

# **Influence of Organic Vapor Annealing on Structure and Property of Conjugated Composite Fiber**

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**Abstract:** In this study, blend fibers composed of poly (vinyl alcohol) (PVA) and poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were prepared via wet-spinning technology. Ethylene glycol (EG) vapor annealing was employed to improve the electrical conductivity and tensile properties of blend fibers. The effects of EG vapor annealing on structures and properties of blend fibers were investigated in detail by analyzing the changes in chemical constituent and structure, molecular structure, surface morphology, surface chemical composition, electrical conductivity, and tensile properties. FT-IR spectroscopy indicates that EG vapor annealing does not change the chemical constituent and structure of blend fibers. Raman spectroscopy shows that vapor annealing leads to conformational changes of PEDOT chains from benzoid structure to quinoid structure. AFM and SEM images show that surface morphology of blend fibers become smoother after vapor annealing. XPS measurement shows that EG vapor annealing induces significant phase separation between PEDOT and PSS, forming an enriched PSS layer on the surface of blend

fibers, thus leading to a thinner insulating PSS layer between PEDOT grains. This conformational change is beneficial to improve the electrical conductivity of blend fibers. The resultant blend fiber reached a conductivity up to  $20.4 \text{ S cm}^{-1}$ . The mechanical properties of blend fibers were also improved by EG vapor annealing, with the Young's modulus and tensile strength increasing from 3.6 GPa and 112 MPa to 4.4 GPa and 132.7 MPa, respectively.

## 1. INTRODUCTION

In recent years, there has been increased interest in research on organic materials used for electronic devices [1-4] and smart textiles [5]. Organic materials are flexible, low-cost and easy to process. These properties made them ideal for fabrication of both flexible devices and textiles in the form of either film or fiber.

Among various conducting polymers, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been regarded as a promising candidate as next-generation organic conductive material in both technological and industrial areas due to their optical transmission property, good thermal and environmental stability, and outstanding processability [3, 6-8]. There have been many articles reported on PEDOT:PSS casting films, such as Chan [9] and Lang [10]. Compared to films, PEDOT:PSS conductive fibers feature electromagnetic shielding property, tunable electrical conductivity, piezoelectricity, electrochemical sensing property and charge storage capability [11-18]. Moreover, molecular chains in fibers could be oriented along fiber axial direction by drawing process, which made conductive fibers have relatively high conductivity.

PEDOT:PSS conductive fiber could be fabricated by wet-spinning technique with hundreds of meters in length. And it's possible that the preparation technique could be scaled up to an industrial process [19]. However, pure PEDOT:PSS conductive fibers are brittle as well as poor in mechanical property, which limit their utility of applications in many fields. In order to solve these problems, some organic polymers, such as polyurethane [20], polyaniline [21-23], and poly(vinyl alcohol)(PVA) [19], have been blended with PEDOT:PSS with an aim of improving mechanical properties. However, the addition of these organic polymers seriously reduces the electrical conductivity of resultant blend fibers due to their electrical insulation properties. Therefore, it is necessary to come up with effective methods to improve the electrical conductivity of these blend fibers. It is well known that doping of polar organic solvents such as ethylene glycol (EG), dimethylsulfoxide (DMSO), and sorbitol with PEDOT:PSS can significantly increase the conductivity up to 2 or 3 orders of magnitude [24, 25]. Moreover, the conductivity could be enhanced to different degrees by various doping methods. Currently, adding an amount of polar organic solvents into the spinning formulation is the most conventional method of solvent treatment. Seyedin et al. [20] reported that high elastomeric fiber composites with high electrical conductivity were successfully prepared by doping of DMSO into mixed spinning formulation composed of PU and PEDOT:PSS. Jalili et al. [5] reported that with a one-step EG-additive wet-spinning process, significant conductivity improvement on PEDOT:PSS fibers was achieved compared to untreated fibers. Okuzaki et al. [11] reported that significant conductivity enhancement of

PEDOT:PSS fibers was achieved by dipping fibers in EG solution for 3 min. These conventional methods of solvent treatment have limitation on increasing the amount of polar solvent because fiber spinnability and softness will deteriorate with the increase amount of solvent [26]. Therefore, a novel method is put forward to enhance fiber conductivity without influencing fiber spinnability and softness.

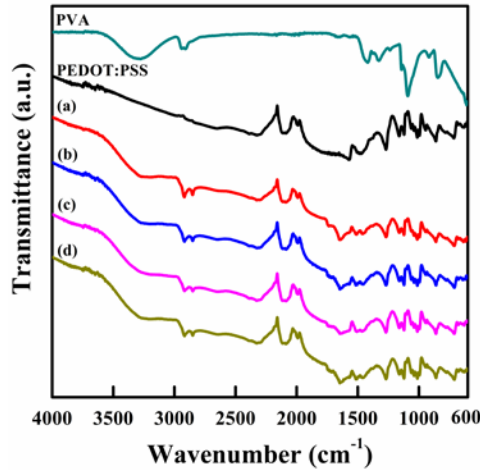
Hence, in this paper, PVA aqueous solution was mixed with PEDOT:PSS aqueous dispersions to prepare PVA/PEDOT:PSS blend fibers via wet-spinning technique. After that, a novel EG vapor annealing treatment was carried out to improve the conductivity of the as-spun PVA/PEDOT:PSS blend fibers. The effects of EG vapor annealing on PVA/PEDOT:PSS blend fibers were investigated in detail by analyzing the changes in chemical components, morphology, conductivity, surface microscopic structure, surface composition and tensile properties. In addition, the mechanisms of the morphological, electrical, componential, and mechanical changes were investigated and discussed in detail.

## **2. RESULTS and DISSCUSSION**

### **2.1 FT-IR spectra**

In order to investigate the effect of EG vapor annealing on chemical structures of PVA/PEDOT:PSS blend fiber, the fourier transform infrared (FTIR) spectroscopy was first carried out by an FT-IR spectrometer. Figure 1 shows the FT-IR spectra of PVA, PEDOT:PSS and PVA/PEDOT:PSS blend fibers annealed for different time, respectively. In the spectra of PVA, the peaks at 2947, 1330, and 849  $\text{cm}^{-1}$  are attributed to C-H symmetrical stretching vibration, C-H in-plane bending vibration,

and C-C stretching vibration of carbon chains, respectively [27, 28]. The peaks at 1420 and 1094  $\text{cm}^{-1}$  correspond to CH-OH bending vibration and C-O stretching vibration, respectively. The absorption band around 3328  $\text{cm}^{-1}$  is attributed to the stretching frequency of -OH group [29]. As for the spectra of PEDOT:PSS, the band at around 2100  $\text{cm}^{-1}$  between 2300 and 1900  $\text{cm}^{-1}$  appears in the spectrum is due to the vibration of  $\text{CO}_2$  molecules [30]. Peaks at 1510 and 1277  $\text{cm}^{-1}$  are assigned to the C=C and C-C stretching vibration of the thiophene ring [29]. The peaks at 1164, 1123, and 1025  $\text{cm}^{-1}$  (two  $\nu_{\text{s-o}}$  bands and one  $\nu_{\text{s-phenyl}}$  band) verify the existence of sulfonic acid group [29]. Peaks at 1066 and 1040  $\text{cm}^{-1}$  correspond to the stretching of C-O-C bonds [30]. And peaks at 952, 858, and 710  $\text{cm}^{-1}$  are related to the stretching vibration C-S bond in the thiophene ring [29, 31]. In the spectra of pristine PVA/PEDOT:PSS blend fiber (Figure 2(a)), the successful formation of blend fiber is confirmed by the presence of characteristic peaks of both PVA and PEDOT:PSS. In addition, compared to the spectra of pristine blend fiber, there are no additional functional groups in the spectra of EG vapor annealed blend fibers (Figure 2(b)-(d)), indicating that vapor annealing treatment does not change the chemical constituents of PVA/PEDOT:PSS blend fiber.

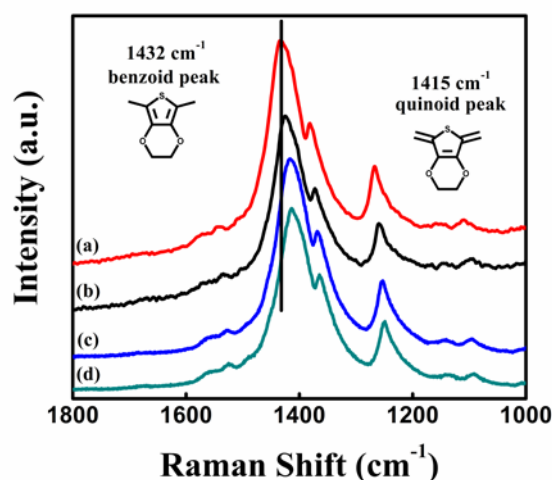


**Fig. 2 FT-IR spectra of PVA, PEDOT:PSS, and PVA/PEDOT:PSS blend fiber annealed by EG vapor for different time: (a) 0min, (b) 10min, (c) 20min, (d) 30min.**

## 2.2 Raman spectra

To explore the molecular structural changes induced by EG vapor annealing, Raman spectra of blend fibers annealed for different time were collected and studied. Figure 2 shows the Raman spectra of blend fibers annealed by EG vapor for different time. In the spectra of pristine PVA/PEDOT:PSS blend fiber(Figure 2(a)), the characteristic peak at  $1432\text{ cm}^{-1}$  was assigned to the stretching vibration of  $C_{\alpha}=C_{\beta}$  on the five-member thiophene ring of PEDOT [32-34], which shifted to red and became weak after EG vapor annealing(Figure 3(b)-(d)), indicating that the resonant structure of PEDOT chain converted from benzoid structure into quinoid structure [35]. These conformational changes were consistent with Ouyang et al [35]. The benzoid structure was regarded as coiled conformation, while the quinoid structure was known as linear or expanded-coiled conformation [35]. According to the related theoretical model of Flory Macromolecular Solution Theory [36, 37], compared to benzoid structure,

quinoid structure was more favorable for inter- and inter chain charge transport in PEDOT, thus lowering the carrier migration energy and improving charge transport rate, which may in turn led to significant enhancement in conductivity of PVA/PEDOT:PSS blend fiber.



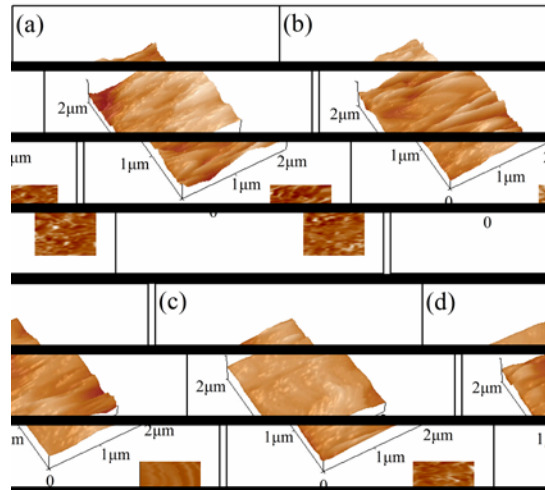
**Fig. 2 Raman spectra of PVA/PEDOT:PSS blend fiber annealed by EG vapor with different time: (a) 0min, (b) 10min, (c) 20min, (d) 30min.**

### 2.3 Morphology

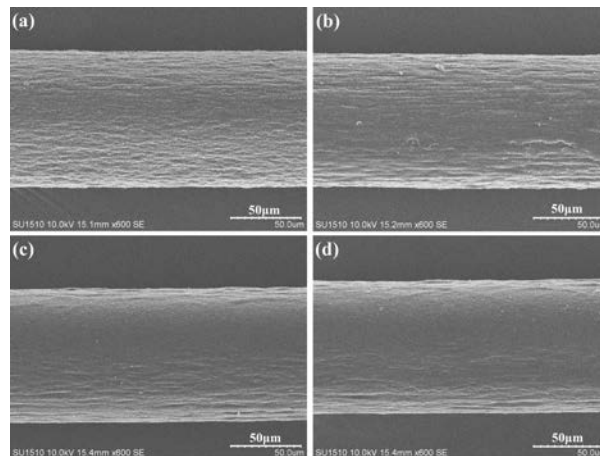
EG vapor annealing influenced not only structures of blend fiber, but also the surface morphology of blend fiber. Atomic force microscopy(AFM) and Scanning Electron Microscope were employed to determine the effect of EG vapor annealing on the surface morphology of blend fiber. Figure 3(a)-(d) shows the height images of PVA/PEDOT:PSS blend fiber annealed by EG vapor for different time; the phase images are presented in the insets of Figure 3(a)-(d). As the annealing time increased from 0 min(pristine) to 30 min, the root-mean-square roughness of blend fiber gradually decreased from 35.8 nm to 18.6 nm, indicating that the surface of blend

fiber became smoother after EG vapor annealing. It can be observed from phase images that as annealing time increased, the clearly revealed PEDOT grains and PSS segments in pristine blend fiber gradually became obscured, indicating that phase separation might occurred between conductive PEDOT grains and amorphous PSS segments in vapor-annealed blend fiber. The presence of PEDOT:PSS was generally regarded as conductive PEDOT grains surrounded by amorphously insulating PSS segments [36,37]. In the pristine blend fiber, the thick and insulating PSS segments hindered the charge transport between adjacent conductive PEDOT grains [12]. After EG vapor annealing, amorphous PSS segments partially moved to the surface of blend fiber, resulting in a highly enriched component of PSS on the surface of blend fiber, as well as thinner PSS layer and better interconnection between conductive PEDOT chains [12], which may significantly improve the conductivity of PVA/PEDOT blend fiber. With respect to the AFM images, Figure 4(a)-(d) shows the SEM images of blend fibers annealed by EG vapor for different time. Fiber diameters under different annealing time are shown in Table 1. There's no obvious change in fiber diameters. But it can be clearly observed from Figure 4 that the surface of blend fiber became smoother as annealing time increased. The surface morphological changes observed in SEM images were consistent with the changes shown in AFM images. That is to say, amorphous PSS segments partly removed to the surface of blend fiber after EG vapor annealing, which helped to smooth the surface of blend fibers





**Fig. 3 AFM height images of PVA/PEDOT:PSS blend fibers annealed by EG vapor for different time: (a) 0min, (b) 10min, (c) 20min, (d) 30min. The insets of figure 3(a)-(d) are the corresponding phase images.**



**Fig. 4 SEM images of PVA/PEDOT:PSS blend fibers annealed by EG vapor for different time: (a) 0min, (b) 10min, (c) 20min, (d) 30min.**

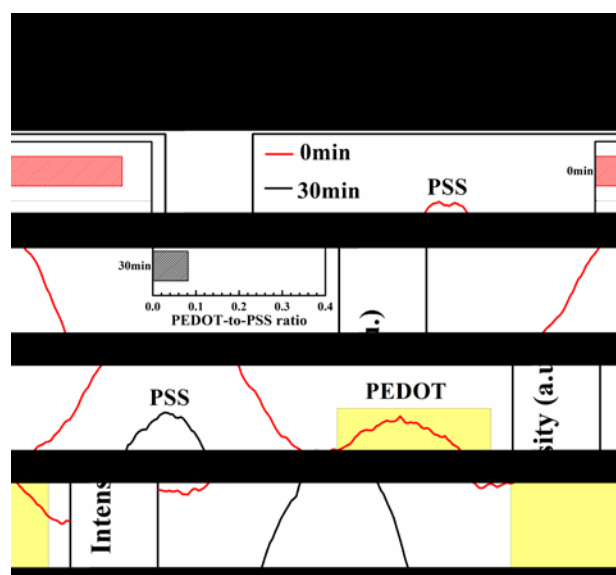
**Table 1 Fiber Diameters at Different Annealing Time**

Annealing Time (min)	Fiber Diameter ( $\mu\text{m}$ )
0	$94.3 \pm 0.7$
10	$93.9 \pm 0.9$
20	$94.1 \pm 1.2$
30	$93.4 \pm 0.6$

## 2.4 XPS analysis

In order to confirm the morphological changes indicated in AFM measurements, X-ray photoelectron spectroscopy (XPS) was used to explore the surface compositional changes of PVA/PEDOT:PSS blend fibers before and after EG vapor annealing. Figure 5 shows the S 2p spectra of PVA/PEDOT:PSS blend fibers before (0 min) and after EG vapor annealing (30 min). The S 2p spectra of PEDOT and the S 2p spectra of PSS have different binding energies due to the sulfur atom in PEDOT existing in the thiophene ring, while the sulfur atom in PSS existing within the sulfonate fragments [38-41]. In Figure 5, the two well-signalized peaks at around 164 eV and 168 eV originate from PEDOT and PSS, respectively [42]. The PEDOT-to-PSS ratio on the surface of blend fiber was calculated by area ratio of the peaks associated with PEDOT and PSS [37]. The ratios were shown in the insets of Figure 5. It can be observed from Figure 5 that the peak corresponding to the PEDOT moiety decreased significantly after EG vapor annealing for 30 min, and the related PEDOT-to-PSS ratio decreased sharply from 0.33 to 0.08, indicating that significant phase separation occurred between PEDOT and PSS, leading to amorphous PSS segments enrich on the surface of annealed blend fiber. These surface compositional changes could well confirm the morphological changes demonstrated in AFM measurements. Furthermore, phase separation between PEDOT and PSS led to insulating and amorphous PSS segments enrich on the surface of annealed blend fiber, resulting in better connection network between PEDOT due to less and thinner PSS

layer acting as barrier between conductive PEDOT grains [12, 36], which might significantly improve the conductivity of PVA/PEDOT:PSS blend fiber.



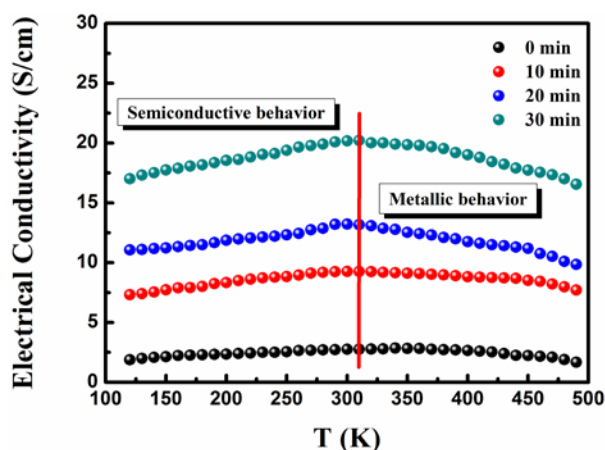
**Fig. 5 XPS( $S_{2P}$ ) spectra of PVA/PEDOT:PSS blend fibers annealed by EG vapor for different time: (a) 0min, (b) 30min. The insets are PEDOT-to-PSS ratios.**

## 2.5 Electrical conductivity

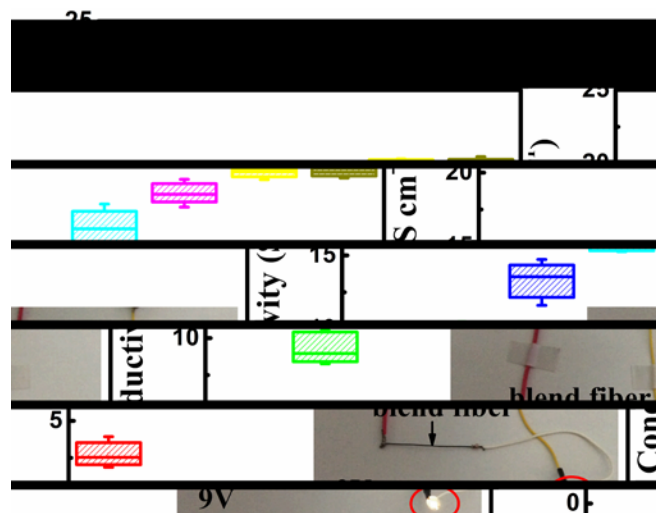
It is well known that better chemical structure, molecular structure, morphology or composition distribution may be more favorable for charge transport in blend fiber [36]. Therefore, in order to investigate the effects of these structural and morphological changes on electrical properties of blend fibers, the electrical properties of PVA/PEDOT:PSS blend fibers annealed for different time were measured. Figure 6 shows the temperature-dependent conductivity of blend fibers annealed for different time. It can be seen from Figure 6 that electrical conductivity of fibers rises at low temperature range (semiconducting characteristics), while declines at high temperature range (metallic characteristics) [12]. The transition temperature is at around 310 K. It is well known that semiconductor-metal transition behavior

widely exists in conductive polymers [15]. The semiconducting behavior could be regarded as carrier hopping or tunneling between PEDOT:PSS grains, while the metallic behavior indicated intra-chain transport [12]. Figure 7 shows the electrical conductivity of blend fibers annealed for different time. As shown in Figure 7, pristine blend fiber had a low conductivity around  $2.5 \text{ S cm}^{-1}$ , and the conductivity gradually improved as the vapor annealing time increased. Above an annealing time of 20 min, the conductivity remained constant above  $19.2 \text{ S cm}^{-1}$ . The conductivity was then basically remained unchanged after 25 min. A peak conductivity of  $20.4 \text{ S cm}^{-1}$  was obtained under the annealing time of 30 min. Furthermore, fiber with the peak conductivity had an amazing ability to lighten an LED bubble as shown in the inset of Figure 7. The improvement in conductivity was well consistent with the structural and morphological changes mentioned above. On the one hand, EG vapor annealing resulted in conformational changes of PEDOT chain from benzoid structure to quinoid structure, which lowered the charge migration energy in blend fiber and in turn led to a remarkable increase in fiber conductivity [35]. On the other hand, EG vapor annealing induced significant phase separation between PEDOT and PSS, leading to a part of amorphous and insulating PSS segments enrich on the surface of blend fiber, which formed a better connection between conductive PEDOT grains due to a thinner insulating PSS layer between PEDOT grains [36]. However, over an annealing time of 30 min, the fiber conductivity showed a slight decline owing to a dewetting phenomenon [43, 44], indicating that an overlong annealing time might result in an unstable conductivity. The evaluation of conductivity stability of blend

fiber under room temperature within a period of time is shown in Table 2. Fiber that annealed by EG vapor for 30 min could obtain a stably high conductivity of  $20 \text{ S cm}^{-1}$ , and this value was nearly 9 times higher than that of pristine blend fiber. Therefore, it was obvious that EG vapor annealing was an effective method to improve the conductivity of PVA/PEDOT:PSS blend fiber.



**Fig. 6 Temperature-dependant electrical conductivity of PVA/PEDOT:PSS blend fibers annealed by EG vapor for different time.**



**Fig. 7 Conductivity of PVA/PEDOT:PSS blend fibers annealed by EG vapor for different time. The inset is the demonstration of an LED bubble lightened by PVA/PEDOT:PSS blend fiber that annealed by EG vapor for 30 min.**

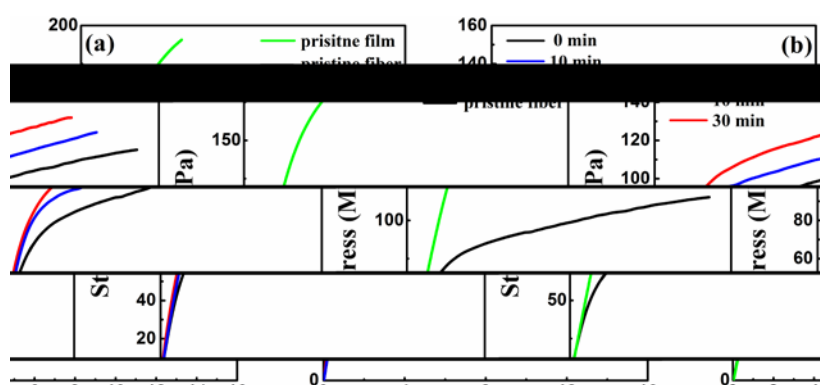
**Table 2 Evaluation of Conductivity Stability After a Period of Environmental Exposition**

Time (min)	Conductivity ( $\text{S cm}^{-1}$ )
30	$20.0 \pm 0.3$
60	$20.0 \pm 0.1$
120	$19.3 \pm 0.4$
240	$19.1 \pm 0.6$

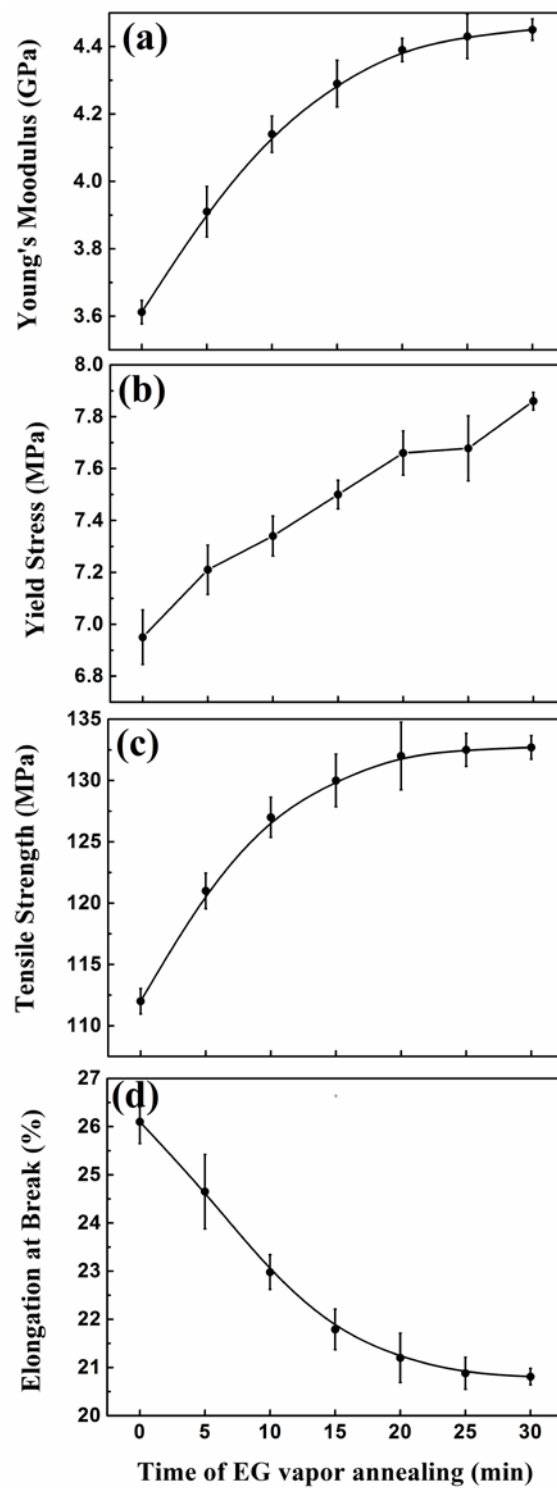
## 2.6 Tensile properties

In fact, EG vapor annealing not only improved the conductivity of PVA/PEDOT:PSS blend fiber, but also enhanced the tensile properties of blend fiber. For comparison, stress-strain curves of untreated casting film with respect to untreated blend fiber are represented in Figure 8 (a). It can be observed from Figure 8 (a) that Young's modulus (7.4 GPa) and tensile strength (190.0 MPa) of cast film were both higher than those of blend fiber. Cast film has a relatively more even structure than blend fiber due to the possible structural defects formed during the fast dehydration process within fiber [45]. Representative stress-strain curves of blend fibers annealed for 0 min, 10 min and 30 min respectively are shown in Figure 8 (b). In order to investigate the effects of EG vapor annealing on tensile properties of blend fibers, the Young's modulus, yield stress, tensile strength, and the elongation at break of blend fibers annealed for different time were measured as shown in Figure 9. It can be observed from Figure 9 that tensile properties of blend fibers were dramatically improved by EG vapor annealing, with Young's modulus and tensile strength increased from 3.6 GPa and 112.0 MPa to 4.4 GPa and 132.7 MPa, respectively. This result can be explained by the conformational changes resulted from vapor annealing.

EG vapor annealing made PEDOT chain converted from benzoid structure to quinoid structure, corresponding to  $C_{\alpha}=C_{\beta}$  on each thiophene ring turning into  $C_{\alpha}-C_{\beta}$  [46], while  $C_{\alpha}-C_{\beta}$  connecting two adjacent thiophene rings turning into  $C_{\alpha}=C_{\beta}$  [46]. This conformational changes weakened the internal rotation interaction of single bond, thus enhancing the molecular chain rigidity [42, 47]. Therefore, as annealing time increased, the Young's modulus of blend fiber increased, while the elongation at break of blend fiber decreased. It is understandable that the interaction among PEDOT chains with linear structure is stronger than that among PEDOT chains with coiled structure [35]. The quinoid-structural PEDOT chain could intertwine with PVA chains more tightly due to its linear or expanded-coiled structure, which would decrease the number of structural defects at which deformation or fractures usually took place due to stress concentration [11], and thus improved the tensile strength of blend fiber.



**Fig. 8 Representative stress-strain curves of: (a) unannealed PVA/PEDOT:PSS blend fiber with respect to unannealed PVA/PEDOT:PSS blend film, (b) PVA/PEDOT:PSS blend fiber annealed by EG vapor for different time.**



**Fig. 9** Tensile properties of PVA/PEDOT:PSS blend fibers annealed by EG vapor for different time: (a) Young's modulus, (b) yield stress, (c) tensile strength, (d) elongation at break.



### 3 CONCLUSIONS

In conclusion, EG vapor annealing induced significant phase separation between PEDOT and PSS, forming an enriched PSS layer on the surface of blend fiber, leading to thinner insulating PSS layer and better connection between conductive PEDOT grains, which helped to improve the conductivity of PVA/PEDOT:PSS blend fiber. EG vapor annealing also led to conformational changes of PEDOT chain from benzoid structure to quinoid structure. The resultant PVA/PEDOT:PSS blend fiber showed an enhanced conductivity up to  $20.4 \text{ S cm}^{-1}$ . As vapor annealing time increased, the Young's modulus and tensile strength of blend fiber increased from 3.6 GPa and 112 MPa to 4.4 GPa and 132.7 MPa respectively, while the elongation at break of blend fiber decreased.

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