triangular nanoplates and nanorods. 2005. 289(2): p. 402-409.
- Rosa, R.M., et al., Simultaneous photo-induced cross-linking and silver nanoparticle formation in a PVP electrospun wound dressing. 2017. 207: p. 145-148.
- 127. Kirchmeyer, S. and K. Reuter, *Scientific importance, properties and growing applications of poly(3,4-ethylenedioxythiophene).* Journal of Materials Chemistry, 2005. **15**(21): p. 2077-2088.
- 128. Selvaganesh, S.V., et al., *Chemical synthesis of PEDOT–Au nanocomposite.*2007. 2(11): p. 546.
- 129. Behniafar, H. and H. Moaref, *Modified solution technique for preparing poly(3,4-ethylenedioxythiophene)* and a *Poly(3,4-ethylenedioxythiophene)/silver nanocomposite: Optical and thermal behavior.* 2013. **130**(4): p. 2707-2712.

- Behniafar, H., D.J.D.M. Yousefzadeh, and Polymers, *Chemical synthesis of PEDOT/Ag nanocomposites via emulsion technique in silver colloid.* 2015. **18**(1): p. 6-11.
- 131. Hong, J.-Y. and S. Huh, Facile preparation of SERS-active nanostructured Au spheres by simple reduction of AuCl4- ions with EDOT. Journal of Colloid and Interface Science, 2014. 418: p. 360-365.
- 132. Zhang, Z., B. Zhao, and L.J.J.o.S.S.C. Hu, *PVP protective mechanism of ultrafine silver powder synthesized by chemical reduction processes.* 1996.
  121(1): p. 105-110.
- 133. Sameen, A., et al., *Nanopackaging of silver using spice extract and their characterization.* 2014. **3**(3): p. 52-56.
- 134. Wang, H., et al., *Mechanisms of PVP in the preparation of silver nanoparticles.* 2005. **94**(2-3): p. 449-453.
- 135. Debnath, D., et al., *Solid-State Synthesis of Silver Nanoparticles at Room Temperature: Poly (vinylpyrrolidone) as a Tool.* 2010. **31**(6): p. 549-553.
- 136. Chan, W.K., *Metal containing polymers with heterocyclic rigid main chains.* Coordination Chemistry Reviews, 2007. **251**(17-20): p. 2104-2118.
- Mumtaz, M., et al., *Hybrid PEDOT–metal nanoparticles–new substitutes for PEDOT: PSS in electrochromic layers–towards improved performance.* European Journal of Inorganic Chemistry, 2012. 2012(32): p. 5360-5370.
- 138. Jönsson, S., et al., *The effects of solvents on the morphology and sheet resistance in poly (3, 4-ethylenedioxythiophene)–polystyrenesulfonic acid (PEDOT–PSS) films.* 2003. **139**(1): p. 1-10.
- Mumtaz, M., et al., *Hybrid PEDOT–metal nanoparticles–new substitutes for PEDOT: PSS in electrochromic layers–towards improved performance.* 2012. 2012(32): p. 5360-5370.
- 140. Conyers, J.L. and H.S.J.T.J.o.P.C.B. White, *Electrochemical growth of Ag2S* on Ag (111) electrodes. Coulometric and X-ray photoelectron spectroscopic analysis of the stepwise formation of the first and second monolayers of Ag2S. 1999. **103**(11): p. 1960-1965.
- 141. Salvioni, L., et al., *Negatively charged silver nanoparticles with potent antibacterial activity and reduced toxicity for pharmaceutical preparations.*

2017. **12**: p. 2517.

- 142. Sharonova, A., et al. *Synthesis of positively and negatively charged silver nanoparticles and their deposition on the surface of titanium.* in *IOP Conference Series: Materials Science and Engineering.* 2016. IOP Publishing.
- Lee, C.J., M.R. Karim, and M.S.J.M.L. Lee, *Synthesis and characterization of silver/thiophene nanocomposites by UV-irradiation method.* 2007. **61**(13): p. 2675-2678.
- 144. Gholami-Shabani, M., et al., *Antimicrobial activity and physical characterization of silver nanoparticles green synthesized using nitrate reductase from Fusarium oxysporum.* Applied biochemistry and biotechnology, 2014. **172**: p. 4084-4098.
- 145. Paul, D., *Polymer blends: phase behavior and property relationships*. 1986, ACS Publications.
- Lopez-Barron, C.R. and C.W. Macosko, *Characterizing interface shape evolution in immiscible polymer blends via 3D image analysis.* Langmuir, 2009. 25(16): p. 9392-9404.
- 147. Ruegg, M.L., et al., Microphase and Macrophase Separation in Multicomponent A/B/A – C Polymer Blends with Attractive and Repulsive Interactions. Macromolecules, 2006. **39**(3): p. 1125-1134.
- Fic, K., G. Lota, and E. Frackowiak, *Electrochemical properties of supercapacitors operating in aqueous electrolyte with surfactants.* Electrochimica Acta, 2010. 55(25): p. 7484-7488.
- 149. Manoharan, K. and S. Bhattacharya, Superhydrophobic surfaces review: Functional application, fabrication techniques and limitations. Journal of Micromanufacturing, 2019. 2(1): p. 59-78.
- 150. Li, Y.D., et al., *Eliminating the Detrimental Effect of Secondary Doping on PEDOT : PSS Hole Transporting Material Performance.* Chemsuschem, 2021. 14(21): p. 4802-4811.
- 151. Palama, I.E., et al., *Bioinspired design of a photoresponsive superhydrophobic/oleophilic surface with underwater superoleophobic efficacy.* Journal of Materials Chemistry A, 2014. **2**(41): p. 17666-17675.

- 152. Beaugendre, A., et al., *Self-stratifying coatings: A review.* Progress in Organic Coatings, 2017. **110**: p. 210-241.
- 153. Han, J.W., et al., *Highly stretchable, robust, and conductive lab-synthesized PEDOT:PSS conductive polymer/hydroxyethyl cellulose films for on-skin health-monitoring devices.* Organic Electronics, 2022. **105**.
- Zhou, H., et al., Graphene-Based Intrinsically Stretchable 2D-Contact Electrodes for Highly Efficient Organic Light-Emitting Diodes. Advanced Materials, 2022. 34(31): p. 2203040.
- 155. Brewis, D., *Surface analysis and pretreatment of plastics and metals*. 1982: Macmillan Publishing.
- 156. Mandolfino, C., Polypropylene surface modification by low pressure plasma to increase adhesive bonding: Effect of process parameters. Surface and coatings technology, 2019. 366: p. 331-337.
- 157. Pandiyaraj, K.N., et al., *Modification of surface properties of polypropylene* (*PP*) film using DC glow discharge air plasma. Applied Surface Science, 2009. 255(7): p. 3965-3971.
- 158. Yasuda, H.K., *Plasma polymerization*. 2012: Academic press.
- 159. Pandiyaraj, K.N., et al., *Adhesive properties of polypropylene (PP) and polyethylene terephthalate (PET) film surfaces treated by DC glow discharge plasma.* Vacuum, 2008. **83**(2): p. 332-339.
- Jin, W.-Y., et al., Ultra-smooth, fully solution-processed large-area transparent conducting electrodes for organic devices. Scientific reports, 2016. 6(1): p. 1-10.
- Li, W., et al., *Transparent Surfactant/Epoxy Composite Coatings with Self-Healing and Superhydrophilic Properties.* Macromolecular Materials and Engineering, 2019. **304**(7): p. 1800765.
- 162. Morent, R., et al., Comparison between XPS-and FTIR-analysis of plasmatreated polypropylene film surfaces. Surface and Interface Analysis: An International Journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films, 2008. 40(3-4): p. 597-600.
- 163. Sciarratta, V., et al., *Plasma functionalization of polypropylene with acrylic*

acid. Surface and Coatings Technology, 2003. 174: p. 805-810.

- 164. Socrates, G., *Tables and charts.* Infrared and Raman Characteristic Group Frequencies, 2001.
- 165. Ren, Z., et al., *Hemocompatibility evaluation of polyurethane film with surface-grafted poly (ethylene glycol) and carboxymethyl-chitosan.* Journal of applied polymer science, 2013. **127**(1): p. 308-315.
- 166. Li, Y., et al., *Eliminating the Detrimental Effect of Secondary Doping on PEDOT: PSS Hole Transporting Material Performance.* ChemSusChem, 2021. 14(21): p. 4802-4811.
- 167. Murff, S., J. Barlow, and D. Paul, *Environmental-Stress Crazing and Cracking of Poly (methyl Methacrylate)-Poly (vinylidene Fluoride) Blends*. 1986, ACS Publications.
- Zhou, J., et al., *The temperature-dependent microstructure of PEDOT/PSS films: insights from morphological, mechanical and electrical analyses.* Journal of Materials Chemistry C, 2014. 2(46): p. 9903-9910.
- Jang, J.-H., et al., Accelerated Testing Method for Predicting Long-Term Properties of Carbon Fiber-Reinforced Shape Memory Polymer Composites in a Low Earth Orbit Environment. Polymers, 2021. 13(10): p. 1628.
- Zhou, J. and J.P. Lucas, *Hygrothermal effects of epoxy resin. Part II:* variations of glass transition temperature. Polymer, 1999. 40(20): p. 5513-5522.
- 171. Ellis, T. and F. Karasz, *Interaction of epoxy resins with water: the depression of glass transition temperature.* Polymer, 1984. **25**(5): p. 664-669.
- Sharp, N., et al., *Effects of water on epoxy cure kinetics and glass transition temperature utilizing molecular dynamics simulations.* Journal of Polymer Science Part B: Polymer Physics, 2017. 55(15): p. 1150-1159.

## **Korean abstract**

본 연구의 목적은 PEDOT:PSS 를 이용한 전극의 새로운 합성 방법을 제시하고 투명성, 신축성 및 형상기억 성능을 가진 전극을 제작하는 것이다. 이를 위한 일련의 연구들이 다음의 순서로 진행되었다.

기존의 PEDOT:PSS 합성 방법의 한계를 극복하기 위해 산 촉매나 강한 산화제가 필요하지 않은 자발적인 산화 환원 반응을 통해 PEDOT:PSS 와 은나노파티클의 복합체를 in-situ 로 합성하는 방법을 제시하였다. 복합체 형성에서 용매의 영향을 분석하였고, 이를 통해 유기 용매인 아세토니트릴에서 고품질의 PEDOT:PSS-AgNP 나노복합체가 형성되었다. 또한, 고분자 첨가제인 PSS 이온과 PVP 의 영향도 분석하였다. PSS 이온의 첨가로 인해 PEDOT:PSS 가 형성되었으며, 적은 양의 PVP 를 첨가함으로써 더 작은 크기의 잘 분산된 은나노파티클이 포함된 나노복합체를 제조했다. 또한. 나노복합체 제작 메커니즘을 제시하였다. 마지막으로, 제조한 나노복합체가 포함된 섬유를 전기방사와 자외선 환원법으로 제작하였다. 다음으로는 다양한 기능성을 가진 PEDOT:PSS 기반 전극을 제작하였다. 우선, 투명성과 신축성을 가진 전극을 제작하기 위해 PDMS 와 결합한 복합체를 제작하였다. 고분자 혼합물의 각 요소에 대한 표면 에너지를 계산하고 이를 통해 기판과의 친밀성 차이를 통한 수직 상분리를 이끌어냈다. 이러한 수직 상분리를 통해 비율이 매우 낮은 PEDOT: PSS 가 복합체 아랫면에 연속적인 매트릭스를 가지게 되어 높은 전도도를 가졌다. 각 고분자 혼합물의 비율 별 표면 형태를 분석하였고 연속적인 PEDOT:PSS 매트릭스에 고립된 섬 형태의 PDMS 가 분포되어있는 구조가 비율에 관계없이 형성되는 것을 확인하였다. 복합체 필름을 이용하여 높은 투명도를 가지면서 매우 높은 신축성을 확보한 전극을 개발하였다.

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마지막으로 이전에 존재하지 않은 형상 기억 성능을 가진 PEDOT:PSS 기반 전극을 제작하였다. 형상 기억 성능을 확보하기 위해 형상 기억 에폭시 수지와의 결합을 통한 복합체를 제작하였다. PEDOT:PSS 와 에폭시 수지의 적은 표면 에너지 차이를 극복하기 위해 기판을 화학적 수정을 하였다. Air-plasma 공법을 통해 기판의 표면을 친수성으로 만들어 표면 에너지를 높였다. 수직 상분리를 통해 비율이 낮은 PEDOT:PSS 가 아랫면에 연속적인 매트릭스를 형성한다. 복합체의 표면 형태를 분석하여 바다-섬 구조를 가지며 이에 대한 메커니즘을 제시하였다. 복합체 필름은 에폭시 수지 덕분에 형상기억 성능을 가지고 있으며, 형상 기억 반응을 일으킬 때도 전기 전도도가 유지되는 특징을 보였다. 기존 연구들에서 제시되었던 신축성, 유연성 및 투명성을 넘은 형상 기억 성능을 확보한 새로운 형태의 스마트 전극을 제시하였다.

핵심어: PEDOT:PSS, 자발적 산화 환원 반응, 상 분리, 신축성, 형상 기억 학번: 2017-26851