Effect of liquid immersion of PEDOT: PSS-coated polyester fabric on surface resistance and wettability

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Abstract
Coating of textile fabrics with poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) is one of the methods used for obtaining functional or smart applications. In this work, we prepared PEDOT:PSS polymer with certain additives such as polyethylene glycol, methanol (MeOH), and ethylene glycol on polyester fabric substrates by a simple immersion process. Surface resistance was measured and analyzed with analysis of variance to determine the coating parameters at 95% confidence level. Fourier transform infrared (FTIR) analysis and scanning electron microscopy (SEM) study of the samples were performed. Contact angle and washing fastness measurements were conducted, to observe the wettability and washing fastness of the samples, respectively. Surface resistance values were decreased by a factor of 100, due to conductive enhancers. As the immersion time and temperature condition varies, surface resistance showed no difference, statistically. FTIR analysis supports the idea that the mechanism responsible for the conductivity enhancement is the partial replacement of PSS from PEDOT chain by forming a hydrogen bond with hydroxyl ion (OH) of the conductive enhancers. A SEM images showed that PEDOT:PSS is well distributed to the surface of the fabrics. Contact angle measurements showed morphology change in the samples. The conductivity was reasonably stable after 10 washing cycles. Altogether, an effective simple immersion of coated polyester fabric is presented to achieve functional textiles that offer a broad range of possible applications.

Keywords: immersion, surface resistance, contact angle, polyethylene glycol, methanol

(Some figures may appear in colour only in the online journal)
polymers (ICPs) has been the most extensively studied. Fibers or polymers that can function as electronic components such as sensors and actuators are an exciting prospects for new textile these technologies. Knowledge of integrating polymers with textiles as sensors and actuators to environmental stimuli has great importance for smart or functional applications.

It is generally accepted that conductive polymers, or more precisely, ICPs are an ideal candidate for smart or functional textile applications due to their good electronic conductivity and mechanical properties [1]. Conductive polymers can be integrated with textile materials through different methods like coating [2, 3], inkjet printing [4], and screen printing of conductive polymers on different substrates [5], to develop smart textiles. PEDOT:PSS can be deposited using common techniques employed for the deposition of waterborne coatings and it is thermally stable [6], flexible [7], and does not crack when the coated fabric is bent.

Coating process has been used for the production of conductive textiles by using polypyrrole and polyaniline [8], and PEDOT:PSS [9]. PEDOT:PSS is a mixture of two monomers. The first one is PSS that consist of polystyrene sulfonate, which is deprotonated; and carry a negative charge and act as a counter ion. The other is 3, 4-ethylenedioxythiophene (PEDOT); is a conjugated polymer and carries a positive charge and is based on polythiophene [10].

The conductivity of PEDOT films can be enhanced dramatically if the dispersions contain high boiling polar solvents such as ethylene glycol (EG), sorbitol or dimethyl sulfoxide (DMSO) [11–16].

From this literature, we can understand that efforts have been made to improve the conductivity of aqueous PEDOT dispersions starting from 80 s cm$^{-1}$ and now reaching 1000 s cm$^{-1}$. Using organic compounds, including high boiling solvents like methyl pyrrolidone, DMSO, sorbitol, ionic liquids, and surfactants added to PEDOT:PSS; conductivity increases by many orders of magnitude.

Conductive enhancers help the partial reduction of excess PSS that surrounds the conducting PEDOT:PSS grains in proposed to lead an increased connectivity and parallel arrangements between the PEDOT grains in the film and hence higher conductivity. A previous study suggested the potential of using PEDOT:PSS dispersion conductive material with polyurethane (PU)-based coating of poly (ethylene terephthalate) (PET) textiles can be used as functional material [9].

Coating formulations of PEDOT:PSS with different molecular weight and concentrations of polyethylene glycol (PEG) [17] have been used for enhancing the conductivity of the polymer for ITO-free solar cells. However, these were applied on a glass substrate, not textiles. The data in [18] has shown that a simple treatment of PEDOT:PSS films with methanol can enhance the conductivity of PEDOT:PSS with a glass substrate. Conductivity enhancement of PEDOT:PSS film through a treatment with aqueous solutions of CuBr$_2$ (Copper (II) bromide) and InI$_3$ (Indium (III) iodide) on a glass substrate has also been reported [19].

Observations in papers [9, 20, 21] suggested that temperature, a conductive enhancer (EG), and polyurethane binder play an important role on the surface resistivity of PEDOT:PSS-coated polyester fabric. To our knowledge, these studies did not recognize the challenges of leveling (decreasing of surface tension) and increase in coating weight. Research has tended to focus on increasing the conductivity of PEDOT:PSS rather than the effect of pre-mixing of conductive enhancers on the surface tension of the coating paste, which creates a leveling problem in coating application. These differences are examined in this paper. In addition to this, we did not find any research that has been used PEG and MeOH as conductive enhancers for textile substrates using PEDOT:PSS.

The purpose of this research paper is to immerse PEDOT:PSS-coated polyester fabric with different conductive enhancers rather than pre-mixing with coating paste. A simple and cost effective immersion process was applied.

In immersion process, conductive enhancers can be used several times so that water pollution can be reduced. In the coating process, the conductive enhancers [9] have contributions to the weights of the finished coating while in immersion process the conductive enhancer was removed by curing and does not contribute to the weight of the finished coating. Solvent-borne formulations with naturally or deliberately lower surface tensions wet readily and transfer well onto most substrates, even though they may raise coefficients of spreading on select substrates. Adding the conductive enhancers before coating application lowers the surface tension. In this paper, we argue that although good wetting may require a reduction in surface tension, higher surface tension promotes leveling as stated in [22]. This approach provides effective methods of enhancing the conductivity of PEDOT:PSS without affecting the surface tension of coating paste and weight of the finished coating.

Wettability of the PEDOT:PSS-coated substrate by water is also an indication of the removal of hydrophobic PSS from the surface of the PEDOT:PSS film [23, 24]. This property was quantified by contact angle measurement and Fourier transform infrared (FTIR) analysis. This indicates that there is a morphology change when PEDOT:PSS is treated with organic chemicals. More details on the change on morphology and conductivity films have been affirmed using tunneling microscopy [25].

2. Experimental

2.1. Materials

Plain woven fabric of spun multi-filament PET fibers with a GSM of 158; 30 ends cm$^{-1}$; and 22 picks cm$^{-1}$; scoured and heat-set by the supplier (Almedahl-Kinema AB, Sweden) was used as the substrate. PEDOT:PSS aqueous solution (Heraeus GmbH, Germany) with a concentration of 1.3% by weight; and a PSS to PEDOT ratio of 2:5 was used as a conductive agent. Methanol alcohol (99.8% anhydrous), EG (99.8% anhydrous), and polyethylene glycol (PEG300 lab grade) (supplied by Sigma-Aldrich) were used as a conductivity enhancers. HEUR (hydrophobically modified ethoxylated urethane) symbolized by Gel L75N (Borchers GmbH/IMCD
Sweden AB) with a solid content of 48 wt%, according to the manufacturer was used as a rheology modifier. Performax 16297 G (Diaz Kemi, Sweden) was used as a binder (the solid content has been determined to 35 wt% through drying according to a previous report [9]). A DuPont Zonyl FSO-300 (solids content of 40 wt% according to the manufacturer); surfactant was added to all the aqueous dispersions prepared as a wetting agent. All chemicals were used as received.

2.2. Methods

2.2.1. Sample preparation. Coating chemicals were prepared by mixing the ingredients according to the recipe given in table 1 with a mechanical stirrer for 5 min; at speed of 500 rpm; after which the solutions were homogeneous with a naked eye.

2.2.2. Coating. The coating process was performed with a laboratory coating machine (coating applicator) at a gap height of 200 μm using constant coating speed manually. The samples were dried at 50 °C for 30 min and annealed at 90 °C for 30 min at air and vacuum condition. In order to limit the number of experimental runs, a general factorial design with three replicates was selected. Replication is essential to estimate the interaction between the factors and one way ANOVA was used to see the effect of each parameter. A total of 36 runs were performed. The next step was to randomize the order of the treatments, which is the foundation underlying the use of statistical methods in experimental design.

2.2.3. Liquid immersion. The first method is to coat the polyester fabric with PEDOT:PSS polymer dispersion first for a while, followed by drying, to fix the polymer; the second method is to immerse or soak the PEDOT:PSS-coated fabric in a solution containing EG, MeOH, and PEG for 5 and 15 min with a liquor ration of 1:10; finally curing of the immersed samples at 100 °C for 30 min under air and vacuum condition.

2.2.4. Surface resistance measurement. Surface resistance measurements were obtained using a multimeter (Agilent 34401A) in a four-point probe resistance mode and in-house designed (Van der Pauw Method) at 29%–30% RH and 19 °C–20 °C after conditioning the sample at 65% ± 2% RH and 20 °C ± 2 °C for more than 18 h. The measurements were made both in the warp and weft directions with three readings each, the average readings were reported.

2.2.5. FTIR analysis. The FTIR spectra were obtained using a Nicolet iS10 FTIR spectrophotometer at a frequency range of 4000–500 cm⁻¹ (a resolution of 4 cm⁻¹) for 256 scans, with diamond ATR mode. The version of the software used was OMNIC. To collect FTIR spectra, untreated polyester fabric, coating without and with EG, and immersion with EG samples were examined for comparison purposes.

2.2.6. Scanning electron microscopy (SEM). Images were taken with a Leo Ultra 55 SEM equipped with a field emission gun (LEO Electron Microscopy Group, Germany) and a secondary electron detector. The acceleration voltage was 3 kV. Samples were cut by a razor blade. All samples were sputtered with gold.

2.2.7. Wettability study. Wettability of PEDOT:PSS-coated fabrics was determined by water contact angle measurement using Theta optical tensiometer setup; sessile drop technique and young Laplace analysis mode. The drop size was 3000 μl at a drop rate of 0.5 μl s⁻¹. The average contact angle values were obtained by measuring the contact angles at three various positions on the samples, and the standard deviations were calculated to observe the error on the average for each material.

2.2.8. Washing fastness test. The washing fastness of the samples against surface resistance values was examined. Therefore, domestic laundry washing and drying procedures of type 3 A reference for textile testing (ISO 6330:2012); were performed to observe the durability of samples immersed for 5 min and selecting one of the three samples with the lowest surface resistance with 100% polyester ballast against washing.

3. Results and discussion

The work presented here provides a different strategy of enhancing the electrical conductivity of PEDOT:PSS-coated fabrics using immersion method. Post-treatment of PEDOT: PSS-coated fabrics using organic solvents resulting in comparable results as that of the usual pre-mixing methods using PEDOT:PSS.

Samples were prepared based on conductivity enhancers EG, MeOH, and PEG via air and vacuum conditions using immersing the PEDOT:PSS-coated PET fabrics at various times. Specimens were found to be electrically conductive and less hydrophilic.

We used four-probe methods for electrical surface resistance measurement, contact angle study, to observe hydrophilicity change and FTIR spectroscopy for spectra characterization of specimens.
Surface resistance measurements were carried out 5 times both in the warp and weft directions of the specimen; average and standard deviations were reported.

To understand the mechanism of conductivity enhancement of PEDOT:PSS films, before and after PEG, MeOH, and EG treatment; the surface resistances of the specimens were measured. The statistical surface resistance values of the samples are shown in Figure 1.

In comparison to the control (C⁵) value, the immersed specimens yield low surface resistance value, this is attributed to the partial reduction of the insulator PSS chain from the PEDOT:PSS film. The immersion of samples after coating led to a decrease in surface resistance which is a fundamental step for enhancing the conductivity of the polymer film and showed that PEG, EG and MeOH used as a conductivity enhancer. The decrease in surface resistance may suggest that some PSS chains leave the PEDOT:PSS film after the treatment with these chemicals.

An increase in immersion time for both methods did not show a difference in surface resistance statistically, indicating that the reaction of enhancers with PEDOT:PSS needs less time only. The surface resistance for both types of drying was almost the same; this means varying drying temperature conditions had little influence on surface resistance of PEDOT:PSS coated fabrics.

The FTIR spectroscopy measurements were taken under ambient conditions in order to compare the spectra of immersed (with EG) specimens against the untreated fabric, control fabric (coated without EG), and coated with EG; the results are shown in Figure 2.

As seen from Figure 2, the most remarkable spectra shift, with respect to control (pristine film), is observed for the sample with EG-immersed, which shows very strong peaks at 3300, 2937, 2874 and around 1000 cm⁻¹. Whereas, the other samples do not show much variation than the control sample. Another effect, due to the immersion of samples with EG, is the decrease of the band intensity at 1712 cm⁻¹. It is, therefore, presumed that these new bands are associated with the existence of some other components present in the sample as a result of additional functional groups due to EG addition. New bands correspond to functional groups of EG (with molecular chemical structure (HO–CH₂–CH₂–OH) (from the repeating unit of PEG) [26].

Thus, our result confirmed that the successful introduction of conductive enhancers to the specimens by immersion method in comparison to the coating method.

It has been reported that when PEDOT:PSS polymer treated with PEG, the hydroxyl ion of PEG forms a hydrogen bond with polystyrene sulfonic acid and hence partial removal of PSS from PEDOT chain [27]. Since PSS is hydrophilic and moves towards the surface of the PEDOT film, it has the tendency to reduce hydrophilic behavior of the specimen after immersion. According to the literature [28], polar solvents has a tendency to reduce the fundamental band gap. It can be observed that in Figure 2 major vibration polar and strong band, carbonyl (–C=O, 1712 cm⁻¹) [29], changed into fewer intensity bands and believed to be due to the addition of EG by immersion that has altered PEDOT:PSS chains by forming hydrogen bond with PSS and carbonyl group. Hydrogen bond not only plays an important role in creating hydrophobic domains and conformational arrangements (crystalline) but also has a tendency to transfer part of its bond to the carbonyl group of the neighboring polymer [30]. Therefore, introducing EG via immersion of PEDOT:PSS-coated fabric has a modified structure not only in the PEDOT:PSS but also in polyester fabric, and hence not only weaken the electrostatic interaction between PEDOT cationic chains and PSS anionic chains but also decrease the polarity of carbonyl group of polyester fabric; resulting in reduced hydrophilicity of the sample. Such bands observed on FTIR have contributed to enhancing electrical conductivity and structural re-arrangements of PEDOT:PSS and decrease the hydrophilic behavior of the polyester fabric.

Observation of the treated EG and untreated samples with SEM confirmed that immersion technique produces more uniform fabric surface than those of coating method as shown in Figure 3. The morphology of the samples is highly dependent on the coating application.

This uneven distribution of PEDOT:PSS is created due to leveling problems as described in [22]. The leveling problem occurs because of pre-mixing with EG reduces the surface tension of the solution, and hence unevenness occurs during coating.

Water contact angle measurement was examined to characterize the hydrophilicity behavior of the sample. The results are shown in Figure 4. Samples of PEDOT:PSS coated fabric with methanol, EG, and PEG (molecular weight 300) show variation in contact angle values to the control sample.

All samples were hydrophilic. However, regarding the control fabric, there was a clear difference in chemically immersed samples, which shows a higher contact angle (low hydrophilicity). The comparison between contact angles before and after chemical immersion clearly indicates increased in hydrophobicity. This effect can be explained by

![Figure 1. Surface resistance values treated samples under (■) MeOH-air, (●) EG-air, (▲) PEG-air, (▼) MeOH-vacuum, (►) EG-vacuum, and (◄) PEG-vacuum condition.](image-url)
considering that hydrophilic PSS being partially removed when the PEDOT:PSS-coated fabric is immersed in PEG, methanol, and EG.

Ouyang et al. have reported that an increased interchain interaction occurs due to conformational changes in PEDOT:PSS chain when treated with solvents like EG and sorbitol. The result can be explained by a change from a coil to a linear structure. Similarly, the study in has shown an increased and improved connectivity between the PEDOT:PSS grains in the film due to the partial reduction of PSS chain as proposed in figure 5.

The addition of EG to PEDOT:PSS can cause structural re-arrangement as reported in [11], due to the removal of PSS chain from the surface of PEDOT:PSS. This conformational change in orientation increases the interchain and intrachain charge/ion carrier mobility and hence the conductivity improved.

The possible morphological changes of PEDOT:PSS film after the immersion in EG, PEG and methanol based on the contact angle measurement can be formulated (see figure 5). For the films without PEG, EG, and MeOH, the PEDOT crystals surrounded by PSS showed amorphous arrangement; however, after the addition of these chemicals PSS chains reorganized to the outer surface and the PEDOT crystals
The increase in conductivities of the films by PEG, EG, and MeOH chemicals post-treatment arise from the rearrangement of the PEDOT segments leading to better connections between the conducting PEDOT chains. This rearrangement also causes aggregation of PSS chains that itself reduces the energetic charge barriers between PEDOT:PSS grains, and hence increases conductivity too.

The MeOH, EG, and PEG treatment screens the ionic interaction between PEDOT film and PSS ion by forming hydrogen bonding with PSS, leading to better phase separation between PEDOT film and PSS, linearly oriented PEDOT chains, as proposed in figure 5. Thus, it is clearly to understand that the transition from coil structure to a linear structure is due to the conformational change of PEDOT chains, resulting in the partial removal of PSS from the film surface, and hence the conductivity enhancement of coated fabric. The decrease in hydrophilicity of the specimens also attributed to the change in the polarity of the carbonyl group of the polyester fabric as mentioned in the FTIR analysis section.

The results of the wash fastness tests on electrical surface resistances of samples with air condition at 5 min immersion time are presented in figure 6. There was a clear increase in surface resistance for all samples after each washing cycle and their surface resistance increased by a magnitude of 100 after 10 wash cycles. Despite the low surface resistance of value of PEDOT: PSS-coated and immersed samples, polymer-based electronics materials are highly sensitive to reactions, such as humidity, and temperature, which often critically affect the electrical performance and reproducibility.

Interests are growing to observe the stability and durability of polymers, such as PEDOT:PSS, suffers from short lifetime due to its hygroscopic nature. The results of the washing experiment showed that the samples are still reasonably conductive after 10 successive washing cycles. The surface resistance values increased slowly in immersed samples than that of the control one. This may be attributed to fabric surface became less hydrophilic when treated with the chemicals, and hence less accessible by water molecules during washing. The results showed a comparable washing fastness as in [21] and can have still enough conductivity for e-textile applications.

4. Conclusions

A simple method was used to significantly enhance the conductivity of PEDOT:PSS-coated textile substrate through a treatment with a solution of PEG, methanol, and EG. A decrease in surface resistance by a factor of 100 was observed. The conductivity enhancement did not depend on the time of treatment and the kind of drying conditions. The conductivity enhancement is attributed to the reduction of PSS from the PEDOT:PSS film. FTIR spectra confirmed EG successfully introduced using immersion technique.

The contact angle measurement showed an increase by 40%–62% from the untreated fabric, this indicates that PSS was partially removed from the PEDOT:PSS chain and hence hydrophilicity of the coated sample decreased.

In summary, the coating of the polyester substrate with PEDOT:PSS in this study offers low surface resistance achieved by simple and cost effective immersion of coated samples with methanol, PEG, and EG solutions. Pre-mixing of conductive enhancers (liquids) subject to reduce the surface tension of the paste as confirmed by SEM images, which affects leveling of the coating. The paper solves the above problem. It is possible to produce a highly conductive polyester fabric with PEDOT:PSS by immersing into liquids without affecting leveling which can be used for wireless communication systems in the healthcare application.

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