The Effects of Acidic Secondary Dopants to the Electrical Conductivity of PEDOT: PSS Fabrics

Dania Adila Ahmad Ruzaidi1, Fifi Alfiani Suhaimi1, Muhammad Adam Saripudin1, Rosmahmahadamani Ramli1, Hazwane Osman2, Nur Izatul Muhammad Nadzri3, Mohd Mazamir Mahat1

1Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
2Centre of Foundation Studies UiTM, Universiti Teknologi MARA (UiTM), Cawangan Selangor, Kampus Dengkil, 43800, Dengkil, Selangor, Malaysia
3Center of Excellence Geopolymer & Green Technology (CEGeoGTech), Universiti Malaysia Perlis, 02600, Arau, Perlis, Malaysia

Abstract. Conductive polymers commonly used as fillers to enhance electrical properties of composite’s system. However, the low conductivity performance of conducting polymers, namely poly(3,4-ethylenedioxythiophene): poly (4-styrene sulfonate) (PEDOT: PSS), constrains their utilization in the field of conductive textile technology in inventing an advanced textiles’ fabric. Maintaining the stability of impregnated PEDOT: PSS fabrics at the microscopic level remains doubtful and unclear. Nowadays, researchers are actively pursuing the introduction of secondary dopants into PEDOT: PSS dispersion to overcome this challenge. In this study, a conductive PEDOT: PSS fabric via immersion technique was prepared and its effects on conductivity upon doped-secondarily by two different dopants; hydrochloric (HCl) and p-toluenesulfonic (p-TSA) acids was revealed. The volume percentage (vol.%) of the secondary dopants (1, 3, 5, 7, 9 vol.%) were varied to find the optimal vol.% for getting the great value of conductivity of the doped PEDOT: PSS fabrics. These fabrics were then analyzed by using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR), Electrochemical Impedance Spectroscopy (EIS), and Scanning Electron Microscopy (SEM) to investigate their conductivity performances chemically. It is found that the conductivity values were affected by varying the strength of the acids. It is concluded, that the 7 vol.% and 5 vol. % of HCl and p-TSA, respectively, gave the highest electrical conductivity values of the PEDOT: PSS fabrics. These findings can be used to provide direction and guidance to researchers in advancing the fields of textiles, electronics and advanced materials.

1 Introduction

Smart textiles are classified as textiles that can sense or respond to environmental stimuli exerted on them. From everyday use to health-related applications, new utility, comfort, and aesthetic values are some of the cultural demands driving the smart textile materials’ advancement. Our smart textiles are made up of conductive fabrics which conduct a certain amount of electric current for stimuli detection purposes. Generally, conductive fabrics can be mainly prepared by using two methods. First, conductive materials such as conducting polymers or metal nanoparticles can be added during the spinning process to obtain conductive fibres [1]. The obtained conductive fibres made of conductive polymers exhibit excellent electrical signal detection and transmission performance owing to their superior conductivity, piezoelectric induction and charge storage [2]. Secondly, conductive fabrics can be prepared by covering, depositing and embedding the surface with conductive materials through dipping, immersion, or spray-coating technique [3]. Previous studies claimed that conductive particles on the surface of the fabrics usually tend to aggregate and easily peel off from the fabrics, thereby diminishing the responses to external stimuli [4]. A promising strategy to overcome the adhesion failure under a high level of strain is to covalently integrate and evenly distribute diverse types of bridging groups onto the surface of the textile or fibre, which can improve the durability of the sensing layer to friction and strain. In addition, the introduction of a multifunctional interfacial layer between the fibrous substrate and conductive nanomaterials is significant in improving the durability of the sensor and heat resistance of the fibrous substrate [5]. In biomaterial textile application fields, the biocompatibility level of smart textile materials is still doubted due to the acidic-based processes used. Apart from that, many components and electro-active materials incorporated into fabrics do not satisfy the textile specification regarding stability, comfort, washability, versatility, and protection for the climate, or even safety for a potential wearer [6].

The incorporation of one of the most researched conducting polymers (CPs), Poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS) into fabrics was numerously studied to improve the electrical conductivity performances of conductive fabrics [7]. Due to its conductivity, clarity, and low redox potential, PEDOT: PSS has numerous advantages over metal materials. PEDOT is insoluble in water making it difficult to be processed. To overcome this problem, polyelectrolyte PSS will be added to stabilize the PEDOT [8]. The attachment of PEDOT particles to the
fibris structure of fabrics depends on the fibre chemistry and the fibre’s surface roughness. In addition, the electrical and mechanical properties of conductive materials can be controlled by the centralization of oxidants, the pre-treatment process of the first unblemished texture, including the conductive texture, type and post-medicines process. According to past research, incorporating other CPs such as Polyaniline (PANI) into fabric results in a wavy pattern of electrical conductivity at ambient conditions [9,10]. This is may be due to the nature of PANI, which is a non-conductive polymer at the rudimentary level and has low stability. Thus, in this study, PEDOT: PSS was chosen to act as an electrical filler in polyester fabrics. In order to increase the electrical conductivity of PEDOT: PSS, a secondary doping process was introduced at the early fabrication level. Some of the dopants that can be added into PEDOT: PSS dispersion to enhance its conductivity performances are strong and weak acids; hydrochloric acid (HCl), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄) and p-Toluene sulfonic acid (p-TSA) [11]. The incorporation of acids will contribute more H⁺ ions in the PEDOT: PSS system. This will physically change the electrical state of PEDOT: PSS by narrowing the gap between its valence band and the conduction band. Though the acids used might agitate the biocompatibility performance of fabrics, alkaline treatment can be proposed at the later part of fabrication process, to neutralize the fabrics. According to previous research, alkaline treatment did improvise the conductivity of fabrics.

The polyester fabrics were submerged into PEDOT: PSS solution containing HCl and p-TSA acids in this research. The concentration of secondary dopants was varied into 1, 3, 5, 7, and 9 vol. % as suggested in previous studies to find the best concentration value which can contribute to higher electrical conductivity of PEDOT: PSS fabrics. Polyester fabric types were chosen for this experiment due to their excellent mechanical properties compared to other fabrics such as cotton. The electrical conductivity performance of doped fabrics was evaluated by using the Electrochemical Impedance Spectroscopy (EIS). Meanwhile, the morphology and chemical structure of fabrics were examined and recorded by using Scanning Electron Microscopy (SEM) and Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) analyses, respectively. Throughout this article, the change in PEDOT: PSS fabrics’ electrical conductivity performance was discussed together with their micrographic structure captured. This finding reveals the electrical conductivity post-effects of PEDOT: PSS fabrics when HCl and p-TSA are introduced at different vol.%. This simultaneously contributes ideas for the development of conductive-wearable smart textiles.

## 2 Materials and Methods

### 2.1 Materials

3,4-ethylenedioxythiophene (EDOT) monomer, poly (styrene sulfonate) (PSS), ammonium persulfate (APS), hydrochloric acid (HCl), p-Toluene sulfonic acid (p-TSA), and ethylene glycol (EG) were all purchased from Sigma Aldrich (St. Louis, MO, United State of America) while polyester fabrics were purchased from JAKEL Textile, Malaysia.

### 2.2 Synthesis of Conductive PEDOT: PSS Dispersion

PEDOT: PSS was synthesised with the aid of an oxidant, ammonium persulfate (APS) through chemical oxidative polymerization method [12]. Briefly, 0.5 mL EDOT was mixed with 3.0 mL PSS solution containing 148.7 mL deionized water and was left stirring for 30 min. Next, 1.0 mL of ammonium persulfate (oxidant) was added and stirred for another two hours to form PEDOT: PSS dispersion. The formation of a dark blue colour solution indicates that a polymerization process of PEDOT: PSS has completely taken place.

### 2.3 Preparation of Doped-PEDOT: PSS Fabrics

For the PEDOT: PSS doping process, five separate concentrations of HCl and p-TSA (1, 3, 5, 7, and 9 vol.%) were prepared through acid dilution method with the use of deionized water and ethylene glycol (EG), respectively. PEDOT: PSS was added into each prepared acid and was left stirring for 5 min. To prepare the doped PEDOT: PSS fabrics, a 16 cm² of polyester fabrics were submerged into each prepared doped-PEDOT: PSS solution for 30 min followed by 24 hours drying process of fabrics at room temperature.

### 2.4 Characterizations of Doped PEDOT: PSS Fabrics

#### 2.4.1 Scanning Electron Microscopy (SEM) analysis of Doped PEDOT: PSS Fabrics

The morphological studies of fabrics were held by capturing the micrograph structure of doped-PEDOT: PSS fabric samples with the addition of different vol. % of secondary dopants (HCl and p-TSA) by means of Scanning Electron Microscope (SEM). All samples (n = 11 with 1 control sample) underwent a gold-sputter coating process for conductive purposes. SEM analysis was performed with 500× magnification.
2.4.2 Attenuated Total Reflectance-Fourier Transform Infrared (ATR FTIR) of Doped PEDOT: PSS Fabrics

All doped-PEDOT: PSS fabric samples were characterized by using Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy (ATR-FTIR). Spectral analysis was performed using Spectrum software (Version 10, Perkin Elmer Ltd, UK) to detect the possible chemical interactions between the component presence within doped PEDOT: PSS fabrics. The number of waves was set between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\) and 4 scans were performed for each measurement. Prior to sample measurement, a background spectrum was recorded and all spectra were baseline corrected.

2.4.3 Electrochemical Impedance Spectroscopy (EIS) Analysis of Doped PEDOT: PSS Fabrics

The conductivity of doped PEDOT: PSS fabric samples were determined by using HIOKI 3520 LCR Hi-Tester Electrochemical Impedance Spectroscopy (EIS) in a frequency range of 100 Hz to 10000 Hz at room temperature. A cylindrical probe was used to detect the charges flow throughout the fabrics. For every operating frequency, the impedance was obtained accordingly. Consequently, the values of impedance were used in the calculation to determine the conductivity value of fabric samples.

3 Results and Discussion

3.1 Morphology of Doped PEDOT: PSS Fabrics

Allison et al. (2017) reported that the PEDOT monomer can be polymerized on the textile substrate (fiber, yarn, fabric or garment form) by in situ, vapor phase or electrochemical polymerization by using EDOT and appropriate chemicals like oxidants [13]. This proves that the use of PEDOT has received attention among textile researchers. In Fig. 1, the micrograph structure of fabric samples captured from SEM analysis shows that PEDOT: PSS was successfully incorporated along with the structure of fibrils. According to previous studies, the presence of precipitates along the polyester fibrils was proved to be the doped-PEDOT: PSS precipitate [14]. In this case, PEDOT: PSS is known as the electrically conductive fillers. Thus, these evenly distributed precipitates are somehow related to the electrical conductivity performances of fabrics. The precipitation formation might come from the insoluble cations and anions reactions of PEDOT: PSS in an aqueous solution forming the ionic solid called a precipitate. As in Fig. 1, 5% HCl-doped PEDOT: PSS fabric fibrils seem to be stickier where the fibrils are attached to each other compared to 5% p-TSA-doped PEDOT: PSS fabric fibrils. Fig. 1 shows 9% HCl-doped PEDOT: PSS fabric portrays the breakage of glued fibrils structure and damaged fibres. Meanwhile, the p-TSA-doped PEDOT: PSS fabric shows more smaller precipitation formed along with the structure of fibrils at 5 vol. % compared to the 9 vol.%. Generally, the presence of acids causes some PSS ions get neutralized by the protons of hydrogen ions, causing the weakening of Coulombic attraction between PEDOT and PSS. This later initiate the removal of insulating PSS, hence increase the conductivity of PEDOT: PSS [15]. Relating to the EIS results discussed in section 3.3 Electrical Conductivity Performance of Doped-PEDOT: PSS Fabrics, this concludes that increased acid concentration has resulted in an increase in conductivity. Different type of acids will show different conductivity responses. For instance, in the case of HCl, the addition of more than 7 vol.% of acids causes the electrical conductivity experienced a little drop but still at the same magnitude \(10^{-3} \text{ S cm}^{-1}\). Meanwhile, it can be observed that after adding more than 5 vol.% of p-TSA, the conductivity of PEDOT: PSS has dropped in which the conductivity reduced to a lower magnitude, \(10^{-4} \text{ S cm}^{-1}\) to \(10^{-5} \text{ S cm}^{-1}\). It has been observed that more precipitates form on the surface of the fibres as more concentration of dopant introduced. In case of the relationship of morphology and conductivity, it can be notified that when the concentration of acid is saturated (higher concentration), the structure of fibre is damage which leads to the drop of conductivity. The high acid concentration led to the polymer chain being disrupted, resulting in a reduction in the electrical conductivity value. To enhance the conductivity, the increase of acid concentration is required, however, post-optimum conductivity obtained. The residue of the acid can lead to the reduction in the electrical conductivity value because the degradation of polymer chains is more dominating [16].
3.2 Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) of Doped-PEDOT: PSS Fabrics.

The ATR-FTIR analysis confirmed the chemical bonding and functional groups present in doped-PEDOT: PSS fabrics. The ATR-FTIR plot includes the lowest (1 vol. %) and highest (9 vol.%). acids percentage since the functional group detected for all samples are quite the same. Fig. 2 (a) shows the ATR-FTIR plot of HCl-doped PEDOT: PSS fabrics, whereas Fig. 2(b) shows the ATR-FTIR plot of p-TSA-doped PEDOT: PSS fabrics at different vol.%. Generally, the C=C bond of PEDOT: PSS was detected at 2964.20, 2966.43 and 2967.40 cm⁻¹. The peaks at 1711.41, 1712.89 and 1713.29 cm⁻¹ indicate a carbonyl double bond of the carboxyl group [17]. The overlapping of peaks might occur due to the shifting of C=C bond of PEDOT from 1600 to 1750 cm⁻¹ area. In the fingerprint region, a strong signal was found at 1500 cm⁻¹ informing the presence of PSS aromatic rings. The addition of HCl and p-TSA acids into PEDOT: PSS fabric shows a broad absorption band in the range of 2900 to 3100 cm⁻¹, indicating the presence of hydrogen bonds. Both HCL and p-TSA doped PEDOT: PSS fabrics plots show similar wavenumber shifting.

3.3 Electrical Conductivity Performance of Doped PEDOT: PSS Fabrics

Fig. 3 depicts the conductivity of PEDOT: PSS fabric doped with different concentrations of HCl and p-TSA acids (1, 3, 5, 7 & 9 vol.%) characterized by using Electrochemical Impedance Spectroscopy (EIS). The optimum conductivity of HCl doped PEDOT: PSS fabric and p-TSA doped PEDOT: PSS fabric were found to be 3.67×10⁻³ S cm⁻¹ and 5.88×10⁻³ S cm⁻¹ at 7 vol.% and 5 vol.%, respectively. Due to the existence of H⁺ ions in HCl and p-TSA, PSS will be bound
with the H+ ions and thus weakening the coulombic attraction between PEDOT and PSS causes charges hopping to quickly occur [18]. Hence, conductivity increased. The presence of EG in p-TSA dopant solution increases the conductivity of PEDOT: PSS considerably. According to previous studies, numerous organic solvent dopant types have been proven to improve the conductivity of PEDOT: PSS such as EG, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and tetrahydrofuran (THF) [19]. In some cases, phase segregation of PSS occurred when introducing EG as an organic solvent. Thus, theoretically weakening the PSS shells that encapsulate the PEDOT grains contributes to the formation of smaller PEDOT: PSS precipitations along with the fibril structure. Overall, by comparing the HCl doped PEDOT: PSS fabrics with p-TSA-doped PEDOT: PSS fabrics, the use of EG as a p-TSA solvent has significantly enhanced the electrical conductivity of PEDOT: PSS and improve the distributions of PEDOT: PSS precipitation on fibrils. This is maybe due to the p-TSA weak acid properties which are not causing damage to the fibril structure of fabrics.

![Figure 3. EIS plot of electrical conductivity value executed by (a) HCl-doped PEDOT: PSS fabrics and (b) p-TSA-doped PEDOT: PSS fabrics.](image)

4 Conclusions

The EIS analysis reveals the potential of HCl and p-TSA to increase the electrical conductivity of PEDOT: PSS fabric. HCl-doped PEDOT: PSS fabrics recorded the highest conductivity value at 7 vol.% while p-TSA-doped PEDOT: PSS fabrics were at 5 vol.%. The contribution to higher electrical conductivity was due to the attachment of PEDOT: PSS precipitation along with fibril structure of fabrics. The attachment of PEDOT: PSS precipitates can be evenly distributed to all over fabric surfaces with the use of EG as solvent during the fabric’s immersion process. Increasing acid’s concentration was not necessary since this leads to the breakage of fibrils.

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