Stretchable and Conductive Polymer Films Prepared by Solution Blending

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Ⓢ *Supporting Information*

ABSTRACT: Stretchable and conductive materials can have important application in many areas, such as wearable electronics and healthcare devices. Conducting polymers have very limited elasticity because of their rigid conjugated backbone. In this work, highly stretchable and conductive polymer films are prepared by coating or casting aqueous solution of poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) and a soft polymer, including poly(ethylene glycol), poly(ethylene oxide), or poly(vinyl alcohol). The soft polymers can greatly improve the stretchability and the conductivity of PEDOT:PSS. The elongation at break can be increased from 2% up to 55%. The soft polymers can also enhance the conductivity of PEDOT:PSS from 0.2 up to 75 S cm^{-1}. The conductivity is further enhanced by adding dimethyl sulfoxide (DMSO) or ethylene glycol (EG) into the aqueous solutions of the polymer blends. Polymer blends with an elongation at break of close to 50% and a conductivity of 172 S cm^{-1} are attained.

KEYWORDS: *elastic, conductive polymer, stretchable conductor, PEDOT:PSS, polymer blend*
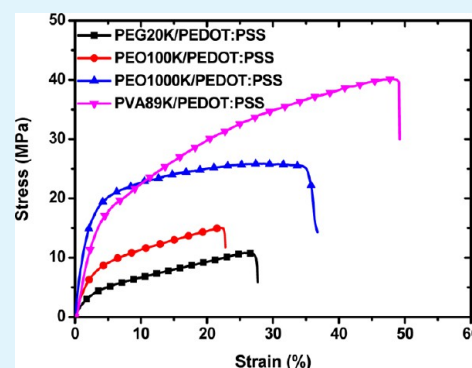
1. INTRODUCTION

Stretchable electronic devices have received more and more attention, because they can be important units in many systems, such as displays, robots, wearable electronics, and healthcare equipment.[1−4] Apart from the active materials, a stretchable electronic device requires compliant electrodes. The compliant electrodes should follow the mechanical movement of the active materials and maintain high conductivity at large strain. However, traditional conductors like metals are not stretchable, while traditional elastomers like polyurethane (PU) and poly(dimethylsiloxane) (PDMS) are not conductive. Therefore, it is significant to develop new materials with both high stretchability and conductivity. A couple of methods were developed to fabricate stretchable conductors. One is to process metal wires or carbon nanotubes into a wavy or tortuous shape.[5,6] Another method is to incorporate conductive fillers, such as metal nanoparticles,[7−11] carbon nanotubes,[4,12−16] and graphene,[17−20] into elastomers. However, these methods have drawbacks, such as poor processability and unsatisfactory performance in terms of conductivity, flexibility, and elongation.[5,21]

Conductive polymers can be good candidates for stretchable electrodes. Conductive polymers have high mechanical flexibility but limited elasticity, since their conjugated backbone is rigid.[22−24] Methods have been developed to increase the stretchability of conducting polymers. For example, Yoshikawa et al. blended polyaniline with polyurethane elastomer.[25] Although the polymer blends could be stretched up to 200%, their conductivity was only 10^{-6} S cm^{-1}.[25] Blends of polypyrrole and polyol-borate composite films were synthesized by electrochemical polymerization of pyrrole at the presence of polyol-borate in

solution. The polymer blends exhibited a conductivity of 116 S cm^{-1} and an ultimate elongation of 23%.[26] Stoyanov et al. covalently bonded polyaniline to a soft triblock copolymer (poly(styrene-*co*-ethylenebutylene-*co*-styrene) grafted with maleic anhydride and then mixed it with elastic copolymer poly(styrene-*co*-ethylenebutylene-*co*-styrene (SEBS). They observed a conductivity of 100 S cm^{-1} and an ultimate elongation of 180%.[27,28] Hansen et al. reported blends of polyurethane (PU) and poly(3,4-ethylenedioxythiophene) (PEDOT).[29] The blend films were prepared by spin coating a solution of 3,4-ethylenedioxythiophene (EDOT), an oxidation agent, and PU and postcoating heating. The polymer films could be stretched by more than 100% and have a conductivity of 100 S cm^{-1}. However, these conductive polymers have poor solution processability. Efforts were also made to increase the elasticity of solution-processable poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS, chemical structure shown in Figure 1). PEDOT:PSS is the most successful conductive polymer in terms of the practical application.[24,30−33] It can be dispersed in water and some polar organic solvents. In a comparison with other conducting polymers like polyaniline and polypyrrole, PEDOT:PSS can have higher conductivity and transparency in the visible range.[24,34,35] It has been used in capacitors,[36,37] sensors,[38] soft actuators,[39] electrode materials, and optoelectronic displays.[40,41] However, PEDOT:PSS cannot be used for a compliant electrode because of its limited elasticity.[21,42] To increase its elasticity, Chiu et al. dispersed
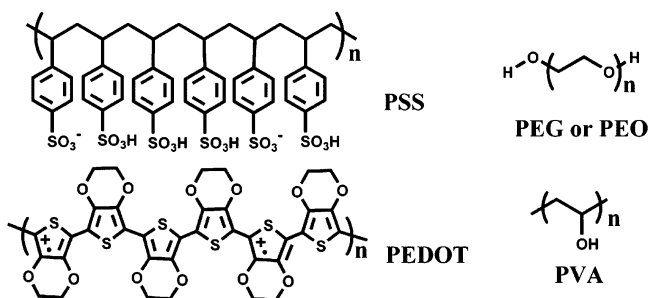
Figure 1. Chemical structures of PEDOT:PSS, PEG (PEO), and PVA. PEG and PEO are different in the molecular weight. When the molecular weight is lower than 100 000, the polymer is usually referred as PEG. PEO has molecular weight of higher than 100 000.

poly(*n*-butyl acrylate−styrene) (P(BA−St)) into PEDOT:PSS aqueous solution.[21,43] Surfactants were needed to stabilize P(BA−St) in water. The PEDOT:PSS/P(BA−St) blends can have an ultimate elongation of 97% and a conductivity of 63 S cm^{-1}. Because P(BA-St) can be dispersed in water only at the assistance of surfactants, the structure and properties of the blends are strongly dependent on the surfactants.

It is significant to develop a facile method to prepare solution-processable conducting polymers with high elasticity. In this work, we report highly elastic and conductive polymers by blending PEDOT:PSS with a water-soluble soft polymer, such as poly(ethylene glycol) (PEG), poly(ethylene oxide) (PEO), or poly(vinyl alcohol) (PVA). The soft polymers improve both the stretchability and the conductivity of PEDOT:PSS. The ultimate elongation is increased from 2% up to 55%, and the conductivity is enhanced from 0.2 up to 75 S cm^{-1}. The conductivity is further improved to higher than 100 S cm^{-1} by adding dimethyl sulfoxide (DMSO) or ethylene glycol (EG) into the aqueous solutions of the polymer blends.

2. EXPERIMENTAL SECTION

2.1. Preparation of Polymer Blends. PEDOT:PSS aqueous solution (Clevios PH 1000 Lot 2014P0146) was purchased from Heraeus. PEDOT:PSS had a concentration of 1.3% by weight in the solution, and the PSS-to-PEDOT weight ratio was 2.5. All other chemicals, including PEG20K (M_n = 20K), PEO100K (M_v = 100K), PEO1000K (M_v = 1000K), PVA89K (M_w = 89K−98K), DMSO, and EG, were supplied by Sigma-Aldrich. All the chemicals were used as received without further purification. Glass substrates were provided by the Continental Lab.

An aqueous solution of PEDOT:PSS and a soft polymer was prepared by adding the soft polymer into the PEDOT:PSS aqueous solution. The weight fraction of the soft polymer was defined as the weight ratio of the soft polymer to the total weight of both the soft polymer and PEDOT:PSS. The solution was stirred at 70 °C overnight. Thin polymer blend films were prepared by spin coating an aqueous solutions of PEDOT:PSS and a soft polymer on glass substrates with a size of 1.3 × 1.3 cm^2, which were precleaned sequentially with detergent, deionized (DI) water, acetone, and isopropyl alcohol. The polymer blend films were then dried at 110 °C on a hot plate for 40 min. A thick polymer blend film was prepared by drop-casting the solution of polymer blend on glass substrate and then dried at 70 °C in an oven for 3 h. After being cooled to room temperature, the thick polymer films were peeled off from substrate and were cut into rectangle strips of 20 × 2 mm^2 for mechanical and electrical tests.

2.2. Materials Characterization. The electrical conductivities of thin polymer films by spin coating were measured by the van der Pauw four-point probe technique with a Keithley 2400 source/meter. Indium was pressed on the four corners of each polymer film on the glass substrate to facilitate the electrical contact. The conductivities of thick

polymer films by drop casting were measured by the four-point probe technique with the four copper wires in parallel. The 4 wires were connected to the polymer film with Ag paste. The tensile properties were measured using an Instron Model 3345 Materials Testing System with a 10 N load cell at a strain rate of 3 mm min^{-1}. The thicknesses of the thin films were measured with an Alpha 500 step profiler, while the thicknesses of the free-standing composite films were determined with a Mitutoyo digimatic micrometer. Atomic force microscopic (AFM) images were acquired using a Veeco Nano Scope IV Multi-Mode AFM operated in tapping mode.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties of Polymer Blends. The stress−strain behaviors of neat PEDOT:PSS and soft polymers that are used to form blends with PEDOT:PSS were investigated first (Figure 2 and Figure S1). Neat PEDOT:PSS films has very
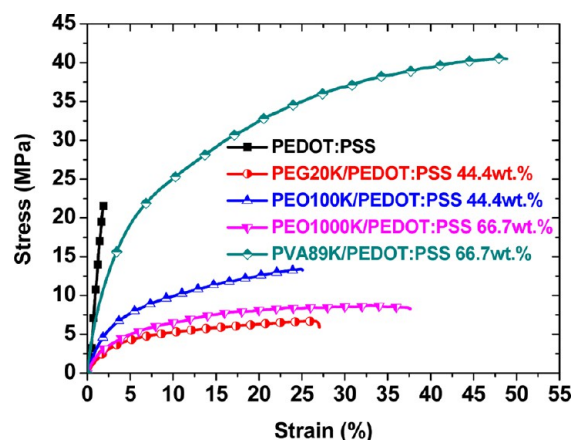

Figure 2. Representative stress−strain curves of neat PEDOT:PSS and polymer blends of PEDOT:PSS with soft polymers.

limited elasticity. Its elongation at break is about 2%, and its tensile strength is 21 MPa. The high tensile strength and low elongation at break can be attributed to the rigid conjugated PEDOT chains. In contrast, the tensile strengths of PEG20K, PEO100K, and PEO1000K are significantly lower than that of PEDOT:PSS. The elongations at break are 1% and 2.1% for PEG20K and PEO100K, respectively, whereas it is 280% for PEO1000K. The high elongation at break observed on PEO of high molecular weight is consistent with that reported by Banthia et al.[44] Although PEG20K and PEO100K have flexible polymer chains, their elongations at break are low because of their high crystallinity. The dependence of the flexibility on the molecular weight is ascribed to the crystallite sizes. As shown in Figure S2, large crystallites could be observed in pure PEG20K and PEO100K films by optical microscopy. But the PEO1000K film is quite uniform, indicating more amorphous structure than PEG20K and PEO100K. PVA89K exhibits a tensile strength comparable to PEDOT:PSS, but its elongation at break is about 230%. The high tensile strength is due to the hydrogen bonds among the PVA chains. This is similar to that reported in the literature.[45]

A polymer blend was prepared by adding a soft polymer into the PEDOT:PSS aqueous solution. Figure 2 presents the representative stress−strain curves of blends of PEDOT:PSS with PEG20K, PEO100K, PEO1000K, and PVA89K. Blending a soft polymer significantly changes the mechanical properties of PEDOT:PSS (Figure S3). The incorporation of PEG20K, PEO100K, or PEO1000K lowers the tensile strength while increases the elongation at break, while PVA89K can simultaneously
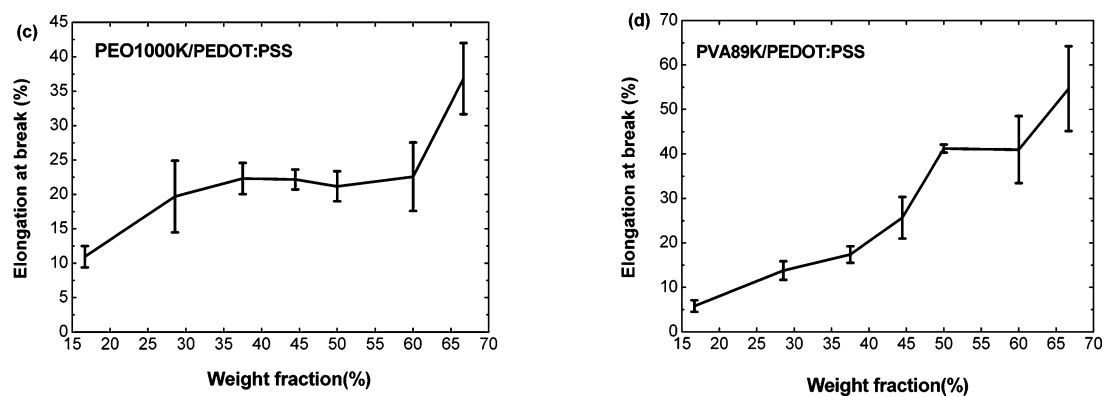
Figure 3. Variation of the elongations at break of the polymer blends with the weight fraction of (a) PEG20K, (b) PEO100K, (c) PEO1000K, and (d) PVA89K to PEDOT:PSS.
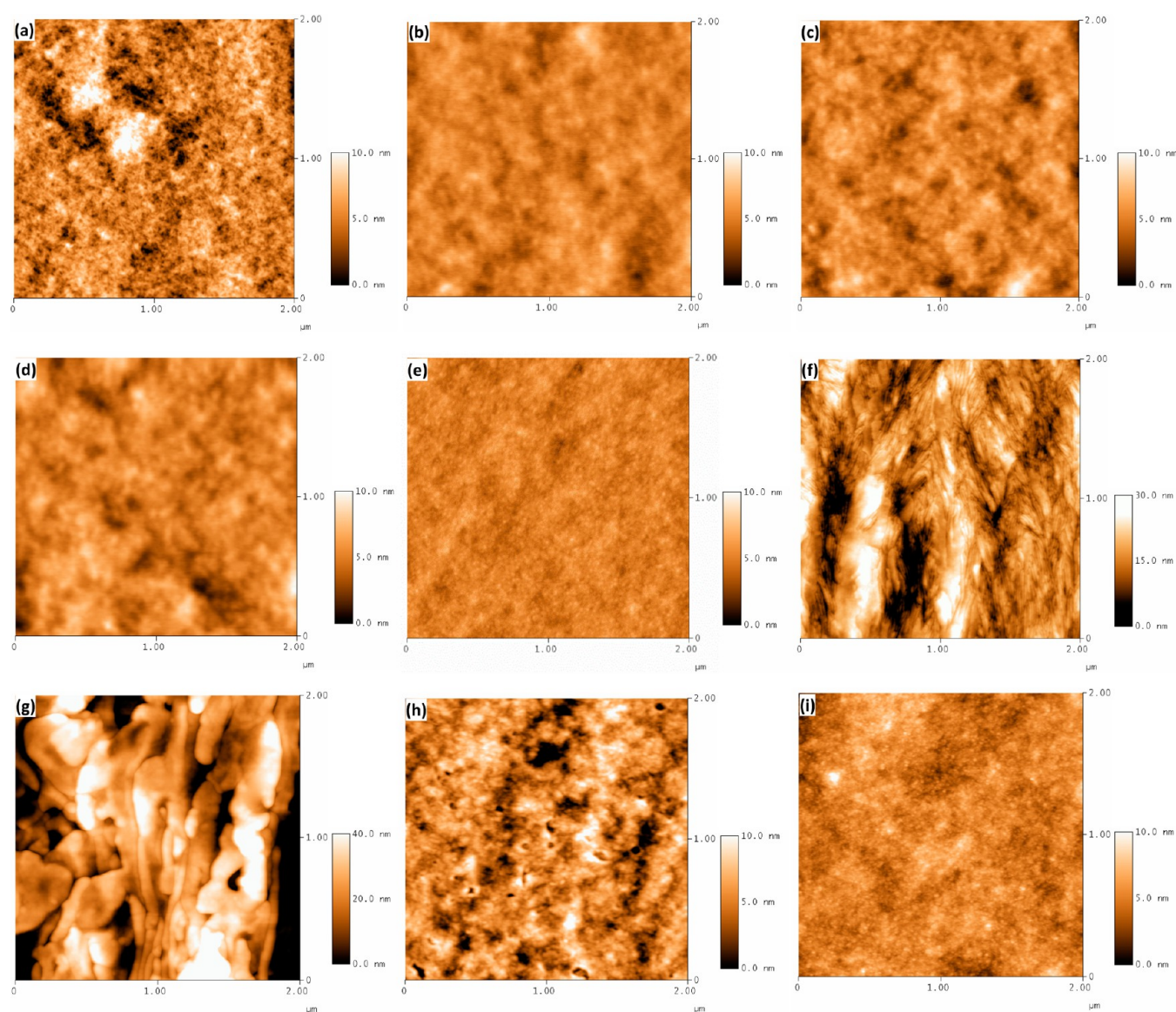
Figure 4. AFM images of polymer films: (a) PEDOT:PSS, (b and f) PEG20K/PEDOT:PSS, (c and g) PEO100K/PEDOT:PSS, (d and h) PEO1000K/PEDOT:PSS, (e and i) PVA89K/PEDOT:PSS. The soft polymer weight fractions are 44.4 wt % for parts b−e and 66.7 wt % for parts f−i.

increase the tensile strength and the elongation at break. But further increase in the weight fraction of PEO1000K or PVA89K to 75.0 wt % leads to a gel, and the gel cannot be processed to free-standing polymer films.

As shown in Figure 3, there is an optimal loading for PEG20K or PEO100K in the polymer blends in terms of the elongation at break. The elongation at break at first increases with the increase of the soft polymer loading, reaches the maximum at a weight fraction of 44.4 wt %, and then decreases with a further increase in the loading of the soft polymer. The decrease of the elongation at break for the polymer blends at high loading of PEG20K and PEO100K may be due to formation of large crystallites. For blends of PEDOT:PSS with PEG20K or PEO100K, the soft polymer begins to form crystallites when its weight fraction reaches 37.5 wt % as revealed by differential scanning calorimetry (DSC, Figure S4). The increase in the soft polymer loading leads to higher crystallinity of the polymer blends (Table S1). Thus, at a high weight fraction such as 60.0 or 66.7 wt %, the polymer blends of PEG20K and PEO100K become brittle, similar to the pure PEG20K and PEO100K films.

The mechanical properties of PEO1000K/PEDOT:PSS and PVA89K/PEDOT:PSS at high loading of these soft polymer are different. Their elongation at break keeps increasing with the increase of the soft polymer loading the polymer blends. At a high polymer weight fraction of 66.7 wt %, PEO1000K/PEDOT:PSS and PVA89K/PEDOT:PSS exhibit the highest elongations at break of 36.8 ± 5.2% and 54.7 ± 9.5%, respectively.

AFM images were acquired to study the surface morphology of the polymer blend films by drop casting (Figure 4). The AFM images of the polymer blends at soft polymer weight fraction of 44.4 wt % are relatively smooth for all the soft polymers, including PEG20K, PEO100K, PEO1000K, and PVA89K. The domains are small. The root-mean-square (RMS) roughness is 1.79 nm for the neat PEDOT:PSS film, and it is 0.90, 1.11, 1.16, and 0.65 nm for PEG20K/PEDOT:PSS, PEO100K/PEDOT:PSS, PEO1000K/PEDOT:PSS, and PVA89K/PEDOT:PSS, respectively. The AFM images suggest that the soft polymer can blend well with PEDOT:PSS at such a ratio. The good miscibility of these soft polymers with PEDOT:PSS is presumably related to the interaction between the soft polymers and PSSH. The hydroxyl group of PSSH can form a hydrogen bond with the oxygen of the soft polymers. The interaction becomes even stronger for PVA that has hydroxyl groups as well. Because the soft polymer can strongly interact with PSS, it can have an effect on the conformation of the PEDOT chain and lead to the change in the conductivity.[41,46]

As observed by DSC, the crystallinity of the polymer blends depends on the loading of the soft polymer. The AFM images become different when the loadings of the soft polymers are high. When the soft polymer weight fraction increases to 66.7 wt %, crystallites in several hundred nanometer to micrometer size can be observed for PEG20K/PEDOT:PSS and PEO100K/PEDOT:PSS. Their RMS roughnesses increase to 5.02 and 13.58 nm, respectively. The large crystallites make the polymer blends brittle and break at low elongation. These AFM images are consistent with the mechanical properties of the polymer blends.

However, the AFM images are quite smooth for PEO1000K/PEDOT:PSS and PVA89K/PEDOT:PSS even at the soft polymer weight fraction of 66.7 wt %. The domain size is less than 100 nm, and no large crystallite can be observed. Their RMS roughnesses are only 1.97 and 1.09 nm, respectively. The crystallization of PEO becomes difficult at high molecular weight, so that it gives rise to a much smoother AFM image for PEO1000K/PEDOT:PSS than that of PEG20K/PEDOT:PSS and PEO100K/PEDOT:PSS. At the soft polymer weight fraction
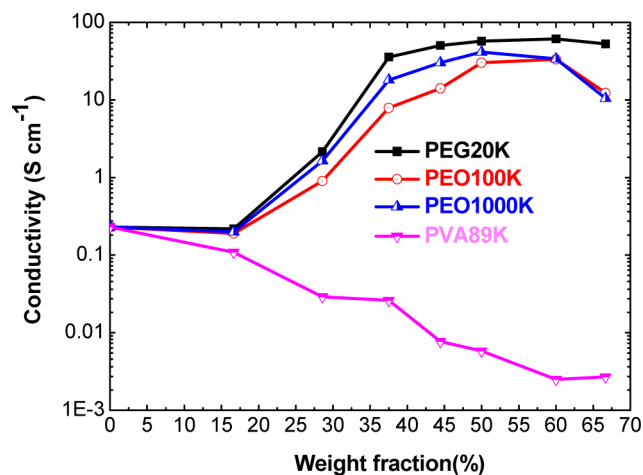

Figure 5. Variation of the conductivities of thin polymer blend films prepared by spin coating with the weight fraction of the soft polymer.
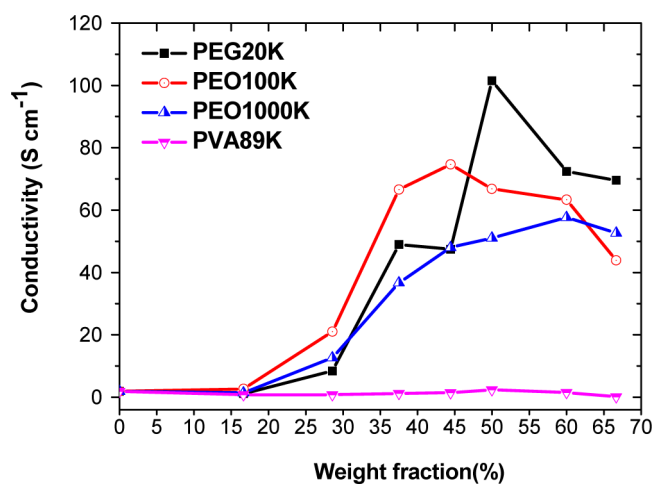

Figure 6. Variation of the conductivities of thick free-standing polymer films with the weight fraction of soft polymer in the blend.

of 66.7 wt %, the PVA89K/PEDOT:PSS film is the smoothest among the polymer blends. This is related to the strong interaction between PVA and PEDOT:PSS.

3.2. Conductivity of Polymer Blends. Apart from the stretchability, the conductivity is another important parameter for the application of conducting polymers as the stretchable electrode. The conductivities of thin films of PEDOT:PSS/soft polymer bends prepared by spin coating were measured. As shown in Figure 5, the conductivity of PEDOT:PSS can be significantly enhanced when it is blended with PEG20K, PEO100K, or PEO1000K. The conductivities first increase with the increase of the polymer loading and then decrease with the further increase in the polymer loading. The optimal conductivities are 61, 33, and 41 S cm^{-1} for PEG20K/PEDOT:PSS, PEO100K/PEDOT:PSS, and PEO1000K/PEDOT:PSS, respectively. In terms of the conductivity, the optimal weight fractions of soft polymers are 60.0, 60.0, and 50.0 wt % for PEG20K/PEDOT:PSS, PEO100K/PEDOT:PSS, and PEO1000K/PEDOT:PSS, respectively. The conductivity change by blending PEG or PEO is similar to that in literature by blending poly-(ethylene glycol) with a molecule weight below 6000 to PEDOT:PSS.[41,47,48] The conductivity enhancement can be attributed to the screening of the Coulombic interaction between PEDOT and PSS by the soft polymers. The screening can lead to
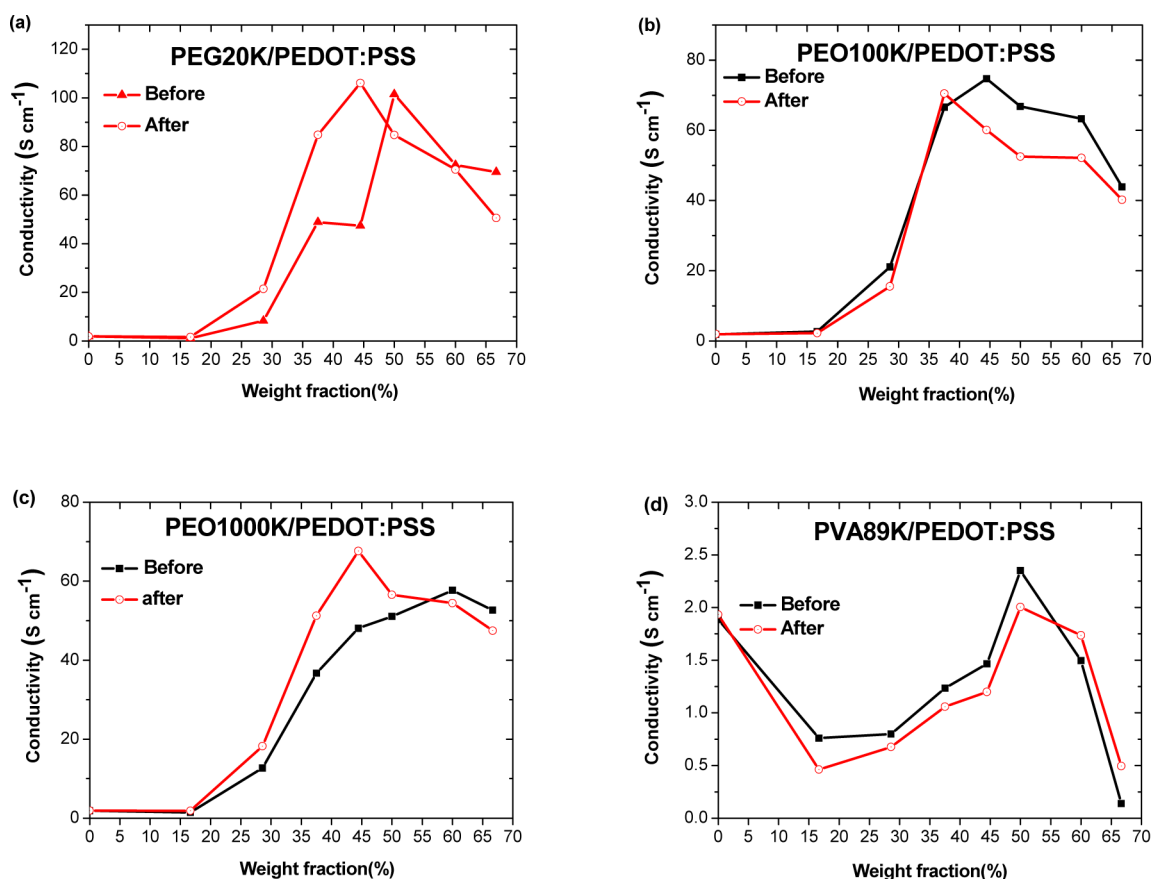
Figure 7. Conductivities of free-standing thick polymer blend films before and after tensile experiment: (a) PEG20K/PEDOT:PSS, (b) PEO100K/PEDOT:PSS, (c) PEO1000K/PEDOT:PSS, (d) PVA89K/PEDOT:PSS.

phase segregation of PSSH from PEDOT:PSS and change of conformation of PEDOT chains from coil to extended coil or linear. This effect is confirmed by the morphological change of the blend films (Figure S5). A neat PEDOT:PSS film has small grains (Figure S5a). The grain size increases after the blending of a soft polymer (Figure S5b−e). However, because the soft polymers are insulators, the conductivity of the polymer blends decreases when the loading of the soft polymers is too high. Thus, there is an optimal loading of the soft polymers in terms of the conductivity.

PVA89K gives rise to a different effect on the conductivity of PEDOT:PSS. The conductivity continuously decreases with the increase of the PVA89K loading in the polymer blend. It decreases by 2 orders in magnitude when the weight fraction of PVA89K reaches 66.7 wt %. The different effects on the conductivity of PEDOT:PSS can be ascribed to the different interactions of these soft polymers with PEDOT:PSS. PVA89K can have for strong hydrogen bonds with PEDOT:PSS.[49−51] For PVA89K/PEDOT:PSS blend films, the PEDOT:PSS grain sizes are almost unchanged compared with those of neat PEDOT:PSS and are well-dispersed in the blend films (Figure S5f). Thus, the conductivity decreased when there is more insulated PVA89K in the blend films.

The conductivity of thick free-standing polymer films fabricated by drop casting aqueous solution of PEDOT:PSS and a soft polymer were also investigated. As shown in Figure 6, the effects of the soft polymers on the conductivity of thick polymer films are similar to that on the thin polymer films by spin coating. When PEG20K, PEO100K, or PEO1000K is blended with PEDOT:PSS, there is an optimal loading of these soft

## Table 1. Conductivities of Polymer Blends of a Soft Polymer with PEDOT:PSS at Optimal Loading of the Soft Polymers[a]

additive	PEG20K (44.4 wt %)	PEO100K (44.4 wt %)	PEO1000K (66.7 wt %)	PVA89K (66.7 wt %)
none	47.4	74.6	52.6	0.14
5 vol % DMSO	130	238	105	142
3 vol % EG	176	245	135	172

[a]The polymer blends were prepared from aqueous solutions added with DMSO or EG.

polymers in the blends in terms of their conductivities. The highest conductivity is 101 S cm^{-1} for PEG20K/PEDOT:PSS at PEG20K weight fraction of 50.0 wt %. It is 74.7 S cm^{-1} for PEO100K/PEDOT:PSS at PEO100K weight fraction of 44.4 wt % and 57.7 S cm^{-1} for PEO1000K/PEDOT:PSS at PEO1000K weight fraction of 60.0 wt %. The conductivity of PVA89K/PEDOT:PSS film also decreases when the loading of PVA89K is very high.

The polymer chains can be oriented and finally break down during a tensile experiment. The conductivities of the blend films after breakdown by the tensile experiment were measured along the tensile direction (Figure 7). The conductivity of the polymer blends after the tensile experiment is not too different from that before the tensile experiment.

3.3. Conductivity Enhancement of Polymer Blends by Organic Solvents. For the application as the stretchable electrode, the conducting polymers should have high stretchability and high conductivity. Table 1 lists the conductivities of the polymer blends with the optimal soft polymer loading for the
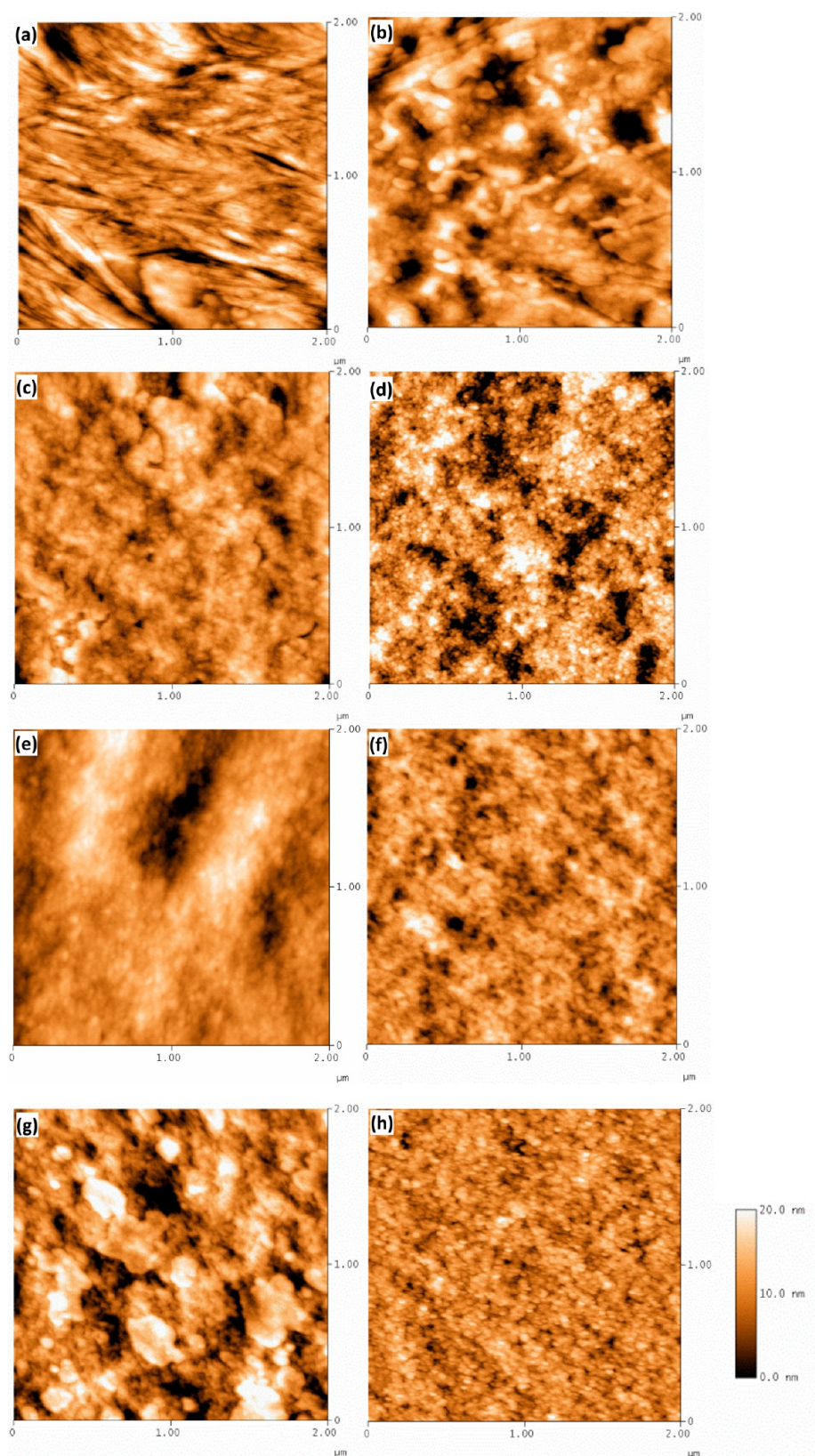
Figure 8. AFM images of polymer films of (a and e) PEG20K/PEDOT:PSS, (b and f) PEO100K/PEDOT:PSS, (c and g) PEO1000K/PEDOT:PSS, (d and h) PVA89K/PEDOT:PSS. A 5 vol % DMSO solution was added into the polymer blend solutions for parts a–d; 3 vol % EG was added into the polymer blend solutions for parts e–h.

elongation at break. Although PVA89K/PEDOT:PSS exhibits the highest elongation at break among these polymer blends, its conductivity is only 0.14 S cm^{-1}.

Organic solvents, including DMSO and EG, were added into the aqueous solutions of the polymer blends to further increase their conductivities.[24,40,41,52] As shown in Table 1, DMSO or EG
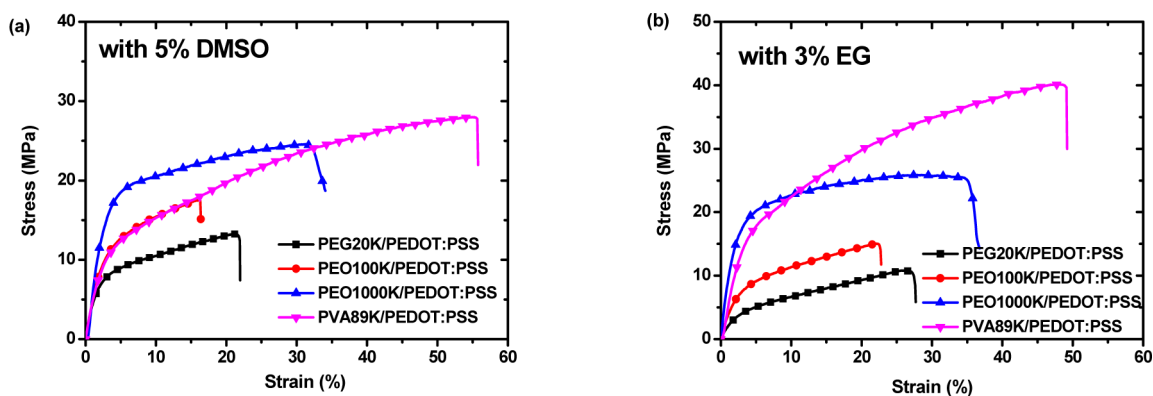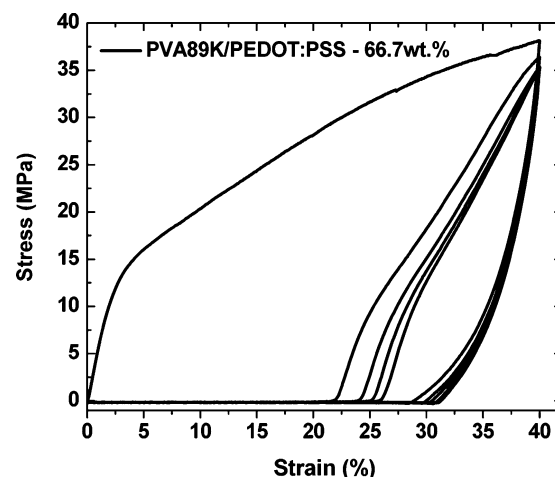
Figure 9. Stress−strain curves of free-standing PEDOT:PSS/soft polymer blends prepared from their aqueous solution added with (a) DMSO and (b) EG.
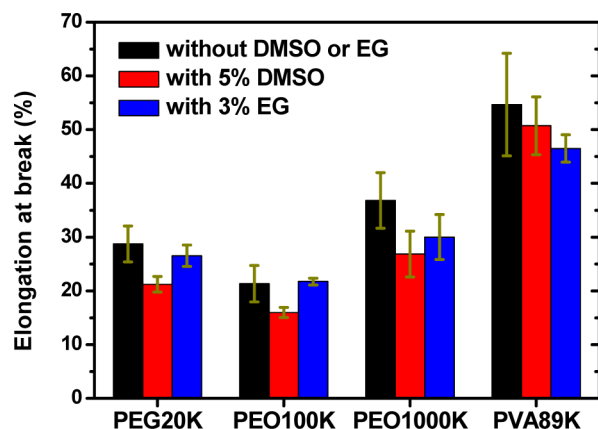
Figure 10. Elongation at break of the soft polymer/PEDOT:PSS blends prepared from their aqueous solutions without additive or with added DMSO or EG.

Figure 11. Stress−strain curves of PVA89K/PEDOT:PSS-66.7 wt % (with 3 vol % EG as additive) blend film during the 40% cyclic strain.

can significantly enhance the conductivity of the polymer blends, particularly for PVA89K/PEDOT:PSS. EG gives rise to even higher conductivities for all the polymer blends. By the addition of 3 vol % EG, the conductivity increases to 176 S cm^{-1} for PEG20K-PEDOT:PSS, 245 S cm^{-1} for PEO100K-PEDOT:PSS, 135 S cm^{-1} for PEO1000K-PEDOT:PSS, and 172 S cm^{-1} for PVA89K-PEDOT:PSS. The conductivity enhancement can be attributed to the additive induced phase segregation of PSSH from PEDOT:PSS and conformational change of PEDOT chains from coil to extended coil or line.[24,41,53] This is evidence by their AFM images (Figure 8). After the addition of DMSO or EG, the domains become much larger than that without any additive in the aqueous solutions of the polymer blends. The change in the surface morphology is particularly significant for PVA89K/PEDOT:PSS.

3.4. Mechanical Properties of Polymer Blends with Organic Solvent Additive. The mechanical properties of the polymer blend films with EG or DMSO in their aqueous solutions were also studied. Figure 9 presents the stress−strain curves. The elongations at break are presented in Figure 10. The addition of 5 vol % DMSO or 3 vol % EG only slightly lowers the elongation at break for all the polymer blends. PVA89K/PEDOT:PSS always has the highest elongation at break among all polymer blends. At the addition of 5 vol % DMSO, the PVA89K/PEDOT:PSS has a conductivity of 142 S cm^{-1} and an elongation at break of 51%. The conductivity and elongation at break are 172 S cm^{-1} and 47%, respectively, when 3 vol % EG is added.

The elasticity of the polymer blends was investigated. A 40% cyclic strain of the highly stretchable PVA89K/PEDOT:PSS (with 3 vol % EG as additive) is present in Figure 11. In the initial cycle, the blend film can recover 11.4% strain after the release of the stress. The plastic deformation could be attributed to the plastic property of PVA. The blend film can recover ca. 9% strain after five cycles.

4. CONCLUSION

A facile method is presented to prepare highly stretchable and conductive polymer films by adding a soft polymer, including poly(ethylene glycol), poly(ethylene oxide), or poly(vinyl alcohol) into the PEDOT:PSS aqueous solution. The soft polymers can greatly improve the stretchability and the conductivity of PEDOT:PSS. The elongation at break is about 2% for neat PEDOT:PSS, and it is increased up to 55% by blending with PVA. The soft polymers can also enhance the conductivity of PEDOT:PSS from 0.2 up to 75 S cm^{-1}. The conductivities of the polymer blends are further enhanced by adding DMSO or EG into the aqueous solutions of the polymer blends. PVA89/PEDOT:PSS can exhibit an elongation at break of close to 50% and a conductivity of 172 S cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04492.

Stress—strain cure of neat PEDOT:PSS and soft polymers as well as blend films; optical microscopic images of neat polymers; DSCs of polymer blends; and table of the melting point, latent heat of melting, and crystallinity of polymers and polymer blends; AFM images of polymer blend films prepared by spin coating (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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