

Effect of solvent on electrical conductivity and gas sensitivity of PEDOT:PSS polymer composite films

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ABSTRACT: Poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) was blended with polyethylene oxide (PEO) and polyvinyl alcohol (PVA) and composite film was cast. Additional solvents of dimethyl sulfoxide (DMSO) and ethylene glycol (EG) were mixed and their effects on electrical conductivity and structural changes were investigated. The electrical conductivity increased in response to the additional solvent, leading to an increase in the PEDOT ratio relative to the control. PEDOT:PSS/PEO composite film had a much higher electrical conductivity than PEDOT:PSS/PVA. When blended with PEO, the quinoid structure revealed by Raman spectroscopy increased relative to the PVA-blended case, indicating higher electrical conductivity. The current–voltage response and gas sensitivity showed much better performance in PEDOT:PSS/PEO/DMSO composite film. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42628.

KEYWORDS: blends; films; structure–property relations

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INTRODUCTION

Conductive polymers have gained a great deal of interest owing to their potential use in low-cost, lightweight, and flexible organic electronic devices. Additionally, transparent conductive films (TCFs) have received attention because of their widespread applications in electronic devices, such as photovoltaics, solar cells, electronic displays, organic light emitting diodes, and touch panels.^{1–4}

Among various conductive polymers, poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) has been widely applied as a conductive polymer. PEDOT:PSS has many advantages including transparency, high conductivity, low surface roughness, and flexibility. PEDOT:PSS can easily provide electrical conductivity on various substrates via simple processing methods such as solution casting.⁵ PEDOT itself is difficult to process; however, its processability can be improved by the addition of PSS during synthesis.⁶ The amount of PSS in PEDOT:PSS reduces the electrochemical properties of PEDOT. Additionally, PEDOT:PSS has many advantages, including high conductivity, good transparency, low surface roughness, low cost, and high flexibility.^{4,5} The conductivity of aqueous solutions of PEDOT:PSS can be improved by the addition of polar solvent, and dimethyl sulfoxide (DMSO) and ethylene glycol (EG) have been shown to significantly enhance the electrical

properties of PEDOT:PSS relative to other polar solvents.^{1,3} Previous investigations of PEDOT:PSS have focused on their deposit coatings on silicon wafers or indium-tin oxide glass (ITO).^{7,8} PEDOT:PSS water based suspensions are not easy to use alone owing to their low viscosity because the polymer concentration is not high enough to be processed. To improve the processability of PEDOT:PSS, polymers can be blended; however, abrupt decreases in electrical conductivity are unavoidable and blended polymers are limited. Even blending of polymer with PEDOT:PSS results in reduced electrical conductivity, and the enhanced processability enables new applications in flexible devices such as sensors and actuators as long as some electrical conductivity is retained.

In this study, we investigated how to increase electrical conductivity when PEDOT:PSS was blended with other polymers. To accomplish this, we selected water soluble polymers such as polyethylene oxide (PEO) and polyvinyl alcohol (PVA) for blending with PEDOT:PSS aqueous solution to enhance processability and attempted to generate polyethylene oxide (PEDOT:PSS)/(PEO) and polyvinyl alcohol (PEDOT:PSS)/(PVA) hybrid films. The effects of additional solvent and blended polymer on the electrical conductivity and gas sensitivity of the composite films were then investigated.

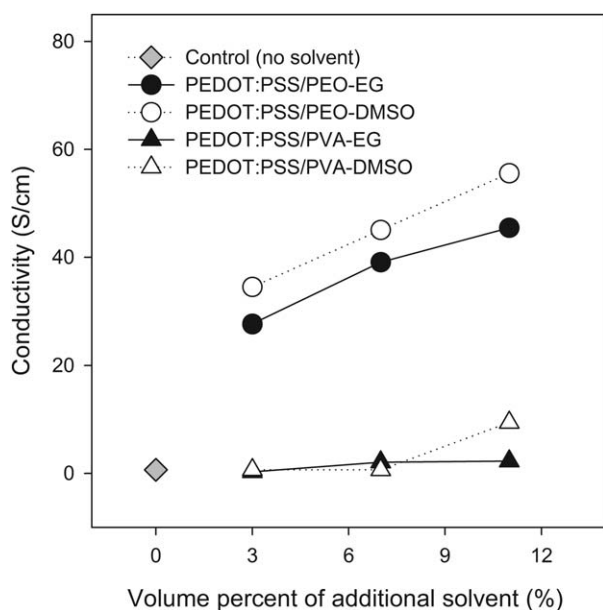


Figure 1. Electrical conductivity of PEDOT:PSS composite films.

EXPERIMENTAL

Materials and Preparation of PEDOT:PSS/Polymer Composite Films

A commercially available PEDOT:PSS aqueous solution (Clevios PH-1000) with a PEDOT:PSS concentration of 1.3 wt % was obtained from Heraeus, Germany, while DMSO and EG were purchased from Daejung Chemicals, Korea. PEDOT:PSS was mixed with different amounts of DMSO and EG (3%, 7%, 11%) while stirring continuously for 6 h at 70°C on a hot plate. When more than 11% solvents were added, it was difficult to cast the PEDOT:PSS/polymer composite film. PVA (Dongyang Chemical) and PEO (Sigma Aldrich) were subsequently added to further improve the processability. The degree of polymerization (P_n) of PVA was 1700 and the viscosity average molecular weight (M_v) of PEO was 100,000. The 10 wt % for both PVA and PEO was dissolved in distilled water for 2 h at 90°C. The blend volume to volume (v/v) ratio of PVA or PEO to PEDOT:PSS was 1/1. The mixed aqueous solutions were bar-coated on flexible PET substrates, after which samples were dried in a vacuum oven for 12 h at 60°C to remove the moisture. The film thickness of the samples was fixed at 2 μm .

Characterization

The electrical conductivity of PEDOT:PSS composite films was measured by a four-point probe technique using an EP MCP-T360 (Mitsubishi), which is a portable surface resistivity meter. Atomic force microscopy (AFM) images were obtained using a Nano Scope IIIA (DI Instruments) in tapping mode. The scan size was $5 \times 5 \mu\text{m}$ and the scan rate was 2 Hz with a 20 nm data scale. Raman spectra were measured using a Nicolet Almega XR system (Thermo Scientific). The laser power was 1% and the laser wavelength was 532 nm. X-ray photoelectron spectroscopy (XPS) was performed using a K-Alpha system (Thermo Scientific), and the current–voltage curve was monitored using a Keithley 4200 source meter (Keithley Instruments Inc.). Gas sensing was conducted using a 2-point probe in a gas

chamber containing NH_3 gas at 25 ppm and room temperature. An interdigitated electrode with 100 μm spacing was used to measure the current change with time when NH_3 gas was introduced to the gas chamber.

RESULTS AND DISCUSSION

Figure 1 shows the electrical conductivity of (PEDOT:PSS)/PEO or PVA composite films with DMSO or EG levels ranging from 0 to 11 vol %. Both PEO and PVA are water soluble polymers that can be blended with a PEDOT:PSS water suspension; however, they showed different effects on the electrical conductivity of the composite films. PEDOT:PSS and PEO (or PVA) composite films without additional solvent showed nearly no electrical conductivity because of the very low electrical conductivity of blended PEO or PVA, while the conductivity increased

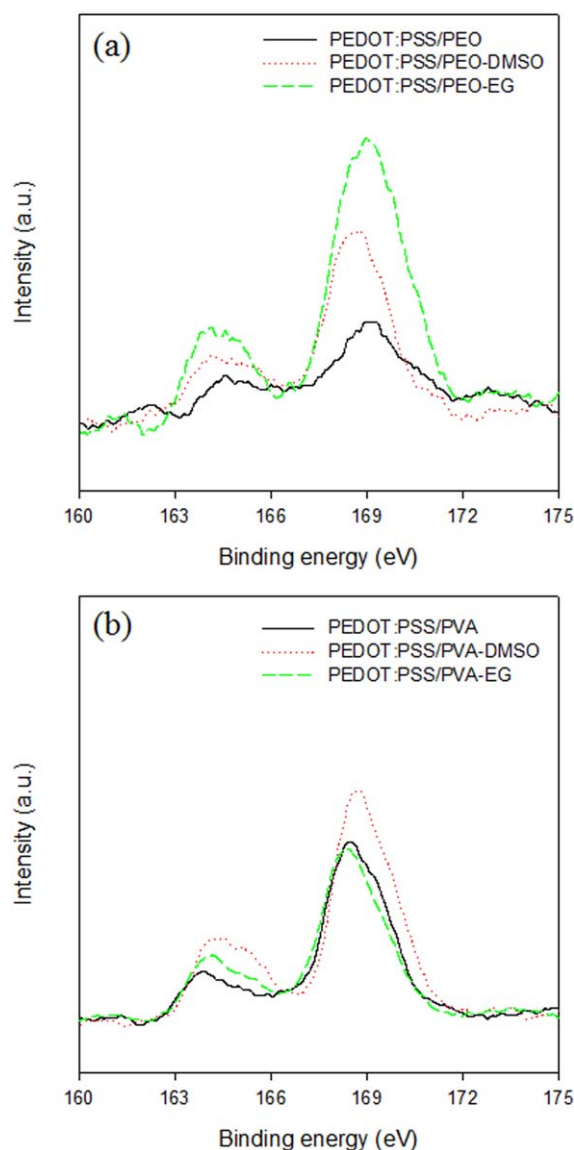


Figure 2. XPS spectra for S 2p of PEDOT and PSS in (a) PEDOT:PSS/PEO/solvent and (b) PEDOT:PSS/PVA/solvent composite films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

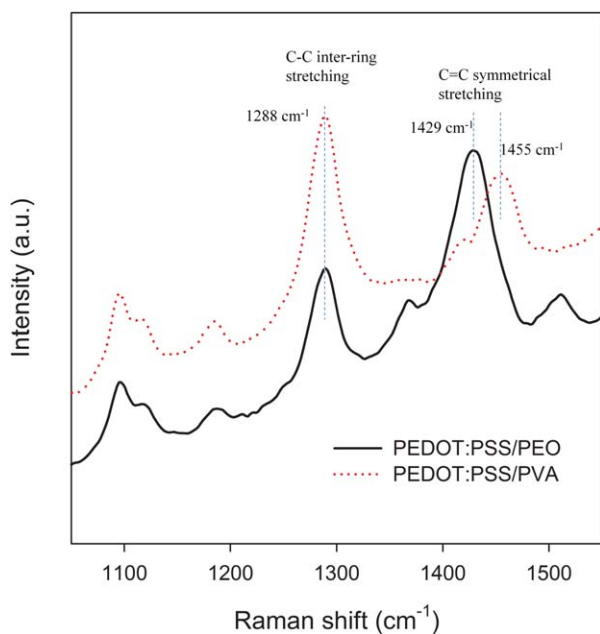


Figure 3. Raman spectroscopy of (PEDOT/PSS)/PEO and (PEDOT/PSS)/PVA composite films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in response to the addition of DMSO and EG. The conductivity of PEDOT:PSS/PEO-blended composite film reached 56 S/cm when DMSO was added at 11 wt %. The electrical conductivity of PVA-blended composite film was very small when compared with that of PEO. When the PEO was blended with PEDOT:PSS in the presence of DMSO or EG, there was a large increase in electrical conductivity. The effects of DMSO on electrical conductivity were greater than those of EG. In the case of PVA-blended PEDOT:PSS composite film, only a small increase in electrical conductivity was observed when a large amount of DMSO of 11 wt % was added. There was no significant difference in the response to DMSO or EG.

Figure 2 shows the XPS spectra with the sulfur (S) 2p of PEDOT and PSS peaks. Two peaks were assigned as S 2p for PSS at 165 eV and for PEDOT at 169 eV.^{9,10} The S 2p peak intensity of PEDOT increased relative to the control [Figure 2

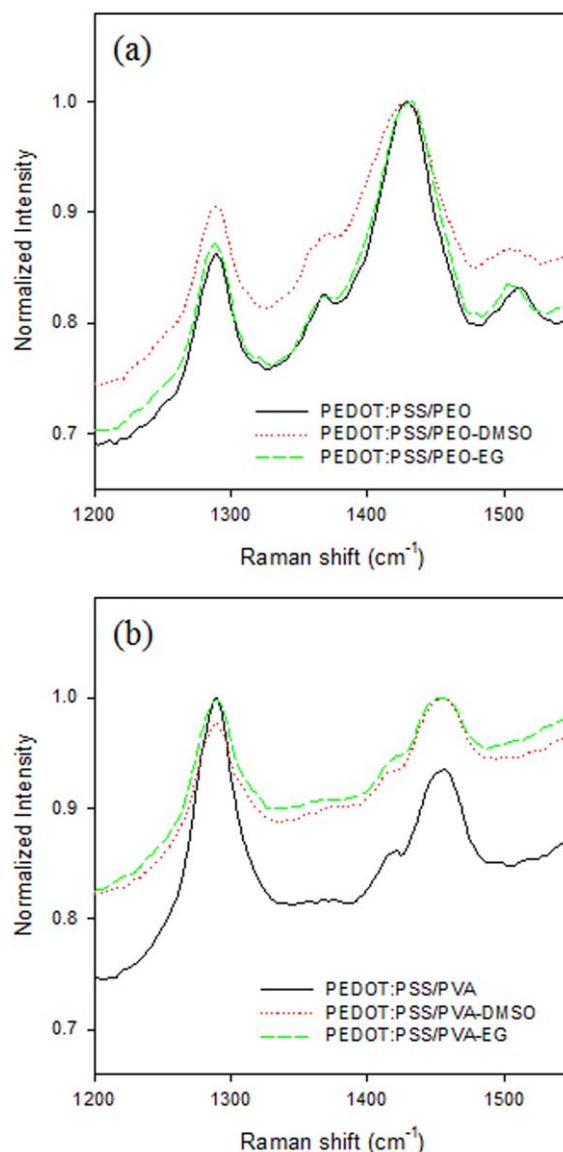


Figure 5. Normalized Raman spectroscopy of (a) PEDOT:PSS/PEO and (b) PEDOT:PSS/PVA composite films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

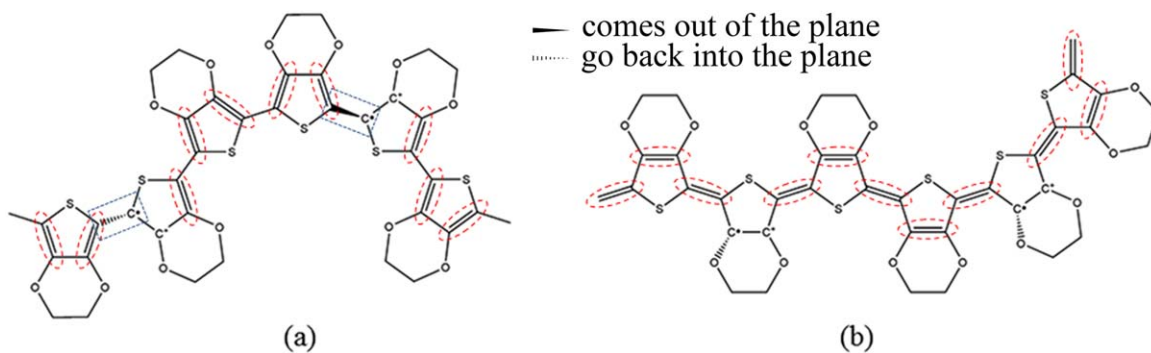


Figure 4. (a) Benzoid and (b) quinoid structures of PEDOT main chain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

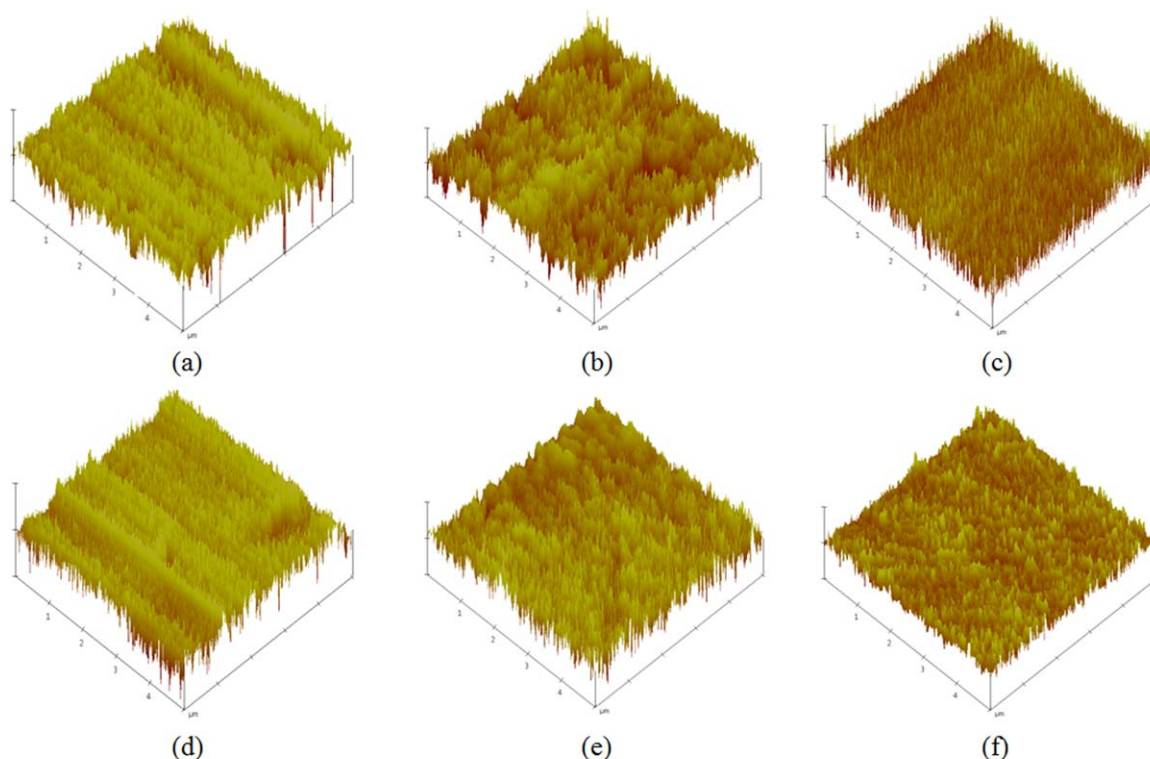


Figure 6. AFM images of PEDOT:PSS composite films: (a) PEDOT:PSS/PEO, (b) PEDOT:PSS/PEO-DMSO, (c) PEDOT:PSS/PEO-EG, (d) PEDOT:PSS/PVA, (e) PEDOT:PSS/PVO-DMSO, and (f) PEDOT:PSS/PVA-EG. Solvent content was fixed at 12 vol %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(a)] when DMSO and EG were added, revealing the effects of solvent addition on electrical conductivity. These results indicate that the PEDOT ratio in the PEDOT:PSS suspension increased in response to the addition of solvent; hence, the electrical conductivity of the solvent added PEDOT:PSS film sample increased relative to the control. Excess PSS may have been removed by the addition of solvents, leading to enhanced electrical conductivity. Hu *et al.*¹¹ and Crispin *et al.*¹² reported that the addition of diethylene glycol (DEG) decreased excess PSS, leading to higher conductivity. The S 2p peak intensity of PEDOT for PEO-blended films increased in response to the addition of DMSO or EG, whereas there was a relatively smaller increase in the PVA-blended films [Figure 2(b)].

Figure 3 shows the Raman spectra of PEDOT:PSS composite films for different blended polymers. Characteristic peaks of PEDOT:PSS were observed, including C-C inter-ring stretching at 1288 cm^{-1} and C=C symmetrical stretching at 1429 cm^{-1} for PEO-blended and 1455 cm^{-1} for PVA-blended composite film.^{13,14} A C=C symmetrical stretching band shift toward the lower Raman shift was observed for the PEO-blended composite film, which can explain its higher conductivity relative to the PVA-blended composite film. As shown in Figure 4, the main structures of PEDOT are benzoid and quinoid.^{15,16} Quinoids [Figure 4(b)] are more planar, while benzoids [Figure 4(a)] have a helical structure, with the former resulting in higher electrical conductivity than the latter. As shown in Figure 4, C=C symmetrical stretching for the PEO-blended composite film was stronger in the quinoid structural unit, as indicated by the

higher peak intensity and lower Raman shift (red shift). If the material is strained, a red shift occurs in the Raman spectrum.¹⁶ Comparison of the molecular structures of PEO and PVA revealed that PVA had bulkier side groups than PEO. The PEO structure is more linear than PVA and therefore leads to less impedance of the linearity of the PEDOT:PSS structure than the PVA. As a result, the electrical conductivity of the PEDOT:PSS/PEO composite film is higher than that of PEDOT:PSS/PVA. To enable higher electrical conductivity, the distance between PEDOT chains in PEDOT:PSS polymer complex should be close,¹⁷ in which case PEO is more advantageous than PVA. Finally, mixture of PEO with PEDOT:PSS polymer yielded PEDOT with a much more quinoid structure.

Figure 5 shows normalized Raman spectra to compare the effects of DMSO and EG. The peaks were normalized using the intensity maximum in the range of $1200\text{--}1550\text{ cm}^{-1}$. Ouyanga *et al.*¹⁴ used normalized Raman spectra to explain the effects of

Table I. RMS Roughness of PEDOT : PSS/(PEO or PVA)-Solvent Composite Films

	RMS roughness (nm)		
	No solvent	DMSO 11 wt %	EG 11 wt %
PEDOT:PSS/PEO	1.467	5.352	4.915
PEDOT:PSS/PVA	1.156	5.061	4.526

additional solvent on the increase in electrical conductivity of PEDOT:PSS. Adding additional solvent to PEDOT:PSS solution increased electrical conductivity and broadened the Raman peak of C=C symmetrical stretching at 1430 cm^{-1} .¹⁵ Similar behavior was observed in the present study. Specifically, the C=C symmetrical stretching band broadened for DMSO or EG mixed PEDOT:PSS. Additionally, the broadening of the peak for DMSO was slightly larger than that for EG, revealing that DMSO had higher conductivity than EG (Figure 1). This broadening was not observed in the case of PVA-blended composite film.

Figure 6 shows the AFM images of PEDOT:PSS composite films. The surface root mean square (RMS) roughness of the composite films is summarized in Table I. When no solvent was added, the PEO-blended film showed a rougher surface than the PVA film. A previous study^{11,18} showed that the electrical conductivity was affected by surface roughness, with increased values being observed in response to the addition of EG into the PEDOT:PSS suspension. Moreover, the increase in roughness was shown to be because of the repulsion force of increased conductivity. In the present study, the effects of surface roughness were not severe, but the PEO-blended film showed higher surface roughness. This might also be attributed to the higher conductivity of the PEO-blended than the PVA-blended film. As shown in Table I, the RMS roughness of PEDOT:PSS/polymer composite films increased in response to the addition of solvents for both PEO and PVA.

Figure 7 shows the current voltage (I - V) curves for PEDOT:PSS/polymer composite films. The current responses of PEDOT:PSS/PEO composite films were higher than those of PEDOT:PSS/PVA films because of their higher electrical conductivity. There was a much smaller response in the I - V curve for

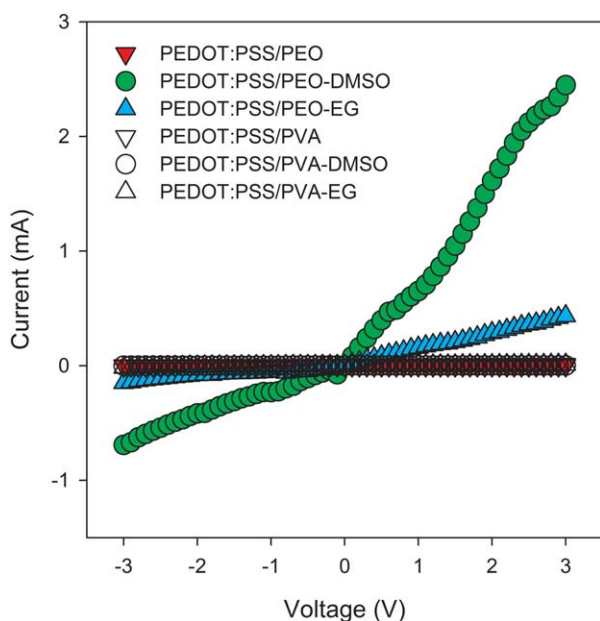


Figure 7. I - V curves of PEDOT:PSS/polymer/solvent composite film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

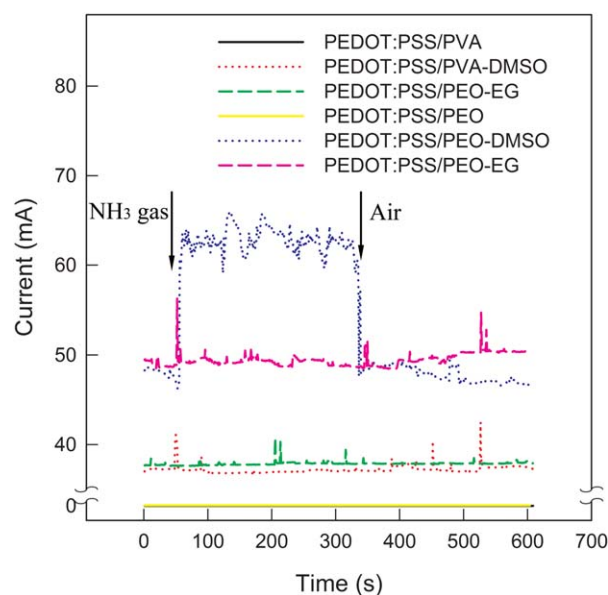


Figure 8. Responses of PEDOT:PSS composite film gas sensors to 25 ppm NH_3 at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PEDOT:PSS/PVA composite films owing to their very low electrical conductivity (Figure 1). The current of PEDOT:PSS/PEO mixed with DMSO was much higher than that of other composite films, demonstrating the good electrical performance of the PEDOT:PSS/PEO-DMSO polymer-blended film.

Figure 8 shows the responses of PEDOT:PSS composite films as sensors of NH_3 gas in the exposure time range of 0–600 s. When NH_3 gas was introduced, the current increased. The change in current response was attributed to the adsorption and desorption of NH_3 molecules of the sensing films. As shown in the figure, the magnitude of the current response is proportional to the I - V response in Figure 7. The results revealed that PEDOT:PSS/PEO-DMSO composite film had greater sensitivity to NH_3 than other composites films. These findings indicate that PEDOT:PSS/PEO-DMSO composite film can be used as gas sensors. Although PEO is a nonconductive polymer that decreases the conductivity of PEDOT:PSS, PEDOT:PSS/PEO composite film can attain a certain extent of electrical conductivity when used as a chemical sensor.

CONCLUSIONS

PEDOT:PSS was blended with PEO and PVA to increase processability. Before blending, DMSO or EG were added to increase the conductivity of PEDOT:PSS. Addition of the solvents resulted in increased electrical conductivity of PEDOT:PSS/PEO-blended film up to 56 S/cm as a result of an increase in the PEDOT ratio relative to the control, with DMSO leading to a greater increase in conductivity. The PEDOT:PSS/PEO composite film had much higher electrical conductivity than the PEDOT:PSS/PVA film. Raman spectroscopy revealed that the blended PEO film had a more quinoid structure than the PVA-blended film, and hence higher conductivity. The current response of the PEDOT:PSS/PEO-DMSO-blended film showed

the highest value, ranging from -1 to 3 mA as voltage increased from -3 to 3 V, indicating good electrical performance. The gas sensing ability of the PEDOT:PSS/PEO-DMSO-blended film showed much better performance than other composites films, and it can be used as a chemical sensor.

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