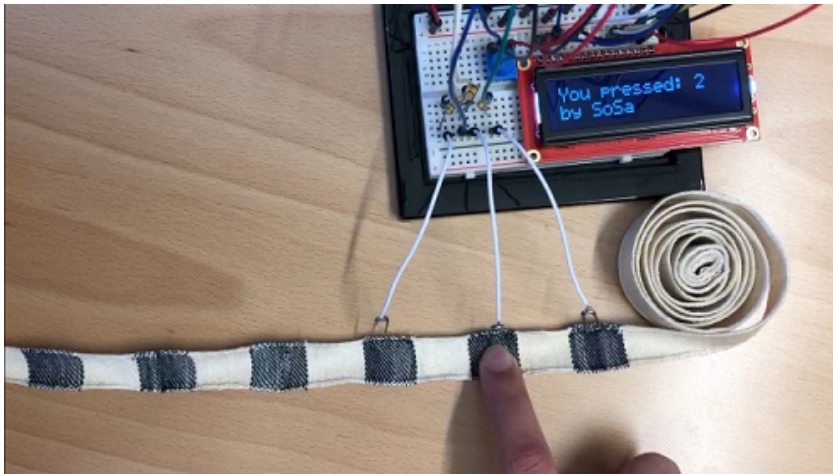




CHALMERS
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Continuously Produced Electrically Conducting Silk Fibers and Their Integration into Functional Fabrics

Master Thesis at Chemistry and Chemical Engineering

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Gothenburg, Sweden 2018

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Abstract

Conducting yarns are of interest for different applications because of their capability to be incorporated into textiles making electronic devices that later can, for example, be used to convert waste heat into electricity. The research available at the present declared that these conducting PEDOT: PSS yarns were produced batch-wise. Therefore, it was of significance to develop a method for continuous dyeing for the production of conducting silk yarns.

In this project a continuously PEDOT: PSS dyed yarn was produced with high conductivity which maintained its properties upon mechanical testing and industrial processing. To produce these dyed threads different parameters were investigated to provide an optimal conductivity. By directing the thread through a dye bath, superior results in conductivity were achieved. Pre-washing a degummed silk yarn in water in combination with small amounts of detergent and ammonia proved to increase the interaction between the coating and the fibers. Further enhancement in conductivity was achieved by the addition of ethylene glycol, as a secondary dopant, to the PEDOT: PSS dye bath. The addition of post-treatment with dimethyl sulfoxide (DMSO) enhanced the conductivity of the dyed yarn by two orders of magnitude compared to a non-secondary doped/post-treated dyed yarn. Additionally, increasing the viscosity of the dye bath in combination with multiple layers of coating improved the conductivity to a value of 74 S/cm and a Seebeck coefficient of 15 $\mu\text{V}/\text{K}$. More than 100 m dyed yarn was produced and the thread was manually woven into a keyboard with alternating conductive sections and non-conductive parts. The dyed thread was connected to a light source and a battery which showed that the thread could conduct current. Additionally, the yarn was both industrially embroidered and woven which illustrated that the thread could survive industrial processing. Washing decreased the resistance of the embroidered textile meaning that the thread could be used in wearable textiles. For future studies, the hope is to integrate the conducting yarn in thermoelectric devices.

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1 Introduction

This section expresses the essential background of electrically conducting silk yarns as well as the motivation behind this work.

1.1 Background

The use of electronics can be seen in many different application fields today and these are expected to increase in the future. The multitude of electronic devices with different functions seems to be integrated into many aspects of everyday life. Therefore, it is a natural progression for textiles to include electronics. The development of these textiles can already be seen in different research. To realize these textiles, electrically conducting fibers must be produced since the fibers are an integral part of e-textiles. It is shown in a recent study that the dyeing of silk yarn with an organic conducting polymer mixture, PEDOT: PSS, at lab-scale provides machine-washable conducting yarns. The research available expresses that these conducting yarns are produced batch wise and it is therefore of importance for the development of this field to generate these yarns at a larger scale[1]. Moreover, electronic textiles can be used in a variety of application fields such as for wearable piezoelectric sensors, biomedical devices, and thermoelectric power generators [2] [3] [4]. Such power generators could generate an electric potential from the temperature gradient between the body and its surrounds [4].

Metals are used in electronic devices that often consist of a rigid design. Metals are stiff materials which makes them unsuitable for wearable e-textiles where stretching and bending occurs [2][5]. Silver is difficult to mine and the consequences of this usage are unknown making the health effects and environmental impact uncertain [6] [7] [8]. In comparison, Ryan et al. show that the conductivity of organic semiconductors is stable during multiple washing cycles making the risk of leakage from chemicals to the environment significantly lower [1].

The conductivity and diameters of conductive commercial threads are presented in table 1. The commercial threads are mostly metal-based and therefore highly conducting. There are also organic conducting threads available on the market with high electrical conductivity, e.g. carbon fibers, but these threads are stiff, brittle and are therefore a suitable material for technical textiles [9]. Two examples of organic commercial threads are carbon fiber and Shakespeare PA + carbon. The Shakespeare PA + carbon thread is structurally more similar to the PEDOT:PSS dyed yarn since it is composed of a PA yarn with an outer layer of carbon. The electrical conductivity for the Shakespeare PA + carbon thread is 0.61 ± 0.01 S/cm and this value is lower than the conductivity for the dyed PEDOT: PSS silk yarn by Ryan et al. which is 15 ± 6 S/cm. It is therefore of interest to develop the PEDOT: PSS dyed silk thread further.

Table 1: The conductivity and diameter of reference samples.

Reference Sample	Conducting Component	Conductivity [S/cm]	Diameter [cm]
Carbon Fiber*	Carbon	$(4.5 \pm 0.4) \cdot 10^2$	0.021 ± 0.001
Stainless Yarn	Stainless Steel	$(17 \pm 0.4) \cdot 10^2$	0.019 ± 0.002
Bekinox PA + Stainless Steel	Stainless Steel	42 ± 7.2	0.029 ± 0.003
Shieldex Yarn PA + Silver	Silver	$(20 \pm 0.9) \cdot 10^2$	0.020 ± 0.003
High Flex Silver	Silver	$(3.4 \pm 0.5) \cdot 10^3$	0.023 ± 0.001
High Flex Copper	Copper	$(2.3 \pm 0.1) \cdot 10^3$	0.024 ± 0.003
Shakespeare PA + Carbon*	Carbon	$(6.1 \pm 0.1) \cdot 10^{-1}$	0.023 ± 0.001
Shieldex 125 μ m Monofilament	Silver	$(24 \pm 1.5) \cdot 10^1$	$(0.135 \pm 0.001) \cdot 10^{-1}$
Bekinox VN 12.1.2.100Z.HT.T10	Stainless Steel	$31 \cdot 10^2$	0.019 ± 0.001

* = Organic

Conducting organic fibers can be manufactured by several different principles e.g. wet-spinning [10]. However, in this project dyeing was used to produce conducting silk threads. The purpose of using coated silk yarns, instead of wet-spun PEDOT: PSS fibers, is to maintain the flexible and durable properties of the pristine yarn [11].

1.2 Aim

The aim of the work is to develop a method for continuous dyeing of conducting silk yarns using a custom-built coating device. The produced yarns will then be characterized and incorporated into a textile that displays electrical functionality.

1.3 Specified aim

The parameters for which the coating device provides the highest conducting yarns are going to be investigated for the further development of the continuous dyeing process. Additionally, pre-treatment of the yarn will be examined to ensure wetting of the dye. It is also of importance to create a suitable composition of the PEDOT:PSS with enhancing additions if deemed necessary to the dyeing bath for the continuous process. Moreover, the effect of post-treatment will be explored and the yarns will be characterized. The investigation will mainly be performed with SEM, light microscopy and tensile testing. Furthermore, electrical characterization will be used to measure the conductivity and Seebeck coefficient. The dyed yarn will be woven into a keyboard, embroidered into a textile and connected to a light source to display electrical functionality. Finally, the embroidered fabric will be washed for several cycles in a washing machine to investigate the change in conductivity with the washing cycles.

2 Theory

In the following section, the meaningful concepts for understanding conducting silk yarns are presented.

2.1 Organic semiconductors

Organic semiconductors consist of an alternating double and single bond structure along the backbone. For conjugated polymers, produced from a chemical coupling of monomers, orbital interaction is observed where the splitting of energy levels for the π and π^* occurs. The valence band is limited by the highest occupied molecular level (HOMO) and it arises from the π -orbitals. However, the conduction band is limited by the lowest unoccupied molecular level (LUMO) and it appears from the π^* . The divide in energy between HOMO and LUMO is called the bandgap. Since the linear chain structure of the polymer is obtained from the σ -bonds the π -orbitals can experience electronic and optical interactions where electrons are delocalized along the backbone or moved to another molecule. Charge transport in organic disordered semiconductors occurs via hopping transport of charge carriers between different discrete energy levels [12] [13].

Doping, when talking about conductive polymers, refers to redox or acid-base reaction. In these cases, new electronic states are created and a previously semiconducting material becomes conductive. N-type dopants are electron donating, making it reducing agents, while p-type dopants are electron accepting, oxidants. Both n-type and p-type dopants are used to change the conductivity of the conjugated polymers [14].

2.2 PEDOT:PSS

PEDOT, when doped, is one of the most highly conductive polymers. PEDOT is a commonly used conductive polymer due to its availability as a polymer dispersion. Since PEDOT is a cationic polythiophene derivative and PSS a polyanion these two form a stable dispersion. This stable polyelectrolyte dispersion complex is easy to make or manufacture at an industrial scale and is used in different deposition methods [14]. See figure 1 for an illustration of the PEDOT and PSS molecular structures.

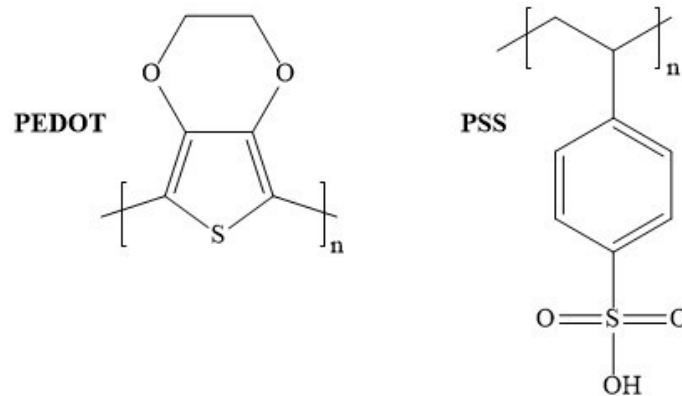


Figure 1: Molecular structure of PEDOT and PSS.

2.3 Silk yarn

The leading producer of silk comes from the silkworms named *Bombyx mori* and this silk is crucial for the textile industry. *Bombyx mori*, also called Mulberry silk, is a natural protein fiber that has been used for centuries due to the materials warmth, softness, and comfortability. Silk is composed of 62,5-67% fibroin fibers, which are covered by sericin that constitutes 22-25% of the silk. The remaining parts are water and salt minerals [15] [16].

Bombyx mori silk fibroin is built up by heavy and light chain subunits. The heavy chain of approximately 350 kDa is substantially hydrophobic and consists of a repeating amino acid sequence. The light chain of about 25 kDa consists of a more undefined, non-repeating amino acid sequence and is more hydrophilic in its nature. The heavy and light chains are linked together by a disulfide bond. The heavy chain has a greater impact on the properties of silk since the silk is mainly composed of the heavier chain [17]. The amino acid sequence of the heavy chain contains crystalline Gly-X repeating units that cover 94 % of the sequence: with X representing 65% alanine, 23% serine, and 9% tyrosine. The crystalline units consist of subunits and within these, the Gly-X alternance is strict which according to Zhou et al. is an inconsistency with the Pauling-Corey model. In this model β -sheets are stacked with alternating layers of glycol-glycol and X-X interactions. Zhou et al. suggests that the subunits provide β -strands with the crystalline units forming two-layered β -sandwiches which result in parallel β -sheets [18]. These sheets provide the material with high tensile strength, high elasticity and thermal stability.

Fibroin is mainly hydrophobic and sericin is hydrophilic, separation is therefore easily performed with water. The separation of harsh and stiff sericin from silk is desired to attain soft degummed silk. Degumming is performed with enzymatic or hydrolytic catalysis which breaks the peptide bonds of sericin. Soap is used for a common degumming method and when combined with alkaline the degumming-rate is enhanced. As the rate increases, the procedure cost decreases due to lower use of soap and time. Under these circumstances, with soap and alkali at pH 9.0-11.5, the degumming occurs due to the higher water solubility and alkali sensitivity of sericin in comparison to fibroin.[15] [19].

Silk is traditionally used in textile manufacturing and can therefore easily be incorporated into textiles without making significant changes to existing techniques, making it cost-efficient. A silk dyeing process can be performed in many ways e.g. continuously and batch-wise. A padding mangle is a continuous dyeing machine where the textile goes through a pad dyebath and is then directed between squeeze rolls to produce homogeneously dyed textiles. One example of a batch dyeing machine is a jigger. In a jigger, the textile is directed backward and forwards through the dye with the help of rotating rolls. The purpose of using coated silk yarns, instead of fabricated PEDOT: PSS fibers, is to maintain the flexible and durable properties of the pristine yarn[11] [20].

When using acid dyes ionic bonds are created between the silk fibers and the dye. At the isoelectric point (pH 3.6-5.2) silk fibers feature neutral NH_2 groups, however under the isoelectric point with the use of acid dyes the NH_2 group of the silk fibers protonate to become cations, NH_3^+ . The acid dye molecules in solution exhibit a negative charge and can, therefore, attract the positively charged sites on the silk. Hydrogen and van der Waals bonds are also present between the silk and dye, however, the ionic bonds have a significantly larger impact. When using a PEDOT:PSS dispersion as an acidic dye with the pH of 2 the anionic PSS is suggested to interact with the cationic sites of silk by electrostatic interactions [1] [21]. [22].

2.4 Secondary doping/post-treatment

A primary dopant is defined as a material that increases the conductivity of conductive polymers by changing their properties. On the other hand, a secondary dopant is explained as an inert material that in combination with the primary dopant changes the properties, even more, resulting in higher conductivity. In contrast to the primary dopant, the removal of the secondary dopant may not change the increased conductivity of the polymer [23].

Yan et al. proposes that the conductivity of PEDOT:PSS increases with the addition of a secondary dopant with a high boiling point, for example, dimethyl sulfoxide (DMSO) or ethylene glycol (EG), due to the solvent's plasticizing ability. Because of this plasticizing ability, the PEDOT:PSS polyelectrolyte complex can at high-temperature re-orientate to improve the contact between the PEDOT molecules. These connections might result in a decrease of the percolation threshold. Another theory, for the higher conductivity, is that the secondary dopant has a high dielectric constant that screens the counterions from the charge carriers. This leads to a decreased Coulomb interaction between the negatively charged PSS and the positively charged PEDOT.[24].

Zhou et al. describe that by combining secondary doping and de-doping with ethylene glycol when making wet-spun PEDOT: PSS microfibers, a record high conductivity of ~ 2800 S/cm is achieved. It is suggested that the consequence of secondary doping with ethylene glycol is the planarization of the PEDOT chains due to dipole-dipole interaction between ethylene glycol and thiophene rings. Because of these interactions, the PEDOT chains are expanded to a more linear structure than previously. When de-doping, the amorphous PSS is removed to a certain extent [10].

According to Kyaw et al. using formamide for post-treatment enhances the conductivity for a PEDOT: PSS film. The polar solvent has a high boiling point and an ability to dissolve PSS. Kyaw et al. suggest that with the addition of formamide some insulating PSS is separated and removed from PEDOT. The mobility is increased due to changes in the position of the conducting PEDOT segments [25].

Alemu et al. propose that methanol can be used as post-treatment for PEDOT: PSS to increase the conductivity by 4 orders of magnitude. The conductivity improvement is, in this work and similarly to the reporting from Kyaw et al., related to the removal and reorientation of PSS [26].

An additional post-treatment of PEDOT: PSS, where the conductivity is increased, is reported by Chou et al. however in case this is realized by using DMSO. The enhancement is as previously mentioned for the other examples also credited to the changes with PSS [27].

When working with different solvents, such as EG, DMSO or formamide it is important to know the health risks. LD50 is defined as is the dose of a substance that is lethal to 50 % of the tested population for a certain time. Oral LD50 (rats) is 4700 mg/kg for ethylene glycol, 14500 mg/kg for dimethyl sulfoxide and 5577 mg/kg for formamide. All substances are harmful, irritant and skin sensitive but EG and formamide are more dangerous to be exposed to since they are carcinogenic. Protective goggles and lab gloves are important in the use of all chemicals [28] [29] [30] [31]

2.5 Seebeck

The Seebeck effect is the resulting voltage that is created due to a temperature difference in between two junctions of materials with different electrical conductivity in the same circuit. The effect is calculated by the Seebeck coefficient:

$$\alpha = \frac{-\Delta V}{\Delta T} \quad (2.1)$$

where ΔV is the Seebeck voltage and ΔT is the temperature difference between the junctions [32].

A common Seebeck coefficient of $14 \pm 1 \mu\text{VK}^{-1}$ is reported by Ryan et al. after secondary doping a PEDOT: PSS dyed thread with EG [1]. A value of $17.4 \mu\text{VK}^{-1}$ for the Seebeck coefficient is obtained by Kyaw et al. after post-treatment of PEDOT:PSS with formamide [25].

2.6 Conductivity

The relationship between the electrical resistance, current, and voltage in an electric circuit is defined by Ohm's law:

$$I = \frac{V}{R} \quad (2.2)$$

where I = current (A), V = potential difference (V) and R = resistance (Ω).

The electrical conductivity, σ is defined as the capability of a material to conduct electrical current and it is related to the electrical resistivity, ρ . The electrical resistivity is the strength for which a material resists current:

$$\sigma = \frac{1}{\rho} \quad (2.3)$$

where σ = electrical conductivity (S/cm) and ρ = electrical resistivity ($\Omega \cdot \text{cm}$).

The electrical resistivity is explained by the following relationship:

$$\rho = \frac{R \cdot A}{L} \quad (2.4)$$

where L = length (cm) and A = area (cm^2).

By combining equation 2.3 with 2.4 the following equation for the conductivity of a thread is obtained:

$$\sigma = \frac{L}{R \cdot A} \quad (2.5)$$

where A is the cross-section area of the thread ($\pi \cdot d^2/4$) [1] [33].

2.7 Mechanical properties of a dyed thread

When forming active layers on textile- and fiber-based devices, intrinsically conductive polymers are an excellent choice of material because of their favorable processing and mechanical ability. Producing, handling and using textiles subjects the material to a considerable amount of strain, stress, and abrasion. For the coated threads to be able to withstand these tough environments the active coating layer should be homogeneous, pliable and compatible with the thread [11].

Ryan et al. performed mechanical testing on PEDOT: PSS dyed silk thread and found the stress-strain curve to be nearly linear. This suggests a stiff thread which does not experience plastic deformation [1].

2.8 Capacitive touch sensing

Capacitance can be explained as the capability of conductors to store electric charge. This property is defined by the conductor's ability to store charge together with the difference in potential that is created when separating two conductors [34].

Two conductors with an intermediary insulating phase are the components which make up a capacitor. When applying this concept to capacitive touch sensing, one of the conductors could be a sensor electrode while the second conductor is the air around the sensor and a conductive entity i.e. a finger. By connecting the sensor to a circuit, one could calculate the capacitance that is obtained when a finger is touching the sensor. Since the capacitance will rise as the two conductors approach each other the change can be detected [35].

3 Method

For the production and the development of electrically conducting silk yarns, literature studies and laboratory work were performed. Mainly for the literature studies, the following databases were used: SpringerLink, Taylor & Francis journals, ScienceDirect, RSC publishing and ACS publications. For the laboratory work, different technical types of equipment were used which will be presented in the section below.

In order to produce continuously dyed threads, different setups were investigated to generate information regarding the optimal settings. The importance of pretreatment of the yarn was also evaluated. The necessity of adding conductivity enhancing material to the dye and the best post-treatment was determined. The coated yarns produced from all the trials were characterized and the results were used to further optimize and develop the process. The threads were integrated into textiles to display electrical functionality. The textile, with the integrated thread, was then washed for several cycles in a washing machine to investigate the change in conductivity with the washing cycles. The strategy for the execution will be described further in the coming passages.

3.1 Materials

Degummed silk (pristine silk 1) was purchased from Aurora Silk while white degummed silk (pristine silk 2) was obtained from Gütermann. PH1000 dispersion (1.1-1.3 wt% solid) was received from Heraeus while ethylene glycol, dimethyl sulfoxide, methanol (99 %) and formamide were purchased from Sigma-Aldrich. Zonyl FS300 was bought from DuPont while silver paint came from Agar Scientific, ammonia (25 %) from Merck Millipore and finally detergent from Zenit AB.

3.2 Characterization

This section clarifies the technical types of equipment that were used for evaluating the conducting silk yarns.

3.2.1 Electrical measurement

Keithley 2400 source meter was utilized in order to measure the electrical resistance of the dyed silk yarns. Two sample pieces of the same thread were placed on one glass slide, silver paint was used to divide the silk yarn into a multitude of measurement sections, every 8 millimeters. Probes were placed at the silver dots to measure the resistance of each segment.

The Keithley 2400 equipment was used to track how the resistance changed upon bending and stretching of the dyed silk yarn. In order to periodically bend and stretch the yarn with a bending diameter of 5 mm, a LEGO construction was created. The resistance was measured after 100 bending cycles and repeated ten times. Silver paint was put on the dyed yarn with copper tape covering it and the probes were clamped onto the copper tape. The Keithley was also used to investigate how the resistance of an embroidered dyed thread changed upon washing. Probes were placed at the embroidered yarn to measure the resistance.

SB1000 equipment together with K2000 temperature controller were used to measure the Seebeck coefficient of a small piece of the conducting silk yarn at 305 K by comparing it with a known reference.

3.2.2 Mechanical measurement

Instron tensile tester 5565A was used in order to determine the difference in the mechanical properties between the raw silk and the dyed silk thread. The tested sample had a length of 5 cm and the testing speed was 10 mm/min.

3.2.3 Optical microscopy

Carl Zeiss A1 optical microscope was utilized to measure the diameter of raw silk and the dyed silk thread. The microscope can polarize light in various ways and can use a variety of techniques to analyze the images. In this instance, brightfield reflected light mode was used with a zoom of 100x.

3.2.4 SEM

To observe the raw and the dyed silk yarn a field emission gun Leo Ultra 55 SEM was employed, at a voltage of 3 kV and 10 kV, together with a secondary electron detector. To obtain suitable samples for cross-section analysis, the samples were placed in liquid nitrogen and cut into small pieces. The samples of two different yarns were investigated, which had been dyed twice, which were either sputtered with gold or un-sputtered. Additionally, two threads of silk 1 which were coated once with either low or high viscosity dye were investigated.

3.2.5 Viscosity measurement

The viscosity was measured at different shear rates with the instrument Discovery HR-3 hybrid rheometer for one PEDOT: PSS/DMSO solution and several PEDOT: PSS/EG solutions, these were evaporated at 50 °C at a time range of 2.5 - 47 h. Two reference samples of non-evaporated PEDOT: PSS and PEDOT: PSS/EG were also investigated.

3.3 Setup of continuous dyeing process

Different setups for the continuous dyeing process were explored to generate the highest conductivity for the dyed yarn.

Setup 1: For the first setup, the thread was licked-rolled on the top of a wheel that rotated with a certain speed that was influenced by the rotational frequency f_1 in a color bath that coated the thread. The yarn was then dried and collected around a coil with a frequency of f_2 , see figure 2. Yarns were dyed with different settings for f_1 and f_2 to determine the influence of the rotational frequency on the conductivity.

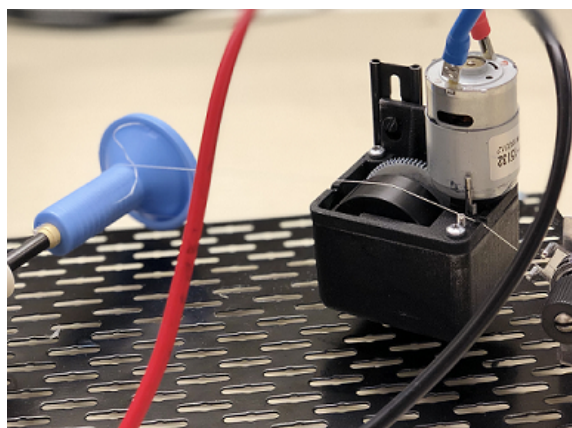


Figure 2: The figure illustrates setup 1 for the continuous dyeing process.

Setup 2: In comparison to the first setup the thread was directed three times on top of the dyeing wheel, then dried and collected on the rotating coil, see figure 3. The optimal rotational frequencies which were decided with setup 1 were used for this setup.

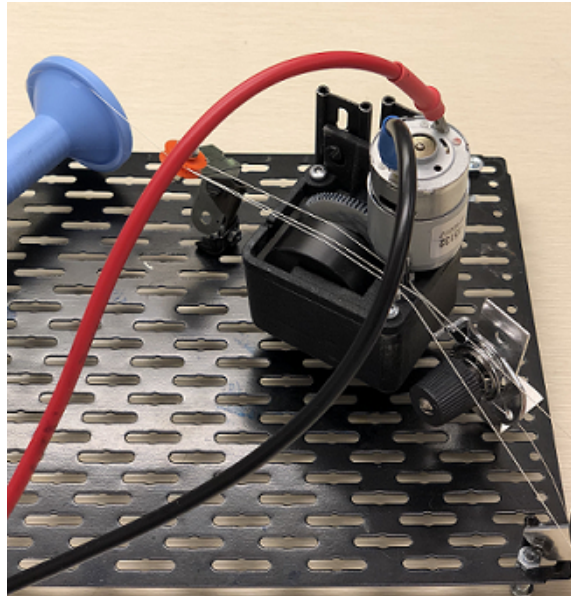


Figure 3: The figure displays setup 2 for the continuous dyeing process.

Setup 3: For setup 3 the device was converted from a lick roll to a continuous pad dyeing setup. The thread went under the wheel and through the dyebath to then, similarly as the previous setups, be dried and collected, see figure 4. New settings for the rotational frequencies of f_1 and f_2 were tested to attain the highest conductivity of the coated yarns.

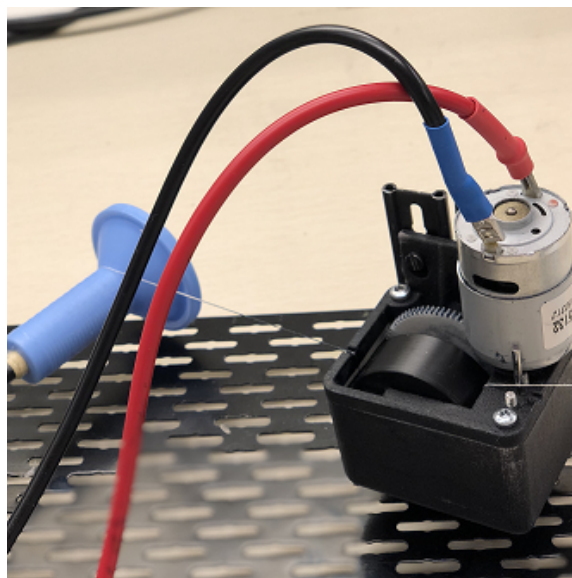


Figure 4: The figure displays the continuous dyeing process with setup 3.

3.4 Pre-treatment

Bombyx mori degummed silk yarn was used for the continuous dyeing process. To get optimal conductivity of the dyed thread a number of pre-washing methods were tested and compared to a dyed thread without pre-washing.

Pre-wash 1: The pre-treatment was carried out in a beaker with a bath mass ratio of 1:50 (yarn:water). $4 \text{ g/dm}^3_{\text{water}}$ was added equally of Zenit detergent and ammonia to the bath that had a temperature of $40 \text{ }^\circ\text{C}$ and was stirred for 17 min. This pre-wash method was done to explore the difference between the conductivity of an unwashed and a pre-washed thread.

Pre-wash 2: For pre-wash 2 the previously mentioned bath recipe was used but performed at room temperature. Dyed thread prepared with pre-wash 2 was compared to the trial with pre-wash 1, this was done to determine the significance of the temperature for the pre-treatment.

Pre-wash 3: The pre-washing was carried out continuously with the optimal settings of setup 1 by passing the thread through a wash bath.

Pre-wash 4: This washing method was the same as pre-wash 1 but with the absence of ammonia.

For further investigation, the dyeing of a wet thread was performed and this was done to determine the influence on the conductivity. One sample was prepared with pre-wash 2 while two others were prepared with pre-wash 4. One of those two samples treated with pre-wash 4 was dyed while it was wet and the other one was dried before coating.

3.5 Dyeing of silk yarn

Pre-wash 1 and setup 1 were used to obtain dyed thread. The dye bath was for this instance a PEDOT: PSS solution with 0.2 wt% surfactants. The conductivity of this dyed thread was compared to a dyed thread without the addition of surfactants. This was done to see how the addition of surfactants would influence the conductivity. The coated thread was always dried after dyeing.

The influence of adding a secondary dopant was investigated with dye setup 1 or 3. For dye setup 1, 5 vol% EG was added to the PEDOT: PSS dye bath and pre-wash 1 thread was dyed in this solution. However, for dye setup 3, pre-wash 3 yarn was coated with PEDOT: PSS solution that was mixed with 5 vol% DMSO.

For de-doping, pre-wash 2 yarn was dyed in PEDOT: PSS/EG dye bath with setup 3 and then the dried yarn was placed in EG de-doping solvent for 1h and 20 min. One piece of the coated yarn was not placed in the de-doping solvent for comparison. Some samples were immersed in MeOH, DMSO or formamide as post-treatment. The PEDOT: PSS dyed yarn was placed in a beaker of MeOH for 5 min or formamide for either 10 min or 1h 20 min. Additionally, the post-treatment with DMSO was performed under the same conditions as previously mentioned for EG de-doping.

The viscosity was increased by evaporating water from PEDOT: PSS/EG solutions. The solutions were placed on a heating plate with a magnetic stirrer at 50 °C and 180 rpm for a time range of 2.5 - 47 h. After 2.5 h pre-wash 1 yarn was dyed with setup 3 and a piece of the thread was placed in either EG or DMSO for 1 h 20 min, this was also done at 16 h 30 min of evaporation. At 16 h 30 min, a sample was also investigated by immersing it in MeOH for 1h 20 min as post-treatment.

To examine the impact of post-treatment time on the conductivity, pieces of coated yarns were placed in DMSO for either 1 h, 1h 20 min or 3 h. For the 1 h 20 min post-treated sample, the process of coating and post-treating was repeated twice to see how layering impacted the conductivity. After 43 h of evaporation, the yarn was dyed and DMSO post-treated once for one sample and twice for another sample. The only differentiating parameter for the 46 h evaporated solution was that DMSO was added as a secondary dopant. The solution which was evaporated for 46.5 h was utilized when dyeing the 100 m of yarn.

However, after 47 h, different silk threads were investigated which were dyed and post-treated twice. One of the silk thread was the degummed silk thread (pristine silk 1) which had been used throughout the project while the other one was a white degummed silk thread (pristine silk 2).

3.6 Continuous dyeing of 100 m silk yarn

For extensive continuous dyeing, 100 m of silk yarn 1 was collected around a cone and placed in a beaker and washed according to pre-wash 2. The thread was dyed with setup 3 where the viscosity of the dye had been increased in advance and the secondary dopant EG had been added to the dye bath. The coated thread was then dried as it was gathered around the coil. For a video of the continuous dyeing see [link](#). The yarn was transferred to a cone again and then post-treated with DMSO. After the post-treatment, the thread was dried and the collected yarn was used in a repeating cycle which resulted in a yarn that had been coated and post-treated twice. Two 100 m samples with different viscosities were prepared with this method.

In order to estimate the amount of PEDOT: PSS in the twice dyed silk thread the weight was measured before and after dyeing. 2.5 cm of the 100 m sample was compared to 2.5 cm of pre-washed silk yarn 1.

3.7 Electrical conductivity over time

The electrical resistance over time of the dyed silk yarns was measured for the continuously produced 100-meter thread. The electrical resistance over time was measured in a similar manner as described in the section for electrical measurements.

3.8 Integration of the dyed yarn

In order to determine if the thread could survive industrial processing, a piece of 100 m thread was sent to the Smart Textiles Lab at the University of Borås. PEDOT: PSS dyed yarn was industrially woven into polyethylene (PE) and the weaving was carried out in an industrial-type jacquard loom. The weave structure was a plain weave which is relatively tough on the fibers in the weft as they cross over/under every warp thread. To investigate how the electrical conductivity had changed after the weaving, silver paint was used to divide the thread into sections of 0.8 cm. Eight measuring points were investigated in total.

In addition to industrial weaving, weaving was performed by hand in a weaving loom with the 100 m yarn. For a video of the manual weaving see [link](#). The purpose of manually weaving was to create a keyboard with alternating electrically conductive sections and non-conducting parts. The thread that was used for the warp was mercerized cotton (16000 m/kg) while pristine silk yarn 1 and thread from the produced 100 m yarn was used for the weft. The reed had 9 dents per cm, where two threads went through each dent, however, there was one thread through each heddle. The textile pattern that was used was a weft-faced twill. Totally a 2 cm wide band with a length of 1.5 m was woven, six conductive keys were created where each section

had a length of 2 cm. Capacitive sensing was used to attain a signal by touch to the electrically conducting segments.

To illustrate that the thread can conduct current, two parallel pieces of dyed yarn from the 100 m thread were connected to a battery on one end and to a light source on the other. Additionally, the yarn was industrially embroidered with a Tajima TMBP-S1501C electronic automatic embroidery machine. The thread was embroidered into a cotton material with a speed of 600-700 stitches/min to see if the yarn could manage to conduct after the processing. Different symbols and texts, such as SoSa and CHALMERS, were embroidered into the material. For a video of the embroidery process see link. The SoSa embroidered fabric was then washed for several cycles in a washing machine with hand wash program (30 °C and 900 rpm). The conductivity was measured at each letter S periodically to investigate the changes with the washing cycles, see figure 5.

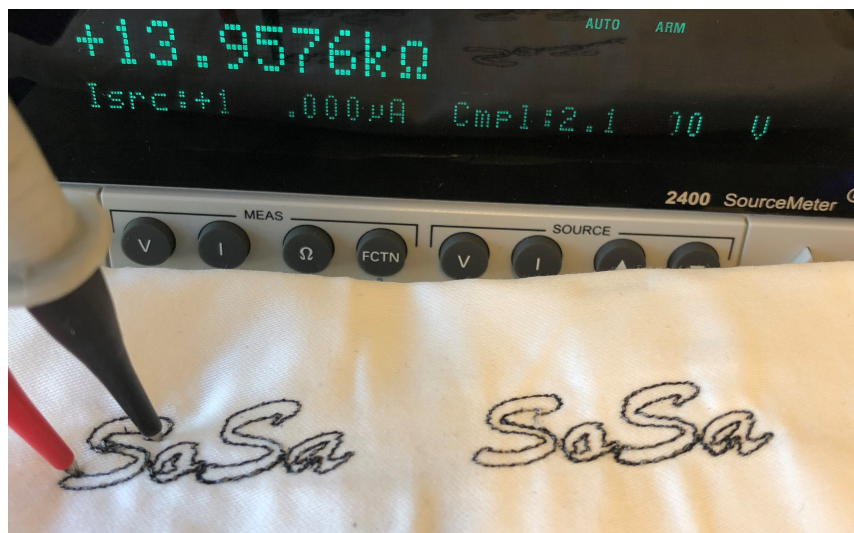


Figure 5: The figure displays the conductivity measurement for the embroidery.

4 Results

In this section, the characterization results from the continuously dyed threads are presented. Within this work, a sample was defined as a continuously dyed yarn. The results are divided into electrical measurements, mechanical measurement, optical microscopy, SEM and viscosity which clarify the difference in properties between dyed silk yarns and pristine silk yarns.

4.1 Electrical measurement

The electrical results are presented in the coming sections and in table 2. This table illustrates the parameters that were changed in order to attain the highest conductivity for the dyed yarns. The values of viscosity, which are presented in the table, are retrieved from table A1 from Appendix A.

Table 2: Electrical results for changes of different parameter.

Sample	Pre-wash	Setup			Dyeing			Post-treatment		Conductivity [S/cm]
		Type	f_1	f_2	Secondary	Viscosity	Surf-	Solvent	Time	
			[rpm]	[rpm]	dopant	[Pa·s]*	actant		[h]	
1	-	1	4.5	110	-	-	Yes	-	-	$(1.4 \pm 0.6) \cdot 10^{-3}$
2	-	1	43	28	-	-	Yes	-	-	$(1.5 \pm 0.7) \cdot 10^{-3}$
3	-	1	5.0	13	-	-	Yes	-	-	$(7.1 \pm 6.0) \cdot 10^{-4}$
4	1	1	43	28	-	-	Yes	-	-	$(4.5 \pm 2.0) \cdot 10^{-3}$
5	-	1	43	28	-	-	-	-	-	$(1.2 \pm 1.0) \cdot 10^{-4}$
6	1	1	43	28	-	-	-	-	-	$(6.5 \pm 2.0) \cdot 10^{-3}$
7	1	1	43	28	EG	-	-	-	-	$(7.5 \pm 3.0) \cdot 10^{-3}$
8	1	1	43	28	-	-	-	MeOH \square	0.08	$(1.6 \pm 0.4) \cdot 10^{-2}$
9	2	1	43	28	-	-	-	-	-	$(3.9 \pm 1.0) \cdot 10^{-3}$
10	3	1	43	28	-	-	-	-	-	$(2.1 \pm 1.0) \cdot 10^{-4}$
11	2 wet	1	43	28	-	-	-	-	-	$(8.9 \pm 4.0) \cdot 10^{-4}$
12	4 wet	1	43	28	-	-	-	-	-	$(4.7 \pm 3.0) \cdot 10^{-5}$
13	4	1	43	28	-	-	-	-	-	$(6.2 \pm 4.0) \cdot 10^{-4}$
14	2	2	43	28	-	-	-	-	-	$(2.5 \pm 2.0) \cdot 10^{-3}$
15	2	3	43	28	-	-	-	-	-	$(7.3 \pm 2.0) \cdot 10^{-3}$
16	2	3	43	3.5	-	-	-	-	-	$(1.2 \pm 0.3) \cdot 10^{-2}$
17	2	3	3.5	3.5	-	-	-	-	-	$(1.7 \pm 0.3) \cdot 10^{-2}$
18	2	3	3.5	3.5	EG	-	-	EG	1.33	3.8 ± 0.3
19	2	3	3.5	3.5	EG	-	-	-	-	$(3.0 \pm 1.0) \cdot 10^{-2}$
20	2	3	0	3.5	EG	0.205	-	EG	1.33	7.6 ± 1.0
21	2	3	0	3.5	EG	0.205	-	DMSO	1.33	7.5 ± 2.0
22	2	3	0	3.5	EG	0.920	-	EG	1.33	11 ± 3.0
23	2	3	0	3.5	EG	0.920	-	DMSO	1.33	19 ± 3.0
24	2	3	0	3.5	EG	0.920	-	MeOH	1.33	1.6 ± 0.4
25	2	3	0	3.5	EG	0.920	-	DMSO	1.00	9.9 ± 1.0
26	2	3	0	3.5	EG	0.920	-	DMSO	3.00	8.3 ± 2.0
27 (2 layers)	2	3	0	3.5	EG	0.920	-	DMSO	1.33	26 ± 5.0
28	2	3	0	3.5	EG	28.23	-	DMSO	1.33	8.9 ± 2.0
29 (2 layers)	2	3	0	3.5	EG	28.23	-	DMSO	1.33	49 ± 11
30 (2 layers)	2	3	0	3.5	EG	68.26	-	DMSO	1.33	74 ± 18
31 (2 layers)**	2	3	0	3.5	EG	68.26	-	DMSO	1.33	59 ± 8.0
32	2	3	0	3.5	EG	50.15	-	DMSO	1.33	-
33 (2 layers)	2	3	0	3.5	EG	50.15	-	DMSO	1.33	66 ± 12
34	2	3	0	4.0	EG	85.08	-	DMSO	1.33	33 ± 5.4
35 (2 layers)	2	3	0	4.0	EG	73.67	-	DMSO	1.33	49 ± 4.3
36 (2 layers)	2	3	0	3.5	EG	6.28	-	Formamide	0.17	52 ± 8.7
37 (2 layers)	2	3	0	3.5	EG	6.28	-	Formamide	1.33	43 ± 6.8
38	2	3	0	3.5	DMSO	52.67	-	DMSO	1.33	37 ± 3.6
39 (2 layers)	2	3	0	3.5	DMSO	52.67	-	DMSO	1.33	41 ± 6.6

Wet = The thread was kept wet after pre-washing and dyed whilst it was wet.

2 layers = The yarn was dyed and post-treated twice.

* = At the share rate 1 s^{-1} .

** = Silk 2.

4.1.1 Setup of continuous dyeing process

This study started by exploring the influence of rotational frequency, of the dyeing wheel and the rotating coil, on the conductivity for setup 1. By comparing samples 1, 2 and 3 it can be seen in table 2 that the best result was for sample 2 with $f_1=43$ and $f_2=28$. The dyeing of yarns with setup 2 proved to be challenging since the thread was drawn excessively until it broke. For setup 3 the lowest rotational frequency for the dyeing wheel and the rotating coil proved to give the highest conductivity, this was determined by comparing samples 15, 16 and 17. By relating sample 18 and 20 it was observed that switching of f_1 and keeping the rotational frequency of $f_2=3.5$ gave a further increase in conductivity.

Three setups for the continuous dyeing process were investigated in this project. The most favorable conductivity was for setup 3 where the thread was directed through the dye bath, see figure 6. This can be observed in table 2 by comparing the conductivity of sample 9, 14 and 15. Sample 9 with setup 1 had a conductivity of $(3.9 \pm 1.0) \cdot 10^{-3}$ S/cm, while sample 14 with setup 2 had $(2.5 \pm 2.0) \cdot 10^{-3}$ S/cm and finally sample 15 with setup 3 had a conductivity of $(7.3 \pm 2.0) \cdot 10^{-3}$ S/cm.

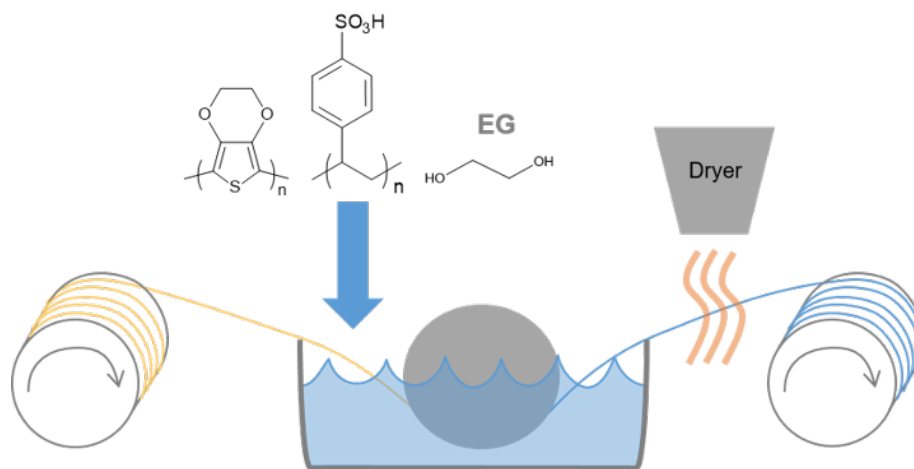


Figure 6: Illustration of the continuous dyeing process.

4.1.2 Pre-treatment

To determine which pre-treatment that gave the highest resulting conductivity of dyed thread, seven different pre-wash methods were analyzed (samples 5, 6, 9-13). The highest conductivity was attained for sample 6 with pre-wash 1 which was $(6.5 \pm 2.0) \cdot 10^{-3}$ S/cm. Hence, pre-washing at elevated temperature gave a better result than; pre-washing at room temperature, dyeing a wet thread, pre-washing without ammonia and not pre-washing at all.

4.1.3 Dyeing of silk yarn

To explore the significance of surfactants in the dyebath samples 4 and 6 were related to each other where sample 4 had surfactants and sample 6 did not. Sample 6 had a higher conductivity than sample 4. Additionally, for comparing samples without pre-wash, see sample 2 and 5, the sample with surfactants in the dye bath gave a better result. However, sample 6 with pre-wash 1 and no additionally added surfactants proved to give a higher conductivity than for sample 2 with surfactants and no pre-wash.

Samples 6 and 7 were compared to see the impact of the addition of a secondary dopant on the conductivity. Sample 7, with EG as a secondary dopant, gave a conductivity of $(7.5 \pm 3.0) \cdot 10^{-3}$ S/cm which was higher than without the addition of EG. Using EG as a secondary dopant proved to give a higher conductivity instead of DMSO as a secondary dopant, this can be seen with samples 33 and 39 in table 2.

Moving on to see the impact of de-doping, sample 18 with EG gave two orders of magnitude higher conductivity than the non-doped sample 19. Post-treatment in EG, DMSO or MeOH (samples 22-24) resulted in a conductivity which was highest for DMSO, followed by EG and finally MeOH. The optimal post-treatment time was measured with samples 23, 25 and 26 and it was determined to be 1 h 20 min.

Furthermore, the impact of viscosity on the dyeing of the yarns was observed by comparing for example sample 20 with 22, sample 21 with 23 or samples 29 with 30. These comparisons showed that an increase in viscosity gave a higher conductivity.

Another interesting parameter to analyze was the impact of layering on the conductivity. Sample 28 had one layer as opposed to sample 29 which consisted of two layers, as seen in table 2 the conductivity is one order of magnitude higher for the yarn with two layers. Two different yarns were also investigated; silk yarn 1 resulted in a conductivity of 74 ± 18 S/cm and silk 2 gave 59 ± 8 S/cm, see sample 30 and 31.

4.1.4 Continuous dyeing of 100 m silk yarn

2.5 cm of sample 35 weighed 0.001 g while pre-washed thread weighed 0.0005 g. This gave the result that the coated thread contained 50% PEDOT: PSS dye.

4.1.5 Bending test and Seebeck

By periodically bending and stretching the yarn with a LEGO construction the resistance changed from 0.30 k Ω to 0.31 k Ω for dyed silk 1. In figure 7 it is observed that the change to 0.31 k Ω happened after 600 bending cycles, however, the conductivity was stable for the remaining 400 cycles. The bending test was also performed for dyed silk 2 which showed unstable conductivity, therefore there were no obtained results for this type of yarn.

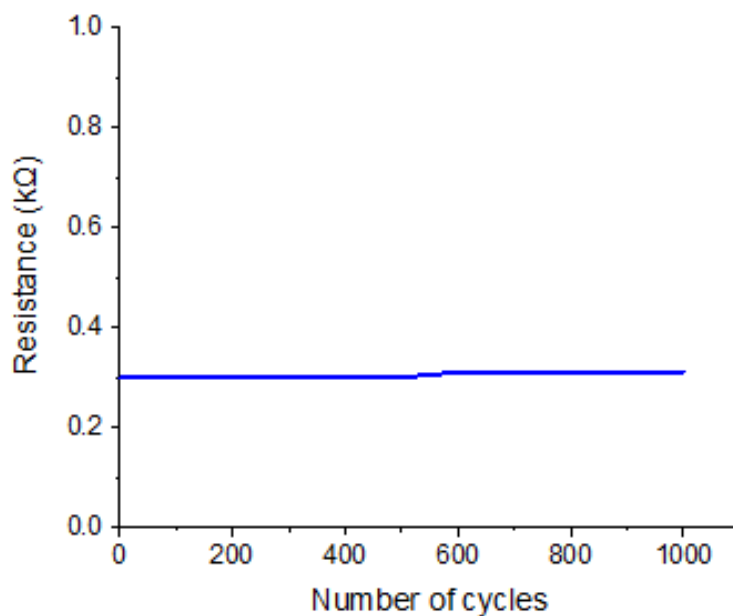


Figure 7: Change of resistance with bending cycles.

Furthermore, the Seebeck coefficient was measured to $15 \pm 1 \mu\text{VK}^{-1}$ for PEDOT: PSS/EG coated silk yarn 1 that was DMSO de-doped.

4.2 Mechanical measurement

In order to determine if dyeing changed the mechanical properties of the thread, tensile testing was performed on both coated and uncoated silk yarns. The samples that were investigated were pristine silk yarn 1 and 2 and PEDOT: PSS/EG coated silk yarn 1 and 2 that were DMSO post-treated (sample 30 and 31). The coated thread displayed similar values for Young's modulus, the stress and strain at break as the corresponding pristine yarn, see table 3. Hence the properties of the thread

remained intact despite two layers of coating.

Table 3: Tensile testing for coated and uncoated silk threads.

Sample	ϵ_{break} [mm/mm] $\cdot 10^{-2}$	σ_{break} [MPa]	E [MPa]
Pristine Silk 1	9.4 ± 1.0	129 ± 12.7	$3\,203 \pm 407.0$
Pristine Silk 2	13 ± 0.8	168 ± 5.00	$2\,404 \pm 338.0$
Dyed Silk 1 (2 layers)	10 ± 0.3	133 ± 8.70	$2\,886 \pm 627.0$
Dyed Silk 2 (2 layers)	13 ± 1.4	158 ± 10.6	$2\,832 \pm 335.0$

4.3 Optical microscopy

By using an optical microscope the following diameters for silk threads were measured, see table 4. Pristine silk 1 had a larger diameter compared to the same thread with two layers of dye (sample 30). However, for silk 2 the larger diameter belonged to the dyed thread (sample 31).

Table 4: Diameters for dyed and undyed silk 1 and 2.

Sample	Diameter [mm]
Pristine Silk 1	0.258 ± 0.026
Pristine Silk 2	0.245 ± 0.023
Dyed Silk 1 (1 layers)	0.242 ± 0.015
Dyed Silk 1 (2 layers)	0.239 ± 0.017
Dyed Silk 2 (2 layers)	0.255 ± 0.018

4.4 SEM

The SEM images illustrate the distribution of dye through the cross-section of the silk yarns. The twice dyed yarn 1 (sample 30) exhibited a covering layer of PEDOT:PSS around the thread, see figure 8a. Thinner sheets were also seen in between and covering the fibers, see figure 8b. In comparison to the undyed thread (figure 8c), which did not possess the membrane-like coating, the fibers in the PEDOT:PSS dyed yarn were more tightly packed. The un-sputtered image of twice dyed silk 1 revealed bright centers, these indicated regions without PEDOT:PSS that were lacking in conductivity. However, around these non-conducting regions, the membrane-like surface seemed to be conductive and the dye has penetrated a little into the fibers.

For dyed silk 2, which was coated twice (sample 31), the membrane-like coating was observed here as well, see figure 9a. However, the distribution of the non-conducting regions was more displaced throughout the yarn. Fewer sheets were seen between the fibers compared to silk 1, see figure 9b. On the surface of the undyed silk yarn 2 (figure 9c) there seemed to be small particles which were not present on silk yarn 1.

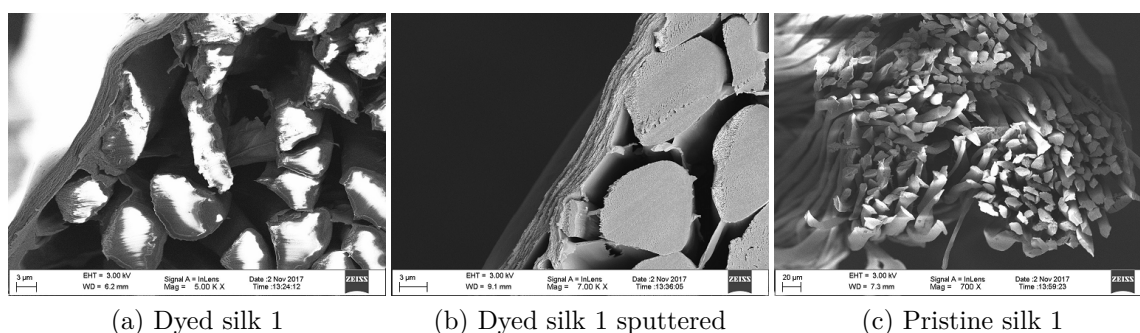
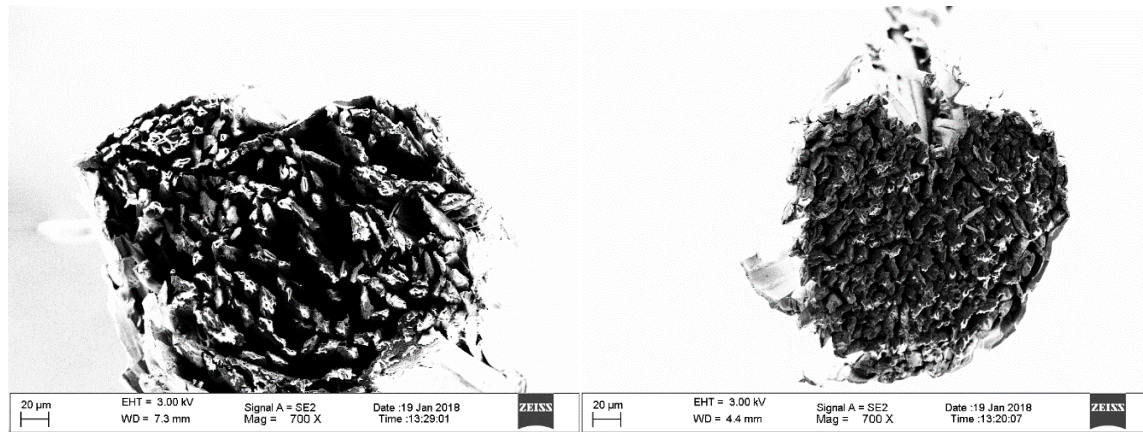


Figure 8: SEM images of cross sections for silk yarn 1.



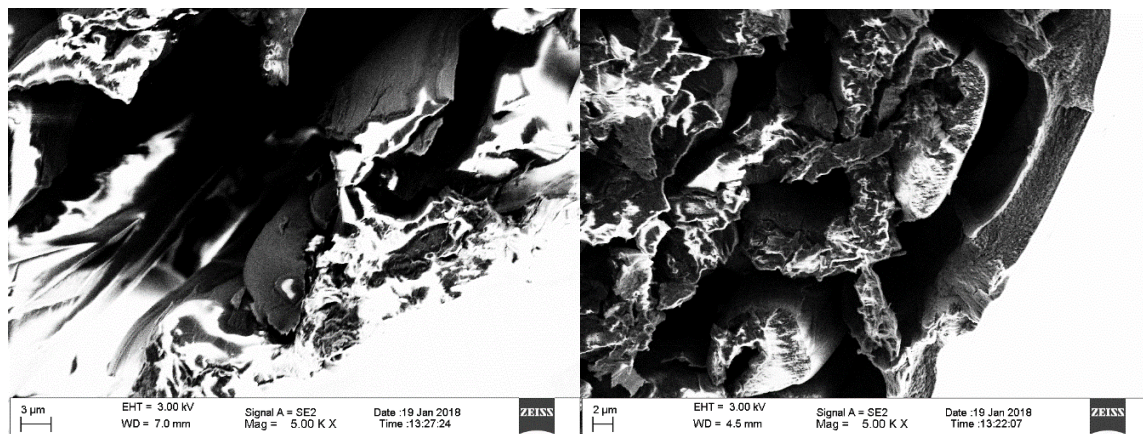
Figure 9: SEM images of cross sections for silk yarn 2.

The SEM images below illustrate the cross section of two yarns which were dyed once with either low or high viscosity. The sample with the lowest viscosity dye was sample 23. For the sample with higher viscosity (sample 32) it can be observed from the SEM images, see figure 10b, that the conducting dye had penetrated the fibers to a larger extent than for the sample with lower viscosity, see figure 10a. The SEM images also reveal brighter fibers for sample 23 and darker for 32 which indicates high conductivity for 32. It can be seen for sample 32 that the conducting layer around the yarn is not fully covering all the fibers with one dyeing cycle. However, in image 10a it is difficult to differentiate how the dyeing layer is covering the sample 23. In figure 10d, a clear covering layer can be observed while in figure 10c it is difficult to distinguish the membrane-like coating.



(a) Entire cross section of sample 23.

(b) Entire cross section of sample 32.



(c) Sample 23 zoomed in.

(d) Sample 32 zoomed in.

Figure 10: SEM images of cross sections for sample 23 and 32, which are coated once.

4.5 Viscosity

The viscosity was changed by evaporating water from PEDOT: PSS/EG or PEDOT: PSS/DMSO sample, this was done at a time range of 2.5-47 h. The change in viscosity can be observed at different shear rates in figure 11 where both axes are on a logarithmic scale. A reference sample of nonevaporated PEDOT: PSS/EG is illustrated with a black line in 11. An increase of evaporation time increases the solid content of the solution.

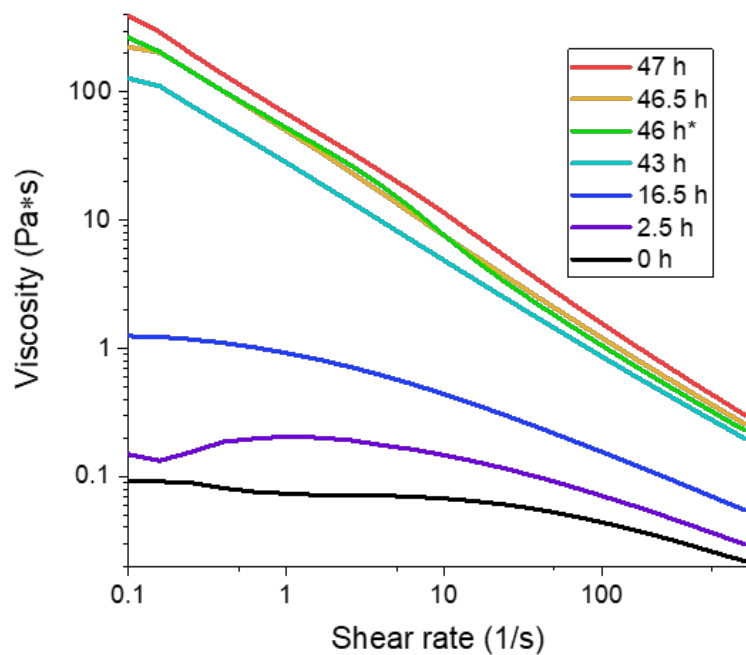


Figure 11: The viscosity of PEDOT:PSS/EG at different shear rates.

* = PEDOT:PSS/DMSO

4.6 Electrical conductivity over time

The change over time of the electrical conductivity for sample 35 is illustrated in the graph below. The conductivity decreased slightly over time and then levels out.

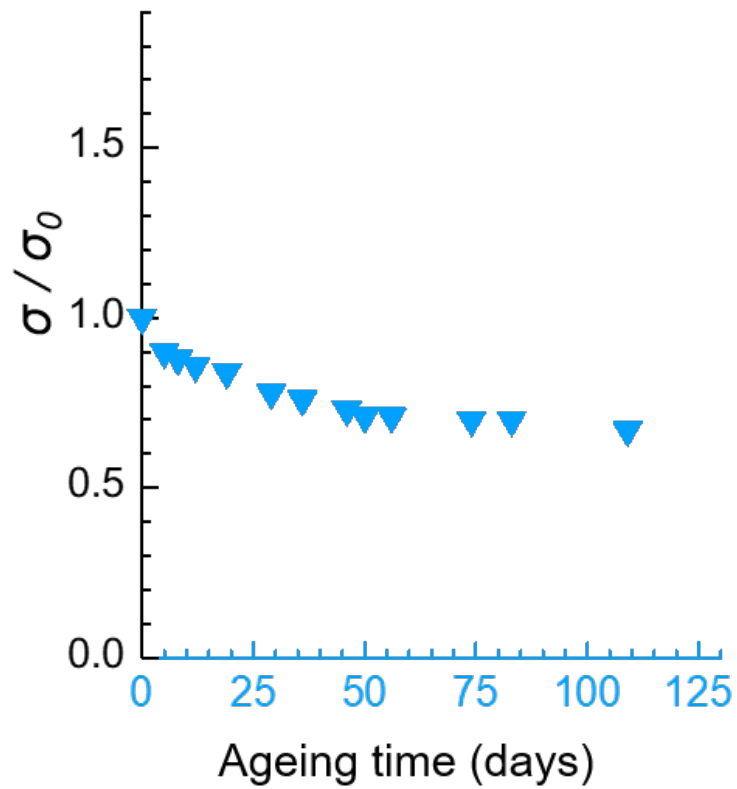


Figure 12: Conductivity relative to initial conductivity over time.

4.7 Integration of the dyed yarn

Sample 30 which was industrially woven by the Smart Textiles Lab showed no indication of delamination after weaving, see figure 13. The electrical conductivity after weaving with an industrial loom is shown in table 5. Half of the measurement points maintained a high electrical conductivity after a plain weaving structure.

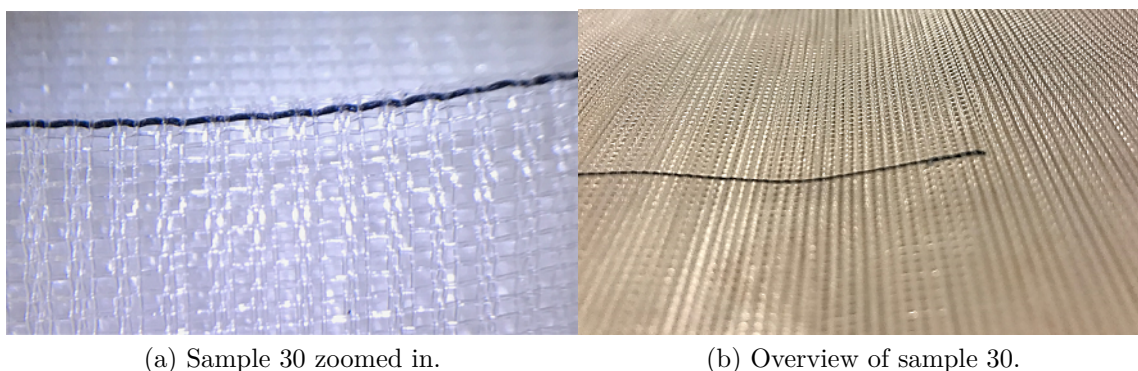


Figure 13: Dyed thread that was industrially woven with a Jacquard loom.

Table 5: Electrical conductivity for eight sections of sample 30 after weaving with an industrial loom.

Measuring points	Electrical conductivity [S/cm]
1	1.13
2	1.20
3	22.65
4	31.57
5	26.74
6	21.39
7	27.91
8	14.70

Furthermore, sample 33 which was manually woven together with non-conductive

yarn to create a keyboard maintained its conductive function after being woven. This can be seen in figure 14 since the segments which were integrated with the PEDOT: PSS dyed yarn responded to touch. For a video of the functioning of the keyboard see link.

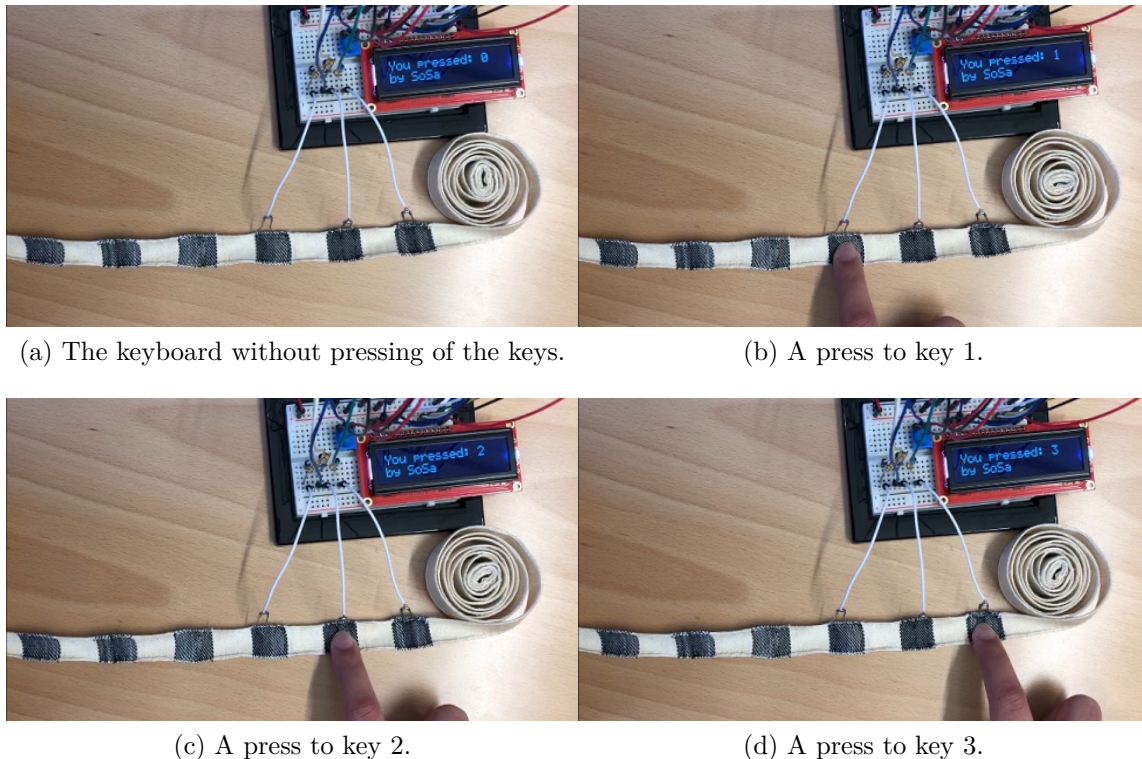


Figure 14: Function illustration of the keyboard.

Additionally, the image below shows that the thread can conduct current when connected to a battery on one end and to a light source on the other. For a video of the light sequence, see link.

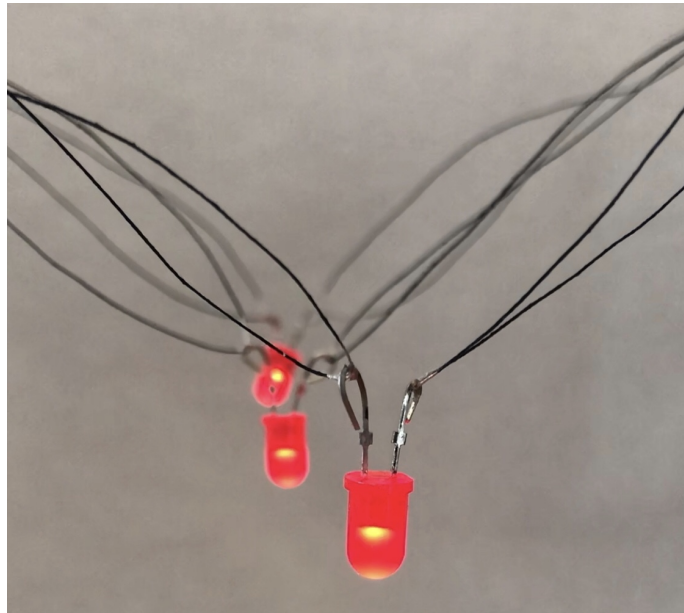


Figure 15: Dyed thread connected to a light source.

The dyed thread survived industrial embroidery since the resistance could be measured. Furthermore, the embroidered text conducted current once it was connected to a battery and a light source, see figure 16.



Figure 16: Embroidered thread connected to a light source.

A multitude of different patterns were embroidered with the dyed silk yarn and the thread did not rupture during this process. The image below illustrates an embroidered heart 17.



Figure 17: An embroidered heart with the PEDOT:PSS dyed thread.

The resistance of the embroidered SoSa text decreased after one washing cycle and was quite stable the remaining 9 washing cycles, see figure 18.

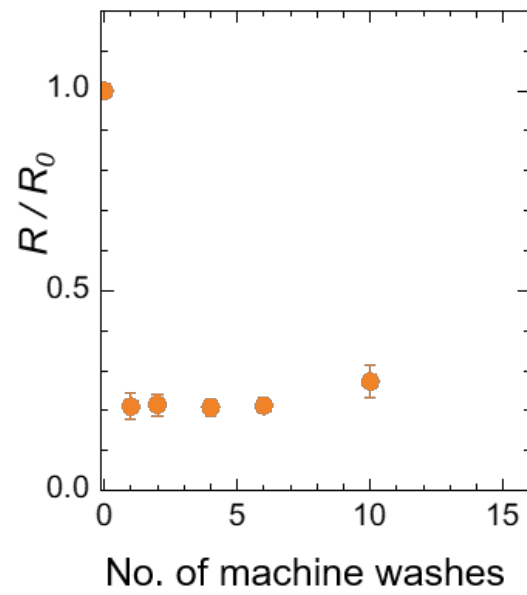


Figure 18: Resistance relative to initial resistance with number of washing cycles.

5 Discussion

In the following sections, the results will be discussed.

5.1 Setup of continuous dyeing process and pre-washing methods

Setup 3 gave superior results in conductivity in comparison to setup 1 and 2. The reason might be that the silk yarn spent more time in the dye bath since the yarn went through the dye bath instead of being directed to the top of the coating wheel. By passing the yarn through the dye and switching of f_1 the time for which the yarn spent in the bath and the contact area between the dye and yarn were further increased. This facilitated the penetration of dye into the fibers. For setup 2 the thread was pulled too much, this might be the reason for the low penetration since the spaces between the fibers were narrower.

Pre-washing improved the conductivity of a dyed thread. Pre-washing the degummed thread could result in a further removal of sericin or in the decrease of the surface energy between the dye and the yarn and allow for a better dyeing coverage. Pre-washing at an elevated temperature gave better results than pre-washing at room temperature. However, energy could be saved by not increasing the temperature but for higher conductivity, the elevated temperature should be used.

5.2 Dyeing of silk yarn

It was proposed in previous studies that the conductivity could be enhanced by the addition of a secondary dopant, this was proven in this project by adding EG or DMSO to the dye bath. EG as secondary dopant gave a higher conductivity compared with DMSO as a secondary dopant. The reason for this could be that EG had a better plasticizing ability meaning that the PEDOT: PSS molecule could, therefore, be reoriented to improve the PEDOT contact. However, DMSO proved to give the highest conductivity for the post-treatment compared to the other solvents and this could be due to a higher separation and removal of PSS from PEDOT.

Additionally increasing the viscosity proved to be an efficient way of increasing the conductivity since the PEDOT: PSS concentration was increased. Two layers of coating gave a better result than one layer, therefore, increasing the coating thickness by adding more layers could enhance the conductivity further. Multiple coating layers could, on the other hand, change the mechanical properties to such a degree that the dyed yarn would possess totally different characteristics than that of pristine silk yarn, yet two layers did not have a significant impact.

5.3 Seebeck

By comparing the Seebeck coefficient for the PEDOT: PSS/EG dyed thread, which was de-doped with DMSO, with the Seebeck coefficient from previous studies it was determined that the values were similar. This indicated that the changes of parameters in this work compared to the previous studies did not change the Seebeck coefficient.

5.4 Optical microscope and SEM

It was observed with an optical microscope that for pristine silk 1 the diameter decreased with the number of coating layers. However, for silk 2 the larger diameter belonged to the twice dyed thread. The reason for this could be that the fibers in silk 1 were more tightly packed once it was dyed. In the SEM images, it seems that the dye in silk 2 did not penetrate the fibers to the same degree as it did for silk 1, see figures 8a and 9a. This could be the reason for the lower conductivity of silk 2, the larger diameter and for the unstable conductivity upon bending. When observing the SEM images there seemed to be small particles on the surface of the undyed silk yarn 2 which were not present on silk yarn 1. The only difference between these two silk yarns was that silk yarn 2 was colored white and therefore the particles on the surface might be titanium dioxide particles. The particles on the surface of the fibers could be the reason for why the PEDOT:PSS did not interact with the fibers as well as it did for silk yarn 1.

A concept for the interaction between the dye and the yarn could be that with the first dyeing cycle the dye penetrated the fibers and started the covering layer while the second dyeing cycle completed the covering layer around the whole yarn. This due to the fact that the thread that was dyed once did not possess an entirely covering layer around the yarn while the thread that had been coated twice seem to be totally covered. By dyeing the sample with a higher viscosity dye the concentration of conducting PEDOT was increased within the yarn. However, more time had passed since the production of sample 23 compared to 32 when the samples were investigated with SEM and this could have affected the results since the conductivity is slightly lower with time.

5.5 Continuous dyeing of 100 m silk yarn

The dyeing method that gave a slightly higher conductivity for the produced 100 m of yarn had a rotational frequency of 3.5 rpm for the collecting coil (sample 33). However, for sample 35 where 100 m of yarn was produced the rotational frequency had to be increased to 4 rpm since there was a problem with the engine. Therefore, the time for which sample 35 spent in the bath was less than sample 33, resulting in a decrease of dye penetration into the fibers for sample 35 and a lower electrical conductivity. For previous samples, an increase of viscosity gave a slightly higher conductivity although this was not the case for the 100 m produced yarns since the viscosity for sample 35 was higher than for sample 33. This could be due to the engine problem or to the fact that the viscosity for sample 35 was much too high leading to a reduction of penetrating dye.

When investigating the difference in weight of an uncoated and coated yarn it was revealed that the coated thread (sample 35) had doubled in weight compared to the pristine silk thread. This suggests that copious amounts of dye had penetrated into the silk thread. The SEM images also confirmed that the dye had diffused to a large extent into all of the investigated yarns. Additional observation of sample 35 showed that the conductivity decreased slightly with time and then stabilized. The reason for this could be that the outer coating layer interacted with air leading to a conductivity decrease. However, when the interaction was complete the conductivity stabilized.

5.6 Integration into a textile

For sample 30, which was integrated into PE using an industrial loom, half of the measurement points maintained a high electrical conductivity after a plain weaving structure. It was primarily the measurement points in the middle of the thread that maintained their conductivity. This may be because the ends of the thread were more exposed to the environment or that those part might have been more handled during the industrial processing than the middle sections. Another factor that influenced the conductivity of the incorporated yarn was that it had been several

months since the production of the yarn when it was actually integrated. This could have had an impact on the results since the conductivity decreases slightly with time.

Moreover, sample 33 managed to maintain its conductive ability despite the rough conditions when manually weaving a keyboard. In addition, the threads responded to touch even though it had been months since the production of the yarn, meaning that the slight decrease of resistance did not have a significant impact on the function of the PEDOT: PSS dyed yarn.

The set up were approximately 12 cm long PEDOT: PSS dyed yarns were connected to a light source and a battery demonstrated that the produced threads were sufficiently homogeneously dyed to provide a conductive pathway. The lights also indicated that the wire had a high enough electrical conductivity for current to pass from the battery to the light source.

The embroidered CHALMERS text that was connected to a light source indicated that the thread retained its conducting properties after the embroidery. The thread did not rupture during the embroidery meaning that the mechanical properties of the dyed yarn were suitable for this industrial process.

The washing of the embroidered thread showed a reduction of the resistance after the first wash cycle. This resistance decrease could be due to the addition of surfactants from the detergent which might have made the PEDOT molecules organize more closely. Excess of PSS could have been removed with washing which could also be the reason for the reorientation of PEDOT. The dyed yarn seemed to be improved after washing meaning that the thread would be suitable in wearable textiles.

6 Conclusion

Continuously dyeing a pre-washed thread with a setup where the thread went through the dye bath gave superior results in conductivity. The addition of EG, as a secondary dopant, and DMSO as post-treatment proved to be two efficient conductivity enhancers. The results were further improved by increasing the viscosity of the dye bath in combination with multiple layers of coating. Furthermore, the dyed yarn maintained its conductive properties after mechanical testing and industrial embroidery/weaving. Washing decreased the resistance of the embroidered textile meaning that the thread could be used in wearable textiles. The functionality of the yarn was also proven by weaving a keyboard where capacitive sensing was used to obtain a signal from the press of a finger. The dyed yarn was additionally used to connect a battery to a light source.

7 Future work

It is of relevance to increase the coating thickness by adding multiple layers, this until the dyed thread does not possess the same properties as the pristine yarn. Since the thread was improved upon washing the addition of a washing step should be investigated and implemented into the process. Additionally, it would be interesting to examine the effect of the detergent on the embroidered fabric by washing the textile in only water at 30 °C or in water at 30 °C together with a detergent. This investigation would determine if the reduction in resistance, where the coating layer was self-healed, was due to washing with a detergent or simply by washing with water. If the resistance decrease is proved to be due to the detergent, it would be interesting to continue washing with other detergents to see if the resistance could be further decreased. Analysis with SEM and EDS could help determine what happened on the surface of the washed embroidered text. Furthermore, it could also be of interest to investigate the cross-section of a washed yarn with SEM to see what happened inside the yarn during the washing. Continuing on, the hope is to create an n-type fiber and to connect this with the p-type fiber in order to produce thermoelectric devices.

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Appendix A Specific values of viscosity at share rate $1 s^{-1}$

The viscosity was measured at different shear rates for one PEDOT:PSS/DMSO solution and several PEDOT:PSS/EG solutions which were evaporated at $50\text{ }^{\circ}\text{C}$ at a time range of 2.5 - 47 h. Shear rate $1 s^{-1}$ was selected to retrieve a specific value for the viscosity.

Table A1: The viscosity for six different samples

Sample	Viscosity [$\text{Pa} \cdot (\text{at the share rate } 1 s^{-1})$]
Evaporation for 2.5 h	0.205
Evaporation for 16.5 h	0.920
Evaporation for 43 h	28.23
Evaporation for 46 h*	52.67
Evaporation for 46.5 h	50.15
Evaporation for 47 h	68.26

* = PEDOT:PSS/DMSO