THE EFFECTS OF ORGANIC SOLVENTS ON THE MORPHOLOGY AND CONDUCTIVITY OF THE PEDOT:PSS NANOFIBERS

A Thesis

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by

Meryem Oznur Pehlivaner

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ABSTRACT

In this study, the effect of solvents on the morphology and conductivity of Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) nanofibers was investigated. Conductive PEDOT:PSS nanofibers were electrospun by dissolving a fiber forming polymer, polyvinyl alcohol (PVA), in an aqueous dispersion of PEDOT:PSS. The conductivity of PEDOT:PSS nanofibers was enhanced 15 fold by addition of DMSO and almost 30-foldby addition of ethylene glycol to the spinning dopes. This improvement is attributed to the change in the conformation of the PEDOT chains from the coiled benzoid to the extended coil quinoid structure as confirmed by Raman spectroscopy, X-Ray Diffraction (XRD), and Differential Scanning Calorimetry (DSC) results. Scanning Electron Microscopy (SEM) images showed that less beady and more uniform fiber morphology could be obtained by incorporation of ethylene glycol in to the spinning dopes.

BIOGRAPHICAL SKETCH

Meryem Oznur Pehlivaner received her B.S. degree from the Department of Textile Engineering, Istanbul Technical University, Istanbul, Turkey in 2009. She received her M.S. degree from the Department of Materials Science and Engineering, Istanbul Technical University, Istanbul, Turkey in 2011. In 2011, she was awarded a fellowship by the Higher Education Council of Turkey for M.S. study in the field of Fiber Science at Cornell University. This thesis is part of her graduating requirements to receive the Master of Science degree in the field of Fiber Science in Fiber Science and Apparel Design department.

To Vural Kara, Nuri and Zeliha Pehlivaner, my lovely sisters, nieces and nephew

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1. Introduction

Electrically conductive polymers have both the physical and chemical properties of organic polymers as well as the electrical properties of metals. Conductive polymers have the ability to conduct ions in addition to electrons and holes. Because of their excellent properties, they have broad application areas including organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs), organic photovoltaics (OPVs). Recently, there is an incremental interest in conductive polymers for diverse biomedical applications; such as sensors, bioelectronics and tissue engineering scaffolds due to their long term stability, better mechanical compatibility, higher signaling sensitivity[1]. More sensitive results/signals can be recorded by using conducting polymers. Conducting polymers also show better long term stability compared metals. The soft nature of the conducting polymer provides better mechanical compatibility with tissue. There are many researches which show the advantages of the electro-deposition or electrochemical polymerization of conducting polymers on neural probes/electrodes compared with traditional electrodes[2].

PEDOT:PSS (Figure 1.1), a conducting polymer, attracts special attention because it has superior conductivityas well as electrochemical, thermal, and oxidative stability. Due to these excellent properties, PEDOT:PSS has broad applications in areas of flexible electrodes, electrochromic displays, and transistors[3-5]. Since it is biocompatible, and more stable to oxidation compared to other conductive polymers, it is also preferred for biomedical applications. Polypyrrole shows cytotoxicity for long period of exposure to current (96 h exposure to 1mA) and has lower oxidative stability compared to PEDOT. Polyaniline needs some modifications to use to render it biocompatible while maintaining the desirable electrical properties of material[6]. However, when compared with other conducting polymers, PEDOT:PSS shows lower conductivity, generally less than 1 S/cm for thin films[7].

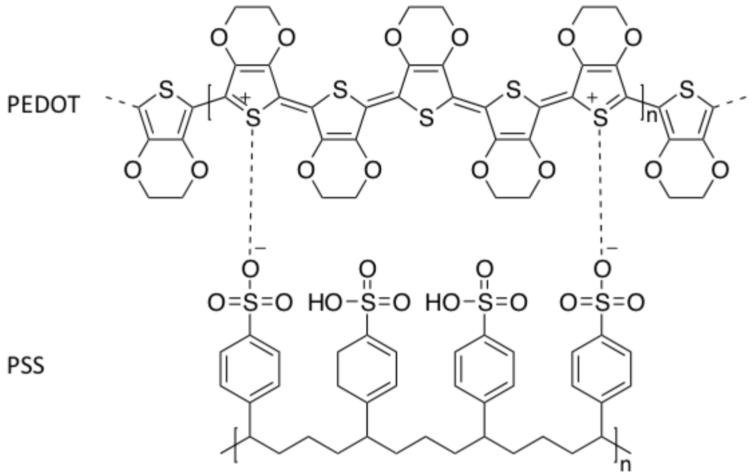

Figure 1.1. Chemical structure of PEDOT:PSS

Incorporation of some organic solvents such as ethylene glycol (EG), poly(ethylene glycol) (PEG), dimethyl sulfoxide (DMSO), or sorbitol, in an aqueous dispersion of PEDOT:PSS, results in an improvement of the conductivity of PEDOT:PSS thin films[7-14]. Several theoriesfor mechanism by which the conductivity is increased have been presented such as conformational change in PEDOT structure, removal of insulating PSS 'shell', and decrease in Coulomb interaction between PEDOT and PSS chains. Ashiwaza et al. observed enhancement in the conductivity of PEDOT:PSS thin films after adding various amounts of ethylene glycol and suggested that the added solvent reduced the effective energy barrier for hopping charge carriers between localized states[7]. Kim et al. observed an increase in conductivity after adding DMSO, DMF or THF to the aqueous dispersion of PEDOT:PSS[14]. They noted that polar organic solvents with high dielectric constants induce a screening effect between positively charged PEDOT chains and negatively charged PSS chains by reducing the Coulomb interaction between them. Jönsson et al. demonstrated that conductivity was enhanced by adding sorbitol and,-N-methylpyrrolidone in PEDOT:PSS aqueous dispersion[13]. They concluded that solvents wash away the excessive non-conductive PSS 'shell' which surrounds the PEDOT:PSS grains and increases the PEDOT-to-PSS molar ratio. Ouyang et. al. proposed that ethylene glycol treatment induces a conformational change of the PEDOT chain from coil to extended coil or linear structure and suggested that the new linear or extended coil structure would improve conductivity through increased interaction between the PEDOT chains[8].

In addition to films, the effects of solvents on the conductivity of PEDOT microfibers have also been investigated. Okuzaki et al. fabricated highly conductive PEDOT:PSS microfibers by wet spinning followed by dip treatment in ethylene glycol. They explained the mechanism of conductivity improvement as removal of the insulating PSS layer from the surface of the PEDOT:PSS grains. They found that dip treatments in ethylene glycol increased not only electrical properties but also mechanical properties of fibers. This enhancement of mechanical properties was attributed to the molecular change in PEDOT molecules from the amorphous state to the crystalline state[15]. Most research with regard to solvent effects on PEDOT:PSS has been explored with thin films prepared by casting[16], spin coating[13], or with micro fibers produced by wet spinning[17]. Solvent effects on PEDOT:PSS in the nanofibrous form has not been investigated. Electrospinning is a novel, simple, cost effective and rapid method to produce ultra thin fibers from polymer melts and solutions [18,19,20]. High voltage supply is used in this non-mechanical, electrostatic technique to create an electrical potential between a grounded target and the surface of the polymer solution droplet. When the applied electric force overcomes the surface tension of the polymer solution, a jet is produced, and solvent molecules begin to evaporate rapidly. Polymer fibers with diameters between a few nanometers to several micrometers are accumulated on the surface of the collector. By controlling parameters such as polymer solution concentration, the strength of the applied electric field, and the distance between the spinneret and collector, fiber properties can be adjusted [21]. A schematic drawing of the electrospinning process is shown in Figure 1.2.

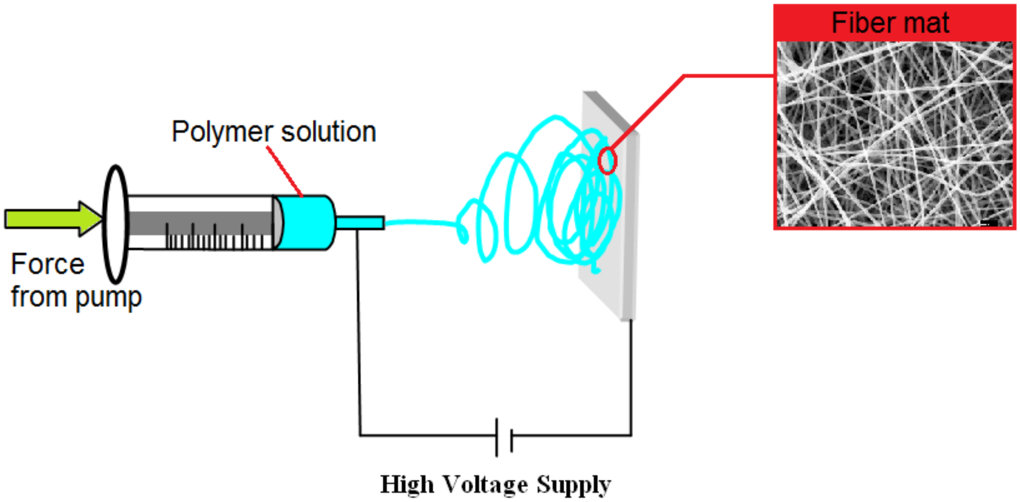

Figure 1.2. Electrospinning setup

This study utilizes the conductive properties of PEDOT:PSS in the form of high surface area nanofibers and seeks to investigate the effect of solvents on fiber properties. Conducting PEDOT:PSS nanofibers are potential candidates for use in highly sensitive, real-time electrically based sensors for radiation detection[22] and, nanomaterialsforbiosensorapplications in solution-processablemicrofluidicdevice[23] due totheir extremely large surface-to-volume ratio, 3D structure, hydrophilicity and small diameters around 150 nm. Both thin films and wet-spun micro fibers have some limitations for these applications, because thin films cannot provide 3D structure, large surface area to volume ratio, and wet-spun PEDOT:PSS microfibers have a large fiber diameter of around 5 μm compared to nanofibers[24].

Investigation of the solvent effects on electrospun PEDOT:PSS nanofibers is more challenging with a greater parameter space than film and microfiber studies, because the properties of added solvents also play an important role on electrospun nanofiber morphology. There are several electrospinning parameters which may be influenced by adding organic solvents. The optimum combination of solution, experimental parameters and the appropriate solvent selection has to be determined to produce ultra thin and greater conducting fibers from solution.

In this study, PEDOT:PSS nanofibers were obtained by electrospinning an aqueous dispersion of PEDOT:PSS with PVA as a carrier. PVA is selected as a fiber forming polymer due to its water solubility and biocompatibility. The different solvents including DMF, DMSO, THF, EG, PEG were used as secondary solvents to investigate their effects on fiber morphology. Those producing the best results (EG and DMSO) were then investigated further to examine their impact on the conductivity of PEDOT:PSSnanofibers.

2. Materials and Methods

2.1. Materials

An aqueous dispersion of PEDOT:PSS (Heraeus PH 1000, 1.3 wt.%), poly (vinyl alcohol) (PVA) (M_w~78,000, Polysciences, Inc) and nonionic surfactant Triton X-100 were used. DMSO (99.9%, Fisher Chemical), DMF (Fluka), THF (Mallinckrodt Chemicals), PEG (Mn~400, Sigma Aldrich) and EG (Macron Chemicals) were used as solvents. All materials were used as received without any purification.

2.2. Electrospinning

5wt. % was selected as an optimum solvent concentration because no significant improvement in nanofiber morphology was noted with a lower concentration (2.5 wt.%). At higher concentrations, as shown in Figure 2.1., excess solvent was unable to evaporate during electrospinning, producing solvent droplets on the nanofibrous mat.

Firstly, 4 wt.% PVA was added to the aqueous dispersion of PEDOT:PSS and stirred on a hot plate by magnetic stirrer at 95 °C for 3-4 hours. Then5 wt.% solvent and 0.5 wt.% Triton X were added to the solution and thoroughly vortexed for 2 minutes to make a homogenous spinning dope. PEDOT:PSS nanofibers were obtained without addition of secondary solvents and used as control samples to investigate the solvents effect on nanofibers. The composition of PEDOT:PSS in nanofibrous mat is approximately 24-27 wt.% and the composition of PVA in nanofibrous mat is approximately 76-73 wt.%. The polymer solutions were electrospun at room temperature using applied voltage of 15 kV and a feed rate of 0.54 ml/hour. The distance between the spinneret and the aluminum collector was 11 cm.

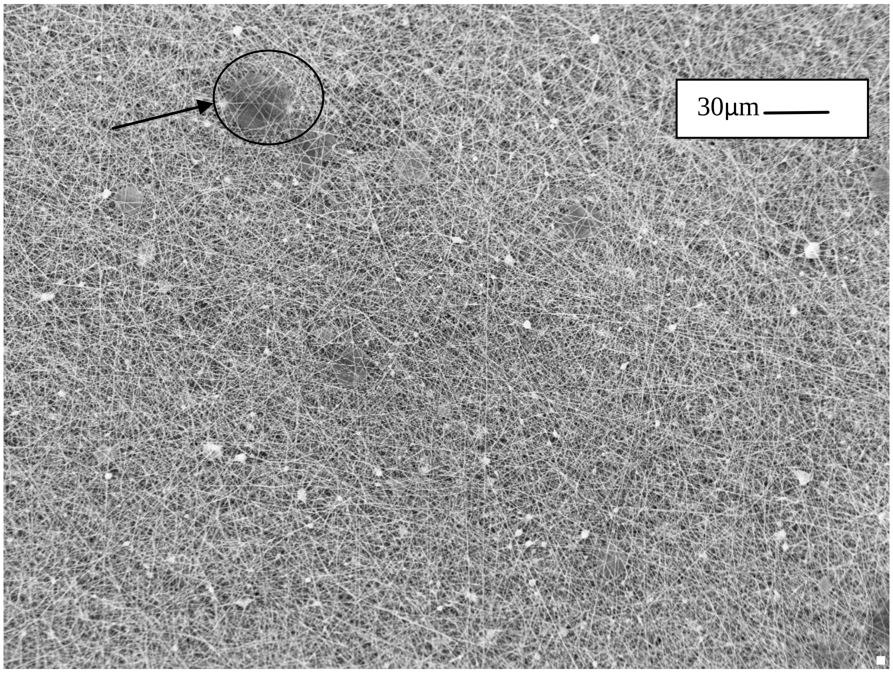

Figure 2.1. SEM image of nanofibrous mat electrospun from spinning dope with 10 wt.% DMSO

2.3. Nanofiber Conductivity

To measure nanofibrous mat conductivity, nanofibers were electrospun on glass slides. Conductance was measured using two-point probe method in accordance with ASTM 4496-04. The current corresponding to the applied voltage was measured with digital multimeter (Model 2400, Keithley). Before measuring the conductance, the fiber samples were conditioned in desiccator for 24 hours. Each sample was measured ten times in different directions. Average values are reported. To measure one nanofiber conductivity, PEDOT:PSS nanofibers were spun onto a two point electrode substrate (Figure 2.2) of an interdigitated microelectrode array (IDMA) which consists of 75 pairs of electrode fingers, each 15 mm wide and spaced by 5 mm and 5mm long. The electrodes were made with 35 nm Au on top of a 5nm thick adhesion layer. As a voltage sweep (− 0.5 to 0.5 V) was applied to a sample at a sweeping rate of 100 mV/s, the conductance of nanofibers was measured using a two-probe method in accordance with ASTM 4496-04 by an Keithley 2400 Source Meter and then the conductivity was calculated.

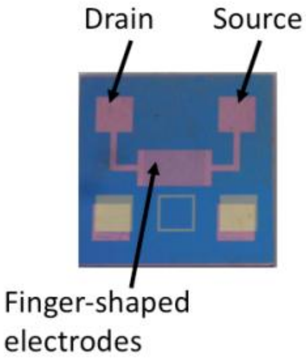

Figure 2.2. A two-point probe silicon-gold transistor with PEDOT:PSS nanofibers.

2.4. GTA vapor crosslinking

PEDOT:PSS nanofibers obtained from 4 wt. % PVA in PEDOT:PSS aqueous dispersion with 5 wt.% of EG were selected for crosslinking studies. The crosslinking process was carried out by placing the 2x2 cm^2 PEDOT:PSS nanofibrous membrane together with a supporting aluminum foil in a sealed desiccator containing 10 ml of aqueous glutaraldehyde solution in a Petri dish for 12 hours[25]. After crosslinking, in order to remove residual GTA and partially enhance the crosslinking, the samples were exposed to heat at 112 °C for 12 hours[26,27].

2.5. Characterizations

Morphology of the PEDOT:PSS nanofibers was examined by SEM (Leica 440). Fibers were collected onto aluminum foil and Au-Pd coated for 30 seconds prior to examination. The average fiber diameter was calculated from SEM images, measuring up to 50 fibers per sample. PEDOT:PSS distribution in final fiber composition was characterized by using electron probe micro analyzer (EPMA) (JEOL 8900). Both energy dispersive X-ray (EDS) and wavelength dispersive energy spectroscopy (WDS) were used to collect characteristic Kα X-ray emission of sulfur atoms in PEDOT:PSS molecules.Thermogravimetric analysis (TGA Model Q500, TA Instrument, New Castle, DE) was used to analyze the thermal properties of all specimens. All TGA tests were performed under a nitrogen atmosphere by keeping the flow rate of 60 ml/min, between 0°C and 300 °C and at a scanning rate of 10 °C/min. The surface morphologies of the PEDOT:PSS films were studied by atomic force microscopy (AFM), using Veeco Dimension 3100. For each sample, an area of 1x1 µm was scanned using tapping mode. To understand the mechanism for the increase in conductivity, the PEDOT:PSS fibers were probed by using a RenishawInVia Confocal Raman microscope and a 785 nm laser source. Differential scanning calorimetry (DSC, Model Q2000, TA Instrument, New Castle, DE) was used to analyze the glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH_f) and crystallinity of PEDOT:PSS nanofibers. All DSC analyses were performed under a nitrogen atmosphere by keeping the flow rate of 50 ml/min, between 0°C and 300°C and at a scanning rate of 5°C/min.XRD patterns of the electrospinning fibers were recorded with a Scintag X-ray diffractometer, operating in theta-theta geometry using C_u Kα radiation at 40 kv and 40 mA in the 2θ range of 9–36.

3. Results and discussion

3.1. Fiber morphology and PEDOT:PSS distribution in nanofibrous mat

SEM images of PEDOT:PSS nanofibers are shown in Figure 3.1. The average diameters of PEDOT:PSS calculated with ImageJ^{TM}are shown in Figure 3.2. PEDOT:PSS nanofibers, and the nanofibers electrospun from solutions with 5 wt.% DMF and THF, showed beads and average fiber diameters between the beads were statistically equal. Addition of 5 wt% DMF or

5 wt.% THF did not affect the resulting fiber structure. Nanofibers electrospun from solutions with 5wt.% PEG exhibited branched fiber morphology, and had higher average nanofiber diameter compared to other fibers. Due to its high molecular weight, PEG does not evaporate during electrospinning. While some fibers were formed, electrospray also occured. For this reason, PEG is not suitable for integration into this electrospinning system. Conversely, it was found that the number of beads decreased significantly and the average fiber diameter increased when fibers were electrospun from solutions with 5 wt.% EG or DMSO. The most uniform fiber morphology was obtained by adding 5 wt.% EG to the solution.

The differences between fiber morphologies after adding DMF, DMSO, THF, and EG, could not be explained by changes in typical electrospinning variables. Spinning conditions including feed rate, applied voltage, ambient humidity and collection distance were held constant throughout all experiments. Solution variables including solution conductivity and viscosity were measuredbefore and after the addition of these solvents. No significant difference in viscosity (0.5 Pa.s at shear rate of 27.09s^{-1}, shear stress of 54.87 Pa) was observed. The solution conductivity of samples was high reflecting the high conductivity of PEDOT:PSS, and exceeded the measurement limit of the conductivity meter. The addition of solvents did not decrease the solution conductivity to measurable values.

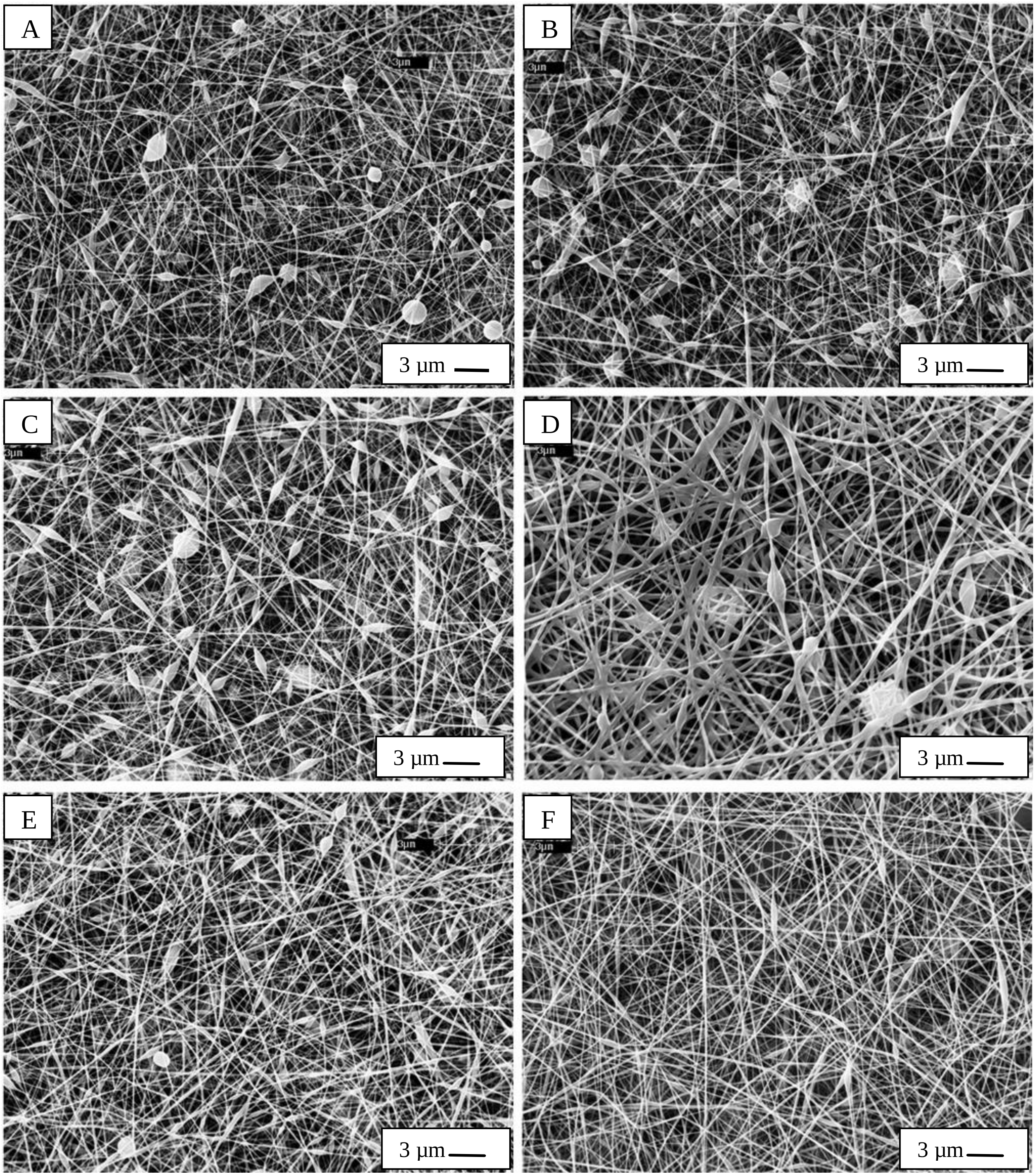

Figure 3.1. SEM images of (A) PEDOT:PSS nanofibers and nanofibers electrospun from spinning dope with 5 wt.% of (B)DMF, (C)THF, (D) PEG, (E) DMSO, (F) EG.

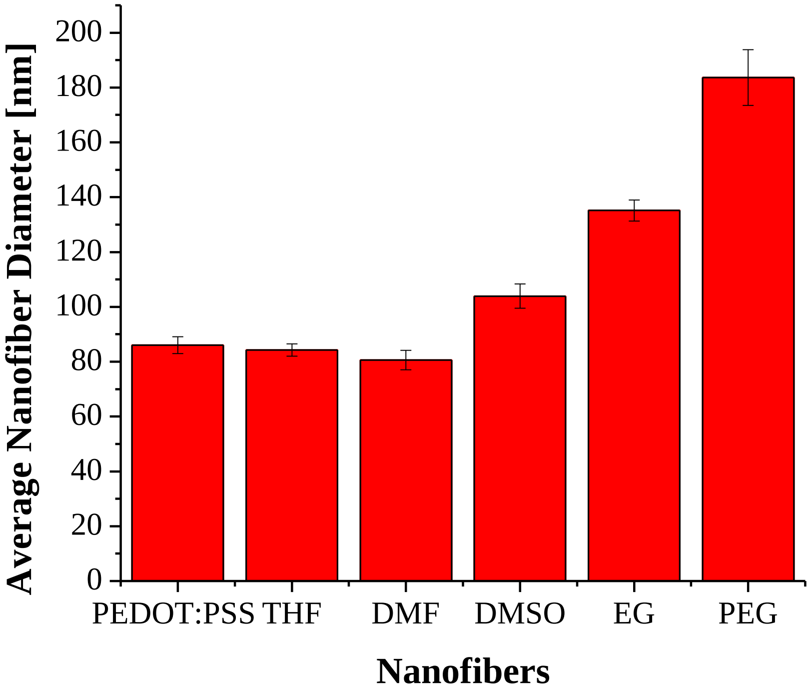

Figure 3.2 Nanofiber diameter as a function of addition of 5 wt. % organic solvents in spinning dopes.

Although no changes in bulk properties of the spinning dope were observed, the added solvents may have had an effect on the spinability of the solution by, as Ouyang stated, changing the conformation of PEDOT from a coil form to an extended coil form. The differences inthe fiber morphologies, with decreasing bead formation on addition of DMSO and EG, may also correlate with this mechanism. A polymer with a linear/extended chain conformation is more easily electrospun than a polymer with a random coil conformation[28]. The change in conformation from coil to extended coil may increase the spinability and improve fiber morphology. DMSO and EG may have greater effect on the extending the PEDOT chain and increasing the spinability of PEDOT:PSS to result in more homogenous fibers.

To see the effect of solvents on the distribution of PEDOT:PSS within the nanofibers, nanofiber mats were examined using EPMA. Since the sulfur atoms in this system are attributable solely to the PEDOT:PSS, distribution of PEDOT:PSS on the nanofiber mat could be mapped. Two samples which showed different fiber morphology (beady and uniform) were selected to elicit PEDOT:PSS distribution. Figure 3.3. shows PEDOT:PSS distribution in PEDOT:PSS nanofiber mats electrospun from spinning dopes containing EG, and spinning dopes containing DMF. The increased number of blue and green spots and their homogenous distribution in the PEDOT:PSS nanofiber mat with electrospun from spinning dopes with EG, confirmed the dispersion of PEDOT:PSS evenly throughout the mat. On the other hand, several large bright spots on the EPMA map of the PEDOT:PSS nanofiber mat electrospun from spinning dopes with DMF indicated the heterogeneous distribution of PEDOT:PSS. These results confirmed that when spinability of dopes was low, PEDOT:PSS concentrated within beads. Conversely, the PEDOT distribution in nanofiber was continuous when spinability and overall fiber uniformity were improved. Previous studies have shown that DMSO and EG treated PEDOT:PSS films also have higher conductivity than DMF and THF treated films[14]. For further investigation, EG and DMSO were selected as solvents because they had more uniform fibers and more evenly distributed PEDOT:PSS in the system than THF, DMF or PEG.

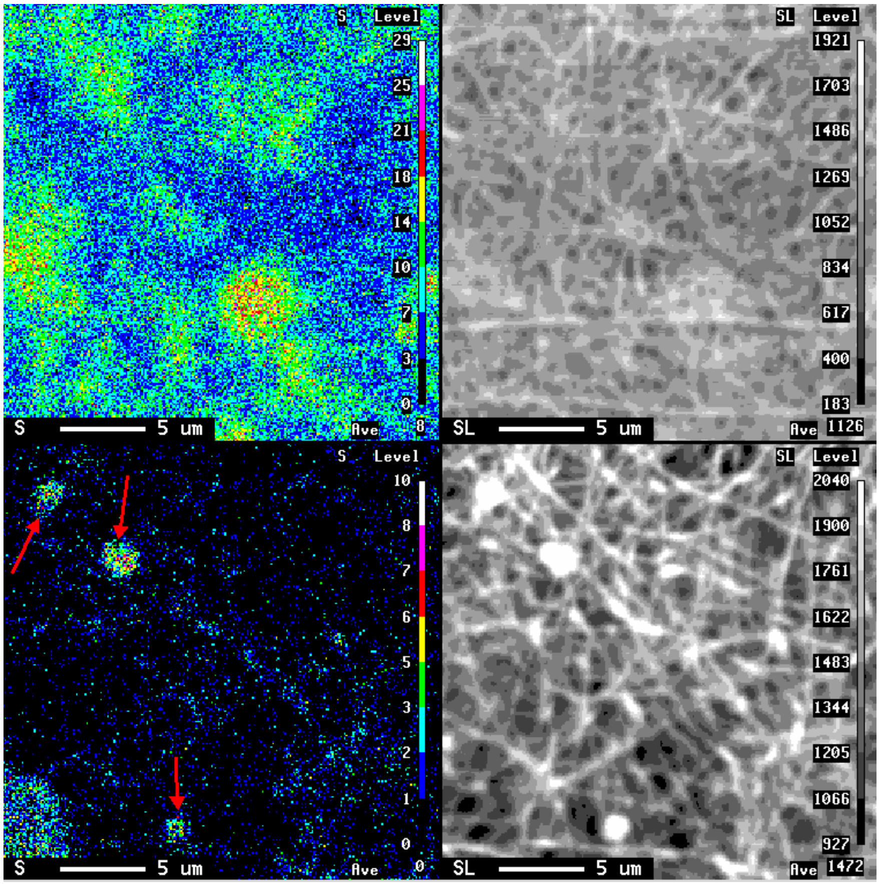

Figure 3.3. Comparison of the sulfur map of PEDOT:PSS nanofibrous mat electrospun spinning dopes with EG (top) and DMF (bottom), the color bars on the side of the left images indicates the sulfur concentration from lowest (black) to highest (white).

3.2. Electrical conductivity

The room temperature conductivity of PEDOT:PSS nanofibrous mats and nanofibrous mats electrospun from spinning dopes with EG and DMSO are shown in Figure 3.4. PEDOT:PSS nanofibrous mats with no addition of EG or DMSO have very low conductivity. However, there is a significant increase in conductivity when 5 wt.% EG or DMSO is added to the solution before electrospinning. The conductivity of PEDOT:PSS nanofibrous mats is enhanced by almost 30-fold when EG is added to the spinning dopes and by 15-fold when DMSO is added to the spinning dopes. It is evident that EG is the optimum solvent to improve both conductivity and morphology of PEDOT:PSS nanofibers. PEDOT:PSS nanofibrous mat conductivity is higher than previously reported hybrid nanofibrous mat conductivity [29,30]. It is difficult to compare nanofibrous mat conductivity results with PEDOT:PSS microfibers and thin films due to the porosity in the fiber mats and non-homogenous structure of the fiber mats. To compare the conductivity results with microfibers and thin films, finger-shaped electrodes were used and single nanofiber conductivity is calculated. The most conductive nanofibers, spun from solution with 5 wt.% EG, was selected for single nanofiber conductivity measurement. The conductance of nanofibers, on the finger-shaped electrodes was measured as 3.8E-04 Swhich was equivalent to the resistance of 2.63 kΩ. The nanofiber conductivity could be calculated using the known variables (fiber diameter: 135 nm, distance between electrodes: 5 μm). The number of fibers on the 75 pairs of electrodes was around ten, as determined using an optical microscope. Therefore, the PEDOT:PSS nanofibers had an electrical conductivity on the order of 180 S m^{-1}. Although the amount of PEDOT:PSS in nanofibers is less than 30 %, nanofiber conductivity is higher than the conductivity of untreated films[13,14] (5 S/m) and microfibers[31] (40-100 S/m) but it is less than solvent treated films and microfibers due to the presence of nonconducting PVA in nanofibers..

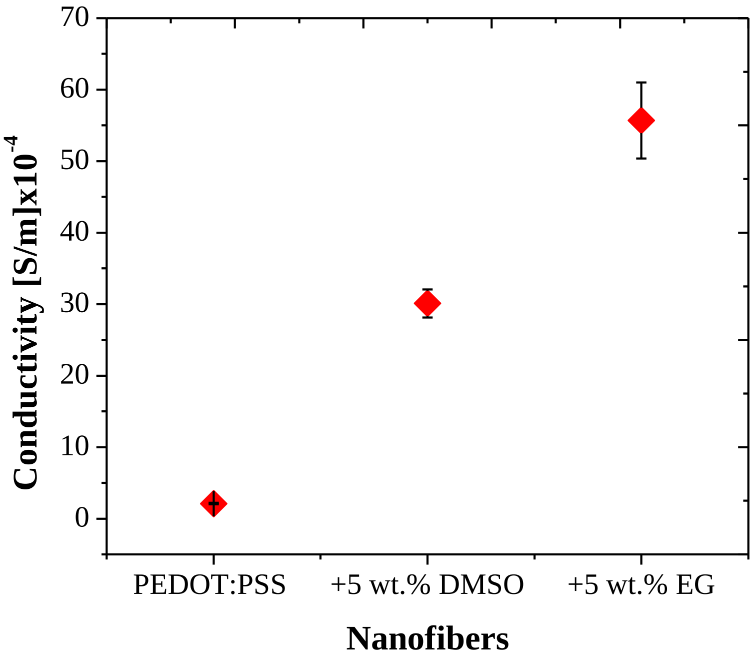

Figure 3.4. Room temperature conductivity of nanofibrous mats

3.3. AFM measurements

The morphology of treated and untreated PEDOT:PSS films was studied with AFM. Figure 3.5 shows AFM images of the PEDOT:PSS films. After EG and DMSO addition (the same amount in the spinning dopes), large domains appeared and the surface roughness of the films increased because of the conformational changes in the PEDOT structure as previously reported[8].

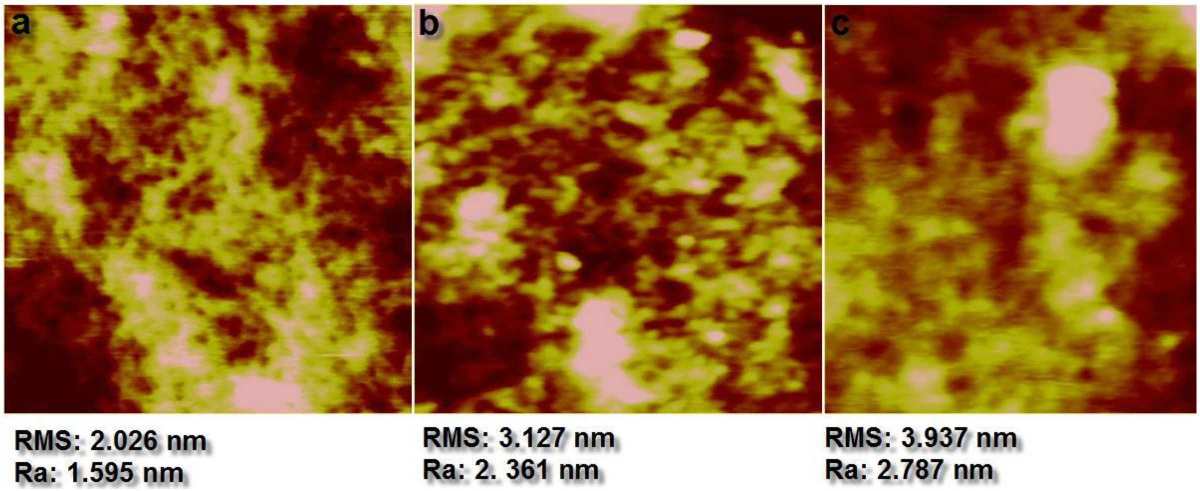

Figure 3.5 AFM images of electrospun PEDOT:PSS films (a)pristine films (b) EG treated films (c) DMSO treated films.

3.4. Raman spectroscopy and Molecular Structure

To understand the mechanism for the relationship between PEDOT chain conformation, fiber morphology and conductivity enhancement, the nanofibers, electrospun with and without addition of EG and DMSO, were studied by Raman spectroscopy. Raman spectroscopy is commonly used to investigate the change in molecular orientation of PEDOT:PSS films and fibers after solvent treatment[8,17]. The Raman spectra of PEDOT:PSS nanofibers, are shown in Figure 3.6. The most clear difference was observed for the strongest band between 1400 and 1500 cm^{-1} associated with the symmetric $C_{\alpha}=C_{\beta}$ stretching from the thiophene rings. The addition of either DMSO or EG resulted in a shift at 1427 cm^{-1} by 2 cm^{-1}. This shift is attributed to the transformation from molecular structures of PEDOT:PSS from benzoid to quinoid[17](Figure 3.7). Quinod is more conductive form of PEDOT and the favored structure of extended coil conformation, conversely, benzoid is less conductive form of PEDOT and the favored structure for random coil conformation[17]. The benzoid structure includes two conjugated π-electrons on the C_α=C_β bond and the quinoid structure does not include any conjugated π-electrons on the C_α-C_β bond. The symmetrical C_α=C_β stretching has been interpreted as a transformation of the benzoid structure to the quinoid structure[8,17]. PEDOT:PSS nanofibers may have both resonant structures, but after addition of EG or DMSO to the spinning dopes, the benzoid structure is thought to transform the quinoid. This results in a dominance of the quinoid structures in the linear or extended coil formation. The use of either EG or DMSO as solvents, both of which resulted in increased conductivity of fibers also show the conformational changes of PEDOT chains from coil to extended coil/linear conformations. Extended coil/linear conformations increase inter-chain interactions among the PEDOT chains and thereby increasing the conductivity.

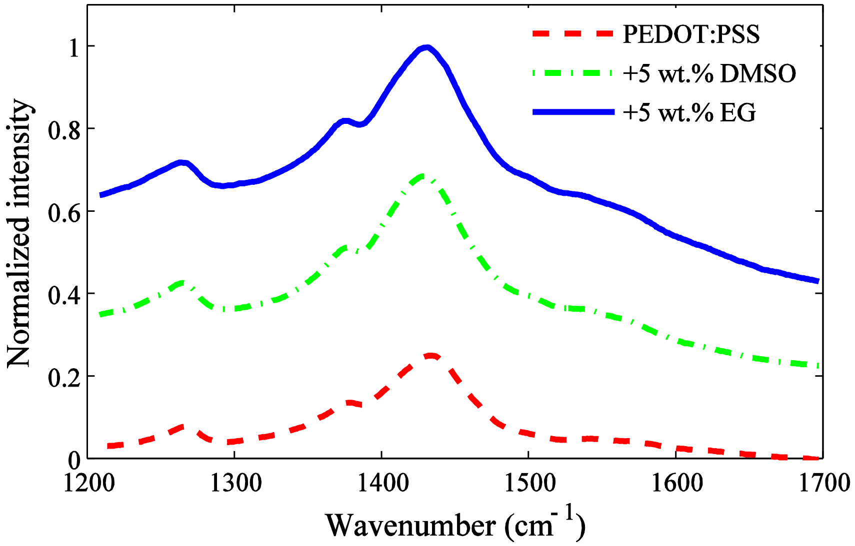

Figure 3.6. Raman spectra of electrospun PEDOT:PSS nanofibers

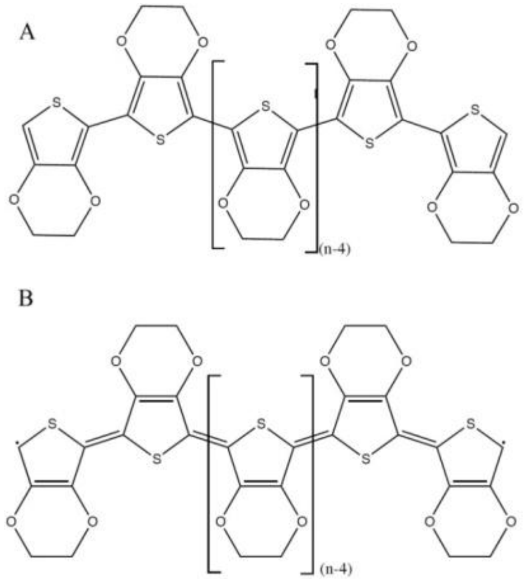

Figure 3.7. Resonant structures of PEDOT (a) benzoid structure (b) quinoid structure

3.5. DSC analysis, XRD patterns and chain conformation

The change of coil conformation from random coil to extended coil would also be expected to result in crystallinity of nanofibers. The change in crystallinity of nanofibers were investigated by DSC and XRD. Fig. 3.8. shows the DSC curves of the PEDOT:PSS electrospun nanofibers and Table 3.1 shows the DSC data of electrospun nanofibers . The first feature of the DSC curves indicates that the glass transition temperature (T_g) of nanofibers. The glass transition temperature for PVA nanofibers has been seen at around 82-85 °C in previous studies[32].The high glass transition temperature of PEDOT:PSS nanofibers is observed at 92.3 °C in our study. Adding EG or DMSO to the solution, decreased the glass transition temperature from 92.3 °C to 84.1 °C and 87.9 °C respectively due to the plasticizing effect of the solvents. A single melting temperature is observed at 165.8 °C for PEDOT:PSS nanofibers. By adding EG or DMSO to the spinning dopes, melting temperature increased from 165.8 °C to 167.6 °C and 174.0° C, respectively. The measured enthalpy value of PEDOT:PSS nanofibers is ΔH= 201.4

J/g. Addition of EG and DMSO to the spinning dopes increased the enthalpyΔH=297.4 J/g and ΔH=247.6 J/g, respectively. The maximum enthalpy value was obtained from the PEDOT:PSS nanofibers electrospun using dopes with 5 wt.% EG. The crystalline melting temperature for PVA nanofibers has been observed at 230 °C and the %100 crystalline PVA enthalpy value found in literature isΔH_c=138.6 J/g [25,32]. Both the decreasing melting temperature and the high enthalpy values observed in this research are attributed to the contribution of PEDOT:PSS and a strong association between PVA and PEDOT:PSS. This association increases as the PEDOT:PSS increasingly adopts the extended coil conformation. The increased enthalpy correlates with the improved fiber morphology, increased conductivity and PEDOT:PSS confirmation shift towards more extended chains.

Table 3.1.DSC data obtained from the electrospun nanofibers

Nanofibers	**Tg (°C)**	**Tm (°C)**	**ΔH (j/g)**
PEDOT:PSS	92.3	165.8	201.4
DMSO	87.9	174.0	247.6
EG	84.1	167.6	297.4

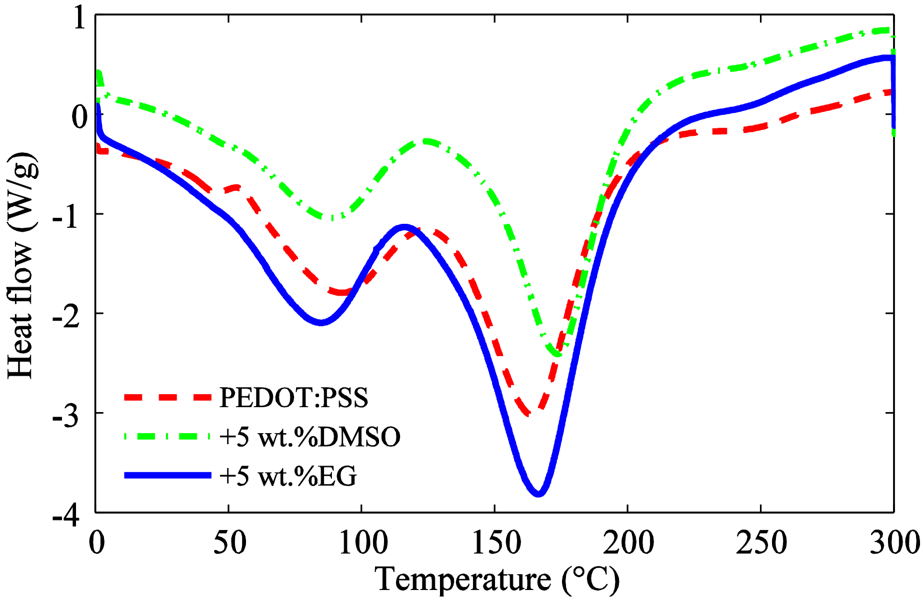

Figure 3.8. DSC thermograms of electrospun PEDOT:PSS nanofibers

The XRD patterns of various PEDOT:PSS nanofibers are shown in Figure 3.9. PVA has diffraction peaks at 16.0°, 19.4°, and 22.7° and, PEDOT:PSS has diffraction peak at around 25°. Jia et al. stated that if there is no interaction or only weak interaction between components in polyblend fibers, there would be two different crystalline peaks for each component[33]. In our study, only one diffraction peak is seen for all nanofibers around 19.0° since the strong interaction between PEDOT:PSS and PVA .The diffraction peak is seen at $2\theta = 19.0°$ for PEDOT:PSS nanofibers. The addition of DMSO or EG to the solution shifts the peak from 19.0° to 19.3° and 19.7° respectively. XRD results showed that fibers with EG or DMSO have larger and sharper peaks compared to the PEDOT:PSS nanofibers.Depression of the PVA peaks at 16.0° and 22.7°, the increase in degrees from 19.0° to 19.7°, sharper-larger peaks indicate the formation and development of new crystalline structure[34]. The increased crystallinity was consistent with the change in PEDOT structure from coiled to extended coil chain conformation.

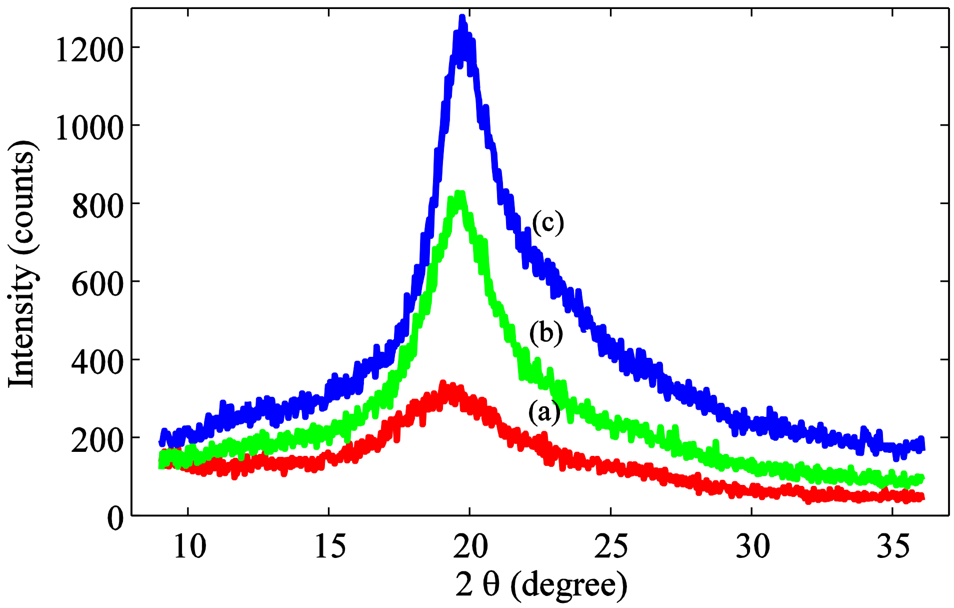

Figure 3.9. XRD patterns of (a) PEDOT:PSS nanofibersand nanofibers were electrospun from spinning dope with 5 wt.% of (b) DMSO, (c) EG

3.6. *Thermal Gravimetric Analysis (TGA)*

To determine whether residual solvents remain and asses influence of solvents on the thermal stability in nanofibrous mats, the fibers were analyzed with TGA. DMSO has lower boiling temperature (189 °C) and smaller density (1.09 g/ml) compared to boiling temperature (195 °C) and density of EG (1.11 g/ml), due to these properties, DMSO may evaporate faster and remain less or none in nanofibers than EG. Figure 3.10. shows the TGA curves of electrospun nanofibers. The first weight loss between 30-120 °C could be attributed to the desorption of physically adsorbed water. The second weight loss between 120-220 °C is about the same for all samples, due to the decomposition of doping material of PEDOT:PSS[31] and side chain of PVA[35], however, the second weight loss starts at a lower temperature for nanofibers electrospun from spinning dope with EG. This difference may indicate the existence of the residual EG in PEDOT:PSS nanofibrous mat. The third weight loss which starts around

270 °C shows the degradation of PSS[31]. Although, there is not an certain weight loss related with the solvents, DSC results showed that the glass transition temperature was decreased when solvents added to the spinning dope, small amount of EG and DMSO may remain in nanofibers and act as a plasticizer and decrease the thermal stability of nanofibers, especially nanofibers which were electrospun from solution with 5 wt.% EG. Due to higher evaporation rate of DMSO, it did not affect the thernal stability a lot compared to EG.

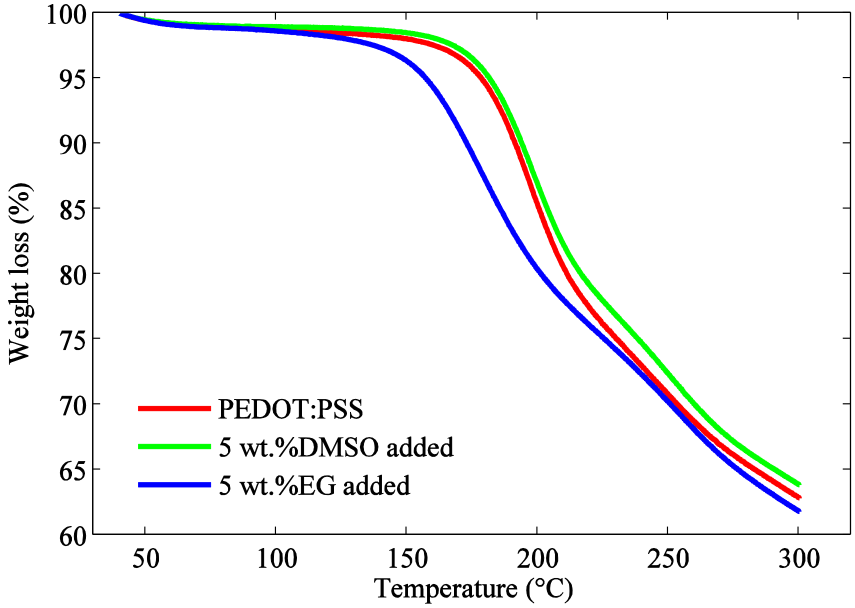

Figure 3.10. TGA thermograms of electrospun PEDOT:PSS nanofibers

3.7. Cross-linking studies

Crosslinking studies were carried out to improve the water resistant-ability of the material. Since PEDOT:PSS and PVA are water soluble, just a drop of water is enough to destroy the nanofibrous structure as shown in Fig.3.11(A).

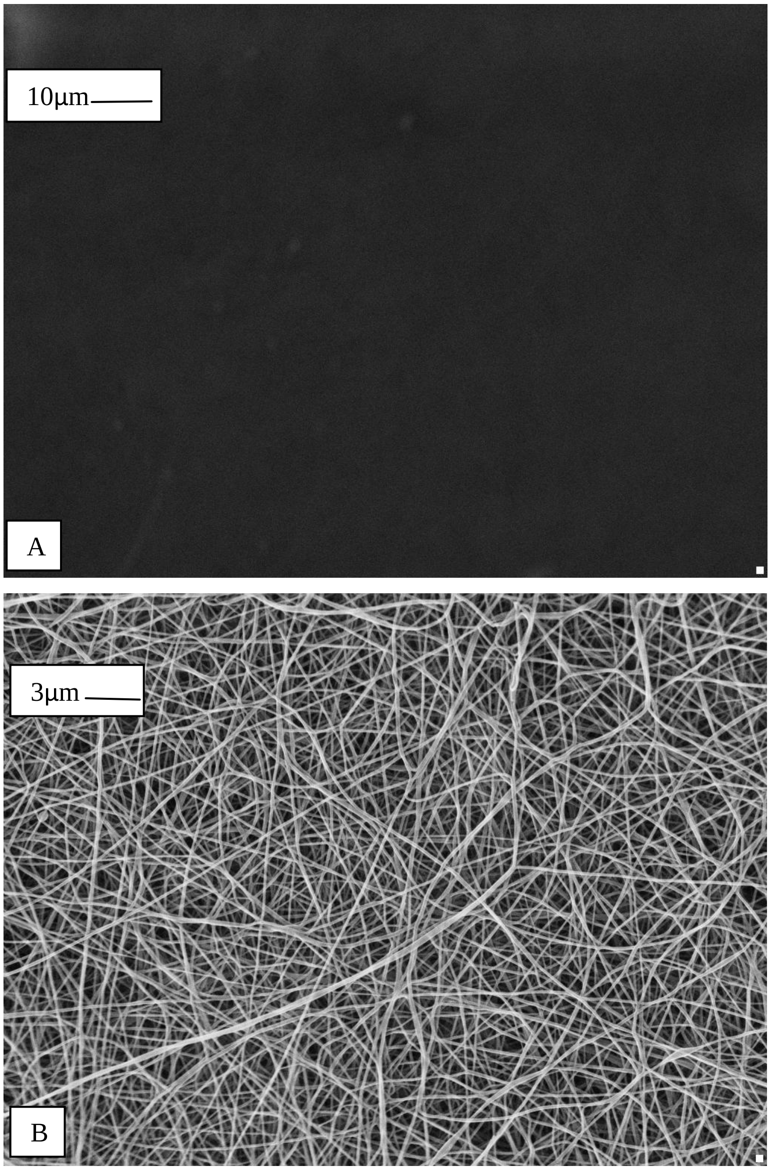

Figure 3.11. Morphologies of PEDOT:PSS nanofibers (A) the smeared surface layer of PEDOT:PSS nanofibrous membrane after adding a drop of water (B) crosslinked electrospun PEDOT:PSS nanofibers after immersed in DI water for 2 days.

By placing the PEDOT:PSS nanofibrous membrane in a sealed desiccator filled with saturated GTA vapor, the PEDOT:PSS fibers could be reasonably crosslinked. After GTA vapor crosslinking, the color change was observed, the membranes became visibly yellowish. When compared to original PEDOT:PSS nanofibers, the crosslinked fibers maintained their fiber morphology after being immersed in DI water for 2 days as shown Fig.3.11 (B).

4. Conclusion

In this study, different solvent effects on fiber morphology was investigated. Adding EG and DMSO to the spinning dopes resulted in transformation of PEDOT:PSS chains from random coil to extended coil conformation. The transformation from random coil to extended coil not only increased the conductivity by increasing the inter-chain interactions among the PEDOT chains, but also improved the fiber morphology and spinability of the solution. DSC investigations indicated the increase in crystallinity after solvent addition to the solution and the strong interaction between PEDOT:PSS and PVA. XRD results showed the formation and development of a new crystalline structure, when EG or DMSO added to the spinning dopes. The most uniform and conductivenanofibers resulted from introducing EG to the dopes.

5. Recommendations for Future Studies

Microbial fuel cells (MFCs) are promising candidates for generating electricity while cleaning the waste water. In these systems, exoelectrogenic bacterias on anode are used to extract electrons, then electrons are transferred to cathode by using external circuit[36]. The surface area, bonding between anode and bacterias, and bacterial activity play an important role on high power generation. Currently, carbon cloth, carbon mesh[37] and graphite fibers[38] are used as an anode material, however, the production of these fibers is expensive, they have larger diameter compared to nanofibers, and their surface area to volume ratio is not as high as nanofibrous mats. To increase the surface area of the anode material, gas treatment applied on carbon fibers[39], but this treatment cost is highly expensive and is not suitable for industrial applications. Bacterial activity can be increased by using nanofibrous mat as an anode. Also, the bonding between bacteria and nanofibers may have higher than bonding between bacteria and carbon cloth or graphite fibers. Conductive PEDOT:PSS nanofibers are potential candidates for anode material in MFCs due to their high conductivity, high surface to volume ratio, low cost, and small diameter around 150 nm. These nanofibers will be used as an anode material and the effect of surface area, and fiber diameter on exoelectrogenic bacteria bonding, bacterial activity and power generation will be investigated. The clogging may be a problem for saturated waste water treatment due to the small pore sizes in nanofibrous mats, and biodegradability of these nanofibers may limit their operating time.

In this study, 1.3-1.6 wt.% of PEDOT:PSS was used. Recently, 3-4 wt.% PEDOT:PSS is commercially available. To produce higher conductive nanofibers, new 3-4 wt.% PEDOT:PSS will be used in spinning dope before electrospinning and the wt.% of PVA will be decreased. In this way, the overall conductivity of nanofibers will be increased.

Humidity has a negative effect on conductivity of PEDOT:PSS, and PVA is a water soluble material. Because of these reasons, GTA vapor crosslinking method was used in this study to make PEDOT:PSS nanofibers insoluble in waterand eliminate the humidity effect on PEDOT:PSS, however, the effect of crosslinking on nanofiber conductivity and PEDOT:PSS molecular structure has not been investigated yet. For future study, PEDOT:PSS nanofibers will be exposed to GTA vapor with different time intervals and solubility test will be performed and the effect of crosslinking on fiber conductivity will be investigated. Crosslinked and un-crosslinked nanofibers conductivity will be measured under different humidity environment.

Our previous study show thatthese nanofibers are promising candidates for use in highly sensitive, real-time electrically based sensor for radiation detection. When PEDOT:PSS nanofibers were exposed to radiation, they loose their conductivity, however, the effect of conductivity on degradation mechanism has not been investigated.

Due to the hydrophilic, high surface to volume ratio and conducting properties, these nanofibers are excellent candidates for biological and chemical detection systems based on microfluidic device. Their performances on detecting some analytes in microfluidic devices will be investigated.

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