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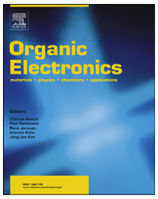

The impact of solvent doping on the morphology and performance of spray-coated PEDOT:dPSS: A USANS and SANS study

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ABSTRACT

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is used in a broad range of organic electronics devices, where their performance can be dramatically enhanced by solvent processing. The morphological changes that occur with solvent processing, as well as the impact of deposition technique, are not well understood, but this understanding is crucial to rationally tune the performance of PEDOT:PSS. In this study, the change in the morphology and conductivity of spray-coated PEDOT:PSS films with pre- and post-deposition processing in the presence of polar solvents is investigated by means of neutron scattering. Deuterium labeling of PSS is used to distinguish between the PEDOT and PSS phases. Changes in the morphology of PEDOT:deuterated PSS (PEDOT:dPSS) films with the addition of 5% dimethyl sulfoxide (DMSO) to the pre-deposition PEDOT:dPSS solutions enhances the conductivity by *ca.* 60-fold, and is further enhanced by *ca.* 2-fold by soaking the films in ethylene glycol (EG). Neutron scattering reveals that the morphology of the spray-coated PEDOT:dPSS film consists of a two-phase structure on the micron to nanometer length scales, where more locally ordered PEDOT-rich fibril-like domains are dispersed on the smallest length scale. Upon DMSO addition, the PEDOT:dPSS domain sizes decrease dramatically. However, with soaking in EG, the sizes of the local domains increase isotropically. Thus, the enhanced electrical conductivity of the spray-coated PEDOT:dPSS with solvent doping is dominated by morphological changes, and not changes in the PEDOT:dPPS composition in these spray-coated films.

1. Introduction

PEDOT:PSS is one of the most promising electrically conducting polymers, as it has application in many low-cost high volume devices, including flexible electrodes, electro-chromic displays, transistors and organic thermoelectrics [1–3]. Among the important properties of this polymer are its intrinsic high conductivity, the ability to tune the conductivity, transparency to light in thin films, mechanical flexibility, electrochemical, thermal, and oxidative stability [4]. Currently, PEDOT:PSS holds one of the highest thermoelectric efficiencies among organic thermoelectrics [5]. For optimal organic thermoelectric performance, the ability to improve the electrical conductivity while maintaining a low thermal conductivity is highly desirable. One promising method to improve the electrical conductivity of PEDOT:PSS has been identified as doping with organic solvents, such as dimethyl sulfoxide (DMSO), ethylene glycol (EG), poly(ethylene glycol) (PEG), or sorbitol, in an aqueous dispersion of PEDOT:PSS [6–14]. Moreover, conductivity of PEDOT:PSS dried films can be further improved by their immersion in polar solvents or exposure to their vapors [7,14,15]. Unfortunately, there is not a clear understanding of how the presence of the dopants in the polymer solution or solvent treatment of the dried films alters the morphology and functionality of the PEDOT:PSS film [16,17]. Yet, this understanding is critical to developing processing protocols that cannot only improve, but optimize the performance of PEDOT:PSS. It is clear that a crucial first step is to

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correlate the morphology of the PEDOT:PSS to its performance.

Moreover, the impact of the deposition method of the PEDOT:PSS film on the change in performance with doping is not well understood. While most studies have focused on the use of spin-coating as a deposition technique, this is not compatible with roll-to-roll or large-area manufacturing. Spray-coating, ink-jet printing and doctor-blading are deposition techniques that can be performed at a high production speed and are compatible with various substrates, and thus are more scalable. Thus, there is also a need to understand the impact of deposition technique on the morphology and performance of doped PEDOT:PSS films.

Several conceptual models that suggest a mechanism by which doping with polar organic solvents enhances the conductivity of PEDOT:PSS have been presented [7,10,11,13,18–22]. Among these, a change in the conformation of the PEDOT chain [23], removal of excess insulating PSS [19], and a decrease in the Coulombic interaction between PEDOT and PSS chains upon doping have received the most attention [17]. Most studies, however, employ surface characterization techniques such as atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) or bulk methods that do not have the resolving power to distinguish between PEDOT and PSS phases [7,13,24,25] that are required to elucidate the bulk morphology of the PEDOT:PSS blend. For example, Ouyang et al. attributed the enhanced conductivity of PEDOT:PSS films with doping of organic solvents, such as ethylene glycol, 2-nitroethanol, methyl sulfoxide or 1-methyl-2-pyrrolidinone, to the enhanced inter chain interaction among the PEDOT chains [13]. This increased interaction is purported to be the result of changes in the PEDOT conformation from a coil to an extended coil or linear structure [13]. AFM and XPS studies by Jonsson et al. attribute the enhanced performance of PEDOT:PSS films doped with sorbitol, isopropanol or NMP to the removal of excess PSS that resides in an insulating “PSS-shell” surrounding the conducting PEDOT:PSS grains [18]. The loss of this PSS leads to a better connectivity between the conducting grains in the film. Kim et al. noted that the incorporation of polar organic solvents such as DMSO, DMF or THF enhanced the charge carrier properties of PEDOT:PSS free standing membranes [11]. They credit the enhanced characteristics to a solvent-induced screening effect that reduces the Coulomb interaction between positively charged PEDOT chains and negatively charged PSS chains [26]. Similarly, Ashizawa et al. investigated the charge carrier characteristics of PEDOT:PSS as a function of the amount of polar solvent that is added to the PEDOT:PSS mixture [10]. The enhanced charge carrier properties in these studies were attributed to the reduced effective energy barrier for hopping of charge carriers between localized PEDOT states [10]. It is interesting that the solvent treatments not only enhance the functional performance but also alter the mechanical properties. Okuzaki et al. showed that EG treatment of PEDOT:PSS microfibers enhanced both electrical and mechanical properties, which were attributed to molecular changes in the PEDOT domains from an amorphous state to a crystalline state [20]. Very recently, Ouyang et al. studied the conformational changes in a drop-cast PEDOT:PSS film at the microscale and concluded that PSS forms a transparent rim around the PEDOT:PSS film [27]. These investigations, however, do not discuss the changes in the bulk morphology of PEDOT:PSS that occur in the presence of a polar solvent. A more thorough understanding of the changes to the PEDOT:PSS morphology with pre- and post-deposition solvent processing is needed to optimize the performance of PEDOT:PSS in many applications.

In this study, the development of the morphology of spray-coated PEDOT:dPSS in the presence of primary and secondary solvent dopants was investigated with ultra-small angle and small angle neutron scattering (USANS and SANS, respectively). Contrary to other studies, isotopic labeling is used as a mechanism to highlight the structure of the PEDOT and PSS domains individually, where the neutron-based techniques utilized in this study provide bulk structural information over a wide range of length scales (1.5 nm-84 μm).

The doping conditions that were studied mimicked those reported in the work by Kim et al., which reported the highest recorded thermoelectric figure-of-merit for PEDOT:PSS [14]. In this procedure, a 1.3% PEDOT:PSS aqueous solution with a PEDOT to PSS ratio of 1:2.5 is first doped with 5 vol% of DMSO in the pre-deposition solution. The PEDOT:PSS film is then soaked in EG for 120 min to optimize its performance. In this manner, the thermoelectric performance of PEDOT:PSS was tuned by changing its morphology and composition to achieve orders of magnitude improvement in its thermoelectric efficiency.

The USANS patterns were analyzed using the two-phase Debye-Anderson-Brumberger (DAB) model [28]. The SANS data were analyzed with two linearly combined models: I) DAB and a triaxial ellipsoid model or II) DAB and an elliptical cylinder model. Both combination models provide crucial insight into the equilibrium size and compositions of the coexisting PEDOT and PSS phases. For the as-cast film and for each of the doped conditions, the in-plane conductivity and Seebeck coefficient were also determined. These functional characteristics are correlated to the morphology and composition of the PEDOT: deuterated PSS (PEDOT:dPSS) film that is determined by neutron scattering. These analyses therefore provide direct evidence of the importance of the size and composition of PEDOT and PSS phases on the performance of these films, a crucial relationship that is difficult to identify using other characterization methods.

2. Results and discussion

The contrast between PEDOT and PSS are limited in electron-, X-ray- or neutron- based characterization techniques, making it very difficult to distinguish the precise morphology of the blend. However, the neutron scattering length densities of PEDOT (~1.7×10^{-6}Å^{-2}) and dPSS (~4.1×10^{-6}Å^{-2}) provide sufficient contrast to distinguish the PEDOT-rich and PSS-rich domains by neutron scattering, as well as the changes in the morphology when films are prepared in the presence of dopants. Thus, to investigate the morphology of pristine spray-coated PEDOT:PSS and the corresponding changes in morphology with solvent processing, PEDOT:deuterated PSS in an aqueous medium was synthesized. Annealing the films at 140 °C for 15 min evaporates the water and dopant from the film post-deposition [29]. The USANS and SANS profiles of I) pristine PEDOT:dPSS, II) a PEDOT:dPSS film that is deposited from an aqueous solution with 5 vol.% DMSO and III) a PEDOT:dPSS film that is deposited from an aqueous solution with 5 vol.% DMSO and subsequently soaked for 120 min in EG are shown in Fig. 1. Length scales that are monitored by combining SANS and USANS profiles extend from angstroms to microns. The USANS profiles follow the changes in structure on the micrometer length scale while the SANS data monitor the changes in the structure of the sample on the nano-meter to angstrom length scales.

The effects of solvent doping on the structure of the PEDOT:dPSS blend are clearly visible across these length scales where the changes in structure due to the presence of DMSO are more prominent relative to the changes in structure due to the soaking in ethylene glycol (EG). This difference might be attributed to the physical state of the PEDOT:dPSS when the doping was completed, i.e. DMSO was added to the pre-deposition solution (primary doping) and the doping with EG was performed on dried PEDOT:dPSS films (secondary doping). In the solution state, the polymers are much more mobile, and therefore morphological