Effects of Organic Solvent Doping on the Structural and Conductivity Properties of PEDOT: PSS Fabric

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Abstract. The development of highly conductive fabrics for application in electronic textiles on non-rigid substrates has gained much interest owing to their potential for realizing next-generation wearable conductive fabrics. Besides, it could be used as a portable device in the energy and healthcare industries. However, pristine PEDOT: PSS has been reported to have low conductivity values due to excessive PSS chains that wrapped up around the PEDOT conductive chain structure. In this context, one of the most successful techniques to include dopant is to use ethylene glycol (EG) to improve the conductivity of poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS). Immersing or coating of fabrics with PEDOT: PSS is one of the facile methods used for obtaining functional and smart properties. Our studies prepared conductive polymer; PEDOT: PSS with ethylene glycol (EG) dopant at different concentrations on polyester (PES) fabric substrates by a facile immersion process. The effect of the different concentrations of EG on the conductivity is shown when Electrochemical Impedance Spectroscopy (EIS) is conducted. It shows that 6% v/v of EG gives the optimum conductivity value up to 4.06 x 10^{-3} S cm^{-1}. Meanwhile, Scanning Electron Microscopy (SEM) imaging is focusing on the morphology of the immersed fabric. The improvement in crystallinity of the doped PEDOT: PSS was revealed and evaluated using X-ray Diffraction (XRD). As a result, it has been demonstrated that EG is an excellent dopant because it efficiently increases the electrical conductivity and crystallinity of PEDOT: PSS fabric.

1 Introduction

Conductive polymers (CPs) or intrinsically conducting polymers (ICPs) are organic polymers that allows the electrical conductivity because of the presence of π-conjugated systems that allow charge mobility [1-2]. Polyaniline (PANI), polypyrrole (PPy), polyacetylene (PA) and poly(3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS) are some examples of CPs. They become popular choice due to their advantages including light weight, cost-effective, adjustable electrical conductivity, flexibility, biocompatibility and processability. By selecting CPs, idea to replace metal to a more compatible material can be achieved [3]. PEDOT: PSS is reported has potential to be used in wide range of applications including supercapacitors, biosensors, electronic and thermoelectric devices [4-6]. Nevertheless, the coiled structure of pristine PEDOT: PSS shows a significantly low conductivity value (0.1 S cm^{-1}) which limits its potential uses [7]. Therefore, doping process is introduced. Doping is the process where impurities or electron is added into the system causing in the ability of electrical charges passes through the polymer backbone. Several types of organic solvents such as dimethyl sulfoxide (DMSO) and ethylene glycol (EG) that act as a dopant was introduced to boost up the electrical conductivity of the PEDOT: PSS. Phase separation between PEDOT and PSS would occur and expedite the better connectivity between the PEDOT grains. This is where the conformational changes happen from coil to linear of PEDOT: PSS chains. As a result, the charge hopping in the PEDOT grains is easier and faster [8].

PEDOT: PSS has emerged in the trend of conductive fabrics possessing good mechanical flexibility while maintaining electrical conductivity. Fabrics such as cotton and polyester (PES) can portray different properties of electrical conductivity, surface morphology and physical properties. This is due to the nature of their physical structure and the distribution of PEDOT: PSS on their structure. Moreover, PES-type fabric provides good attachment and longevity of PEDOT: PSS precipitates onto
the fiber structure [9]. Due to these characteristics, we utilised an immersion method to fabricate a conductive PEDOT: PSS fabric. However, the low conductivity values of PEDOT: PSS have become a concern and need to be improved to allow this type of conductive polymer to be used in a variety of fields. Therefore, dopant EG was used to test the conductivity of PEDOT: PSS at different concentrations (2% v/v, 4% v/v, 6% v/v, 8% v/v, and 10% v/v). Electrochemical Impedance Spectroscopy (EIS), Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD) are used to determine the conductivity, morphology, and crystallinity of the fabricated fabrics after the immersion process. This study provides more understanding on the structural changes that lead to the conductivity enhancement of PEDOT: PSS fabric.

2 Experimental

2.1 Materials

Polyester fabric (50 cm X 50 cm) was purchased from Jakel Trading Sdn Bhd. Sigma-Aldrich (St. Louis, MO, USA) provided the 3,4-ethylenedioxythiophene (EDOT) monomer, poly (styrene sulfonate) (PSS), ammonium persulfate (APS), ethylene glycol (EG), and ammonium persulfate (NH₄)2S2O8.

2.2 Synthesis of PEDOT: PSS

PEDOT: PSS was synthesised with the aid of an oxidant, which is ammonium persulfate (APS) by chemical oxidative polymerization. A 0.05 mL of EDOT and 0.3 mL of PSS (1:6) ratio was mixed in 14.87 mL of distilled water in room temperature for 1 hour. Then, ammonium persulfate (APS) with 1:2 ratio was added into the mixture solution and stirred for 2 hours until the colour turns into dark blue solution.

2.3 Preparation of doped and undoped PEDOT: PSS with EG

A 2% v/v of EG and the PEDOT: PSS solution were added together with 1:1 ratio and swirled slowly to ensure the solution is well mixed. The same step was repeated for different concentration of EG (4% v/v, 6% v/v, 8% v/v and 10% v/v). PEDOT: PSS without the addition of EG was prepared as a control (undoped PEDOT: PSS).

2.4 Immersion of PES fabric dopes and undoped PEDOT: PSS

Fabrics made of polyester (PES) were cut into 5 cm by 5 cm squares. They were immersed in the PEDOT: PSS solution for 30 minutes followed by a drying process. The fabrics were kept in the dark place until further use.
2.5 Material Characterisations

2.5.1 Electrochemical Impedance Spectroscopy (EIS)

HIOKI 3532-50LCR Hi Tester Electrochemical Impedance Spectroscopy at room temperature was utilised with a frequency range of 100 Hz to 1000 kHz. PEDOT: PSS textiles were sandwiched between two stainless steel disc electrodes having a diameter of 2.0 cm. The samples' conductivity (σ) was determined using the formula below:

$$\sigma = \frac{L}{RB \times A}$$

Where L denotes fabric thickness, RB denotes bulk resistance, and A denotes the electrode's contact surface area with the fabric.

2.5.2 Scanning Electron Microscope (SEM)

The morphological evaluation of the PEDOT: PSS fabric samples with varied concentration of EG was performed using a scanning electron microscope (SEM) model TM3030 Plus. All samples (n=6 with 1 control sample) was prepared by coated with gold to ensure the sample is conductive. Then, the sample was mounted on the sample stage by sticking it with carbon tape and placed in the chamber. Sample was viewed and magnified at 200x and 500x.

2.5.3 X-ray Diffraction (XRD)

X-Ray Diffractometer (XRD) Rigaku Model Ultima IV was used in this experiment to measure the crystallinity of the PEDOT: PSS fabric. Besides, it is also used to identify the arrangement of the PEDOT: PSS chain in the whole system. The sample was cut in 1 cm X 1 cm dimension before tamped on the sample holder.

3 Results and Discussions

3.1 Synthesis of PEDOT: PSS

In this work, PEDOT: PSS was created via chemical oxidative polymerization and immersion method to produce conductive fabric. The colour of the fabrics changed from white to green and dark blue after immersing in undoped solution and doped PEDOT: PSS solution, respectively. This is due to the completed polymerization of PEDOT: PSS. The colour of the fabric is darker as increasing the concentration of dopant. The differences in the colour of pre- and post-immersion fabric proved the successful preparation of PEDOT: PSS fabric. In a physical touch, both undoped and doped fabrics form a smooth surface (Fig. 3).
Fig. 3. (a) Bare PES fabric, (b) Undoped PEDOT: PSS fabric and (c) Doped PEDOT: PSS fabric with 6% v/v of EG.

3.2 Electrochemical Impedance Spectroscopy (EIS)

The conductivity values of PEDOT: PSS fabric were measured using the Electrochemical Impedance Spectroscopy (EIS). Fig. 4 shows the bar chart summarized the electrical conductivity values of PEDOT: PSS coated PES fabrics with different concentrations of EG. It shows that the conductivity value is increased after the concentration is increased. PEDOT: PSS fabric with 6% v/v of EG recorded the highest value at 4.06 x 10⁻³ S/cm. This can explained a 6% v/v of EG has imparted the electron migration along the conjugated backbone [10]. Meanwhile, at 10% v/v of EG shows the lowest conductivity measured at 9.42 x 10⁻⁴ S/cm considering the weaker charge carrier mobility in the PEDOT: PSS fabric [8].

Fig. 4. Conductivity values of PEDOT: PSS PES fabrics at different concentrations of EG in (% v/v).

Kroon et al., (2016) stated that PEDOT: PSS is in the core-shell structure, and it is becoming one of the reasons the conductivity is limited. Moreover, the PSS shell is believed to wrap up the PEDOT core resulting in a minimum hopping of charge carrier. Treating PEDOT: PSS with EG can cause phase separation and segregation between PEDOT and PSS by their different hydrophilicities [12]. Therefore, it may reduce columbic interaction and thus causing in the elimination certain amount of PSS from PEDOT: PSS chains [13-14]. As a result, conformational change occurred in the PEDOT: PSS structure transforming the coil into a linear structure (Fig. 5) [15]. The mobility of charge carrier will be easier at 6% of EG as the connectivity between PEDOT grain is improved. Hence, conductivity is enhanced.
3.3 Scanning Electron Microscopy (SEM)

Fig. 6 shows the surface morphology of undoped PEDOT: PSS fabric and PEDOT: PSS fabric doped with 6 v/v% of EG.

Fig. 6. Morphological surface through SEM on (a) undoped PEDOT: PSS fabric and (b) PEDOT: PSS doped with 6% EG fabric under 500x magnification.

In the Fig. 5 (a) and (b), there was randomly distributed PEDOT: PSS precipitate formed on the fiber surface. It may indicate that PEDOT: PSS has been successfully adhered to the surface of the fabrics. This theory is proven by the fact that the CPs are easily absorbed within the fibers [16-17]. As shown in Fig. 5 (b), the amount of precipitate is slightly increased compared to the undoped fabric, resulting in better conductivity as mentioned in the above section.

3.4 X-ray Diffraction (XRD)

Fig. 7 shows the XRD pattern of the PEDOT: PSS fabric with different concentration of EG. There are three (3) obvious peaks in this XRD pattern at 2\(\theta\) = 17.8°, 22.7° and 25.6°. Peak at 2\(\theta\) = 17.7° and 25.6° correspond to the amorphous of PSS and \(n\)-\(n\) stacking \(d\) (010) of the PEDOT thiophene ring, respectively. According to Fig. 6, the peak of the XRD pattern for PEDOT: PSS polyester fabric doped with 6% v/v of EG is slightly increased at 2\(\theta\) = 25° (\(d\) = 3.6 Å) compared to undoped PEDOT: PSS polyester fabric. The sharpness of the peaks slightly increased at 6% v/v of EG, indicating the formation of a linear conformation. It is also mentioned that an increase in the peak intensity suggests an increase in the crystallinity of the PEDOT: PSS system [8]. The enhancement of crystallinity contributes to the electrons hopping in PEDOT grains and thus boost up the conductivity of PEDOT: PSS fabric.
4 Conclusion

PEDOT: PSS was successfully synthesized through a chemical oxidation method. The conductivity of PEDOT: PSS is increased by adding a dopant, EG at different concentrations. PES fabrics can simply be produced by incorporating a CP, PEDOT: PSS through an immersion method. The conductivity of the fabrics can be achieved at $4.06 \times 10^{-3}$ Scm$^{-1}$ using 6% v/v EG concentration. When the concentration of EG is further increased, the conductivity of the PEDOT: PSS fabric is drop. The morphological properties of the fabrics have shown different attributions. In this study, both doped and undoped PEDOT: PSS exhibit a homogenous, uniform, and smooth surface of. The immersion technique may be used to make PEDOT: PSS textiles that are conductive.

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