Electrical Conductivity of Polymer Blends of Poly(3,4-ethylenedioxythiophene) : Poly(styrenesulfonate) : N-Methyl-2-pyrrolidinone and Polyvinyl Alcohol

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ABSTRACT: The goal of this study is to determine the electrically conductivity of the polymers poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) : N-methyl-2-pyrrolidinone (PEDOT : PSS : NMP) and PEDOT : PSS when blended with polyvinyl alcohol (PVA). While the conducting polymers have high conductivity when not blended with PVA, they are brittle and difficult to spin-coat. Thus, the motivation for this study is to develop blends of these two conducting polymers with PVA to produce a material with optimized mechanical properties and that can also be spin-coated. The blends are produced using aqueous preparations of these materials. Mixtures of various weight percentages (wt %) of PEDOT : PSS : NMP and PEDOT : PSS are prepared and spin-coated on glass slides to form thin films. In the blends, the film conductivity increases with increasing content of either PEDOT : PSS : NMP or PEDOT : PSS. For example, 100 wt % of PEDOT : PSS : NMP and 60 wt % of PEDOT : PSS : NMP blended with PVA exhibit conductivities of, respectively, 10 and 4.02 S/cm. In contrast, conductivities of only 0.0525 and 0.000506 S/cm are observed, respectively, for 100 wt % of PEDOT : PSS and 60 wt % of PEDOT : PSS content in the PEDOT : PSS/PVA blends (No NMP). The addition of the NMP enhances the electrical conductivity by two to five orders of magnitude (depending on the amount of PVA in the blend) due to conformational change of PEDOT chains. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 3134–3141, 2012

Key words: MEMS; PEDOT; PEDT; polyvinyl alcohol; NMP; conducting polymers; conductivity enhancement

INTRODUCTION

Throughout the past two decades, the field of microelectromechanical systems (MEMS) has been growing rapidly.[1] It is recognized that the rate of future growth in MEMS applications depends, in part, on the development of the novel functional materials, including polymers.[2] Low cost, easy processing, excellent thermal stability, relatively high flexibility, ability to fabricate films 1–10 μm thick, and low Young's Modulus provide the motivation for the development of synthetic polymer materials for MEMS. Development of conducting polymers[3,4] sparked a wide variety of applications and novel devices in the fields of microelectronics,[5] electroluminescence,[6,7] optical amplifiers,[8,9] and organic transistors.[10,11]

Single component polymers such as polypyrrole, polyimide, poly(3,4-ethylenedioxythiophene) (PEDOT), polydimethylsiloxane, poly(methyl methacrylate), and polyvinyl alcohol (PVA) have found a wide variety of applications in MEMS devices. Additionally, blending of polymers offers means to combine the useful and desired properties exhibited by the individual polymer components with a concomitant enhancement of selected properties. For example, PEDOT,[12–14] a conducting polymer used in organic light-emitting diodes and organic transistors, has high electrical conductivity (up to 500 S/cm) in the doped state, as well as good thermal and chemical stability.[15] However, PEDOT is insoluble in water and is difficult to process, but when polystyrene sulfonic acid (PSS) (which serves as the charge-balancing dopant during polymerization) is added to the mix, the PEDOT : PSS blend forms a highly stable dispersion in water that contributes to ease of processing. In the PEDOT : PSS complex, oligomeric PEDOT segments are tightly attached to PSS chains by means of electrostatic forces.[16] This molecular

interaction results in a water-dispersed polyelectrolyte system with reasonably good film-forming properties, high conductivity (up to about 500 S/cm), and excellent chemical stability as films of PEDOT : PSS have been heated in air at 100°C for over 1000 h with only a minimal change in conductivity.[13]

However, while PEDOT : PSS has a relatively high electrical conductivity, it is mechanically weak. Furthermore, due to the low viscosity of PEDOT : PSS water dispersion, films thicker than 1 µm are difficult to produce using spin coating and at low rotational speeds, the film uniformity is compromised. Creation of films with acceptable flexibility, tear strength, and uniform thickness are additional goals.

PVA, a water soluble synthetic polymer, has excellent film forming, emulsifying, and adhesive properties.[17] In the PEDOT : PSS/PVA blend, PEDOT : PSS provides the electrical conductivity,[12] while PVA serves as a binder,[17] improving the mechanical properties of the polymer blend. Typically, PVA is prepared by partial or complete hydrolysis of polyvinyl acetate to remove the acetate groups. It has a high tensile strength and good flexibility. However, these properties are dependent on humidity. Specifically, at higher humidity levels more water is absorbed into the film and the absorbed water, acting as a plasticizer, leads to a reduction in the tensile strength but increases the elongation and tear strength.

In summary, PVA when blended with PEDOT : PSS should lead to increase in tensile strength, durability, and flexibility of the film. However, as PVA reduces the number of physical contacts between conducting portions of the film, an increase in the wt % of PVA is expected to lead to a reduction in the electrical conductivity. For example, Hopkins and Reynolds[18] find that the electrical conductivity for a 50% blend of PEDOT : PSS and PVA is reduced by more than three orders of magnitude compared to a film of pure PEDOT : PSS.

The electrical conductivity of the PEDOT : PSS/PVA blend can be improved by the addition of different organic compounds called secondary dopants or additives. These include inert solvents (sorbitol, N-methyl-2-pyrrolidinonoe, and polyethylene glycol), some alcohols (dimethyl sulfoxide, N,N-dimethylformamide, and tetrahydrofuran), and other ionic liquids.[19–22] It is reported that a small amount of N-methyl-2-pyrrolidinone (NMP) increases polymer conductivity by two to three orders of magnitude,[14,19,20] because the NMP causes a conformational change in the PEDOT : PSS adduct which leads to an increase in conductivity. It is also speculated[19,20] that the mechanism which causes the conformational change is due to the interaction between the dipole of one polar group of the NMP and the positive charges on the PEDOT chains.

Additionally, another polar group of the organic compound may form a hydrogen bond with the PSS chains so that the organic compound stays in close proximity to the PEDOT chain.[19,20]

The primary goal of this study is to determine the electrical conductivity of PEDOT : PSS : NMP/PVA films and, secondarily, PEDOT : PSS/PVA films with varying weight percentages. The electrical conductivity of PEDOT : PSS : NMP/PVA blends for different weight percentages of NMP is also presented.

EXPERIMENTS

Materials

PEDOT doped with PSS is commercially available in the form of water dispersion (Clevios P V4071 from H.C. Starck). However, a high-conductivity blend, PEDOT : PSS : NMP, (CPP105D from H.C. Starck)[14] is used in this study. The components, weight percentages, functions, and manufacturers of the chemical components of the CPP105D formulation are summarized in Table I. The PEDOT : PSS : NMP blends are prepared by mixing the various components listed in Table I at room temperature for 4 h.

The PVA (98–99% hydrolyzed high molecular weight material from Alfa Aesar with average MW 88,000–97,000) in the blends is used as received and mixed in a 9-wt % water solution at 90°C for 4 h.

Blending

The PEDOT : PSS : NMP (CPP105D, solid content 1.2%) dispersion described in Table I and PVA 9 wt % water solution are blended and stirred with a magnetically driven paddle for 24 h. The two solutions are mixed at solid weight percentages varying from 0 to 100 PEDOT : PSS : NMP (CPP105D) with PVA.

Film processing and thickness characterization

Spin-coated films are fabricated using the PEDOT : PSS : NMP (CPP105D) and PVA blends on glass slides at 500 rpm for 30 s. Subsequently, these films are placed in a vacuum oven at 100°C for 6 h to remove the solvent. The thickness of all of the films is measured using a Digital Instruments Dektek 3 surface profiler.

Electrical properties characterization

The electrical conductivity of the polymer films is measured using a Kelvin four-point probe technique implemented with a LakeShore 7507 system and Hall Measurement System version 2.3.0 software.

TABLE I
CPP105D High Conductivity Formulation[14]

Components	% By weight	Functions	Manufacturers
Baytron P	42.92	Conducting polymer dispersion in water	H.C. Starck
N-Methyl-2-pyrrolidinone	2.58	Conductivity enhancement	EM Science
Silquest A 187	0.86	Form harder, durable films	GE Silicones
Isopropanol	53.34	Reduce surface energy	EMD
Dynol 604	0.30	Wetting agent	Air Products
Total	100.00		

Glass slides with dimensions of 25.4 mm (width) and 76.2 mm (length) are spin-coated with the polymer blends. The films are imprinted with silver epoxy using a stenciling process to create 1-mm wide line contacts with a separation of 15 mm to form surface contacts which do not penetrate the film. For each of the samples, the thickness, t, and width, w, of the films, and the separation, s, of the electrodes are carefully measured. A fixed current, I, is supplied to the outer two electrodes as shown in Figure 1 and the voltage difference, V, between the inner two electrodes is recorded.

The conductivity, σ (S/cm) is determined using the following equation:

$$\sigma = \left[\frac{V}{I} \cdot \frac{w \cdot t}{s} \right]^{-1}$$

where V is the voltage difference, w is the width of the film, t is film thickness, I is the applied current, and s is the electrode separation.

RESULTS

Film thickness

Figure 2 shows the thickness of films spin-coated on glass at a spin rate of 500 rpm as a function of different weight percentages, wt %, of PEDOT : PSS :
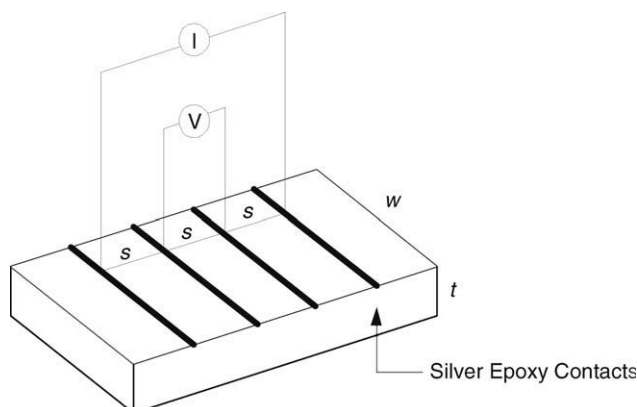
NMP (CPP105D) in PVA. As shown in Figure 2, the film thickness decreases with increasing PEDOT : PSS : NMP weight percentage. For blends with PEDOT : PSS : NMP wt % of 60, 40, and 20 in PEDOT : PSS : NMP/PVA blends, the film thicknesses on glass are, respectively, 0.99, 1.32, and 3.09 μm. This is because of increasing the wt % of PVA (with the attendant decrease in the wt % of PEDOT : PSS : NMP) increases the viscosity of the blend which leads to a thicker film for the fixed spin rate.

Electrical conductivity of the polymer films

The conductivity as a function of PEDOT : PSS : NMP (CPP105D) weight percentage is shown on Figure 3. Corresponding conductivities obtained by Hopkins and Reynolds[18] for PEDOT : PSS/PVA blends (without the NMP additive) are also shown on the same graph. As expected, the conductivity decreases with decreasing PEDOT : PSS : NMP (CPP105D) weight percentage in the PEDOT : PSS : NMP/PVA blends and, at wt % of 100, 60, 40, and 20, the film conductivities are, respectively 10, 4.02, 1.89, and 0.00204 S/cm. Note that for a wt % change from 100 to 30, the conductivity is reduced by a
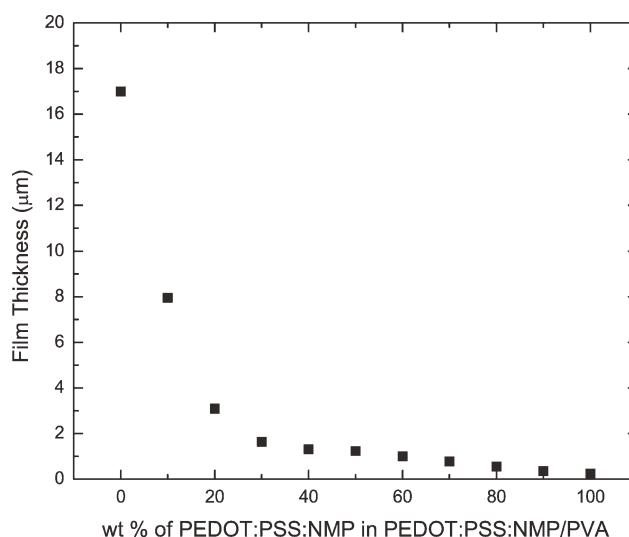

Figure 1 Sketch of modified four-point measurement setup.

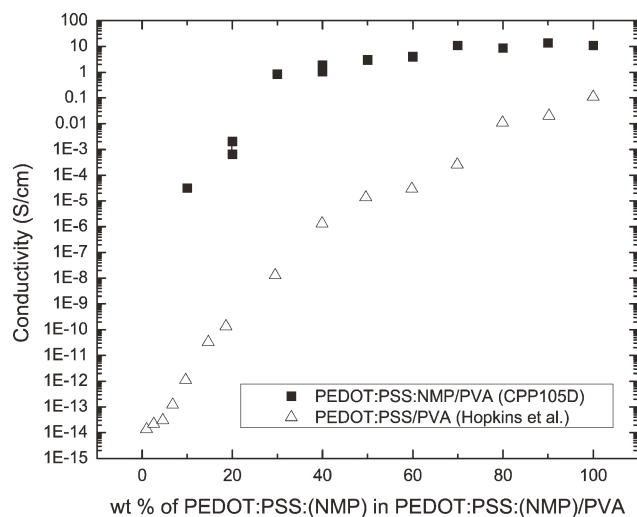**Figure 2** Film thickness versus PEDOT : PSS : NMP/PVA weight percentage.

Figure 3 Electrical conductivity as a function of weight percentage of PEDOT : PSS : NMP in a blend of PEDOT : PSS : NMP/PVA weight percentage and corresponding conductivity measurements of Hopkins and Reynolds[18] for PEDOT : PSS/PVA.

factor of about 20. In contrast, for a wt % decrease from 30 to 10, the conductivity is reduced by about four orders of magnitude. This rapid reduction in conductivity is due to the increasing amount of PVA that crosslinks to the PEDOT : PSS chains. It is this crosslinking that impedes the charge transport and decreases the PEDOT : PSS/PVA conductivity.

It should be noted that, as shown in Figure 3, conductivities of the PEDOT : PSS/PVA blends (without any NMP) as reported by Hopkins and Reynolds[18] are significantly lower than the conductivities of the PEDOT : PSS : NMP/PVA blends for corresponding weight percent polymer blends as reported herein. For example, the conductivity measured by Hopkins and Reynolds[18] is 0.109 S/cm for 100 wt % PEDOT : PSS. This value is significantly lower than the 10 S/cm measured for the same weight percentage blend (but with NMP) in the current study. At lower weight percentages, the difference in the measured conductivity is even larger. For a wt % of 40, Hopkins and Reynolds[18] report a conductivity of 10^{-6} S/cm compared with a conductivity of 1.89 S/cm for a corresponding weight percentage blend of PEDOT : PSS : NMP/PVA as reported herein. Based on the measured variability, the large difference in the measured values for the PEDOT : PSS : NMP/PVA and PEDOT : PSS/NMP blends cannot be attributed to measurement uncertainty but rather can be attributed to the addition of the NMP.

In addition to promoting significantly higher conductivity for the same weight percentage, the data in Figure 3 also demonstrate that the presence of the NMP helps to slow down the rate of reduction in conductivity with decreasing weight percentage of

PEDOT : PSS : NMP where for a wt % decreases from 100 to 40, the corresponding conductivity is reduced only from 10 to 1.89 S/cm by less than one order of magnitude. In contrast, Hopkins and Reynolds[18] find conductivity reduced of five orders of magnitude (from 0.109 to 10^{-6} S/cm) for the same reduction in weight percentage. The large difference in measured conductivity for the same weight percentage with and without NMP is most likely due to the effect of the NMP. However, the difference might, in part, be due to differences in the measurement techniques. While Hopkins and Reynolds also use a modified Kelvin four-point measurement technique to determine the conductivities in the plane of the film for blended films with conductivities greater than 10^{-2} S/cm and corresponding weight percentage of greater than about 80%, they use a two-point technique to determine the conductivity normal to the plane of the film for films with conductivities less than 10^{-2} S/cm. In the Kelvin four-point technique used by Hopkins and Reynolds, the contacts are formed by sputtering 1 cm^2 gold onto the cast films. The contacts used in their two-point measurements are also 1 cm^2 gold contacts but are located on the bottom and top surfaces of the film. In both that work and this study, the probes do not penetrate the film and only make contact at the surface. The conductivities for PEDOT : PSS/PVA blends measured in this study and values reported by Hopkins and Reynolds are shown in Figure 4.

At 80 and 100 wt %, the conductivities measured by Hopkins and Reynolds and those of the present study (for PEDOT : PSS/PVA blends without NMP) are in close agreement. However, there are differences in the conductivity measured for the 60 and 40
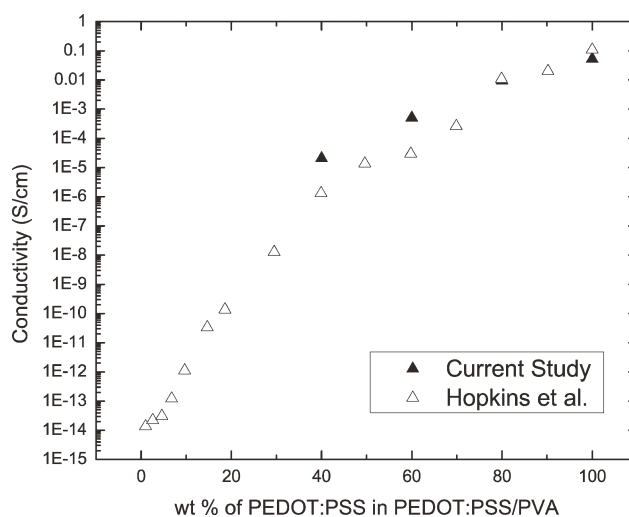

Figure 4 Electrical conductivity as a function of weight percentage of PEDOT : PSS in PVA (without NMP) for results obtained in the current study and that of Hopkins and Reynolds.[18]
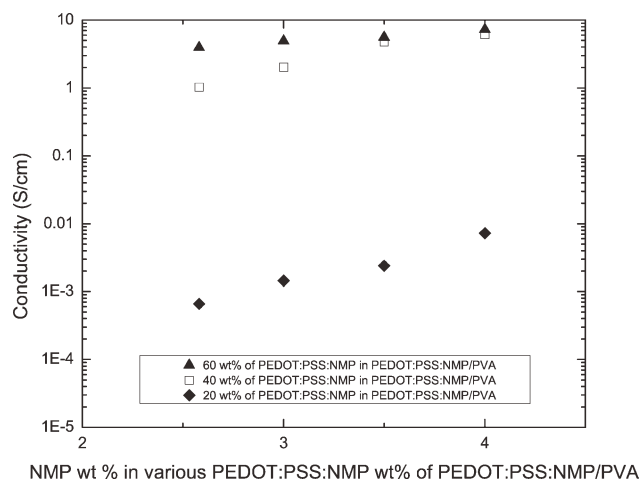
Figure 5 Electrical conductivity measurement of PEDOT : PSS : NMP/PVA with various amounts of NMP.

wt % blends. This difference may be attributed, in part, to the difference in the measurement techniques as described above. For 100 and 80 wt %, a modified four-point Kelvin technique is used in both studies to determine the conductivity in the plane of the film, however, while a four-point technique is used to determine in the plan conductivities for films of 60 and 40 wt %, in this study, a two-point technique (which measures conductivity normal to the plane of the film) is used by Hopkins and Reynolds for the conductivity measurement of the corresponding polymer films. It is possible that differences in conductivity values are due, at least partially, to the differences in conductivity measurement techniques. Another possible reason for the difference is that the film may be anisotropic with different in-plane and perpendicular conductivities. This conjecture is supported by Nardes et al.[23] who finds, for spin-cast PEDOT : PSS films, that there is a variation in excess of two orders of magnitude for the conductivity in the direction normal to the film's surface relative to that parallel to the film's surface.

The data collected in this study clearly demonstrate that the addition of NMP has a dramatic effect on the electrical conductivity. For example, for a 40 wt % blend of PEDOT : PSS/PVA, the addition of NMP leads to increase in conductivity of about five orders of magnitude (Fig. 5).

To explore the effect of NMP on electrical conductivity of PEDOT : PSS : NMP/PVA blends, measurements of conductivity with different amounts of NMP relative to the PEDOT : PSS are performed. In this set of experiments, the wt % of NMP in the PEDOT : PSS varies from 2.58% (the value in the CPP105D blend from H. C. Stark) to 4%. The conductivity of films with NMP weight percentages in a PEDOT : PSS/NMP blend of 2.58, 3, 3.5, and 4% are shown in Figure 5. For PEDOT : PSS : NMP/PVA

blends of 60, 40, and 20 wt %, an increase in the amount of NMP (and a corresponding reduction in the wt % of PEDOT : PSS in the final blend) leads to an increase in conductivity. Specifically, for wt % of 20 and 40 of PEDOT : PSS : NMP/PVA, an increase in wt % of NMP from 2.58 to 4% is shown to increase the conductivity by about one order of magnitude. In contrast, at 60 wt %, the same increase in NMP only leads to a doubling of the conductivity. Thus, an increase in NMP content leads to an increase in conductivity. It is also noted that the higher amount of NMP in the PEDOT : PSS blend reduces the rate of decrease in the conductivity as the weight percentage of PVA is increased.

DISCUSSION

The mechanism of conductivity change in PEDOT : PSS/PVA system

PEDOT is a p-type electronic conductor. PSS is a negative ionic conductor and PEDOT: PSS is a p-type semiconductor.[16] In this study, the conductivity of the blend of PEDOT : PSS and PVA decreases with increasing weight percentage of PVA. The PVA is also observed to significantly decrease the brittleness of the films. Ikkala et al.[24] and Kim et al.[25] have reported that the sulfonate group (SO_3^-) and hydroxyl group (OH^-) readily form a hydrogen bond. This hydrogen bonding can be achieved easily by a simple solubility process. Thus, it is feasible that when PVA is blended with the PEDOT, the OH^- groups of PVA form strong hydrogen bonds with the SO_3^- groups of PSS. This would reduce some negative charge of the PSS (acting as a counter charge to the positive charge in the PEDOT) and reduce the conductivity in the PEDOT : PSS/PVA blend compared to that of the PEDOT : PSS. Another possible explanation is that the number of conducting paths is reduced when the insulating polymer PVA is added to the conducting (PEDOT : PSS : NMP) matrix.

SEM microscopy is utilized to study the NMP and PVA distribution in the PEDOT : PSS matrix. Figures 6(a–c) show the SEM micrographs of PEDOT : PSS : NMP/PVA with wt % of PEDOT : PSS : NMP in the blend corresponding to 80, 60, and 40, respectively. Figures 6(d–f) show the SEM micrographs of PEDOT : PSS/PVA (no NMP) with the wt % of PEDOT : PSS in the blend corresponding to 80, 60, and 40, respectively. The samples have been stained with ruthenium tetroxide to highlight PSS[26] as white bright features in the SEM micrographs. Note that there are three dominant features in the micrographs: small bright areas, broad gray regions, and irregular black features with dimensions of 1–10 μm. The small bright features are assumed to be PSS rich regions
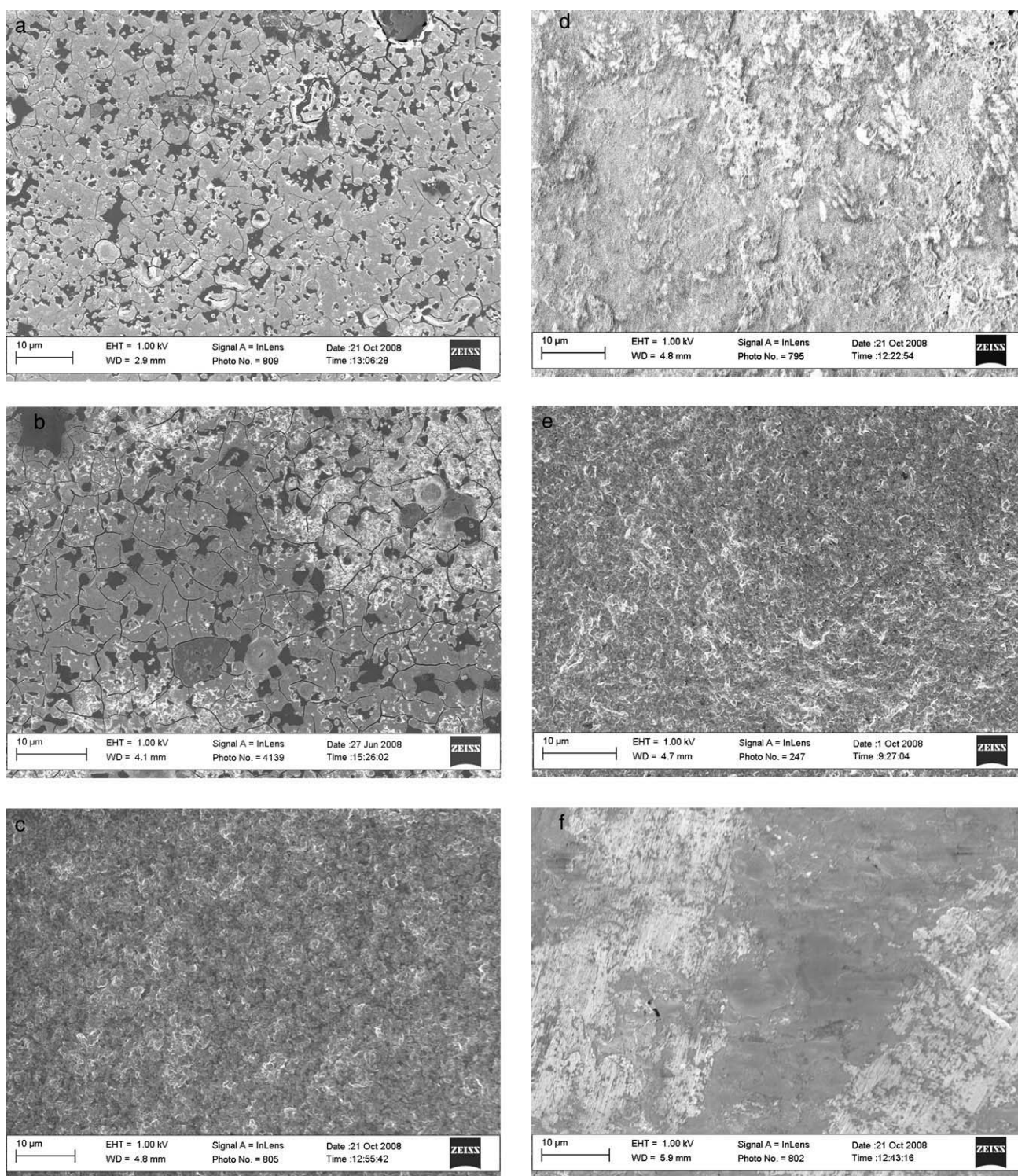
Figure 6 SEM micrographs of (a) 80 wt % PEDOT : PSS : NMP/PVA, (b) 60 wt % PEDOT : PSS : NMP/PVA, (c) 40 wt % PEDOT : PSS : NMP/PVA, (d) 80 wt % PEDOT : PSS/PVA, (e) 60 wt % PEDOT : PSS/PVA, and (f) 40 wt % PEDOT : PSS/PVA.

and bright as a result of the staining. PEDOT is known to be tightly bound to the PSS polymer and is therefore contained in these bright features. The broad gray regions are assumed to be PVA rich as they appear in films with and without the NMP.

The irregular black regions are assumed NMP rich or result from the presence of NMP in the film. As the SEM micrographs show, as the weight fraction of PVA is increased, the surface concentration of PEDOT : PSS decreases. Figure 6(a) features circular
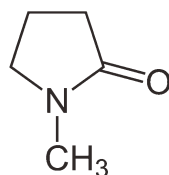
Figure 7 Structure of NMP.

regions of 1–3 μm in diameter with a bright perimeter indicative of a high concentration of PSS in that region. The spatial fraction of bright areas decreases as the fraction of PEDOT : PSS in the film is reduced (the fraction of PVA is increased) as expected [Fig. 6(b,c)]. These observations are consistent with the morphological model of a PEDOT-rich core surrounded by a PSS-rich shell.[27,28] Note that there is a trend as the clustering of PEDOT : PSS rich regions decreases as the wt % of PEDOT : PSS decreases in the samples. The PEDOT : PSS rich regions are most uniformly dispersed in the films with the lowest wt % of PEDOT : PSS.

Effect of NMP on conductivity

The higher conductivity found for the PEDOT : PSS : NMP/PVA blends relative to the PEDOT : PSS/ PVA blends for a given weight percentage results from the inclusion of the NMP (Fig. 7) in the blend. While NMP is a nonconducting organic solvent, its presence leads to higher conductivity. This observation is consistent with previous studies[19,20] where it has been observed that a conductivity enhancement is possible with a number of solvents having two or more polar groups on each molecule. It is likely that the NMP solvent has two effects on the PEDOT : PSS. For NMP, the polar groups of double-bonded oxygen interact with the positive charges on the PEDOT chains causing a conformational change in the PEDOT chains. The polymer changes from a coiled structure to an expanded coil or linear structure. In addition, another polar group forms a hydrogen bond to the sulfonate group (SO_3^-) of the PSS chains so that NMP then leads to closer proximity to the PEDOT chains. As the conductivity of this organic structure is believed to be due to hopping of charge carrier between conducting polymer chains,[4] reducing the proximity between chains enhances the conductivity.

Both the PVA and NMP mechanisms described above, suggest that the OH^- groups of PVA form strong hydrogen bonds with the SO_3^- groups of PSS while one of polar groups of NMP forms a hydrogen bond to the SO_3^- group of PSS chains. We find (see Fig. 5) that increasing NMP in the polymer blend helps to keep high conductivity even in polymers with relatively high wt % of PVA. Therefore, if PVA

is required to be added to the polymer blend to improve mechanical properties and impart the ability to create thicker polymer films, the addition of NMP to the polymer blend will help retain the high conductivity of the blend.

CONCLUSIONS

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT : PSS) is a commercially available, conducting polymer that has a viscosity that is very low to use spin coating to fabricate films thicker than about 1 μm. A mixture of PEDOT : PSS and PVA can be used for spinning films that are 1–3 μm thick and that have enhanced electrical conductivity. Use of NMP in the blend can increase the electrical conductivity by two to three orders of magnitude and films of the blended polymers with a PEDOT : PSS : NMP concentration equal to or greater that 50 wt % have a conductivity greater than 1 S/cm. Thus, it is possible to optimize the electrical conductivity and mechanical properties of polymer films by the addition of PVA and NMP to the polymer blend to achieve the best trade-off between facility in polymer film fabrication and high electrical conductivity.

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