

The Effects of DMSO on Structure and Properties of PVA/PEDOT:PSS Blended Fiber

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(Received August 18, 2015; Revised October 21, 2015; Accepted October 24, 2015)

Abstract: In the present study, novel strong and conductive blended fibers composed of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and polyvinyl alcohol (PVA) were successfully fabricated via a wet-spinning process using spinning formulation prepared by doping DMSO into PVA/PEDOT:PSS aqueous solution. The effects of DMSO on structure and properties of PVA/PEDOT:PSS blended fibers were systematically investigated in detail by analyzing the changes in electrical conductivity, aggregation structure, conformational PEDOT chains, morphology and mechanical properties. The results showed that doping of DMSO induced significant conformational changes in PEDOT chains which in turn led to significant enhancement in electrical conductivity and smoother surface morphology as well as better mechanical properties of PVA/PEDOT:PSS blended fibers. The resultant DMSO-doped PVA/PEDOT:PSS blended conductive fibers exhibited an enhanced electrical conductivity up to 21.16 S cm^{-1} . In addition, as the doping concentration of DMSO increased, the surface of blended fibers became less fluted and smoother. The Young's modulus and tensile strength increased from 3.5 GPa and 115 MPa to 4.95 GPa and 145 MPa respectively, while the elongation at break decreased from 25 % to 17 %.

Keywords: Wet-spinning, Conductive fiber, PVA/PEDOT:PSS, Dimethylsulfoxide

Introduction

Conducting polymers, such as polyaniline [1-3], polypyrrole [4], and recently poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS) [5-7], have attracted extensive attention for use in applications ranging from simple textiles to various functional electronics [8,9]. Among various conducting polymers, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS), one of the most commercially successful conducting polymers, has attracted widespread attention of its excellent performances such as water-solubility, high mechanical flexibility, superior thermal and environmental stability [10-14], providing potential applications for either multifunctional fabric [6] or organic and optical devices [15-18]. At present, one of the major studies on PEDOT:PSS is fabricating high-performance blended polymer fibers using conducting PEDOT:PSS. The as-spun fibers are expected to have not only high conductivity, but also other utility functions.

Conductive polymer fibers produced from PEDOT:PSS [5,6], featuring tunable electrical conductivity, have been widely investigated from both practical and technological perspectives to understand their electrical or mechanical properties and practical use in wearable bionics [19-21], conducting textiles, organic electronics and sensors [22-24]. At present, although PEDOT:PSS conductive fibers have been successfully prepared by the wet-spinning process [23,25], however, these simplex as-spun PEDOT:PSS conductive fibers can't meet the needs of the textile

manufacturing process and application in conducting textile due to their poor mechanical properties, high manufacturing costs, and low conductivity under 1 S cm^{-1} without doping of polar solvents [26]. Therefore, to respond to these needs, various organic macromolecule polymers, such as polyurethane [27] and poly(vinyl alcohol)(PVA) [28], are being actively investigated to blend with PEDOT:PSS as novel blended conductive polymer fibers to improve their mechanical properties and to reduce the manufacturing costs. On the other hand, because these organic macromolecule polymers are basically electrically insulating, the resultant blended fibers are consequently of a low conductivity and even insulating. Therefore, polar organic solvents such as N,N-dimethylformamide, ethylene glycol (EG), dimethylsulfoxide (DMSO), and sorbitol are being actively investigated to dope with these blended fibers to significantly enhance their conductivity [7,19,20].

It is well known that addition or post-treatment of polar organic solvents can significantly enhance the conductivity of PEDOT:PSS fibers or PEDOT:PSS/organic macromolecule polymer blended fibers by up to 2 or 3 orders of magnitude [7,19,20]. Recently, more and more researchers have reported studies on conductivity enhancement of PEDOT:PSS/organic macromolecule polymer blended fibers or PEDOT:PSS fibers by various organic solvents treatment. Seyedin *et al.* [27] reported that high elastomeric fiber composites with high electrical conductivity composed of PU and PEDOT:PSS were successfully prepared by doping of DMSO into homogenous composite formulation composed of PU and PEDOT:PSS. Jalili *et al.* [6] reported that with a relatively simple one-step EG-additive wet-spinning process, significant

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conductivity enhancement on PEDOT:PSS fibers was achieved with regard to an untreated fiber. Okuzaki *et al.* [5] reported that significant enhancement on PEDOT:PSS fibers occurred with a dip-treatment in EG for 3 min. However, there have not been many reports on PEDOT:PSS/PVA blended fibers.

In this work, we doped a certain amount of DMSO into PVA/PDOET:PSS mixed aqueous solution preparing DMSO doped PVA/PEDOT:PSS spinning formulation to fabricate novel, strong, and conductive PVA/PEDOT:PSS blended conductive fibers via a relatively simple wet-spun process. The innovation lies in using water as solvent dissolving PVA, which is environmentally-friendly and cost-effective to a certain extent. Doping of DMSO, induces significant conformational changes in PEDOT chains, which in turn led to obvious enhancement on the conductivity of blended fibers and improvement on surface morphology and mechanical properties of blended fibers. Also, the mechanism of the electrical, conformational, morphological, and mechanical changes induced by DMSO-doped method were investigated in detail.

Experimental

Material

The 99.9 % hydrolyzed PVA (DP=3500) was provided by Kurary Co. Ltd., Tokyo, Japan. PEDOT:PSS aqueous solution (Clevios™ P) was purchased from HC Starck, Inc. Methyl alcohol and dimethylsulfoxide (DMSO) were analytically pure grades.

Preparation of Spinning Formulation

Mixed aqueous solution was prepared from PVA with the concentration of 100 mg mL^{-1} and PEDOT:PSS with the concentration of 5 mg mL^{-1} , in which the content of PEDOT:PSS in PVA/PEDOT:PSS blended fiber is 4.76 %. The mixed aqueous solution was then homogenized at 3000 rpm for 6 h at a constant temperature of 90°C (Wiggins WB3000-D). After that various doping concentrations of DMSO were directly added into the homogenous mixed solution and then continuously homogenized at 3000 rpm for 2 h at 90°C . Thus, the homogenous PVA/PEDOT:PSS spinning formulation doped with various amounts of DMSO was successfully prepared.

Fiber Spinning

PVA/PEDOT:PSS blended fibers were fabricated at room temperature using a custom-made wet-spinning apparatus (Figure 1). The spinning formulation was injected into a 5 ml syringe and then extruded into the coagulation bath containing the non-solvents methyl alcohol, through a needle (20 gauge) with a blunt tip, employing flow rates between 2.5 to 5 mL h^{-1} . The solidified blended fibers then went through two washing baths containing methyl alcohol

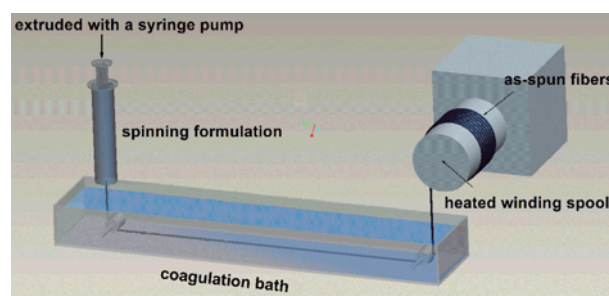


Figure 1. Wet-spinning apparatus.

to remove the remaining DMSO and other impurities in fibers. After the washing process, blended fibers were then collected on a heated winding spool at 120°C for drying the blended fibers. The take-up speed is 0.9 m/min .

Characterizations

Chemical constituents of PVA/PEDOT:PSS blended fibers were measured by a FT-IR spectrometer (Nicolet is 10, Thermo Fisher Scientific). Electrical resistance of the blended fibers were measured at room temperature using a high resistance meter (Keithley 6517B), with two alligator clips clamping two points of the fiber at a distance of 10 mm. Aggregation structure of the blended fibers was characterized using an X-ray diffraction instrument (D8 Advance, Bruker), with Cu-K α radiation ($\lambda=0.15418 \text{ nm}$) at 40 kV and 40 mA, from 5° to 90° in a continuous mode. Raman spectra of the blended fibers were taken using a Renishaw in Via laser confocal Raman spectrometer with a 785 nm laser. Morphology of the blended fibers was observed by a scanning electron microscope (SU1510, Hitachi, Japan). The mean value of fiber diameter was measured using ImageJ analysis software with 10 points taken on each fiber. The mechanical properties of the blended fibers were measured using a tensile testing instrument (KD11, KaiQiang Testing Instruments, Shenzhen) at a constant strain rate of 10 \% min^{-1} . Samples were mounted on paper cards (20 mm length window) with an adhesive tape. The Young's modulus, tensile strength and elongation at break were measured and the mean and standard deviations were calculated for $n=20$.

Results and Discussion

Spinning Formulation

Selection of suitable wet-spinning conditions was vital for preparing continuous PVA/PEDOT:PSS fibers with good electrical and mechanical properties [27]. Fiber quality was mainly influenced by the composition of spinning formulation and the suitable choice of coagulation bath. Pure PVA dispersions were found to be spinnable over the minimum concentration of 70 mg mL^{-1} and with the concentration above 100 mg mL^{-1} , continuous and uniform PVA fibers could be prepared usually over tens of meters. On the basis of

Table 1. Components of spinning formulation

| Samples | PVA (mg ml ⁻¹) | PEDOT:PSS (mg ml ⁻¹) | DMSO contents (wt%) |
|---------|-------------------------------|-------------------------------------|------------------------|
| a | 100 | 5 | 0 |
| b | 100 | 5 | 1 |
| c | 100 | 5 | 3 |
| d | 100 | 5 | 5 |
| e | 100 | 5 | 7 |

previous work, PEDOT:PSS aqueous dispersions were added into PVA aqueous solutions to prepare homogeneous PVA/PEDOT:PSS blended spinning formulation. However, the PVA/PEDOT:PSS blended fibers prepared by the simplex physically-mixing method showed low electrical conductivity that could not meet the needs of antistatic fabrics or conducting textiles. In order to solve this problem, various amounts of DMSO were added as doping agents into the PVA/PEDOT:PSS blended spinning formulation to improve the electrical conductivity and other properties of PVA/PEDOT:PSS blended fibers. The detailed components of the spinning formulation were shown in Table 1.

Fiber Spinning Conditions

Selection of coagulation bath needs to work well for both pure PVA and PEDOT:PSS [27]. Methyl alcohol and acetone both meet the needs of formation of PVA/PEDOT:PSS blended fibers. However, the extremely strongly volatile and toxic properties made acetone a difficult coagulation bath to realize the industrial production process. Therefore, methyl alcohol was chosen as coagulation bath to prepare PVA/PEDOT:PSS blended fibers. The formation of blended fibers was also influenced by the rate of fiber wet-spinning. The continuous fiber production process could not be achieved when the rate was under 2.5 ml h⁻¹. The spinning formulation would be solidified at the spinneret orifice when the rate was over 5 ml h⁻¹. Therefore, a wet-spinning rate of PVA/PEDOT:PSS blended fibers was set as 3.6 ml h⁻¹, which met the needs of both the continuous fiber-production process and the good morphology of blended fibers.

Effect on Structure of PVA/PEDOT:PSS Blended Fibers

Fourier Transform Infrared Spectroscopy (FTIR)

In order to confirm the successful synthesis of PVA and PEDOT:PSS, and to investigate the effect of DMSO on chemical components of PVA/PEDOT:PSS blended fibers, FT-IR spectra of PVA, PEDOT:PSS, pristine PVA/PEDOT:PSS blended fibers, and PVA/PEDOT:PSS blended fibers doped with different concentrations of DMSO were collected by an FT-IR spectrometer. Figure 2 shows the FT-IR spectra of PVA, PEDOT:PSS, and PVA/PEDOT:PSS blended fibers doped with various amounts of DMSO in the range of 600-4000 cm⁻¹. From the FT-IR spectra of PVA, peaks at 841, 1325 and 2947 cm⁻¹ were attributed to C-C stretching vibration,

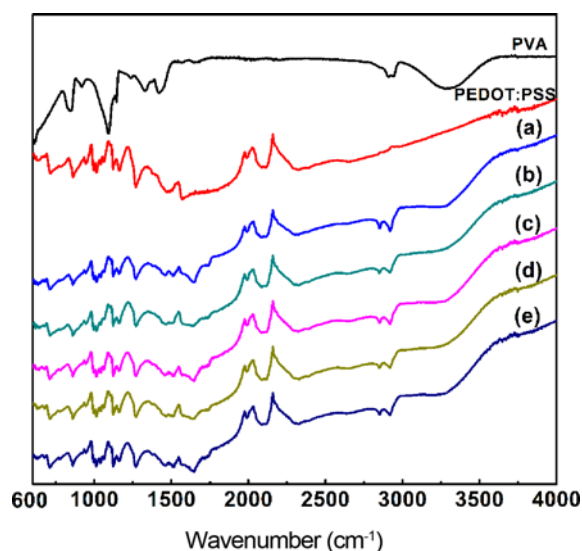


Figure 2. FT-IR spectra of PVA, PEDOT:PSS and PVA/PEDOT:PSS blended fibers at different DMSO-doping contents; (a) 0 %, (b) 1 %, (c) 3 %, (d) 5 %, and (e) 7 %.

C-H in-plane bending vibration, and C-H symmetrical stretching vibration of carbon chains, respectively [29,30]. A broad absorption peak at 3305 cm⁻¹ was assigned to stretch frequency of the -OH group. As for PEDOT:PSS, peaks at 685, 830, and 984 cm⁻¹ were related to the C-S bond stretching vibration in the thiophene ring [31], and peaks at 1519 and 1278 cm⁻¹ were assigned to the C=C and C-C stretching vibration of the thiophene ring [31]. Peaks at 1060 and 1174 cm⁻¹ could be attributed to the stretching of C-O-C bonds [31]. According to the result of the FT-IR spectrum of pristine PVA/PEDOT:PSS blended fibers (Figure 2(a)), the representative spectrum of both PVA and PEDOT:PSS appeared, indicating that PVA and PEDOT:PSS have blended successfully into the PVA/PEDOT:PSS blended fibers. From the FT-IR spectra of blended fibers doped with various amounts of DMSO (Figure 2(b)-(e)), there was no appearance of new functional groups, indicating that doping of DMSO did not change the chemical components and structure of PVA/PEDOT:PSS blended fibers.

XRD

To explore changes in the aggregation structure and crystallization state of DMSO-doped PVA/PEDOT:PSS blended fibers, XRD patterns of pristine PVA/PEDOT:PSS blended fibers, and blended fibers doped with different concentrations of DMSO were collected by X-ray diffraction (XRD). The crystallization property of polymer that on behalf of the piling tightness of polymer molecules, is one of the key factors affecting the electrical conductivity of polymer [32]. Doping of organic solvents may induce transformation on the crystallization property of some conducting polymers, from an original amorphous state into a crystalline state which is highly beneficial for carrier transport [33], and in

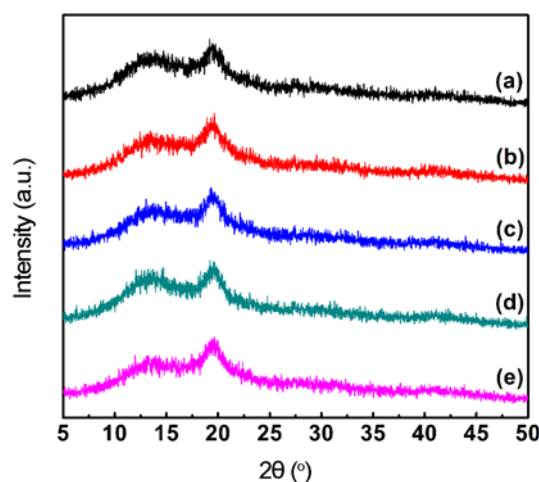


Figure 3. XRD patterns of PVA/PEDOT:PSS blended fibers at different DMSO-doping contents; (a) 0 %, (b) 1 %, (c) 3 %, (d) 5 %, and (e) 7 %.

turn dramatically improve the electrical conductivity of conducting polymers. XRD patterns of PVA/PEDOT:PSS blended fibers doped with various amounts of DMSO are shown in Figure 3. From XRD patterns of pristine PVA/PEDOT:PSS blended fibers (Figure 3(a)), no obvious crystalline diffraction peaks appear, indicating that the aggregation structure of pristine fibers is an amorphous state. As for XRD patterns of PVA/PEDOT:PSS blended fibers doped with various amounts of DMSO (Figure 3(b)-(e)), they are basically the same as that of pristine blended fibers, suggesting that doping of DMSO does not result in crystallization of PVA/PEDOT:PSS blended fibers, and the aggregation structure of blended fibers remains to be an amorphous state. These results suggested that the conductivity enhancement by DMSO doping was not due to the transformation in the crystallization property of PVA/PEDOT:PSS blended fibers.

Raman Spectroscopy

To determine the mechanism of the conductivity enhancement in DMSO-doped PVA/PEDOT:PSS blended fibers, we investigated Raman spectra of the pristine PVA/PEDOT:PSS blended fibers and the DMSO-doped PVA/PEDOT:PSS blended fibers. The effect on conformational changes of PEDOT chains in PVA/PEDOT:PSS blended fibers before and after DMSO doping can be studied in the Raman spectroscopy (Figure 4). In the Raman spectra, the characteristic absorption peak at 1428 cm^{-1} corresponding to the stretching vibration of $C_{\alpha}=C_{\beta}$ on the five-member thiophene ring of PEDOT chains [34-36], shifted to 1411 cm^{-1} and the absorption peak became narrower with a DMSO doping concentration of 7%. This change in the Raman spectra indicated that the $C_{\alpha}=C_{\beta}$ bond converted to the $C_{\alpha}-C_{\beta}$ bond on the five-member thiophene ring of PEDOT chains [37], corresponding to the structure of PEDOT converting from a benzoid structure into a quinoid structure (Scheme 1).

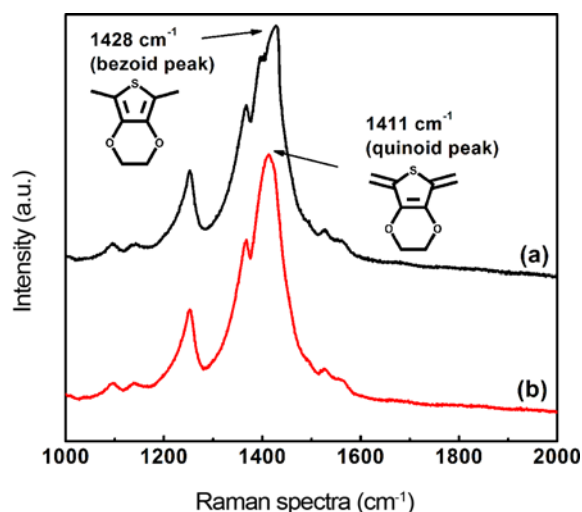


Figure 4. Raman spectra of PVA/PEDOT:PSS blended fibers at different DMSO-doping contents; (a) 0 % and (b) 7 %.



Scheme 1. Transmission of PEDOT chain from benzoid to quinoid structure.

The PEDOT chain with benzoid structure usually behaves as an irregular coil conformation, while a quinoid structure usually behaves as a linear or expanded-coil structure [37]. According to the related theoretical model of Flory Macromolecular Solution Theory [38], a benzoid structure of PEDOT chain leads to high carrier migration energy and low carrier migration rate, thus affecting the electrical conductivity of PVA/PEDOT:PSS blended fibers. While a stretchy-curly quinoid structure results in a sharp increase of ordered structures in PEDOT, which lowers the carrier migration energy and is more favorable for inter- and interchain charge transport [39], thus enhancing the electrical conductivity of PVA/PEDOT:PSS blended fibers. These results suggested that the conductivity enhancement of DMSO-doping PVA/PEDOT:PSS blended fibers could be explained by conformational changes of PEDOT chains in PVA/PEDOT:PSS blended fibers.

Effect on Electrical Conductivity

The electrical conductivity of blended fibers that were doped with different amounts of DMSO were measured using an electrometer. Figure 5 shows the electrical conductivity of PVA/PEDOT:PSS blended fibers doped with various amounts of DMSO. The inset of Figure 5(a) is the

real object of PVA/PEDOT:PSS blended fibers. Figure 5(b) and (c) show that a bulb can be lightened by PVA/PEDOT:PSS blended fibers with a DMSO-doping content of 7%. The pristine PVA/PEDOT:PSS blended fibers had low electrical conductivity of 2.56 S cm^{-1} due to the addition of insulating material PVA. The insulating PVA formed a network inside blended fibers, which consequently increased the energy barrier of the electron transition, and thus decreasing electrical conductivity of blended fibers. However, the electrical conductivity of PVA/PEDOT:PSS blended fibers was significantly enhanced by doping with DMSO. Above a DMSO concentration of 6%, the electrical conductivity of the PVA/PEDOT:PSS blended fibers remained constant at around 20 S cm^{-1} . The highest electrical conductivity of 21.16 S cm^{-1} was obtained with a 7% DMSO concentration.

The conductivity values of DMSO-doped blended fibers were nearly 10 times higher than the pristine PVA/PEDOT:PSS blended fibers. It was obvious that DMSO doping is an effective method to enhance the electrical conductivity of PVA/PEDOT:PSS blended fibers, suggesting that the DMSO-doped PVA/PEDOT:PSS blended fibers could have a better PEDOT:PSS aggregation structure, a better PEDOT:PSS molecular structure or a better fiber morphology for superior charge transport networks and better conducting connections in blended fibers, compared with the pristine PVA/PEDOT:PSS blended fibers without DMSO doping.

Effect on Fiber Morphology

The conformational changes improve not only electrical conductivity but also fiber morphology of the PVA/PEDOT:

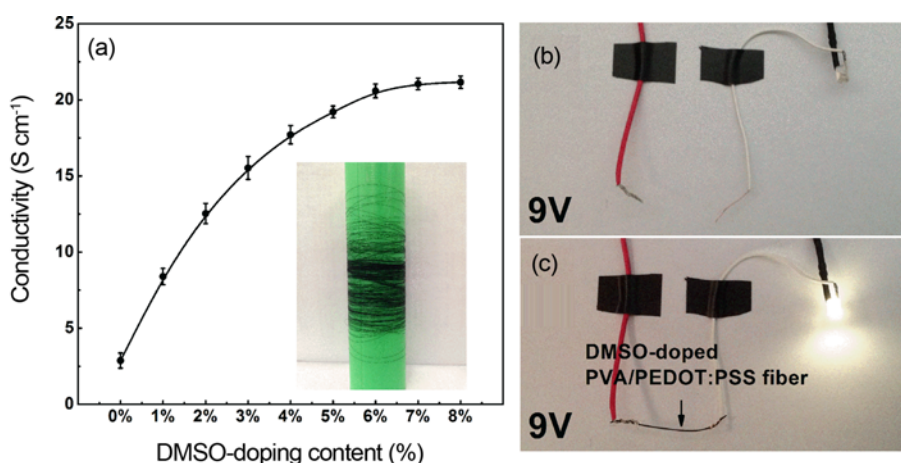


Figure 5. Conductivity and electrical behavior of PVA/PEDOT:PSS blended fibers; (a) conductivity of blended fibers at different DMSO-doping contents (inset is the real object) and (b) bubble-lightening experimental of PVA/PEDOT:PSS blended fiber at DMSO-doping content of 7%.

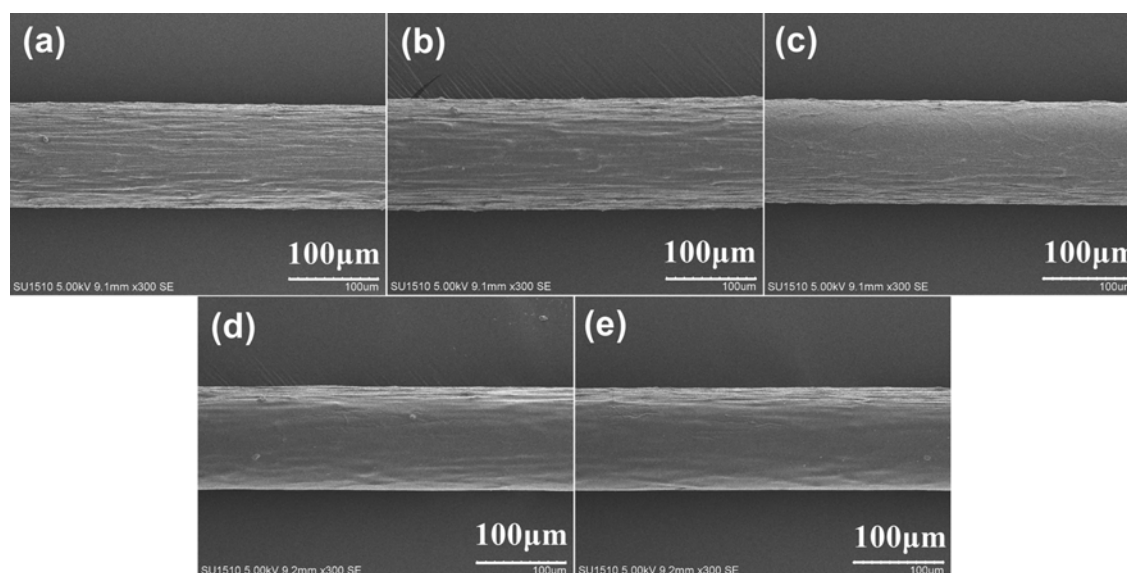


Figure 6. SEM images of PVA/PEDOT:PSS blended fibers at different DMSO-doping contents; (a) 0%, (b) 1%, (c) 3%, (d) 5%, and (e) 7%.

PSS blended fibers. The representative SEM images of PVA/PEDOT:PSS blended fibers doped with various amounts of DMSO shown in Figure 6 demonstrate the change in fiber surface morphology, from a fluted surface to a relatively smooth surface. It can be observed that both pristine and DMSO-doped PVA/PEDOT:PSS blended fibers were straight and continuous with a uniform diameter of $95 \pm 15 \mu\text{m}$. It can be seen that the surface of pristine PVA/PEDOT:PSS blended fibers was full of grooves, while the surfaces of DMSO-doped blended fibers were getting smoother with the increase of DMSO doping concentration. In pristine PVA/PEDOT:PSS blended fibers, coil conformational PEDOT chains in PEDOT:PSS made it difficult to blend uniformly with long linear PVA molecular chains. On the other hand, the formation of an interpolymer network via electrostatic complexation between PEDOT and PSS intertwines each other tightly [17], thus resulting in an uneven structure of PVA/PEDOT:PSS blended fibers. Therefore, one can see that there were many tiny grooves on the surface of pristine PVA/PEDOT:PSS fibers. After doping of DMSO, coil conformational PEDOT chains in PEDOT:PSS transferred into expanded-coil or linear conformational PEDOT chains, thus leading to a more homogeneous intertwining between PEDOT:PSS and PVA molecular chains. On the other hand, the interaction between DMSO and PSS chains lowers the electrostatic forces between PEDOT and PSS [40], indirectly resulting in a more uniform and close-knit structure of PVA/PEDOT:PSS blended fibers, thus leading to a decrease in tiny grooves and a more smooth surface of PVA/PEDOT:PSS blended fibers. These morphological changes are consistent with the changes in the PEDOT molecular chain structure as shown in Figure 4.

Effect on Mechanical Properties

The conformational and morphological changes also affect the mechanical properties of PVA/PEDOT:PSS blended fibers. The mechanical properties of PVA/PEDOT:PSS blended fibers doped with various amounts of DMSO were shown in Figure 7. It can be observed that with the increase of DMSO doping concentration, the Young's modulus and tensile strength of the blended fibers increased from 3.5 GPa and 115 MPa to 4.95 GPa and 145 MPa, respectively, while the elongation at break declined from 25% to 17%. This tensile behavior could be explained by the changes of polymer chain composition comprising hard segments and soft segments whereby the hard segments provide rigidity while the soft segments provide elongation [41-44]. The addition of DMSO made the PEDOT chain transfer from the benzoid structure to the quinoid structure, corresponding to $C_\alpha=C_\beta$ on each single thiophene ring turning into $C_\alpha-C_\beta$ while $C_\alpha-C_\beta$ connecting two adjacent thiophene rings turning into $C_\alpha=C_\beta$, which weakened the internal rotation of single bond, and thereby enhancing the molecular chain rigidity [45]. On the other hand, compared to coil PEDOT chains,

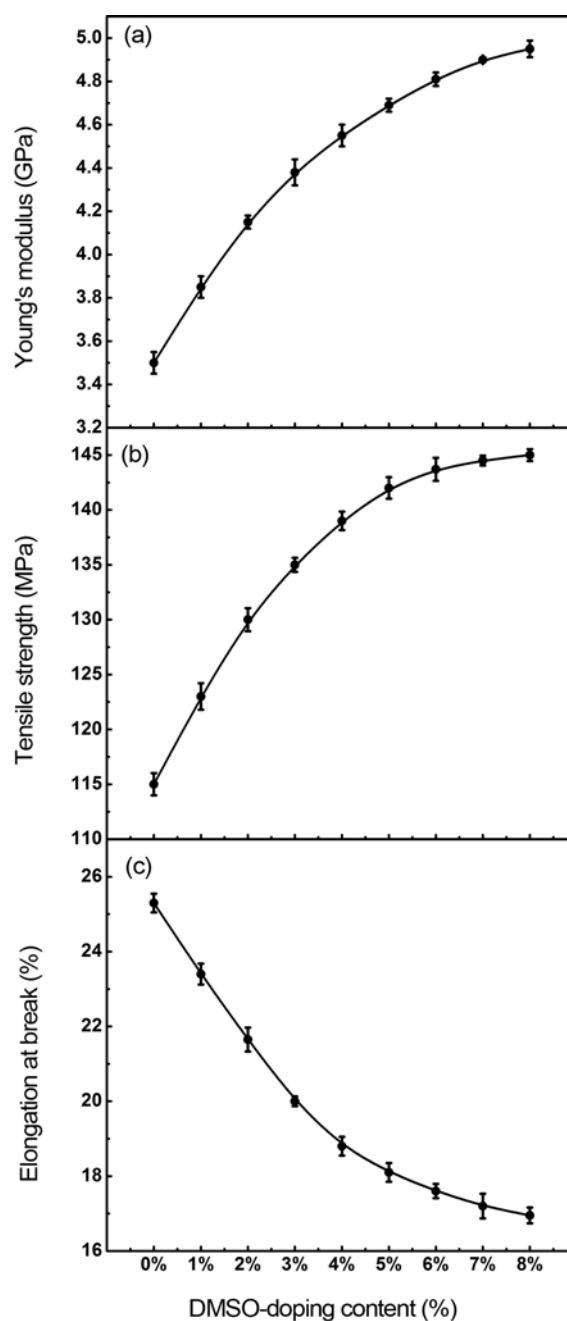


Figure 7. Mechanical properties of PVA/PEDOT:PSS blended fibers at different DMSO-doping contents; (a) Young's modulus, (b) tensile strength, and (c) elongation at break.

stretchy linear PEDOT chains effectively formed a more close-knit intertwining between PEDOT:PSS and PVA molecular chains, which consequently decreased the number of structural defects such as microvoids and microfractures in blended fibers [5]. Therefore, the increase of Young's modulus and tensile strength and the decrease of elongation at break of blended fibers could be fully explained by the increase of the number of hard segments, resulting from the

enhancement of molecular chain rigidity. It is worth mentioning that the as-spun PVA/PEDOT:PSS fibers possess better mechanical properties compared to pure PEDOT:PSS fibers reported previously [6].

Conclusion

In conclusion, doping of DMSO induced significant conformational changes in PEDOT chains which in turn led to enhancement in electrical conductivity, improvement in surface morphology and mechanical properties of PVA/PEDOT:PSS blended fibers. The DMSO-doped PVA/PEDOT:PSS blended fibers exhibited enhanced conductivity up to 21.16 S cm^{-1} with a doping concentration of 7 % of DMSO, 10 times higher than pristine PVA/PEDOT:PSS blended fibers. As the doping concentration of DMSO increased, the surface morphology of blended fibers became less fluted and smoother. In addition, the Young's modulus and the tensile strength increased, while the elongation at break decreased. It should be noted that the DMSO-doped PVA/PEDOT:PSS blended fibers had better mechanical properties compared to pristine PVA/PEDOT:PSS blended fibers, which could basically meet the needs of processing conditions of textile materials.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (NO.21171074/B010201), National High Technology Research and Development Program of China (NO.2012AA030313), and Industrialization Project of College Research Findings of Jiangsu Province (NO. JH10-29).

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