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WEAFING

D3.1 – EAP COATED COMMERCIAL YARN DELIVERED



WEAFING[®]

Wearable Electroactive Fabrics Integrated In Garments

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2 Disclaimer

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3 Abbreviations

Abbreviation	Translation
PPy	polypyrrole
PEDOT	poly(3,4-ethylenedioxythiophene)
PSS	poly(styrenesulfonate)



4 Introduction

All the electroactive yarns start with functionalizing them with the electroactive polymer polypyrrole (PPy). In this Task 3.1 we will fabricate electroactive yarns and electroactive fabrics by coating PPy on commercial yarns. Commercial yarns, that are either passive or electrically conducting, and fabrics that are manufactured by University of Borås (HB) from the same yarns have been coated with the electroactive polymers PPy, poly(3,4-ethylenedioxythiophene) (PEDOT) and hybrid versions thereof using electrochemical, chemical synthesis, and dip coating from commercial solution of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). These developed electroactive yarns and electroactive fabrics will be used in the first generation devices, for developing the first generation in-air yarns in Task 3.3.1 using the coatings of Task 2.1.1, for weaving the first in air yarn Task 4.2.1, (HB) and for testing the soft mechatronics models Task 5.1.2 (University of Twente, UT).

We have investigated the thickness of two EAP coatings: the electrically conductive coating PEDOT:PSS and the electromechanically active coating PPy. We studied the effect of the commercial yarns on the performance with respect to yarn material (Young's modulus, electrical conductivity) and thickness. The actuator performance has been evaluated investing amongst others speed, strain, output stress and force, and the electrochemical parameters (current, potential) and mechanical properties using lever arm system.



5 Materials and Methods

5.1 Optimization of the PEDOT coating

5.1.1 Materials

Dimethyl sulfoxide (DMSO) and pyrrole were acquired from Sigma-Aldrich. Pyrrole was previously distilled under vacuum before use and stored at -20°C . Sodium dodecylbenzenesulfonate (NaDBS) was acquired from TCI Europe and Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) PH1000 from Heraeus Company.

Viscose ring spun 1 ply yarn (Hof Garn Farber GmbH, Germany) with yarn number Nm 60/1 (Ne 36/1) was used for this investigation and cut into different samples with 72.0 ± 0.2 mm length.

5.1.2 Methods

The solid-state conductivity measurements of the uncoated yarns were performed using an Multimatrix® DMM220 digital multimeter. The resistance was measured over 14.00 ± 0.01 mm yarn length. The length of the yarns was obtained using a digital calliper (Mitutoyo Absolute AOS Digimatic) with a precision of ± 10 μm and the thickness using a digital micrometer (Mitutoyo) with a precision of ± 1 μm . Also, the conductivity was calculated using the following expression:

$$\sigma = \frac{1}{\rho} = \frac{l}{A \cdot R} \quad (2)$$

where R is the resistance of a sample between two points of the yarn, l is the length, A is the cross-sectional area, ρ is the resistivity and σ is the conductivity in S/cm.

All the electrochemical experiments were performed in a single compartment three-electrode electrochemical cell, connected to a potentiostat–galvanostat Autolab PGSTAT 204 from Metrohm Company controlled by a personal computer through Nova 2.1 software.

The reference electrode was a BASi MF-2052 Ag/AgCl (3M KCl) electrode. Here every potential is referenced to this reference electrode. Furthermore, all the experiments were performed at room temperature (22°C).

The yarn actuators were constructed following a two-step polymerization process: first a thin layer of highly conducting PEDOT: PSS was deposited on the yarn by soaking a piece of yarn into a PEDOT: PSS solution containing DMSO at different concentrations (from 0 to 80% (v/v)) to ensure sufficient conductivity in the yarn. The yarn was immersed (soaked) into PEDOT:PSS for 1 hour and then dried at room temperature for 24 hours (the yarn became dark blue). Then an active (actuating) layer of PPy was deposited using electropolymerisation in order to form an electroactive yarn.

For electropolymerization, a cylindrical electrochemical cell with a diameter of 4 cm was used. The working electrode (yarn) was set in the centre of the cell, surrounded by a stainless-steel fabric acting as the counter electrode. The PPy coating was obtained in 0.1M NaDBS and 0.1M pyrrole aqueous solution by applying a constant current of 0.5 mA through the yarns for 2500 s. The yarns were pre-tensed by hanging a plastic screw having a mass of 983.160 ± 0.007 mg at the lower end.

To characterise the movement, the yarns were mounted in a square shape electrochemical cell in 175 mL of 0.1M NaDBS aqueous solution. The yarns were again pre-tensed in a similar way as during electropolymerization, using a metallic clamp having a mass of 1049.400 ± 0.006



mg. The movement was recorded using a Dino-Lite Edge digital microscope attached to a personal computer and controlled by DinoCapture 2.0 software (version 1.5.14.G). The scanning electron microscopy (SEM) micrographs were taken using a Leo 1550 Gemini SEM operating at 20.00 KeV. Energy-Dispersive X-ray Spectroscopy (EDX) was used to quantify the elements present in the samples. The detector called X-max, manufactured by Oxford Instruments, and Aztec software was used to quantify the EDX analysis. The yarns were attached to the SEM sample holder based using conducting double-sided copper tape.

5.2 Investigation the effect of PPy coating thickness

5.2.1 Materials

Dimethyl sulfoxide (DMSO) and pyrrole were acquired from Sigma-Aldrich. Pyrrole was previously distilled under vacuum before use and stored at -20°C . Sodium dodecylbenzenesulfonate (NaDBS) was acquired from TCI Europe and Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) PH1000 from Heraeus Company. Nylon based polyamide yarn, PA, 1/78/46, consisting of 46 filaments and nylon based, rib 2×1 knitted fabric PA6, from University of Borås were used for this investigation as received.

5.2.2 Methods

The yarn was cut into pieces of 29.0 ± 0.5 cm. As the yarn tended to uncurl, common Scotch tape was placed at both ends and then cut through so that the uncurling of the yarn was prevented. The yarn was then dip coated in PEDOT:PSS-DMSO mixture. Using a pipette, a mixture of 40 % DMSO and 60 % PEDOT:PSS was applied to the yarn so that it was covered completely and let to soak. After 30 min, the yarn was let to hang vertically until it was dry. When dry, the resistance of the coated layer was measured using a Multimetrix® DMM220 digital multimeter over the entire length of the yarn. This process was repeated three additional times, making the total number of dip coatings four. After the fourth dip coat, the PEDOT:PSS-DMSO coated yarn was cut into smaller pieces. The smaller pieces of yarn received a length of 9.0 ± 0.1 cm. The conductivity of the small pieces of yarn was measured by controlling its resistance, R , to see that they were conductive enough to carry out the electropolymerization of PPy in the second step. Also, the thickness of the PEDOT:PSS-DMSO coated yarns were measured using a micrometer (Mitutoyo). The thickness values were gathered at three points to get an average, two close to each end of the yarn and one in the middle of the yarns.

For electropolymerization, a cylindrical electrochemical cell with a diameter of 4 cm was used. The working electrode (WE, yarn) was set in the centre of the cell, surrounded by a stainless-steel fabric acting as the counter electrode (CE). The PPy coating was obtained in 0.1M NaDBS and 0.1M pyrrole aqueous solution. The electropolymerization of Py onto yarn was performed using a potentiostat (Ivum Compactstat) combined with the software Ivumsoft from Ivum Technologies. The current was set to 0.5 mA and the time was set to either 2500 s, 3750 s or 5000 s to obtain different thicknesses of PPy on the yarn. After electropolymerization, loose material was rinsed off by letting them soak in water for approximately 3 min and then let to dry flat in air. When dry, the average thickness of the yarns were measured in the same manner as previously.

The performance of the yarn actuators was studied by using the Series 300B Lever System from Cambridge Technology, Inc. The software for controlling the electrochemical cell was NOVA 2.1.4. The plastic tube was placed in a clamp on a stand and the yarn was hung in the



lever arm. The plastic tube was filled with 0.1 M NaDBS so that 36.7 ± 4.1 mm yarn was immersed in electrolyte and again an Ag/AgCl RE was immersed in the electrolyte, along with a gold coated silicon wafer as CE. A flat alligator clip was attached the yarn to the WE. The container for the electrochemical cell was made specifically for this experiment and consisted of a 50 mL plastic tube (Sarstedt AG & Co KG), cut in half at 44.8 mm from the cap. The upper part, containing the cap was kept while the bottom part was ignored. In the cap, a hole was drilled in order to thread a yarn through it. The yarn was then glued in place using the two-component epoxy glue Power Epoxy from Loctite. The glue was then let to harden overnight (approx. 12 h). After hardening, a piece of tape was placed on the longer end of the yarn.



6 Results

6.1 Optimization of the PEDOT coating

6.1.1 PEDOT:PSS composition - DMSO content

We investigated the effect of adding DMSO at various concentrations to the PEDOT:PSS solution to increase the conductivity. The viscose yarns were coated with PEDOT:PSS and DMSO ranging from 0 to 80% (v/v), as previously explained, and the conductivity was measured. Figure 1 shows the conductivity of PEDOT:PSS coated yarns as a function of DMSO concentration. It is observed that when no DMSO was used the conductivity of the yarn was low (~ 0.5 S/cm). After adding DMSO the conductivity increased by 3 orders of magnitude, with a maximum conductivity when 40% (v/v) DMSO was added to the PEDOT:PSS before soaking the yarn.

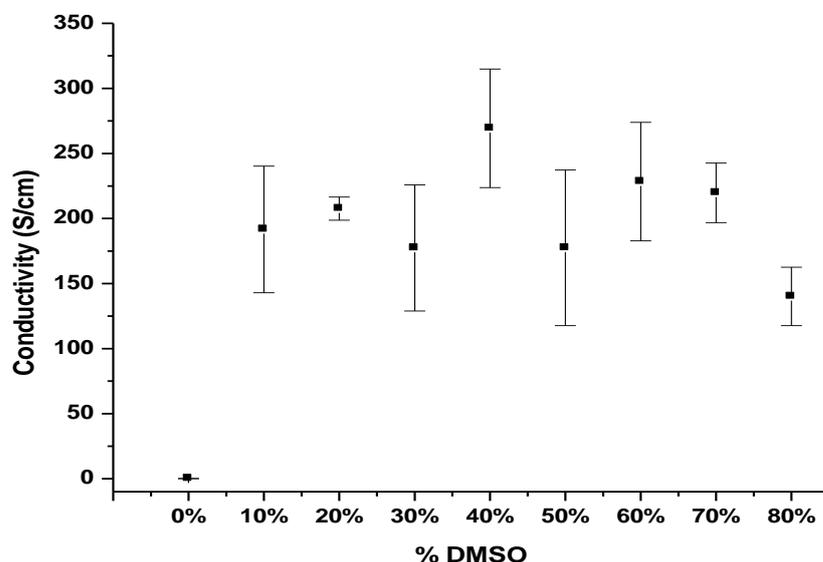


Figure 1. Conductivity vs Concentration of DMSO (v/v) used during PEDOT:PSS soaking to get PEDOT:PSS coated yarns.

6.1.2 Multilayer coatings

In order to further increase the conductivity of the PEDOT:PSS coated yarns, multiple successive PEDOT:PSS coatings were applied. Figure 2 shows the variation the conductivity versus the number of PEDOT:PSS coating layers at different DMSO concentrations. The conductivity when no DMSO was used resulted in the lowest conductivity and showed a linear increase with the number of PEDOT:PSS coating layers. Higher values of conductivity were observed when 40% and 80% (v/v) DMSO were used during PEDOT:PSS soaking, in accordance with results shown in figure 2. In these cases, the conductivity increased up to 4 coatings, after which the conductivity remained constant or even decreased.



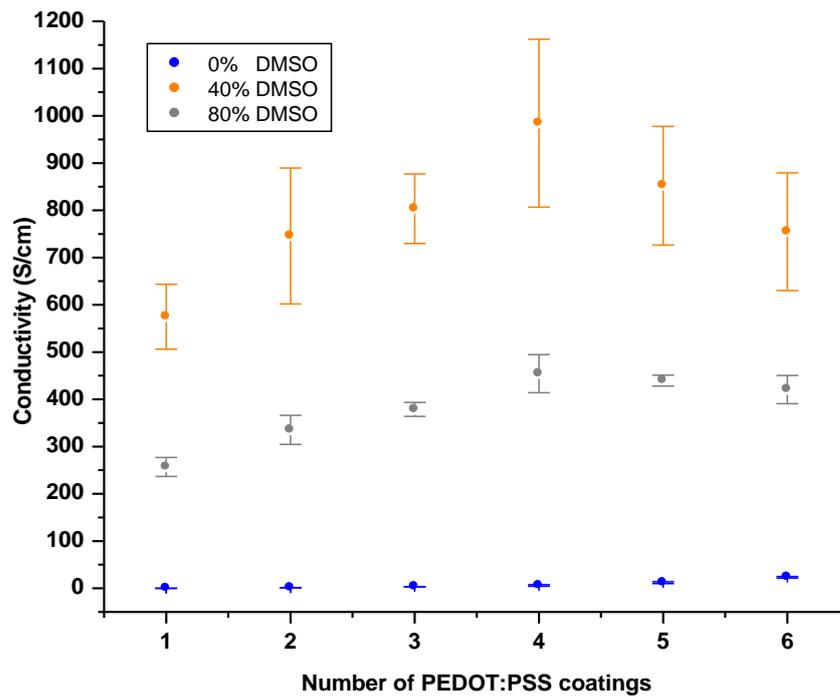


Figure 2. Relationship between the conductivity of PEDOT:PSS coated yarns and the number of PEDOT:PSS coatings. Samples measured between 1 to 6 successive coatings using 0%, 40% and 80% (v/v) DMSO during PEDOT:PSS soaking.

6.1.3 Effect of the DMSO concentration on in the actuation of the yarn

Once the conductivity of the yarns was ensured to be sufficient and optimised, PPy electropolymerization was performed on the PEDOT:PSS coated yarns to provide mechanical actuation.

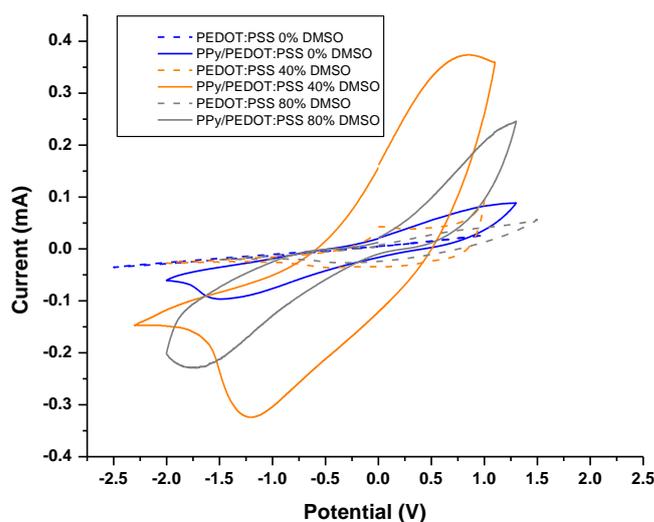


Figure 3. Cyclic voltammograms obtained from PEDOT:PSS and PPy/PEDOT:PSS coated yarns using different DMSO concentrations during PEDOT:PSS coating at scan rate 10 mV s^{-1} after four cycles in 0.1 M NaDBS aqueous electrolyte.

The electroactivity of PEDOT:PSS coated yarn and PPy/PEDOT:PSS coated yarn at different DMSO concentration was investigated using cyclic voltammetry (CV), figure 3. A higher current through the PPy/PEDOT:PSS coated yarns can be observed as compared to the PEDOT:PSS coated yarn. Also, better defined redox peaks can be observed when PPy was present. This points to the fact that the electropolymerized PPy has better electroactive properties than the PEDOT:PSS used on the first coating, so the cation ion drive redox-reaction takes place to a higher extent, doping and de-doping of the sodium cation causing also the elongation and contraction of the yarn. Further comparison also shows that the 40% DMSO present higher currents than using 80% DMSO, as would be expected from the conductivity data in Figure 2.

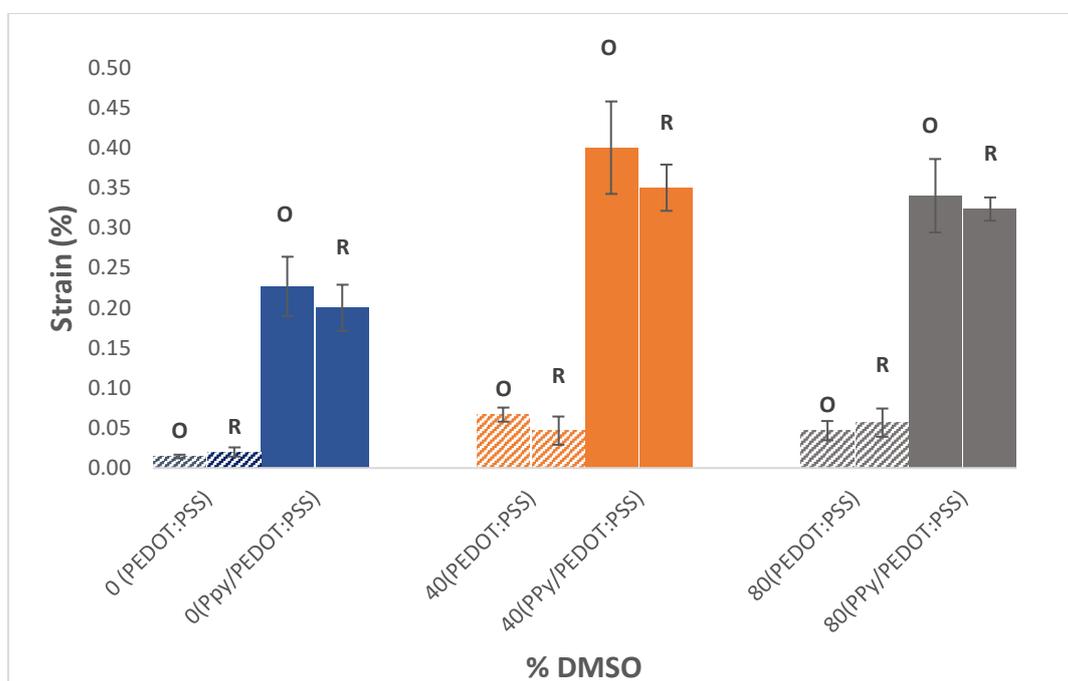


Figure 4. Strain measurements from PEDOT:PSS and PPy/PEDOT:PSS coated yarns obtained during cyclic voltammetry shown in figure 3. O: oxidized and R: reduced.

Next, the exerted linear strain was measured (figure 4). The PPy/PEDOT:PSS coated yarn has a larger actuation than PEDOT:PSS coated yarn pointing to the positive effect of the electrochemically polymerized PPy on the actuation. Furthermore, the actuation strain is higher when DMSO was present during PEDOT:PSS coating.

6.1.4 Effect of the number of PEDOT:PSS layer on the yarn actuation

Higher currents were obtained in the PPy/6PEDOT:PSS (PPy electropolymerized on a yarn with 6 consecutive layers of PEDOT:PSS coating) coated yarn than in PPy/PEDOT:PSS (PPy electropolymerized on a yarn a single PEDOT:PSS coating) coated yarn.

The PPy/6PEDOT:PSS coated yarn presented a better actuation performance than PPy/PEDOT:PSS coated yarn at 0%, 40% and 80% DMSO concentration (v/v), figure 5.



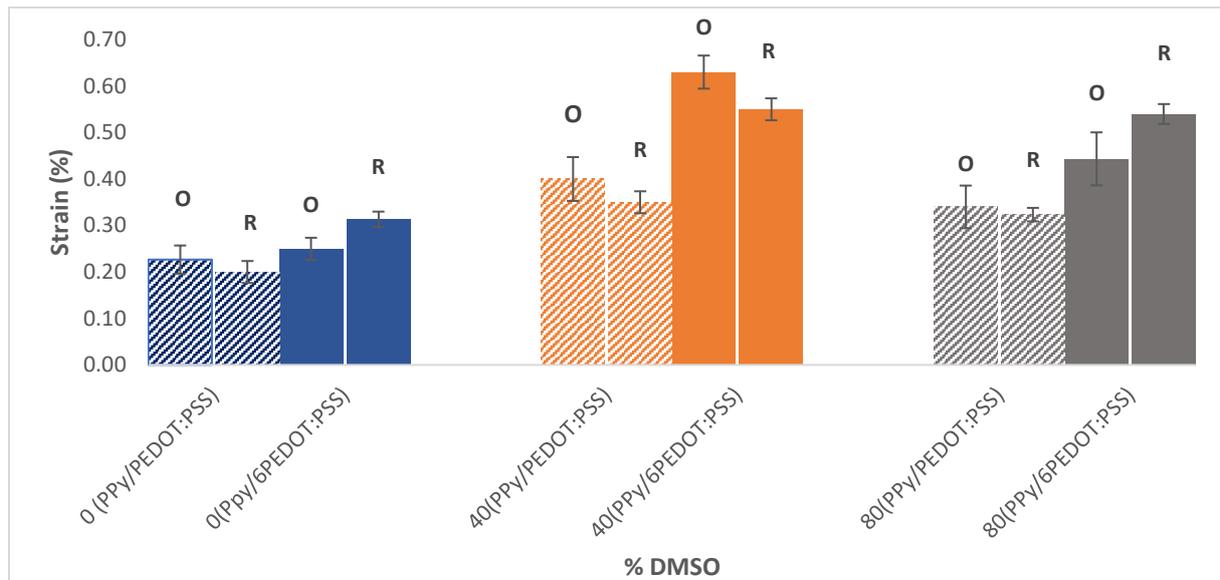


Figure 5. Strain measurements from PPy/PEDOT:PSS and PPy/6PEDOT:PSS coated yarns obtained during cyclic voltammetry.



6.2 Investigation the effect of PPy coating thickness

6.2.1 Yarns

Nylon based polyamide, PA, 1/78/46 were dip-coated into PEDOT:PSS with 40% content (vol) of DMSO for 4 consecutive times, ensuring good conductivity to perform a subsequent electropolymerization of PPy.

Different yarns were electropolymerized for different times (25000, 37500 and 50000 s) to get different thickness of the PPy coatings. The thickness for all yarns increased after electropolymerization. Also, the change of thickness increased with increased electropolymerization time.

All yarns were used in a CV experiment. As PEDOT:PSS also will actuate when exposed to electrical potential, a yarn only coated with PEDOT:PSS (without PPy electropolymerized on top) was utilized as reference in order to confirm the actuation induced by the coating of PPy on PEDOT:PSS coated yarns. Increasing currents were obtained for increasing thicknesses of PPy.

By applying potential steps (chronoamperometry), every yarn moved. The relationship between the obtained strain and the PPy electropolymerization time (thickness) can be seen in figure 6. The obtained strain increases with the thickness of PPy.

Strain vs. electropolymerization time

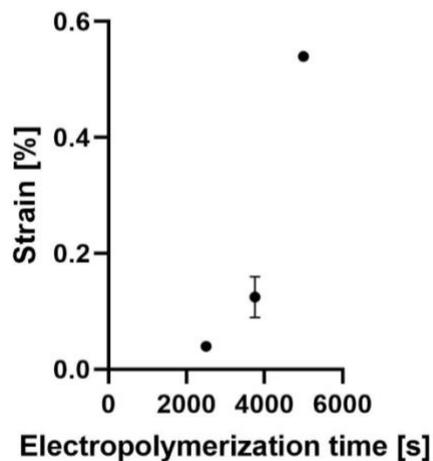


Figure 6. Depicted is the relationship between electropolymerization time and the strain of the yarns, which increases with increasing electropolymerization time.

The speed of the movement also increases with the thickness of PPy, figure 7.

Speed of movement vs. electropolymerization time

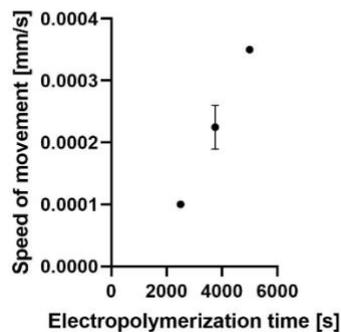


Figure 7. An increasing electropolymerization time showed an increase of speed of movement.

6.2.2 Fabrics

Pieces of 1 × 9 cm fabrics were dip coated together in the same container. The number of dip coats for fabrics were three as the fabrics showed a very little difference in resistance between dip coat 2 and 3, hence three layers of PEDOT:PSS-DMSO was considered sufficient. Also, the change of colour to black indicated PEDOT:PSS-DMSO films on the fabrics, and ocular inspection under light microscope displayed that the dip coating had given uniform coatings of PEDOT:PSS-DMSO.

Compared to the resistances seen in the dip coated yarns, a much lower resistance is exhibited in fabrics.

After electropolymerization of PPy, their voltammograms become broader (rising currents) for rising coating thicknesses.

The strain increases with increasing electropolymerization time (figure 8).

Strain vs. electropolymerization time

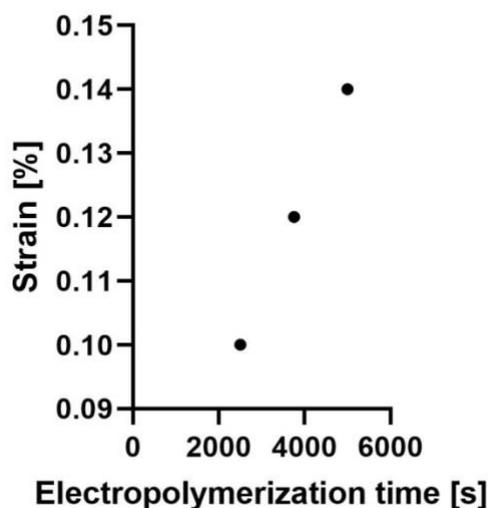


Figure 8. Depicted is the relationship between electropolymerization time and the strain of the fabrics, which increases with increasing electropolymerization time.

Increased PPy thickness gives also faster responses.

7 Discussion

7.1 Optimization of the PEDOT coating

7.1.1 DMSO content

The results are in accordance with some previous studies that have shown an increase of the conductivity of PEDOT:PSS by the addition of DMSO ^[1,2]. This phenomenon is probably due to the elimination of the excess of PSS- from PEDOT: PSS ^[3]. However an excess of DMSO may cause a decreasing of the conductivity due to hydrophobicity of PEDOT:PSS ^[2].



7.1.2 Multilayer coatings

The conductivity increased up to 4 coatings, after which the conductivity remained constant or even decreased. This phenomena is probably related to the hydrophobicity or saturation of PEDOT: PSS ^[4].

7.1.3 Effect of the DMSO concentration on in the actuation of the yarn

A higher electrical conductivity of the PEDOT:PSS coated yarns should promote a more uniform PPy electropolymerisation as well as better oxidation and reduction of the polymerised PPy layer when using a high conducting 'current collector'.

7.1.4 Effect of the number of PEDOT:PSS layer on the yarn actuation

Higher electrical conductivity plays a key role on the electrical current passing through the yarn and its actuation. Mechanism of insertion ions and hydration ions in materials more uniform (thickness) can be play also an important role in the electroactivity ^[5].

7.2 Investigation the effect of PPy coating thickness

7.2.1 Yarns

The change of the yarn thickness increased with increased electropolymerization time, which is expected as a longer time should yield more material ^[6]. With increasing thickness of PPy, literature states that the current should increase as well ^[6].

The strain increases with increasing electropolymerization time. This is expected as more PPy will make the actuation evident and hence Δl can get longer.

Just as for strain, the speed of movement increased with respect to increasing electropolymerization time. A thicker layer having more material available to take part in the redox reactions that are active, hence the contractions and expansions will go faster. Literature have also shown an increase of diffusion rate of ions inside PPy as its thickness increases ^[6].

7.2.2 Fabrics

The strain increases with increasing electropolymerization time. Just as for yarns, this is expected as more PPy will make the actuation of the material more pronounced and hence Δl can get longer. However, the increase of strain with increasing thickness is not as big as for yarns. This could be explained with the presumed thin PPy coating. Thicker films worth to be studied.



8 Conclusion

Electroactive yarns and electroactive fabrics have been fabricated by coating PEDOT:PSS and PPy on commercially available yarns. Optimization regarding the CP layers into textile actuators has been done. The CP yarn and fabric-actuators were prepared using a two-step soak deposition of commercially available PEDOT:PSS solution including the additive DMSO to increase its conductivity and the subsequent electrochemical deposition of PPy. The PEDOT:PSS layer forms an electrically conductive surface, allowing a well-controllable electrochemical deposition of PPy to form an electroactive (actuating) layer. The conductivity and actuation performance of CP yarn-actuators were increased by varying the concentration of DMSO and increasing the number of PEDOT:PSS layers. The obtained yarn-actuators showed electrochemically induced movement having mechanical performance, strain, comparable or better than previous reports of PPy coated yarns. The results showed a five-fold better performance than previously developed textile actuators.

The thickness of the PPy coating has also been studied. The strain and speed of movement increases with increasing thickness of PPy on textile muscles. This hence indicates that thicker layers of PPy is to be preferred with regard to strain and speed of movement when considering both yarns and fabrics.

9 References

- [1] J. D. Ryan, D. A. Mengistie, R. Gabrielsson, A. Lund, C. Müller, *ACS Appl. Mater. Interfaces* **2017**, *9*, 9045.
- [2] J. Y. Oh, M. Shin, J. B. Lee, J.-H. Ahn, H. K. Baik, U. Jeong, *ACS Appl. Mater. Interfaces* **2014**, *6*, 6954.
- [3] N. Kim, B. H. Lee, D. Choi, G. Kim, H. Kim, J.-R. Kim, J. Lee, Y. H. Kahng, K. Lee, *Phys. Rev. Lett.* **2012**, *109*, 106405.
- [4] M. Kuş, S. Okur, *Sensors and Actuators B: Chemical* **2009**, *143*, 177.
- [5] D. Melling, S. Wilson, E. W. H. Jager, *Smart Mater. Struct.* **2013**, *22*, 104021.
- [6] T. F. Otero, J. G. Martinez, *J. Solid State Electrochem.* **2011**, *15*, 1169.

