FABRICATION, CHARACTERIZATION AND APPLICATIONS OF HIGHLY CONDUCTIVE WET-SPUN PEDOT:PSS FIBERS

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FABRICATION, CHARACTERIZATION AND APPLICATIONS
OF HIGHLY CONDUCTIVE WET-SPUN PEDOT:PSS FIBERS

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DISSERTATION

A dissertation submitted in partial fulfillment of the
requirements for the degree of Doctor of Philosophy in the
College of Engineering
at the University of Kentucky

By
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Lexington, Kentucky
2020

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ABSTRACT OF DISSERTATION

FABRICATION, CHARACTERIZATION AND APPLICATIONS OF HIGHLY CONDUCTIVE WET-SPUN PEDOT:PSS FIBERS

Smart electronic textiles cross conventional uses to include functionalities such as light emission, health monitoring, climate control, sensing, storage and conversion of energy, etc. New fibers and yarns that are electrically conductive and mechanically robust are needed as fundamental building blocks for these next generation textiles.

Conjugated polymers are promising candidates in the field of electronic textiles because they are made of earth-abundant, inexpensive elements, have good mechanical properties and flexibility, and can be processed using low-cost large-scale solution processing methods. Currently, the main method to fabricate electrically conductive fibers or yarns from conjugated polymers is the deposition of the conducting polymer onto an inert fiber support by using different techniques. However, the volume occupied by the electrically active coating is generally very small relative to the volume of insulating fiber acting as support. Therefore, when considering the total volume, the bulk electrical conductivity of these coated textiles is usually small, often lower than 10 S/cm, which limits their applications.

An interesting alternate approach would be to fabricate fibers directly from the electrically conductive material avoiding the need for an inert-fiber support. Therefore, in this work, a wet-spinning process for the fabrication of PEDOT:PSS fibers with high electrical conductivity and robust mechanical properties is described. The process includes a coagulating step, a drawing step in a dimethyl sulfoxide bath and two drying steps. The effect that drawing the fibers in the DMSO bath has on the electrical, thermoelectric and mechanical properties of the fibers is studied and correlated to the changes observed in the fibers’ structure. In general, the fibers with the highest state of preferential orientation of crystal planes are also the most conductive and stiffest.

In order to further improve the electrical properties of the fibers, substituting the DMSO drawing step by a sulfuric acid drawing step in the fabrication process is investigated. The sulfuric acid drawn fibers have higher electrical conductivities and better mechanical properties than the DMSO drawn fibers. In fact, electrical conductivities as high as 4039 S/cm and break stresses around 550 MPa are obtained which, to the best of our knowledge, are the highest reported for a PEDOT:PSS fiber. The mechanism by which sulfuric acid enhances the electrical and mechanical properties of the fibers is also
investigated. It is found that the sulfuric acid treatment is very efficient removing PSS from
the fibers while also promoting substitution of PSS by sulfates as counterions. The removal
of PSS and substitution of counterions leads to a reorganization of the crystal structure of
the fibers that is more favorable for charge transport.

The last part of this work focuses on the application of the fibers. The mechanical
properties of the fibers are compared to traditional textile fibers. Additionally, the time
stability of the electrical conductivity of the fibers is also studied. Moreover, the maximum
current carrying capacity or ampacity of the fibers is investigated together with some Joule
heating-based applications such as thermochromic textiles. A thermoelectric textile device
is also demonstrated using the fibers as the p-type legs. Finally, electrochemical
applications of the fibers are discussed and demonstrated.

KEYWORDS: PEDOT:PSS, fibers, electrical conductivity, electronic textiles, wet-
spinning

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Ruben Sarabia Riquelme

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8 April 2020
FABRICATION, CHARACTERIZATION AND APPLICATIONS OF HIGHLY CONDUCTIVE WET-SPUN PEDOT:PSS FIBERS

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8 April 2020
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# TABLE OF CONTENTS

ACKNOWLEDGMENTS ................................................................................................................................. iii

LIST OF TABLES ........................................................................................................................................... viii

LIST OF FIGURES .......................................................................................................................................... ix

CHAPTER 1. OVERVIEW ................................................................................................................................. 1
  1.1 Background and motivation .................................................................................................................. 1
  1.2 Dissertation outline .............................................................................................................................. 2
  1.3 References ........................................................................................................................................... 4

CHAPTER 2. INTRODUCTION ......................................................................................................................... 6
  2.1 Background in band theory and transport phenomena ................................................................. 6
    2.1.1 Conduction and valence bands ................................................................................................. 6
    2.1.2 Density of states, Fermi function and carrier concentration .............................................. 7
    2.1.3 Doping ........................................................................................................................................ 10
    2.1.4 Transport properties ................................................................................................................. 11
      2.1.4.1 Electrical conductivity ........................................................................................................ 11
      2.1.4.2 Seebeck effect ..................................................................................................................... 12
      2.1.4.3 Thermal conductivity .......................................................................................................... 16
  2.2 Fundamentals of conducting polymers .............................................................................................. 18
    2.2.1 Brief history of conducting polymers ...................................................................................... 18
    2.2.2 Transport in conducting polymers ........................................................................................... 21
      2.2.2.1 Origin of the electrical conductivity .................................................................................. 21
      2.2.2.2 Charge transport models in conjugated polymers .......................................................... 24
      2.2.2.3 Model for the thermoelectric power ................................................................................. 27
      2.2.2.4 Thermal conductivity of polymers ................................................................................. 28
    2.2.3 The case of poly(3,4-ethylendioxythiophene) (PEDOT) ..................................................... 31
      2.2.3.1 Oxidative polymerization of EDOT ................................................................................... 32
      2.2.3.2 Crystal structure of PEDOT ............................................................................................ 33
      2.2.3.3 Morphology of PEDOT:PSS .......................................................................................... 35
      2.2.3.4 Electrical conductivity of PEDOT:PSS .......................................................................... 36
      2.2.3.5 Seebeck coefficient of PEDOT:PSS .............................................................................. 39
      2.2.3.6 Thermal conductivity of PEDOT:PSS ............................................................................ 39
  2.3 Conclusions ........................................................................................................................................... 40
  2.4 References ............................................................................................................................................. 41

CHAPTER 3. EXPERIMENTAL METHODS AND CHARACTERIZATION TECHNIQUES ......................................... 47
  3.1 Electrical conductivity ......................................................................................................................... 47
3.1.1 2-probe method ................................................................. 47
3.1.2 4-probe method ................................................................. 48
3.2 Seebeck coefficient ............................................................... 49
3.3 Thermal conductivity ............................................................ 50
3.4 Scanning electron microscope (SEM) ........................................ 51
3.5 Mechanical characterization and linear density measurements .... 52
3.6 Wide-Angle X-ray Scattering (WAXS) ...................................... 52
3.7 X-ray photoelectron spectroscopy (XPS) .................................... 54
3.8 References ............................................................................. 56

CHAPTER 4. WET-SPINNING AND CHARACTERIZATION OF PEDOT:PSS FIBERS ................................................................. 57
4.1 Introduction ................................................................................ 57
4.1.1 Fiber spinning methods .......................................................... 57
  4.1.1.1 Melt spinning ................................................................. 58
  4.1.1.2 Solution spinning .......................................................... 58
  4.1.1.3 Electrospinning ............................................................. 59
4.1.2 Fabrication of electrically conductive conjugated polymer fibers .... 60
  4.1.2.1 Coating of insulating textile fibers with conjugated polymers .... 60
  4.1.2.2 Spinning of conjugated polymer and insulating polymer blends ... 61
  4.1.2.3 Spinning of pure conjugated polymers ................................. 63
4.2 Experimental details on the wet-spinning setup ......................... 68
  4.2.1 Materials ........................................................................... 68
  4.2.2 Dope preparation ............................................................... 68
  4.2.3 Wet-spinning setup ............................................................ 68
4.3 Results and discussion ............................................................ 69
  4.3.1 Wet-spinning process .......................................................... 69
  4.3.2 Critical draw ratios ............................................................ 71
  4.3.3 Diameter and geometry of the fibers ....................................... 72
  4.3.4 Linear density and removal of PSS from the fibers in the DMSO bath .... 74
  4.3.5 Wide-angle X-ray scattering (WAXS) ...................................... 78
  4.3.6 Electrical conductivity ......................................................... 82
  4.3.7 Thermoelectric properties .................................................... 85
  4.3.8 Mechanical properties ....................................................... 88
4.4 Conclusions ............................................................................ 93
4.5 References ............................................................................. 95

CHAPTER 5. ENHANCING THE ELECTRICAL CONDUCTIVITY OF PEDOT:PSS FIBERS BY SULFURIC ACID DRAWING ........................................................................... 101
5.1 Introduction ............................................................................ 101
5.2 Experimental details on the sulfuric acid treatment setups ............ 104
LIST OF TABLES

Table 2.1. Values of the unit cell distances of the PEDOT crystal for different counterions. ........................................................................................................................................................................ 34

Table 5.1. Lateral crystallite size in the a and b directions for the different fiber samples. ........................................................................................................................................................................ 119

Table 6.1. Mechanical and electrical properties of common metals and fibers......... 134

Table 6.2. Performance parameters of previously reported textile thermoelectric devices. ........................................................................................................................................................................ 152
**LIST OF FIGURES**

Figure 2.1. Scheme showing the position of the conduction and valence bands for (a) insulator, (b) semiconductor and (c) metal. ................................................................. 7

Figure 2.2. Representation of three possible positions of the Fermi energy for a semiconductor. (a) Intrinsic semiconductor, (b) p-type semiconductor and (c) n-type semiconductor. The density of states has been represented using a parabolic model. ..... 10

Figure 2.3. Band diagrams showing (a) p-doping (acceptor impurity) and (b) n-doping (donor impurity). ........................................................................................................... 11

Figure 2.4. (a) Scheme of Seebeck effect. (b) Diffusion of majority charge carriers due to a temperature gradient................................................................. 13

Figure 2.5. Diagram explaining the positive and negative contributions to the Seebeck coefficient as a function of the Fermi level position with respect the conduction band for a metal and a heavily doped semiconductor. .................................................. 16

Figure 2.6. Chemical structure of (a) trans-polyacetylene, (b) polyaniline (emeraldine base), (c) polypyrrole, (d) polythiophene, (e) PEDOT and (f) polymer complex PEDOT:PSS showing the negative charges of the counterion stabilizing the positive charges of doped PEDOT. ........................................................................... 20

Figure 2.7. p\textsubscript{z} orbital energy splitting as a function of the number of carbon atoms leading to the formation of energy bands in polyacetylene. ................................................................. 21

Figure 2.8. Band structure changes in conjugated polymers: (a) a neutral chain, (b) a chain carrying a positive polaron and (c) a chain carrying a bipolaron. .............................. 23

Figure 2.9. Intra-chain and inter-chain coupling of bipolaron wavefunctions in polythiophene, which is the origin of bipolaronic bands or networks................................. 23

Figure 2.10. Band structure of (a) polaron network and (b) bipolaron network............ 23

Figure 2.11. Scheme representing the microstructure of semi-crystalline conjugated polymers. The darker regions represent ordered domains of high conductivity where polymer chains have efficient π-π stacking. Lighter regions represent amorphous regions with weak interchain coupling leading to charge localization and thus low conductivity. Long polymer chains (in red) act as bridges between the different ordered regions...... 26

Figure 2.12. Schematic representation of the effect of molecular weight on charge carrier mobility for semi-crystalline conjugated polymers. ................................................. 27

Figure 2.13. Polaron stabilization by additional resonance states in oxygen group substituted polythiophenes................................................................. 32
Figure 2.14. Oxidative polymerization of EDOT to obtain PEDOT using iron (III) chloride as oxidant. .......................................................... 32

Figure 2.15. Schematic representation of the crystal structure of PEDOT.................. 34

Figure 2.16. Scheme of the polyelectrolyte complex structures of PEDOT:PSS showing the PEDOT-rich core (red shadow) – PSS-rich shell (green shadow) gel particles found in PEDOT:PSS water dispersions......................................................... 36

Figure 3.1. Scheme of (a) 2-probe configuration to measure electrical conductivity and (b) plot of $R_{measured}$ versus $L$ to obtain $R_{contacts}$ .............................................................. 48

Figure 3.2. Scheme of the 4-probe configuration to measure electrical conductivity. ..... 49

Figure 3.3. Scheme of the purpose-built setup used to characterize the Seebeck coefficient of the fiber specimens............................................................. 50

Figure 3.4. (a) Scheme of a 2D WAXS pattern and (b) changes in the scattering pattern as a function of the degree of orientation of the crystalline planes from random to perfect orientation.......................................................... 53

Figure 4.1. Schemes of different fiber spinning methods: (a) Melt spinning, (b) dry spinning, (c) wet spinning and (d) electrospinning................................................................. 60

Figure 4.2. Scheme of the continuous wet-spinning process for the fabrication of PEDOT:PSS fibers. Insets are (a) image of the fiber formation in the coagulation bath (scale bar is 10 mm); (b) image of dried fiber before entering the DMSO draw bath (scale bar is 2 mm); (c) image of the same fiber as in panel b visibly swollen by DMSO after exiting the DMSO draw bath (scale bar is 2 mm); (d) image of a fiber on a PTFE spool of 26 mm diameter. ........................................... 69

Figure 4.3. Critical draw ratios as a function of the coagulation bath draw ratio......... 72

Figure 4.4. (a) Diameter versus total draw ratio of the PEDOT:PSS fibers. Plotted values are average values of 50-75 diameter measurements performed on 5 different specimens (10-15 per specimen) and error bars represent the standard deviation within specimens of the same sample. (b and c) SEM cross-section image of fibers spun into a coagulation bath of IPA and 10 vol.% DMSO in IPA, respectively, and stretched through DMSO for a total draw ratio of 1.67. Insets are close-ups to one of the fibers. (d-f) SEM images of fibers spun into 10 vol.% DMSO in IPA and further stretched through DMSO with total draw ratios of 1.58, 1.97, and 2.36, respectively. Scale bars are 10 $\mu$m except in insets that are 3 $\mu$m. ........................................................................ 74

Figure 4.5. Linear density versus the cross-sectional area for all samples.................. 75

Figure 4.6. Linear density as a function of total draw ratio. Linear density is given in denier (grams of fiber per 9000 meter of fiber). The dotted curves are calculated using eq. 4.8 using varying weight percentages of PEDOT in the final fiber................... 77
Figure 4.7. XPS S2p of coagulation bath fibers and DMSO drawn fibers. Intensities normalized to the PSS peak. ................................................................. 78

Figure 4.8. WAXS analysis of wet-spun PEDOT:PSS fibers. 2D WAXS pattern of (a) PEDOT:PSS film, (b) coagulation bath fibers spun into 10 vol.% DMSO in IPA (draw 1.58) and (c) fibers spun into 10 vol.% DMSO in IPA and drawn through a DMSO bath at 2.36 draw ratio. (d) Normalized intensity (with respect to the PSS broad hump) versus 2\theta. (e) Scheme of the PEDOT:PSS crystal structure. Intensity as a function of azimuthal angle for (f) (100) reflections and (g) (020) reflections. ......................................................... 81

Figure 4.9. Electrical conductivity of PEDOT:PSS fibers as a function of total draw.... 83

Figure 4.10. (a) Electrical conductivity as a function of total draw of fibers spun into 10 vol.% DMSO in IPA including DMSO-washed coagulation bath samples which are plotted at 1.5 total draw instead 1.58 to avoid overlap of the symbols and improve clarity. (b) Electrical conductivity (standardized to the initial electrical conductivity) as a function of strain for a coagulation bath sample spun into 10 vol.% DMSO in IPA. For this test the resistance as a function of strain was measured, and then, the electrical conductivity at each strain was calculated assuming constant specimen volume. Values presented are average of 3 specimens................................................................. 84

Figure 4.11. Typical temperature dependence of the resistance normalized to its (vacuum) room temperature value (blue crosses) and fit to 1D-VRH with hopping parameter T0 = 32 K (red curve)..................................................................................... 85

Figure 4.12. (a) Seebeck coefficient as a function of total draw. (b) Thermoelectric power factor as a function of total draw. Seebeck coefficients are the average of 3 specimens per sample. The power factor was calculated using the average values of electrical conductivity and Seebeck coefficient. The error bars represent standard deviation between specimens within the same sample................................................................. 86

Figure 4.13. (a) Average values of the calculated thermal conductivity from samples spun into 10 vol.% DMSO in IPA at different total draws and T = 78 K. (b) Temperature dependence of thermal conductivity for a sample with total draw ratio of 2.36. ..............88

Figure 4.14. Typical stress-strain curves in uniaxial tension of fibers spun into 10 vol.% DMSO in IPA at different draw ratios from 1.58 to 2.36................................................................. 89

Figure 4.15. Single-filament tensile properties of PEDOT:PSS fibers as a function of total draw: (a) Young’s modulus, (b) elongation at break, and (c) break stress. Values are average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample. ................................................................. 90

Figure 4.16. Correlation between polymer chain orientation and electrical and mechanical properties. (a) Electrical conductivity versus (100) Hermans orientation factor, f_{100} and (b) Young’s modulus versus f_{100}. Values are the average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample. ............... 92
Figure 4.17. Electrical conductivity versus Young’s modulus. Values are the average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample. Data encircled as “summer season” or “winter season” are samples that were measured during summer or winter, respectively.

Figure 5.1. Scheme of the sulfuric acid drawing process.

Figure 5.2. (a) Diameter as a function of sulfuric acid immersion treatment time. (b) Linear density of coagulation bath, DMSO drawn and sulfuric acid treated fibers versus total draw. (c) SEM image of a coagulation bath fiber. (d) SEM image of a sulfuric acid treated fiber. (e) SEM images showing several fusion points between fibers after sulfuric acid treatment. (f) Close up image of a fusion point.

Figure 5.3. Electrical conductivity as a function of sulfuric acid immersion treatment time for coagulation samples with total draw of 1.58 and 3.34.

Figure 5.4. Linear density of coagulation bath fibers, DMSO drawn fibers, sulfuric acid immersed fibers and sulfuric acid drawn fibers. Dotted curves represent the linear density of the fibers as calculated with eq. 4.8 using the noted wt.% of PEDOT in the final fiber.

Figure 5.5. XPS spectra of coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers and sulfuric acid drawn fibers that were also immersed in sulfuric acid for 30 min. (a) C1s scan and (b) S2p scan. Intensities are normalized to the maximum intensity.

Figure 5.6. WAXS analysis of PEDOT:PSS fibers. 2D WAXS patterns of (a) coagulation bath fibers, (b) DMSO drawn fibers, (c) sulfuric acid drawn fibers and (d) sulfuric acid drawn fibers that were then immersed in sulfuric acid for 30 min. (e) Integrated intensity (normalized to the maximum intensity) versus 2θ. (f) Scheme of the PEDOT crystal structure.

Figure 5.7. Scheme showing the different proposed changes in the (100) lamella stacking of PEDOT and counterions upon sulfuric acid treatment. Insets show the (100) peaks in the intensity versus 2θ plots.

Figure 5.8. Electrical conductivity as a function of draw ratio for coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers and sulfuric acid drawn fibers that have additionally been immersed in sulfuric acid for 30 min. Values are average of five specimens and error bars represent the standard deviation between specimens within the same sample.

Figure 5.9. Seebeck coefficient and thermoelectric power factor of coagulation bath fibers, DMSO drawn fibers and sulfuric acid drawn fibers.

Figure 5.10. Typical stress-elongation curves in uniaxial tension of coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers and sulfuric acid drawn fibers that were additionally immersed in sulfuric acid for 30 min.
Figure 5.11. Single-filament tensile properties of PEDOT:PSS coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers and sulfuric acid drawn fibers that were additionally immersed in sulfuric acid for 30 min. (a) Elongation at break, (b) break stress and (c) Young’s modulus. Values are average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample. 125

Figure 5.12. Photographs of (a) as-spun PEDOT:PSS fibers and (b) sulfuric acid drawn PEDOT:PSS fibers both being collected into a PTFE spool. Insets are saturated zooms of the marked area to emphasize the change in color. 126

Figure 5.13. Electrical conductivity versus Young’s modulus. Values are average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample. 128

Figure 6.1. Stability of the electrical properties of PEDOT:PSS fiber specimens in (a) laboratory atmosphere and (b) controlled atmosphere. 136

Figure 6.2. Electrical conductivity versus time of specimens cut from the spool with new electrical contacts. 138

Figure 6.3. (a) Resistance (standardized to the initial resistance) of coagulation bath fibers versus increasing current density at different voltage sweep rates until electrical failure. (b) Change in resistance (standardized to the initial resistance) of coagulation bath fibers with time at different constant current densities. 140

Figure 6.4. (a) Resistance (standardized to the initial resistance) of the three types of fibers versus increasing current density at 0.1 mV/s voltage sweep rates until electrical failure. (b) Ampacity as a function of the voltage sweep rate. 141

Figure 6.5. (a) Photographs showing a red LED being lit by passing 1 mA through PEDOT:PSS fiber interconnections sewed to cotton cloth. Inset shows a zoom to the PEDOT:PSS fibers. (b-c) Images showing functional interconnections even after bending the cotton cloth. 142

Figure 6.6. (a) Temperature of a fiber versus time while increasing the current by 0.5 mA each 30 s. (b) Temperature of the fibers as a function of the current density (inset: temperature as a function of power dissipated). 144

Figure 6.7. (a) Temperature response to a step change in current fitted to eq. 5.5. (b) Temperature response to step changes in current (ON: 15 kA/cm², OFF: 0) at different cycle frequencies between 0.017 and 1 Hz. 146

Figure 6.8. Thermochromic PEDOT:PSS fiber bundle sewed on a cotton cloth in its (a) OFF (blue) and (b) ON (white) state. (c) Temperature response of the bundle to a step change in current (inset: infrared image of the thermochromic bundle in its ON state.). 147
Figure 6.9. (a) Scheme of a thermoelectric generator showing p-n couples connected electrically in series but thermally in parallel. (b) Equivalent electrical circuit of a thermoelectric generator.

Figure 6.10. (a) Photograph of the textile thermoelectric device fabricated by sewing PEDOT:PSS fiber bundles and alumel wire to a cotton cloth. (b) Output voltage and output power of the device as a function of output current at $\Delta T = 84$ °C. (c) Output power of the device as a function of $\Delta T$. The dotted curves in (a) and (b) represent the theoretical fit to eqs. 6.7-6.12.

Figure 6.11. Scheme of (a) electrochemical transistor and (b) field-effect transistor both with a positive gate voltage applied.

Figure 6.12. (a) Image of the PEDOT:PSS fiber-based OECT. (b) Output curves showing the dependence of $I_D$ on $V_D$ at different $V_G$ from 0 to 0.7 with $\Delta V_G$ of 0.1 V and channel length of 1 cm.

Figure 6.13. (a) Photograph of an LED attached to a cotton cloth with PEDOT:PSS knitted fiber interconnections with dimming capabilities by including a PEDOT:PSS fiber-based OECT. (b) Photographs showing the LED emitting at different intensities by changing the gate voltage from 0 V to 1 V while applying a constant drain voltage of -3.3 V.

Figure 6.14. (a) Transfer curves showing the dependence of $I_D$ on $V_G$ and (b) transconductance as a function of $V_G$. Both (a) and (b) at different values of $V_D$ from 0 V to -0.6 V with $\Delta V_D$ of -0.1 V and channel length of 1 cm. Solid lines connecting the data point are guides to the eye.

Figure 6.15. (a) Transconductance as a function of gate voltage and amount of fibers acting as channel. Here $V_D$ was kept constant at -0.6 V and the channel length was 1 cm. (b) Transconductance at $V_D = -0.6$ V and $V_G = 0.2$ V as a function of the number of fibers acting as channel (1 cm) showing the linear relationship between these two parameters per eq. 6.15.
CHAPTER 1. OVERVIEW

1.1 Background and motivation

The first evidence of textiles dates back to the late Stone Age. Woven materials were found in Pavlov, Czech Republic dating to c. 26000 years ago [1] and Venus figurines from c. 25000 BC have been depicted with clothing [2]. However, despite the technological advancements in other areas, textiles have remained relatively unmodified until very recently when research efforts have started to focus on the development of electronic textiles (smart textiles or e-textiles). Miniaturization of electronic devices and circuits have allowed them to be embedded in traditional textiles [3] making possible the fabrication of smart textiles with functionalities such as light emission, health monitoring, climate control, sensing, storage and conversion of energy, etc. [4-7]. However, in next generation smart textiles, instead of embedding electronic devices into textiles to impart those functionalities, ideally the constituent fiber itself would have electronic capabilities so that fibers can be arranged into woven patterns and fiber-based electronic devices. To realize this idea, new fibers and yarns that are electrically conductive and mechanically robust are needed as fundamental building blocks [7,8].

Conjugated polymers are promising candidates in the field of electronic textiles because they are made of earth-abundant, inexpensive elements, have good mechanical properties and flexibility, and can be processed using low-cost large-scale solution processing methods. Currently, the main method to fabricate electrically conductive fibers or yarns from conjugated polymers is the deposition of the conducting polymer onto an inert fiber support by using different techniques. Several authors have explored the in-situ polymerization of conjugated polypyrrole and poly(3,4-ethylenedioxythiophene)
(PEDOT) on silk fiber [9], cotton [10], wool [11], or polyester fabric [11,12]. Additionally, water dispersions of PEDOT complexed with the counterion poly(styrenesulfonate) (PSS) or PEDOT:PSS have been widely used to coat textile fibers such as nylon fibers [13], polyester fabrics [14], cotton [15], and silk yarns [16].

Coated fibers are relatively straight-forward to fabricate and retain the mechanical properties of the underlying polymer fibers. However, the volume occupied by the electrically active coating is generally very small relative to the volume of insulating fiber acting as support. Therefore, when considering the total volume, the bulk electrical conductivity of these coated textiles is usually small, often lower than 10 S/cm, which limits their applications [7]. An interesting alternative would be to fabricate electrically conductive fibers directly from the conjugated polymers, not coated fibers, avoiding the need for a non-active fiber support.

The development of such conducting fibers is a problem that falls on the field of materials science and engineering. In this dissertation, a process for the fabrication of PEDOT:PSS fibers with high electrical conductivity and robust mechanical properties is described. Moreover, process-structure-property relationships are sought to understand the electrical and mechanical behavior of the fibers. The fiber geometry offers some unique opportunities such as the study of the effect that polymer chain alignment, packing and preferential orientation has on the properties of the resulting fibers. Finally, potential applications and other interesting aspects of the fibers are also discussed.

1.2 Dissertation outline

Chapter 2 of this dissertation starts introducing fundamental concepts about electron transport in the solid state and continues with a brief history of the discovery of
conducting polymers. The chapter ends describing the unique electronic transport associated with conducting polymers.

Chapter 3 presents some of the methods and characterization techniques used through this dissertation.

Chapter 4 introduces basic concepts regarding polymer fiber spinning and provides a detailed description of the PEDOT:PSS spinning process developed in this dissertation. Additionally, the effect that chain orientation by drawing has on the transport properties of the fibers is discussed.

Chapter 5 describes the use of sulfuric acid post-treatment as an effective way to increase the electrical conductivity of the fibers. The mechanism by which this enhancement occurs is investigated and discussed.

Chapter 6 discusses potential applications of the fibers such as flexible interconnections, textile heaters, thermoelectric generators, electrochemical transistors, thermochromic textiles, … providing preliminary results of the use of the fibers for such applications.

Chapter 7 includes the conclusions of this work together with possible future directions.
1.3 References


CHAPTER 2. INTRODUCTION

2.1 Background in band theory and transport phenomena

2.1.1 Conduction and valence bands

A useful way to differentiate between metals, semiconductors and insulators is in terms of their band structure. While individual atoms have discrete energy levels that electrons can occupy, in crystalline solids there are groups of levels with closely spaced energies referred as to energy bands. An electron can move freely within a band given that there is an empty energy level to which it can move. It is important to introduce here the following concepts: Electrons occupy energy states from lowest to highest energy. The Fermi level is the highest energy state that an electron would occupy at 0 K. The valence band is the highest occupied energy band while the conduction band is the lowest unoccupied energy band. The distance in energy between the valence and conduction band is called the energy band gap, $E_g$. The position of the Fermi level with respect to the conduction and valence bands is a crucial factor for determining electrical properties. Figure 2.1 provides a typical graphical representation of these important concepts.

If the energy gap between conduction and valence band is large the material behaves as an insulator. If the Fermi level lies within a band or there is no energy band gap because the conduction and valence band overlap, electrons can move freely, and the material is a metallic conductor. There is an intermediate case when the energy gap is small enough that thermal energy can bridge the gap for a fraction of electrons. In this case the material is said to be a semiconductor. Figure 2.1 depicts the position of the conduction and valence bands for the different scenarios explained above.
Figure 2.1. Scheme showing the position of the conduction and valence bands for (a) insulator, (b) semiconductor and (c) metal.

2.1.2 Density of states, Fermi function and carrier concentration

Earlier we stated that energy bands are groups of states with closely spaced energies. But how many states and how close? The answer to these questions is the density of states, $D(E)$, defined as the number of states per unit energy per unit volume of the crystal. Another important question that arises is how are these states filled by electrons? This is given by the Fermi function, $f(E)$, which quantitatively describes the probability of an energy state, with energy $E$, being filled (see eq. 2.1). Here, we can introduce a new definition for the Fermi energy, $E_F$, as the energy at which there is a 50% probability for a state to be filled at a finite temperature, $T$.

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$  
\text{eq. 2.1}

where $k$ is the Boltzmann constant.

The basic nature of this function dictates that at ordinary temperatures, most of the levels up to the Fermi level are filled, and relatively few electrons have energy above
the Fermi level. At ordinary temperatures $f(E)$ takes values of 1 almost up to the Fermi level and rapidly approaches zero above it.

The carrier distribution, $n(E)$, per unit energy and unit volume is then given by

$$n(E) = D(E)f(E)$$ \hspace{1cm} \text{eq. 2.2}

and the total carrier density is given by

$$n_{total} = \int_0^{\infty} D(E)f(E)dE$$ \hspace{1cm} \text{eq. 2.3}

However, since only electrons in the conduction band or holes in the valence band are free to move and contribute to electronic transport, we are often more interested in the electron or hole concentration in the conduction or valence band, respectively.

In that case:

$$n = \int_{E_C}^{\infty} D_C(E)f(E)dE$$ \hspace{1cm} \text{eq. 2.4}

is the concentration of electrons in the conduction band and

$$p = \int_0^{E_V} D_V(E)[1 - f(E)]dE$$ \hspace{1cm} \text{eq. 2.5}

is the concentration of holes in the valence band, where $E_C$ and $E_V$ are the energies at the bottom of the conduction band and at the top of the valence band, respectively, and $D_C(E)$ and $D_V(E)$ are the density of states in the conduction band and valence band, respectively.

Based on these definitions it is clear that the position of $E_F$ relative to the conduction and valence bands determines the mobile electrons and mobile hole concentrations. Metals have high charge carrier concentration since the Fermi energy lies within a band. In semiconductors $E_F$ lies in the band gap and we can have three different scenarios depending on its position with respect the bands. \textbf{Figure 2.2} exemplifies these
three scenarios where the Fermi level is situated at different positions within the band gap. An intrinsic semiconductor has the same concentration of electrons and holes and the Fermi level is situated approximately at the center of the energy gap. Whereas, in a p-type or n-type semiconductor the Fermi level is closer to the valence band or the conduction band, respectively, and thus the concentration of either holes or electrons is higher.
Figure 2.2. Representation of three possible positions of the Fermi energy for a semiconductor. (a) Intrinsic semiconductor, (b) p-type semiconductor and (c) n-type semiconductor. The density of states has been represented using a parabolic model.

2.1.3 Doping

Since the charge carrier concentration in semiconductors is intrinsically low, small amounts of impurities are often added to semiconductors to increase it. This is called doping. The impurity is chosen such that it introduces an energy level close to either the
conduction band edge (n-doping) or the valence band edge (p-doping) (see Figure 2.3). Impurity atoms that create an energy state near the conduction band edge are often called donors since they effectively donate an electron to the conduction band, thereby increasing the electron concentration. Such a semiconductor is usually called n-doped or n-type semiconductor. On the other hand, impurity atoms that create an energy state near the valence band edge are called acceptors since they accept an electron from the valence band, thereby increasing the hole concentration. A semiconductor doped this way is usually called p-doped or p-type semiconductor. n-doping effectively shifts the $E_F$ closer to the conduction band edge while p-doping shifts it closer to the valence band edge (see Figure 2.2b-c).

![Band diagrams showing (a) p-doping (acceptor impurity) and (b) n-doping (donor impurity).](image)

**Figure 2.3.** Band diagrams showing (a) p-doping (acceptor impurity) and (b) n-doping (donor impurity).

### 2.1.4 Transport properties

#### 2.1.4.1 Electrical conductivity

The electrical conductivity, $\sigma$, is defined as the degree to which a specified material conducts electricity, calculated as the ratio of the current density in the material to
the electric field that causes the flow of current. It can be easily understood that the degree to which a material conducts electricity depends on the density of charge carriers in the material and how easily or fast they can move. Indeed, \( \sigma \) is often calculated as

\[
\sigma = ne\mu_n + pe\mu_p
\]

where \( e \) is the electron charge and \( \mu_n \) and \( \mu_p \) are the electron and hole mobilities, respectively.

Mobility is an important parameter that determines the velocity at which charge carriers move when they are subject to an electric field. At finite temperature, atoms are constantly vibrating due to thermal excitation. A phonon is the quantum description of one such vibrational motion. An electron traveling through a crystal lattice can be scattered by these vibrations. This is called lattice or phonon scattering. The higher the temperature, the more atoms vibrate, and more scattering events occur. Therefore, mobility usually decreases with temperature. Doping also affects mobility since ionized impurities can act as scattering centers due to Coulomb interactions. In this case, increasing the level of doping results in decreased mobility. Grain boundaries, disorder and other defects also decrease mobility.

2.1.4.2 Seebeck effect

We can consider a circuit formed by two dissimilar conductors, A and B, which are electrically connected in series and thermally connected in parallel such as depicted in Figure 2.4a. If a temperature difference is set across the material A by setting the junctions A and B at \( T_c \) and \( T_h \) with \( T_h > T_c \) and \( \Delta T = T_h - T_c \), an open circuit voltage, \( \Delta V \), is developed and is given by

\[
\Delta V = -\alpha \Delta T
\]

eq. 2.7
where \( \alpha \) is the Seebeck coefficient between the elements A and B and is usually measured in \( \mu V/K \).

A useful way of understanding the Seebeck effect is based on a charge carrier diffusion perspective as shown in Figure 2.4b. When a temperature difference is set across an n-type semiconductor, the majority charge carriers, in this case electrons, tend to diffuse towards the cold side of the material. If the material is p-type, holes diffuse towards the cold side. The unbalanced density of charge carriers across the material sets up a voltage difference. At steady state, the flow of charge carriers due to the temperature difference is equilibrated by an opposite flow of charge carriers due to the voltage difference. Based on this definition, \( \alpha \) is positive for p-type materials and negative for n-type. The phenomenon has some similarities to the spatial gradient in gas particle density that occurs when a temperature gradient is applied to an enclosed gas.

![Figure 2.4.](image)

**Figure 2.4.** (a) Scheme of Seebeck effect. (b) Diffusion of majority charge carriers due to a temperature gradient.

To try to find a physical interpretation of the Seebeck coefficient, we can look at the Seebeck effect from a simplified thermodynamic perspective. Let us consider a closed system where one side is kept at \( T_h \) and other side is kept at \( T_c \) with \( T_h > T_c \) and \( \Delta T = T_h - T_c \).
such that a charge carrier density gradient is developed, thus, an electrochemical potential, $\Delta V$, is also developed. In a stationary state, the electrical energy required to transfer $n$ electrons from the hot side to the cold side against the voltage should equal the thermal energy transported or

$$ne\Delta V = \Delta s\Delta T$$

where $\Delta s$ is the change in entropy density. Using eq. 2.7, we can rearrange the expression to:

$$\alpha = \frac{-\Delta s}{ne}$$

This suggests that electrons carry heat (or entropy) and that the physical interpretation of the Seebeck coefficient is the “entropy per carrier”. However, one must be careful trying to use eq. 2.9 since there are several factors that have not been considered (heat transport by lattice vibrations, other sources of entropy, irreversible processes...). A more rigorous thermodynamic study of the Seebeck effect requires use of non-equilibrium thermodynamics, since electrical and heat transport phenomena are involved. For this, the author refers to the Onsager-Callen theory [1-3] and the work by Goupil et al. [4]. Nevertheless, the physical interpretation of the Seebeck coefficient as the “entropy per carrier” still stands.

A widely used equation for the Seebeck coefficient is the Boltzmann formulation [5]:

$$\alpha = \frac{1}{e} \left( \frac{\int_{0}^{\infty} (E - E_F) \frac{\partial f}{\partial E} D(E) v^2 \tau(E) dE}{\int_{0}^{\infty} \frac{\partial f}{\partial E} D(E) v^2 \tau(E) dE} \right)$$

eq. 2.10
where $\frac{\partial f}{\partial E}$ is the derivative of the Fermi function, also called the Fermi window, which peaks at the Fermi level, $v$ is the group velocity and $\tau(E)$ is the relaxation time.

The term $\frac{(E - E_F)}{T}$ in eq. 2.10 is related to the entropy change in a solid due to the addition of an electron to an electronic state of energy $E$ [6]. The electrons above the Fermi level carry positive entropy, $\frac{(E - E_F)}{T} > 0$, and contribute positively to the Seebeck coefficient while electrons below the Fermi level carry negative entropy, $\frac{(E - E_F)}{T} < 0$, and contribute negatively. A non-zero Seebeck coefficient implies imbalance between these two contributions, which strongly depend on the position of the Fermi level [5]. The level of imbalance between these two contributions also depends on how $D(E)$ changes with energy ($\frac{\partial D(E)}{\partial E}$) near the Fermi level. Figure 2.5 shows these contributions for a metal and a heavily doped semiconductor. In metals, the Fermi level lies within a band where $D(E)$ slightly changes with $E$ (small $\frac{\partial D(E)}{\partial E}$). In this case, the contribution from the electrons above the Fermi level is compensated by the contribution from the electrons below the Fermi level. Indeed, in general, metals have low Seebeck coefficients. In the case of the heavily doped semiconductor, the band gap prohibits electrons below the Fermi level (which would contribute negatively) and, therefore, a large Seebeck coefficient is expected. However, in this latter case the concentration of electrons is lower, and the electrical conductivity is smaller.
Figure 2.5. Diagram explaining the positive and negative contributions to the Seebeck coefficient as a function of the Fermi level position with respect the conduction band for a metal and a heavily doped semiconductor.

2.1.4.3 Thermal conductivity

The thermal conductivity, $\kappa$, of a solid is defined with respect to the steady-state flow of heat, $q$, with a temperature gradient.

$$q = \kappa \nabla (-T)$$

eq. 2.11

The process of thermal energy transfer is a random process. Energy diffuses through the solid encountering frequent collisions, which brings into play the existence of a mean free path [7]. Applying the kinetic theory of gases to solids yields the following expression for the lattice thermal conductivity, $\kappa_L$:

$$\kappa_L = \frac{1}{3} C v_L \ell$$

eq. 2.12

where $C$ is the lattice (phonons) heat capacity per unit volume, $v_L$ is the phonon velocity and $\ell$ is the phonon mean free path.

The phonon mean free path is determined principally by geometrical scattering (i.e. scattering by grain boundaries or imperfections) and scattering by other phonons. The
number of excited phonons with which another phonon can interact is proportional to $T$. Since the collision frequency of a phonon is proportional to the number of phonons with which it can collide, $\ell$ is proportional to $1/T$ when the primary mechanism of thermal resistance is phonon scattering.

Geometrical effects can also limit the mean free path. Geometrical effects may include grain boundaries, chemical impurities, lattice imperfections and amorphous structures. When the length scale between these geometrical effects becomes comparable to the phonon mean free path, scattering by geometrical effects becomes the dominant mechanism and $\kappa_L$ takes the following expression [7]:

$$\kappa_L = C v_L L_{GE} \text{ eq. 2.13}$$

where $L_{GE}$ is the characteristic length between the geometrical effects, which is independent of $T$.

In the above discussion, we assumed that phonons carry all the heat current. However, we stated earlier that electrons also act as heat carriers. Hence, the total thermal conductivity, $\kappa$, has a lattice contribution, $\kappa_L$, and an electronic contribution, $\kappa_e$. The Wiedemann-Franz law relates $\kappa_e$ to the electrical conductivity, $\sigma$ [7,8]:

$$\kappa_e = \sigma LT \text{ eq. 2.14}$$

where $L$ is the Lorenz number, which for simple metals takes the following expression:

$$L = \frac{\pi^2}{3} \left( \frac{k}{e} \right)^2 = 2.45 \cdot 10^{-8} (V/K)^2 \text{ eq. 2.15}$$

Therefore, we can write the following expression for $\kappa$:

$$\kappa = \kappa_L + \kappa_e = \frac{1}{3} C v_L \ell \sigma LT \text{ eq. 2.16}$$
For metals, the electronic contribution usually dominates due to the high electrical conductivity, while for insulators the lattice contribution dominates. In the case of semiconductors both contributions can be significant.

2.2 Fundamentals of conducting polymers

2.2.1 Brief history of conducting polymers

The IUPAC defines a polymer as “a molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.” With uses ranging from fabrics to food packaging, polymers are among the most widely used and important type of materials today. Historically, polymers have been always classified as insulating materials unable to conduct electricity. However, one of the most important breakthroughs in the field was the discovery of conducting polymers in 1977. Alan J. Heeger, Hideki Shirakawa, and Alan G. MacDiarmid published the discovery and investigation of doped polyacetylene (Figure 2.6a), the simplest conjugated polymer that demonstrated an enormous electrical conductivity when doped with halogens [9,10]. In 2000, they were honored with the Nobel Prize in chemistry for this discovery. However, the starting point of conducting polymers dates more than a century before these publications. In 1862, H. Letheby electropolymerized aniline sulfate, yielding a deep blue solid layer on a platinum electrode [11]. Although the nature of the colored product remained unknown at that moment, it is now known as the birth of polyaniline. Later disputes between Richard Willstätter and Arthur G. Green resulted in a deeper understanding of polyaniline and its oxidized states (Figure 2.6b) [12-14]. Nevertheless, it was Marcel Jozefowicz and his group in 1967, who first presented polyaniline as a conductive polymer, having an electrical conductivity in the 10 to 10^{-4} S cm^{-1} range depending on the protic doping [15].
Parallel to the development of polyaniline, the first group of conducting heterocycle polymers appeared, the polypyrroles (Figure 2.6c). In 1963, D.E. Weiss, B.A. Bolto and co-authors described the electronic conduction and chemical structure of polypyrrole [16-18]. And later, in 1967, A. G. Davies and co-authors investigated the polymerization of polythiophenes (Figure 2.6d) as potential candidates for conducting polymers [19].

All these reports led to an exciting period of discovery and development in the field of conducting polymers. Most of the advances during this period, from the 1970s to the 1980s, resulted from improvements in the reproducibility and synthesis of pure polymers with known molecular weight and degree of doping [20]. In 1987, a decade after the discovery of polyacetylene, Naarmann and Theophilou set the world record in electrical conductivity for an organic material at 100,000 S cm⁻¹ with stretched, iodine-doped polyacetylene [21]. However, by the end of the 1980s, the electrical conductivity stability of all these polymers had become an issue. Münstedt wrote that the reason for “the lack of significant technical use of intrinsically conducting organic materials is that of ageing problems” [22] and suggested that the carbenium ion-structures of polyacetylene, polypyrrole, polythiophene, and polyacetylene were not stable under oxygen or humid conditions. Nevertheless, polypyrrole and polythiophene offered slightly higher environmental stability because the electron donating function of the N or S ring atoms stabilizes the conjugated system. Incorporating oxygen substituents at the 3- and 4-positions in the thiophene ring yielded further stability. This led to the invention of poly(3,4-ethylenedioxythiophene) (PEDOT) (Figure 2.6e) by the Bayer AG researchers Jonas and Heywang [23]. PEDOT emerged as a highly conducting polymer with high stability in air, high temperatures and humidity. Later, PEDOT was even made processable
in water by including a water soluble counterion, poly(styrenesulfonate) (PSS), during synthesis to yield the polyelectrolyte complex PEDOT:PSS [24] (Figure 2.6f). Since then the field of conducting polymers has increasingly grown and conducting polymers such as polyaniline, polypyrrole, poly(3-alkylthiophene) and PEDOT are now commercially available and investigated for a wide range of applications.

**Figure 2.6.** Chemical structure of (a) trans-polyacetylene, (b) polyaniline (emeraldine base), (c) polypyrrole, (d) polythiophene, (e) PEDOT and (f) polymer complex PEDOT:PSS showing the negative charges of the counterion stabilizing the positive charges of doped PEDOT.
2.2.2 Transport in conducting polymers

2.2.2.1 Origin of the electrical conductivity

Conductive polymers are conjugated polymers in which a $\pi$ system is formed along the polymer backbone due to single-double bond alternation (sometimes also involving heteroatoms). The carbon atoms form three $\sigma$-bonds and the remaining $p_z$ orbitals engage in the $\pi$ system. The orbital interaction between monomer units leads to energy level splitting forming bonding $\pi$, and antibonding $\pi^*$, orbitals. In long polymer chains this interaction leads to the formation of energy bands similar to metals and semiconductors [25]. Figure 2.7 depicts this using polyacetylene as an example. In polyacetylene each carbon atom forms two $\sigma$-bonds with two other carbons and one with a hydrogen atom. The $p_z$ electron remaining contributes to the $\pi$ system.

![Diagram of polyacetylene and $p_z$ orbitals](image)

**Figure 2.7.** $p_z$ orbital energy splitting as a function of the number of carbon atoms leading to the formation of energy bands in polyacetylene.

Pristine conjugated polymers have a filled valence band and an empty conduction band separated by an energy gap and are typically semiconductors. Similar to inorganic semiconductors, they show low electrical conductivity in their pristine (undoped or neutral)
state. The electronic properties of conductive polymers can be changed by chemical doping or electrochemical doping, in both cases through oxidation or reduction reactions. The introduction or removal of an electron by reduction or oxidation, respectively, leads to the formation of a polaron. A polaron is a charge state accompanied by a structural distortion. The structural distortion introduces changes in the energy level structure. Figure 2.8 shows how the energy levels change for the case of a positive polaron (removal of an electron). One energy level from the conduction band and one level from the valence band are moved into the band gap. An electron is removed from the level moved up from the valence band leaving an unpaired electron behind. If a second electron is removed, a positive bipolaron is formed. A positive bipolaron also has two energy levels within the energy gap, but both are empty. At high oxidation levels, polaron and bipolaron states within a polymer chain can overlap (intra chain coupling in Figure 2.9) forming a one-dimensional polaron or bipolaron band [26]. If the polymer in the solid state is in an amorphous phase, the weak inter-chain electronic coupling does not allow for these bands to extend in three dimensions and localized states appear within the energy gap. In the case of crystalline domains, the short inter-chain distance can result in the overlap of the \( \pi \)-systems resulting in delocalization and formation of polaron or bipolaron networks (Figure 2.9). In a polaron network the Fermi level lies within the half-filled polaron band and the polymer shows metallic behavior (Figure 2.10a). In the case of a bipolaron network, the Fermi level lies in between the bipolaron and the valence bands and the polymer behaves as a semimetal (Figure 2.10b) [27].
Figure 2.8. Band structure changes in conjugated polymers: (a) a neutral chain, (b) a chain carrying a positive polaron and (c) a chain carrying a bipolaron.

Figure 2.9. Intra-chain and inter-chain coupling of bipolaron wavefunctions in polythiophene, which is the origin of bipolaronic bands or networks.

Figure 2.10. Band structure of (a) polaron network and (b) bipolaron network.
2.2.2.2 Charge transport models in conjugated polymers

In spite of the recent developments in the field of conducting polymers, there are still difficulties on determining the transport mechanism of these materials, which is far from being traditionally metallic [28]. These difficulties are related to the fact that conducting polymers are located on an intermediate level in the order-disorder scale as opposed to traditional crystalline metals and semiconductors. Generally, conductive polymers in the solid state show low levels of crystallinity. Structural disorder leads to electronic localization and the appearance of a tail of localized states that extends into the band gap [27,29,30]. Because of such structural disorder, transport models for amorphous semiconductors have been used to model charge transport in conducting polymers. One such model is Mott’s law for variable range hopping (VRH), [5,31] which is used to describe transport in disordered systems by electron hopping between localized states:

$$\sigma(T) = \sigma_0 \exp \left[ -\left( \frac{T_0}{T} \right)^{\gamma} \right]$$

Here $\gamma$ is a parameter that depends on the dimensionality of transport taking values of 0.5, 0.33 and 0.25 for 1D, 2D and 3D VRH transport, respectively. $T_0$ can be interpreted as an effective energy barrier between localized states. $\sigma_0$ is a pre-exponential factor that is also temperature dependent, however, its temperature dependence is often neglected due to the stronger temperature dependence of the exponential [31].

There are some unique features that differentiate conducting polymers from traditional semiconductors. For example, in conjugated polymers dopant ions (or counterions) are positioned at interstitial sites between the polymer chains as opposed to semiconductors where dopants are usually substituted directly into the crystal structure. Further, as opposed to the 3D covalent bond structure of traditional semiconductors,
conducting polymers are comprised of covalently bonded 1D polymer chains with weak interchain coupling [32]. Although, strong electronic coupling occurs within the polymer backbones, interchain transport is required in a typical material since no macroscopic transport can occur from a single individual chain. This requirement is quite important since it makes π-stacking of polymer chains very relevant for charge transport [29]. In conjugated polymers, chains can π-stack forming crystalline regions where the electronic charges are delocalized. These regions can be expected to show metallic behavior as for traditional metals. However, these metallic regions are separated by regions of disordered chains where charge carriers are localized [27-30,32]. The metallic regions are connected by long polymer chains that extend from one crystallite to an adjacent one following a traditional fringed micelle model as shown in Figure 2.11 [33]. In this figure, darker regions represent more ordered metallic domains, while lighter regions represent less conductive amorphous regions. In such microstructure, charges must overcome an energy barrier to move from one metallic region to another through the amorphous or more disordered regions. The quasi-1D VRH model has been proposed to explain conduction in this case, where metallic regions are connected by 1D chains [32]:

\[
\sigma(T) = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{\frac{1}{2}} \right]
\]

eq. 2.18
Figure 2.11. Scheme representing the microstructure of semi-crystalline conjugated polymers. The darker regions represent ordered domains of high conductivity where polymer chains have efficient $\pi-\pi$ stacking. Lighter regions represent amorphous regions with weak interchain coupling, leading to charge localization and thus low conductivity. Long polymer chains (in red) act as bridges between the different ordered regions.

Since long polymer chains are needed to bridge metallic regions, the molecular weight of the polymer is expected to play an important role. Indeed, Noriega et al. [29] studied the effect of molecular weight on charge carrier mobility using poly(3-hexylthiophene) (P3HT). They found that initially the mobility increased as the molecular weight increased, i.e. the average chain length increased. However, at high-molecular weights the mobility reached a plateau (Figure 2.12). This behavior was explained as a trade-off between connectivity of the ordered regions and disorder induced by the long polymer chains. Short polymer chains (low molecular weight) can efficiently stack forming crystalline regions with low degrees of disorder. However, the lack of long polymer chains limits connectivity between these crystalline regions. On the other hand, at high molecular weights, long chains provide enough connectivity between the crystalline regions, but also increase the structural disorder in them (Figure 2.12).
Interestingly, for the polymers studied by Noriega et al. [29], the plateau occurred for chains that were around 50-100 monomer units long. However, recently, Rolland et al. [34] provided theoretical evidence that this plateau also occurred for PEDOT:Tosylate but at much lower molecular weights (at around 9-12 monomer units). This result could explain the high electrical conductivity ($> 10^3$ S/cm) of PEDOT despite its typically low molecular weight (usually between 8-12 monomer units).

2.2.2.3 Model for the thermoelectric power

Eq. 1.10 can be used to derive the Seebeck coefficient for a metal where conduction occurs by motion of electrons at the Fermi level in delocalized states [35,36]:

$$\alpha_m(T) = \frac{\pi^2 k^2 T}{3 e} \left( \frac{d\ln\sigma(E)}{dE} \right)_{E=E_F}$$  \hspace{1cm} \text{eq. 2.19}

Here, $\sigma(E)$ is the electrical conductivity that would be found in the metal for electrons of energy, E. From eq. 2.19, it can be demonstrated [35,36] that $\alpha_m(T) \propto T$ at
high temperatures. If the states are localized and the conduction is instead by hopping between localized states eq. 2.20 can be obtained [37]:

$$\alpha_{VRH}(T) = \frac{k}{2e kT} \left(\frac{d\ln\sigma(E)}{dE}\right)_{E=E_F} \propto \frac{W^2}{T}$$

eq 2.20

where $W$ is the range of energy contributing to the conduction and can be considered as the hopping energy. For 3D VRH, $W \sim k(T_0 T^3)^{1/4}$ and eq. 1.20 gives $\alpha_{3D}(T) \propto T^{1/2}$ [36].

In quasi-1D VRH, the interchain hopping gives $W \sim k(T_0 T)^{1/2}$, and the intrachain hopping, $W \sim kT_0$. The total thermoelectric power is the sum of both contributions and thus, eq. 2.20 yields $\alpha_{1D}(T) \propto 1/T$ [37].

All these contributions can exist in conductive polymers stemming from the metallic character of the ordered regions and the hopping between localized states in the disordered regions. Therefore, a generalized formula can be used for $\alpha(T)$ that accounts for all contributions [32]:

$$\alpha(T) \propto \frac{A_{1D}}{T} + A_{3D} T^{1/2} + A_m T$$

eq 2.21

where $A_{1D}$, $A_{3D}$ and $A_m$ are coefficients related to the volume fraction and electrical conductivity of each domain. Typically, one contribution will be dominant for a certain sample crystallinity and temperature range.

2.2.2.4 Thermal conductivity of polymers

Polymers are typically considered thermally insulating materials with low thermal conductivities on the order of 0.1-1 Wm$^{-1}$K$^{-1}$. However, polymers can in principle achieve greater thermal conductivities than common metals. Indeed, Choy et al. [38,39] demonstrated in the late 1970s that oriented polyethylene could have a thermal conductivity of 14 Wm$^{-1}$K$^{-1}$, comparable to that of stainless steel (10 Wm$^{-1}$K$^{-1}$). More
recently, Shen et al. [40] obtained a record value of 104 Wm$^{-1}$K$^{-1}$ for ultra-drawn polyethylene nanofibers, which is on the same order of magnitude of metals such as aluminum, gold, or copper. Henry et al. [41] using molecular dynamics simulations estimated that the thermal conductivity of a single polyethylene chain could reach 350 Wm$^{-1}$K$^{-1}$.

The reason for the typically low thermal conductivity of polymers resides in their complicated morphology. A single polymer chain can be considered as a 1D crystal in the sense that atoms only arrange periodically in one dimension. In such a system, the number of phonon scattering events is limited and, the mean free path of phonons is increased. Thus, the thermal conductivity is increased (see eq. 2.12). In fact, a theoretical 1D periodic chain [42] can have infinite thermal conductivity and even an individual polyethylene chain [41] can reach incredibly high thermal conductivity given certain conditions. On the other hand, bulk polyethylene has a low thermal conductivity of ~0.33-0.50 Wm$^{-1}$K$^{-1}$ because the chains are entangled and not oriented. The highly entangled and curved nature of polymer chains reduces the thermal conductivity as phonons encounter frequent scattering events [43]. Therefore, increasing crystallinity and alignment of the polymer chains increases the thermal conductivity.

The interaction between different chains also seems to decrease the thermal conductivity. Henry et al. [44] showed by molecular dynamics simulations that starting from an individual polyethylene chain (1D), the thermal conductivity decreased when stacking individual chains into a single sheet (2D) and decreased further when stacking sheets into a single crystal (3D). The decrease in conductivity is attributed to the anharmonic phonon-phonon scattering by neighboring chains. Interestingly, these results
suggest that stronger interchain coupling could lead to decreased thermal conductivity in the chain axis direction.

Molecular weight also affects the thermal conductivity of polymers. Phonons can propagate more easily along chains than between chains and are scattered at chain ends, commonly known as boundary scattering. Thus, increasing molecular weight increases the thermal conductivity for relatively low molecular weights. At higher molecular weights, the phonon mean free path is limited by other scattering events (intramolecular scattering, intermolecular scattering, impurity scattering, etc.) and, thus, the thermal conductivity becomes independent of molecular weight changes.

In general, phonons are affected by multiple scattering processes (phonon-phonon, phonon-impurity, phonon-boundary, phonon-electron). The Matthiessen rule provides a way to combine the effects of all these scattering processes into a single relaxation time, $\tau$ [43]:

$$\frac{1}{\tau} = \sum \frac{1}{\tau_i}$$

where $\tau_i$ is the relaxation time due to the scattering mechanism $i$. The phonon mean free path can be calculated as the product of the relaxation time and the phonon velocity, $\ell = \nu L \tau$. Phonon velocities are intrinsically related to elastic moduli. The carbon-carbon bond is one of the stiffest bonds, leading to the highest phonon velocities [43]. Thus, carbon-based materials such as diamond, carbon nanotubes or graphene, all have high thermal conductivities. Polymer backbones are typically made of carbon-carbon bonds; therefore, it is not a coincidence that individual polymer chains can also have high thermal conductivities.
Thermal transport in polymers has been mostly studied for polyethylene, however, conjugated polymers have the potential to achieve even higher thermal conductivities. This is because the carbon double bond due to sp² hybridization present in conjugated polymers is stiffer than the single carbon-carbon bond. Additionally, the delocalized π-bond constrains the backbone to a plane, thereby increasing the stiffness of segmental rotation [45]. At the present time, thermal conductivities as high as 2.2 Wm⁻¹K⁻¹ and 13 Wm⁻¹K⁻¹ have been measured for oriented P3HT and polyacetylene, respectively [46,47].

2.2.3 The case of poly(3,4-ethylendioxythiophene) (PEDOT)

After the discovery of conducting polymers, the challenge switched to find structures that were stable in air and humid atmospheres. Conjugated polymers with heterocycles were rapidly identified as potential candidates due to the electron donating function of the nitrogen atom in polypyrroles (Figure 2.6c) and the sulfur atom in polythiophenes (Figure 2.6d). Additionally, substituting oxygen bearing functional groups at the 3- and 4-position in polythiophene was found to further stabilize the doped state of the polymer due to additional resonance states (Figure 2.13) [48]. This led to the chemical polymerization of PEDOT from the monomer 3,4-ethylendioxythiophene (EDOT). PEDOT is stable in its doped state in humid air and is capable of achieving high electrical conductivity.
Figure 2.13. Polaron stabilization by additional resonance states in oxygen group substituted polythiophenes.

2.2.3.1 Oxidative polymerization of EDOT

The first synthetic route that was used to produce PEDOT was the so-called oxidative polymerization using iron (III) chloride (Figure 2.14) [48]. This reaction yields doped PEDOT$^+$ stabilized by the counterion FeCl$_4^-$ (or PEDOT:FeCl$_4$) in the form of an insoluble powder with high electrical conductivity.

Figure 2.14. Oxidative polymerization of EDOT to obtain PEDOT using iron (III) chloride as oxidant.

The oxidant salt can be changed to obtain PEDOT with different counterions. For example, a very common oxidant is iron (III) tosylate, to yield PEDOT:Tosylate (PEDOT:Tos) [26,27,49]. The oxidative polymerization usually results in an insoluble intractable powder that is very difficult to process. An important breakthrough in the field was the realization that by adding the water-soluble polymer PSS to the reaction mixture,
the oxidative polymerization of EDOT yields a water-stable dispersion of PEDOT with PSS serving as the counterion (PEDOT:PSS). This dispersion can be processed into films or other geometries using common solution processing techniques such as drop casting, spin coating, doctor blading, spray coating, etc. Moreover, other synthesis routes exist to \textit{in situ} polymerize the material in the substrate of choice. These routes include oxidative chemical vapor deposition (oCVD) \cite{50,51}, vapor-phase polymerization (VPP) \cite{52,53} and electrochemical polymerization \cite{54,55}.

2.2.3.2 \textit{Crystal structure of PEDOT}

\textbf{Figure 2.15} shows a scheme of the crystal structure of PEDOT. The PEDOT chains stack overlapping their $\pi$ orbitals ($\pi-\pi$ stacking) along the $b$-axis with the backbones aligned along the $c$-axis. Lamellae of PEDOT and counterion (shown as a blank box in \textbf{Figure 2.15}) alternatively stack in the $a$-axis direction \cite{56}. The crystal unit cell of PEDOT is orthorhombic (three mutually perpendicular axes of unequal length). The distance $a$ corresponds to the lamella stacking distance of PEDOT and counterion, and, thus, depends on the counterion size. The distance $b/2$ is the $\pi-\pi$ stacking distance between PEDOT chains, and the distance $c$ corresponds to the length of two monomer units of PEDOT. Values for these distances are shown in \textbf{Table 2.1} for different counterions. As can be observed, the main variations in unit cell distance from different counterions occur in the lamellar stacking distance $a$. Small anions such as $Cl^-$ allow for a closer stacking of the PEDOT chains in the $a$-axis direction, while bulky counterions such as PSS result in large stacking distances. The $\pi-\pi$ stacking distance of PEDOT stacks ($b/2$) is commonly found to be around 3.4-3.6 Å which is in good agreement with other poly(3-alkylthiophene)s \cite{56}. 

33
The polymer repeat distance is typically around 7.8 Å in agreement with the length of two monomer units of PEDOT.

Figure 2.15. Schematic representation of the crystal structure of PEDOT.

Table 2.1. Values of the unit cell distances of the PEDOT crystal for different counterions.

<table>
<thead>
<tr>
<th>Counterion</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Tos^- )</td>
<td>14.0</td>
<td>6.8</td>
<td>7.8</td>
<td>[56]</td>
</tr>
<tr>
<td>( PF_6^- )</td>
<td>15.2</td>
<td>6.8</td>
<td>7.7</td>
<td>[57]</td>
</tr>
<tr>
<td>( OTf^- )*</td>
<td>14.0</td>
<td>6.8</td>
<td>7.8</td>
<td>[58]</td>
</tr>
<tr>
<td>( ClO_4^- )</td>
<td>13.2</td>
<td>4.2**</td>
<td>14.2**</td>
<td>[59]</td>
</tr>
<tr>
<td>( Cl^- )</td>
<td>11.0</td>
<td>4.6**</td>
<td>7.9</td>
<td>[60]</td>
</tr>
<tr>
<td>( PSS^- )</td>
<td>22.0</td>
<td>6.8</td>
<td>7.8</td>
<td>[58]</td>
</tr>
<tr>
<td></td>
<td>23.0</td>
<td>7.0</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td>( SO_4^{2-} )</td>
<td>13.4</td>
<td>7.5</td>
<td>-</td>
<td>[62]</td>
</tr>
</tbody>
</table>

*Trifluoromethanesulfonate.

**These values are significantly different to the typical values found in literature without clear explanation.
In terms of crystallinity, small counterions usually promote higher degrees of crystallization. The use of large counterions such as PSS decreases the degree of crystallinity, leading to broad amorphous peaks in the X-ray diffraction pattern [63].

2.2.3.3 Morphology of PEDOT:PSS

Despite the inherently low crystallinity of PEDOT:PSS, the fact that it can be obtained as a water-dispersion and be solution-processed makes PEDOT:PSS a very attractive conducting polymer. PEDOT and PSS form what is called a polyelectrolyte complex. Polyelectrolyte complexes are typically formed by mixing aqueous solutions of oppositely charged polyelectrolytes (commonly named polycations and polyanions) [64]. The Coulomb forces between the two oppositely charged polymers lead to the formation of these complexes that can be water-soluble or insoluble [48]. On one hand, if the polyelectrolytes are mixed in a stoichiometric fashion, insoluble complexes are formed. On the other hand, if one of the polyelectrolytes is in excess, water-soluble particles are formed. Water solubility is improved if the molecular weight of the component in excess is significantly larger than the other component. In the case of PEDOT:PSS, PEDOT is positively charged and acts as the polycation while PSS is negatively charged an acts as the polyanion. PSS as a counterion to PEDOT is always used in excess and has a much higher molecular weight than PEDOT (typically 5-18 EDOT monomers). In fact, commercial formulations have PEDOT:PSS weight ratios in the range of 1:2.5 to 1:20. In water, PEDOT and PSS form stable suspensions of gel particles with a core-shell structure (Figure 2.16). The core is rich in hydrophobic PEDOT segments while the shell is rich in hydrophilic PSS chains [65]. The electrostatic repulsion between gel particles due to the negatively charged PSS-rich shells is what stabilizes the dispersions [48].
Figure 2.16. Scheme of the polyelectrolyte complex structures of PEDOT:PSS showing the PEDOT-rich core (red shadow) – PSS-rich shell (green shadow) gel particles found in PEDOT:PSS water dispersions.

2.2.3.4 Electrical conductivity of PEDOT:PSS

As-processed films of PEDOT:PSS usually have low electrical conductivities in the order of 0.1-1 S/cm. This is because when the colloidal gel particles of PEDOT:PSS are deposited on a substrate and subsequently dried, the core-shell structure is maintained yielding electrically conductive PEDOT-rich domains separated by electrically insulating PSS-rich areas that act as energy barriers for charge transport [65,66].

The electrical conductivity of such films can be improved by secondary doping. Secondary doping refers to the addition of an apparently inert material that induces structural changes in the organization of the polymer chains, leading to conductivity increases up to several orders of magnitude [67]. Secondary doping is not to be confused with primary doping. Primary doping is similar to traditional doping of inorganic semiconductors. However, while traditional semiconductor doping is achieved by substituting impurity atoms into the lattice, in conductive polymers the dopant is a redox agent that either oxidizes (p doping) or reduces (n doping) the polymer chains, thus, changing the charge carrier concentration. One of the main differences between primary
and secondary doping of polymers is that primary doping is a reversible process while secondary doping is irreversible from a spatial and structural point of view.

Typical secondary dopants for PEDOT:PSS are polar solvents with high boiling points such as dimethyl sulfoxide (DMSO) and ethylene glycol (EG). The increase in electrical conductivity can be achieved by either directly adding the secondary dopant to the PEDOT:PSS water dispersion before processing it into film (additive method) or by post-treating the polymer film with the secondary dopant (post-treatment method), e.g. immersing the film in the solvent. Kim et al. [68] reported for the first time the increase of the electrical conductivity of PEDOT:PSS from 0.8 to 80 S/cm by addition of DMSO to the water dispersion. Later, optimization of the process resulted in values in the range of 500-700 S/cm [69]. The increase in electrical conductivity using the additive method is attributed to morphological changes that occur in the material during drying. Water evaporates first from the material due to its lower boiling point leaving behind a solvent mixture rich in secondary dopant. Here, the polar secondary dopant can screen the coulombic interactions between PEDOT and PSS allowing for the PEDOT chains to rearrange in a more favorable way for charge transport [48] (i.e. increase of PEDOT crystallite size and improving π-π interactions between PEDOT stacks [70]). On the other hand, post-treating the PEDOT:PSS samples with secondary dopants also induces these morphological changes and, additionally, can remove excess of insulating PSS. By combining addition of secondary dopant and post-treatments (also with secondary dopants), conductivity values above 1000 S/cm can be achieved [71,72].

On a similar note, recently, the post-treatment of PEDOT:PSS films with sulfuric acid has proven to significantly improve the electrical conductivity to values above those
typically achieved by traditional secondary dopants. PEDOT:PSS films post-treated with dilute sulfuric acid (~1 M) can achieve electrical conductivity values of 2000-2500 S/cm [73,74]. Moreover, if concentrated sulfuric acid is used, the enhancement is more pronounced and electrical conductivity values around 3700-4200 S/cm have been reported [61,75]. The exact mechanism for the enhancement of the electrical conductivity by sulfuric acid treatment is still a topic of discussion in the field. While there seems to be agreement on the effectiveness of sulfuric acid to remove insulating PSS (more effective than DMSO and EG) and promote the crystallization of PEDOT, it is not clear whether sulfate ions partially substitute PSS as counterions and/or if the sulfuric acid treatment induces primary doping of the PEDOT chains, thereby increasing the charge carrier concentration. For example, Xia et al. [73] reported Fourier-transform infrared spectroscopy (FTIR) data of sulfuric acid-treated PEDOT:PSS that suggested that sulfate ions remained in the PEDOT:PSS film even after water wash. However, Kim et al. [61] ruled out the possibility of sulfuric acid to act as dopant or counterion and suggested that it only served as a solvent for PSS.

In terms of transport mechanism, the electrical conductivity of PEDOT:PSS has been typically modelled using 1D-VRH transport (eq. 2.18) describing metallic conductivity in the PEDOT-rich domains moderated by 1D-hopping through insulating PSS barriers [27,76]. The characteristic hopping temperature, $T_0$, has been reported to be 1901 K for pristine PEDOT:PSS [73], 360 K for a EG-treated PEDOT:PSS [77] and 29 K for sulfuric acid-treated PEDOT:PSS [73]. This decrease in $T_0$ indicates a reduction in the energy barrier for hopping by secondary doping, and more effectively by sulfuric acid treatment.
2.2.3.5 *Seebeck coefficient of PEDOT:PSS*

Doped PEDOT:PSS typically has a Seebeck coefficient around 15-20 μV/K [27,74]. Nevertheless, the Seebeck coefficient can be increased by de-doping using reducing agents such as hydrazine [78,79] and sodium borohydride [80]. De-doping reduces the concentration of polaron and bipolarons and increases the number of neutral chains, which in turn increases the Seebeck coefficient but decreases the electrical conductivity.

On the other hand, PEDOT:Tos has been reported to have larger values of $\alpha$ than PEDOT:PSS while also having high values of $\sigma$ [27]. This difference between PEDOT:PSS and PEDOT:Tos has been attributed to better ordering of PEDOT chains in PEDOT:Tos due to the lesser steric effects encountered by PEDOT chains when the smaller tosylate counterion is used instead of the bulky PSS. The increased order leads to delocalization of charge carriers, decreasing the number of localized states near the Fermi level that contribute to charge transport [27].

Acid treatments have also been reported to slightly increase the Seebeck coefficient of PEDOT:PSS [74,81]. The mechanism behind the enhancement in this case is not clear in the literature, although it is believed that it could be related to the increased order of the PEDOT chains after the effective PSS removal by the acid treatment [74].

2.2.3.6 *Thermal conductivity of PEDOT:PSS*

Thermal conductivity of PEDOT:PSS is typically measured between 0.2-0.6 Wm$^{-1}$K$^{-1}$ [82-84]. Thin films are usually anisotropic with the in-plane thermal conductivity being higher than the out-of-plane thermal conductivity [82]. This anisotropy stems from the polymer chains lying in-plane and parallel to the substrate rather than perpendicular to it. Additionally, the thermal conductivity of PEDOT:PSS was reported to decrease from
0.38 to 0.30 Wm$^{-1}$K$^{-1}$ upon removal of PSS by secondary dopants [84]. For high electrical conductivity PEDOT:PSS samples, the electronic contribution to the thermal conductivity can be significant. Liu et al. [85] found that the electronic contribution of the thermal conductivity for PEDOT:PSS followed the Wiedemann-Franz law (eq. 2.14) with the conventional Sommerfeld value for the Lorenz number (eq. 2.15).

2.3 Conclusions

This chapter has first introduced basic concepts related to transport in the solid state and then explored how those basic concepts are applied to transport in conducting polymers. Several of these concepts will be very useful to the reader in subsequent chapters.

Conducting polymers are relatively new compared to traditional insulating polymers and there are several areas that are still a topic of discussion and controversy within the field. The fiber geometry offers some unique advantages to explore these areas. Therefore, this dissertation not only focuses on the fabrication and development of high performance electrically conducting PEDOT:PSS fibers for electronic textiles, it will also investigate some of the more fundamental questions raised during this introductory chapter. For instance, in Chapter 4 we explore the effect that preferred alignment of polymer chains has in the electrical, thermoelectric, thermal, and mechanical properties of PEDOT:PSS; and in Chapter 5 we study the mechanism by which sulfuric acid enhances the electrical conductivity of PEDOT:PSS.
2.4 References


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CHAPTER 3. EXPERIMENTAL METHODS AND CHARACTERIZATION TECHNIQUES

This chapter provides detailed description of the experimental methods and characterization techniques used through this dissertation. But, firstly, some nomenclature that will be widely used in this chapter and through the dissertation must be clarified. A set of fiber spools obtained during one single spin run is referred as a batch. Each of the individual spools that are part of a batch are referred as a sample. Finally, a portion of a sample (e.g. a certain length of fiber cut to be characterized) is referred as a specimen. All samples, regardless of if they pertain to the same batch (same spin run) or not and if they have been obtained using different processing parameters or not, are presented as different data points. Typically, several specimens from a sample are tested for a certain property to obtain an average value and standard deviation of said property for the sample. This means that in some cases two samples may have identical processing conditions but are presented as separate data points. This reveals insight into the reproducibility of the data.

3.1 Electrical conductivity

3.1.1 2-probe method

In this method, two electrical contacts are made to the specimen as shown in Figure 3.1a. Then, a current, \( I \), is passed through the specimen and the voltage drop, \( V \), is measured. Note that, since the voltage drop is measured using the same leads that carry the current, the voltage drop measured also includes the voltage drop due to the resistance of the leads and the contact resistance. A resistance, \( R_{\text{measured}} \), can be calculated using Ohm’s law and is equal to the sum of the specimen resistance, \( R_{\text{specimen}} \), and the contact resistance, \( R_{\text{contact}} \):
\[ R_{\text{measured}} = \frac{V}{I} = R_{\text{specimen}} + R_{\text{contacts}} \quad \text{eq. 3.1} \]

The electrical conductivity of a specimen can be obtained using:

\[ \sigma_{\text{specimen}} = \frac{1}{R_{\text{specimen}} A} \frac{L}{A} \quad \text{eq. 3.2} \]

where \( L \) is the length of the specimen and \( A \) is its cross-sectional area. By combining equations 3.1 and 3.2, the following expression can be obtained:

\[ R_{\text{measured}} = \frac{1}{\sigma_{\text{specimen}} A} L + R_{\text{contacts}} \quad \text{eq. 3.3} \]

Therefore, by measuring the resistance of different specimens with varying length the contact resistance can be found by plotting \( R_{\text{measured}} \) versus \( L \) as shown in Figure 3.1b. Once the contact resistance is known, equations 3.1 and 3.2 can be used to find \( \sigma_{\text{specimen}} \).

**Figure 3.1.** Scheme of (a) 2-probe configuration to measure electrical conductivity and (b) plot of \( R_{\text{measured}} \) versus \( L \) to obtain \( R_{\text{contacts}} \).

**3.1.2 4-probe method**

This method uses a different configuration to avoid the measurement of the contact resistance. In this case four electrical contacts are made to the specimen as shown in Figure 3.2. A current, \( I \), is passed through the two outer contacts while the voltage drop, \( V \), is measured using the two inner contacts. Since the contacts used to measure the voltage drop
and pass current are different, there is no voltage drop due to the leads or the contact resistance and $R_{\text{specimen}}$ can be directly calculated using Ohm’s law. Then, equation 3.2 can be used to obtain the specimen’s electrical conductivity. It must be noted that in this case, the value of $L$ to be used is the distance between the two inner contacts.

![Diagram of 4-probe configuration](image)

**Figure 3.2.** Scheme of the 4-probe configuration to measure electrical conductivity.

Typically, specimens were laid between two copper strips and contacted using silver paint. Then, the resistance was measured using a 2-probe method using a Keithley 2100 microvoltmeter. Initially, the resistance was measured using 4-probe. However, the contact resistance was found to be in all cases small (< 5%) compared to the total resistance of the specimens. Thus, it was decided to switch to a 2-probe method to reduce manipulation of the specimens. The electrical conductivity was calculated from the measured resistance, length and cross-sectional area of each specimen.

### 3.2 Seebeck coefficient

The Seebeck coefficient of the fibers was measured using a purpose-built setup (see **Figure 3.3**). Typically, specimens were laid between two Peltier devices that allowed for precise control of the temperature and contacts were made using silver paint. Two K-type thermocouples were used to monitor the cold-side and hot-side temperatures. The
Seebeck coefficient was extracted as the slope of the $\Delta V$-$\Delta T$ plots and corrected using the Seebeck coefficient of copper (1.9 $\mu$V/K).

![Diagram of the purpose-built setup used to characterize the Seebeck coefficient of the fiber specimens.](image)

**Figure 3.3.** Scheme of the purpose-built setup used to characterize the Seebeck coefficient of the fiber specimens.

### 3.3 Thermal conductivity

The thermal conductivity of the fibers was characterized in collaboration with Prof. Joseph Brill and Dr. Maryam Shahi from the Department of Physics and Astronomy of the University of Kentucky using a self-heating technique [1,2].

If a small current, $I$, flows through a wire of radius $r$ and length $L$, which is thermally grounded at temperature $T_0$ at its ends, the spatial ($z$) dependence of its temperature is governed by:

$$
\frac{I^2 \rho(T)}{\pi r^2} = 4 \sigma \varepsilon (2\pi r)T_0^3 T - \kappa(\pi r^2) \frac{d^2 T}{dz^2}
$$

**eq. 3.4**

Here $\rho$ is the electrical resistivity, $\kappa$ is the thermal conductivity, $\sigma$ the Stefan-Boltzmann constant, and $\varepsilon$ the emissivity, and we assume that the sample is in vacuum. To second order in current, the local temperature will then be:
\[ T(z) = T_0 + \frac{l^2 R}{\kappa L \alpha^2 \pi r^2} \left[ 1 - \frac{\cosh(\alpha z)}{\cosh(\alpha L/2)} \right] \]  

**eq. 3.5**

where \( \alpha \equiv \left[ 8 \sigma \varepsilon T_0^3 / (\kappa r) \right]^{1/2} \) and \( R \equiv L \rho (T_0) / (\pi r^2) \) is the resistance in the absence of Joule heating.

Then the change in the measured resistance will be:

\[ \frac{dR}{dI^2} = \frac{dR}{dT} \frac{1 - \tanh(\alpha L/2)}{\alpha L/2} \]  

**eq. 3.6**

Note that for negligible cooling by thermal radiation (small \( T_0 \) or \( \varepsilon \to 0 \)), eq. 3.6 reduces to:

\[ \frac{dR}{dI^2} \approx \frac{RL}{12\kappa \pi r^2} \frac{dR}{dT} \]  

**eq. 3.7**

The specimens were mounted in 4-probe configuration, with inner contacts separated by 5-7 mm, on four indium pedestals on a sapphire substrate with small drops of melted indium. Then, the resistance of the specimens was measured as a function of the applied current. The measurements were performed at liquid nitrogen temperature such that equation 3.7 could be used to extract the thermal conductivity. Also, measurements were done in vacuum for presumably dehydrated samples.

### 3.4 Scanning electron microscope (SEM)

Imaging of the fibers was performed on a Hitachi S-4800 field emission SEM at 10 kV accelerating voltage and 10 \( \mu \)A beam current. Gold sputtering of the samples was not needed due to the conductive nature of the fibers. Since the diameter of the fibers are needed to calculate the electrical conductivity, each specimen tested for electrical resistance was then placed in the SEM to obtain its average diameter. For each specimen
10 to 15 diameter values were measured at different points, which gave a total of 50-75 measured values per sample. The average value was taken as the average diameter of the sample and error bars represent standard deviation within the same sample. In the case of non-round fibers reported diameters are for an equivalent circular area. For imaging cross-sections, a bundle of fibers was immersed in liquid nitrogen and fractured using a razor blade. The bundle was then transferred to the SEM for imaging.

3.5 Mechanical characterization and linear density measurements

Fibers were tested in uniaxial tension using the automatic single-fiber test system, FAVIMAT+ from Textechno. The pretension was 0.50 cN/tex and the test speed was 5.0 mm/min over a gauge length of 25.4 mm (i.e., 1 inch). Values presented in this work are average values of at least 5 specimens per sample and error bars represent standard deviation.

Additionally, the FAVIMAT+ system was also used to measure the average linear density of each specimen tested using an ultrasonic resonance method. In this method the resonance frequency of the filament is measured at constant gauge length and known pre-tension. The linear density is then calculated using

\[ LD = \frac{T}{4f^2L^2} \]  

\text{eq. 3.8} 

where \( LD \) is the linear density, \( T \) is the applied pre-tension, \( f \) is the fundamental resonant frequency and \( L \) is the gauge length.

3.6 Wide-Angle X-ray Scattering (WAXS)

X-ray are scattered by electrons in materials. From the scattering pattern, information about the structure of the material can be deduced. In wide angle X-ray scattering (WAXS), the Bragg peaks scattered to wide angles by sub-nanometer to few
nanometer structures are analyzed, and it is often used to study the crystalline structure of polymers. 2D WAXS patterns, where the Bragg reflections appear as concentric rings or arcs in a 2D plane, are of particular interest to characterize preferred orientation of crystal planes in anisotropic structures. In 2D WAXS patterns, each ring corresponds to a different Bragg reflection (i.e. different crystal plane) being the radius of the ring proportional to the Bragg angle while the angle made by rotating the radius corresponds to the azimuthal angle (Figure 3.4a). In anisotropic structures with oriented crystal planes, the rings become arcs (which converge to points in ideal, perfectly oriented structures). Figure 3.4b shows a scheme of these concepts.

![Figure 3.4](image)

**Figure 3.4.** (a) Scheme of a 2D WAXS pattern and (b) changes in the scattering pattern as a function of the degree of orientation of the crystalline planes from random to perfect orientation.

Measurements were performed in transmission mode using the Xenocs Xeuss 2.0 SAXS/WAXS system located at the Electron Microscopy Center of the University of Kentucky. The source was GeniX³D Cu ULD 8 keV with wavelength of 1.54189 Å₁. Typically, several fibers were aligned into a bundle and placed in an aperture card. The

---

₁ This value of wavelength was obtained from the software installed in the equipment’s computer by the manufacturer.
aperture card with the aligned fiber bundle was then transferred to the WAXS sample holder and placed at 101.17 mm from the 2D detector (Dectris Pilatus 200 K). Exposure time was 600 s. Data processing to obtain the integrated diffracted intensity versus 2θ and azimuthal angle, Ψ, was performed using the software Foxtrot provided by Xenocs. To measure the WAXS diffraction pattern of unoriented PEDOT:PSS, films were prepared by drying some drops of dope on a flat polycarbonate surface at room temperature. The dried film could be peeled off the surface and transferred to the WAXS sample holder for characterization.

To quantify the degree of orientation of the fibers, the Hermans orientation factor, \( f_c \), was calculated from the WAXS data using

\[
\langle \cos^2 \Psi_{c,Z} \rangle = \frac{\int_0^{\pi} I(\Psi) \sin \Psi \cos^2 \Psi d\Psi}{\int_0^{\pi} I(\Psi) \sin \Psi d\Psi}
\]

and

\[
f_c = \frac{3 \langle \cos^2 \Psi_{c,Z} \rangle - 1}{2} \quad \text{eq. 3.10}
\]

In these equations, Ψ is the azimuthal angle, \( I(\Psi) \) represents the azimuthal intensities, and \( \langle \cos^2 \Psi_{c,Z} \rangle \) is the average cosine square of the angle that the c-plane made with the draw direction, Z [3]. \( f_c \) takes values of 0 for an isotropic material with no preferred orientation, -0.5 when the crystal planes are oriented perpendicular to the draw direction, and 1 for fully oriented planes parallel to the draw direction.

### 3.7 X-ray photoelectron spectroscopy (XPS)

XPS is a technique based on the photoelectric effect for analyzing the surface chemistry of a material. In XPS, a beam of X-rays is irradiated on a solid surface and the kinetic energy of the electrons emitted from the top 1-10 nm of the material is analyzed.
Typically, photoelectron spectra are recorded where peaks in intensity correspond to atoms emitting electrons of a particular energy. By analyzing the energies and intensities of the spectra, identification and quantification of all surface elements (except hydrogen) is possible.

Here, the K-Alpha XPS (Thermo Scientific) with Al Kα X-ray monochromator from the Electron Microscope Center of the University of Kentucky was used to obtain the XPS spectra of PEDOT:PSS fiber bundles placed in an aperture card. The software Avantage provided by Thermo Scientific was used to analyze the data.
3.8 References


This chapter briefly introduces basic concepts of fiber spinning. It then provides a short review on the state-of-the-art polymer-based electrically conductive fibers. The wet-spinning method to fabricate electrically conductive PEDOT:PSS fibers developed during this dissertation is described in detail. Finally, the properties of the resulting fibers are discussed with emphasis on the effect that drawing has on the transport properties and mechanical properties of the fibers. The work presented in this chapter has been reproduced or reproduced in part with permission from “Ruben Sarabia-Riquelme, Maryam Shahi, Joseph W. Brill, and Matthew C. Weisenberger, Effect of Drawing on the Electrical, Thermoelectrical, and Mechanical Properties of Wet-Spun PEDOT:PSS Fibers. ACS Applied Polymer Materials 2019 1 (8), 2157-2167” Copyright 2019 American Chemical Society. The full text of this article can be downloaded at http://pubs.acs.org/ArticlesOnRequest/AOR-hDE9HPJkiZhE3QWVRqYk.

4.1 Introduction

4.1.1 Fiber spinning methods

Fiber spinning is the process of manufacturing fibers by extrusion of a polymer fluid through a spinneret. The polymer fluid can be a melt in the case of thermoplastic polymers (melt spinning) or a solution of a polymer in a suitable solvent (solution spinning). Polymer solutions are often referred to as a ‘dope’. Additionally, there exists a special form of fiber spinning called electrospinning, in which fibers are produced using electrostatic forces instead of mechanical forces. An explanation of these spinning processes is given in the following subsections.
4.1.1.1 Melt spinning

Figure 4.1a shows a simple scheme of a melt spinning set up. A thermoplastic polymer is heated above its melting temperature. Then, the viscous melt is extruded through a spinneret to form filaments. The filaments cool down, solidifying into fibers while being drawn by the rollers. Nylon and polyester fibers are manufactured using this process.

4.1.1.2 Solution spinning

Spinning of polymer solutions can be subdivided into dry spinning and wet spinning. Dry spinning has some similarities with melt spinning (Figure 4.1b). First, a polymer is dissolved into a solvent to form the dope. Then, the dope is extruded through a spinneret into an evaporating tower. Solvent evaporates from the nascent filaments leaving behind the polymer, which solidifies into fibers. Spandex fibers are produced using this method.

On the other hand, in wet spinning, the dope is extruded into a coagulation bath that contains a non-solvent to the polymer or a mixture of non-solvent and solvent, which are highly miscible (Figure 4.1c). When the nascent dope jets enter the coagulation bath, solvent diffuses out of the forming filaments while non-solvent diffuses into them. In this process, the solvent and non-solvent mix. This dual diffusion process leads to the precipitation of the polymer from solution to form solid fibers. Wet-spinning can be further subdivided into wet-jet spinning, if the spinneret is submerged in the coagulation bath, and air-gap spinning, if the spinneret is located above the coagulation bath such that the nascent jets pass through a small air gap before entering the coagulation bath. Air-gap spinning allows for higher extensional forces to be applied to the dope in the air gap since at that
point it has not yet encountered the non-solvent. This leads to increased molecular orientation and, consequently, better tensile properties [1].

Several variables affect the coagulation step such as dope composition, viscosity, flow rate, coagulation bath concentration and temperature, draw ratio, etc. Furthermore, following coagulation, the filaments can be subjected to different post-treatments including washing, drawing, drying, etc.

Acrylic (including carbon fiber precursors), rayon or aramid fibers are produced using wet-spinning methods.

4.1.1.3 Electrospinning

In electrospinning, a polymer solution is charged using a high-voltage source. As the electrostatic repulsion balances the surface tension, a stream of liquid erupts from the solution towards a grounded metal collector (Figure 4.1d). The charged stream dries and is elongated as it flies to the metal collector where fibers are deposited. During the flight, the elongation and thinning that the stream experiences results in fibers with nanometer-scale diameters (nanofibers).

An important difference between electrospinning compared to melt spinning and solution spinning is that the latter produce spools of continuously wound fiber that can then be unwound to be woven, knitted, etc., into a textile material. On the other hand, electrospinning produces non-woven porous fiber mats, which limits their applicability in textiles.
Figure 4.1. Schemes of different fiber spinning methods: (a) Melt spinning, (b) dry spinning, (c) wet spinning and (d) electrospinning.

4.1.2 Fabrication of electrically conductive conjugated polymer fibers

There are three main methods by which electrically conductive fibers based on conjugated polymers are fabricated: (a) coating of insulating textile fibers with conjugated polymers, (b) spinning blends of conjugated polymers and insulating polymers and (c) spinning of pure conjugated polymers.

4.1.2.1 Coating of insulating textile fibers with conjugated polymers

In this method a conjugated polymer is in-situ polymerized or deposited by other means on the surface of an insulating textile fiber such as silk, cotton, polyester, nylon, etc. The core insulating fiber acts as a load-bearing support, ensuring robust mechanical properties while the conjugated polymer coating provides electrical conduction. For example, Xia et al. [2] in-situ polymerized polypyrrole, polyaniline, and PEDOT on the surface of silk fibers obtaining electrical conductivities of 0.4, 0.01 and 0.005 S/cm, respectively, while maintaining the original mechanical properties of the silk fibers. Other authors have reported the in-situ polymerization of polypyrrole and PEDOT on a wide variety of fiber substrates including cotton [3,4], wool [5] or polyester [5,6].
In addition to *in-situ* polymerization, PEDOT:PSS water dispersions have been widely used to dye different fiber substrates in order to obtain electrically conductive textiles. Finefrock et al. [7] coated nylon fibers with PEDOT:PSS to use them as textile thermoelectric generators. Du et al. [8] coated a commercial polyester fabric and obtained an electrical conductivity of 1.5 S/cm. Later, Kirihara et al. [9] reported a conductivity of 30 S/cm by coating cotton fibers. Lastly, Ryan et al. [10] and Lund et al. [11] dyed silk fibers with PEDOT:PSS obtaining electrical conductivities as high as 70 S/cm.

In these coated fibers, the volume occupied by the thin conjugated polymer coating is very small compared to the volume of the insulating fiber acting as support. Thus, the bulk electrical conductivity is usually small, often lower than 10 S/cm, limiting their applications [12].

### 4.1.2.2 Spinning of conjugated polymer and insulating polymer blends

In this method a conjugated polymer is blended with an insulating polymer (typically by dissolving both in a common solvent) and then spun into fibers. The insulating polymer is usually of high molecular weight and improves the spinnability of the conjugated polymer.

Wet spinning of blends of PEDOT:PSS and polyacrylonitrile (PAN) resulted in electrically conductive fibers with a conductivity of 5 S/cm for a content of 1.83 wt.% of PEDOT:PSS in the final fiber [13]. Later, Wang et al. [14,15] obtained by wet spinning PEDOT:PSS/polyvinyl alcohol (PVA) blended fibers with conductivities around 20 S/cm for 4.76 wt.% PEDOT:PSS in PVA.

The mechanical properties of the blended fibers are usually determined by the insulating polymer since it is typically used in higher proportion. This has led authors to explore blending elastomers with conjugated polymers to obtain highly stretchable
electrically conductive fibers. For example, blends of P3HT and the elastomer poly(styrene-\(\beta\)-isobutylene-\(\beta\)-styrene) (SIBS) with 87.9 wt.% SIBS were able to withstand strains up to 975 % before breaking, with electrical conductivities as high as 0.38 S/cm at zero strain [16]. More recently, Seyedin et al. [17] wet spun blends of PEDOT:PSS and polyurethane (PU) to fabricate strain responsive PEDOT:PSS/PU fibers. A fiber made with a composition of 13 wt.% PEDOT:PSS could withstand strains up to 350 % and had an electrical conductivity of about 10 S/cm at zero strain.

Blends of conjugated polymers and insulating polymers are also used in the electrospinning of electrically conductive nanofiber mats. The rheological properties of the polymer fluids are very important in electrospinning to achieve continuous spinning. Unfortunately, conjugated polymers typically have limited solubility and low average molecular weight which prevents them from reaching the required viscosities for electrospinning. Moreover, the conjugated nature of conducting polymers makes for a rigid backbone, resulting in low levels of polymer chain entanglement to survive the large elongations experienced during jet flight [18]. For these reasons, a soluble, high-molecular weight, insulating polymer is blended with the conjugated polymer to control the rheological properties and enable stable and continuous electrospinning. Electrospinning of conjugated polymers such as PEDOT:PSS, polypyrrole (PPy) or polyaniline (PANi) has been reported by blending typical insulating polymers such as poly(ethyleneoxide) (PEO) [19-21], poly(methylmethacrylate) (PMMA) [22,23], poly(vinylpyrrolidone) (PVP) [24,25] or PVA [26,27].

Conjugated polymer/insulating polymer blended fibers present the advantage of decoupling the electrical conductivity from the mechanical properties. For example,
stretchable and electrically conductive fibers such as the ones obtained by blending PEDOT:PSS with elastomers have potential applications as strain sensors. However, the dilution of the electrically conductive material into an insulating matrix results in relatively small values of electrical conductivity, limiting their applications.

4.1.2.3 Spinning of pure conjugated polymers

To overcome the electrical conductivity limitations of coated fibers or blended fibers authors have explored the direct spinning of pure conjugated polymers into fibers.

PANi was the first conjugated polymer to be spun into fibers [28,29] using wet spinning. Mattes et al. [30] pioneered the one-step wet spinning of PANi fibers using emeraldine base PANi dissolved in mixtures of pyrrolidine and N-methyl-2-pyrrolidone (NMP). Pyrrolidine acted as a gel inhibitor, reducing the viscosity of the solutions and delaying gelation. The PANi/solvent mixtures were extruded through a 2.5 cm air gap into a water coagulation bath. As-spun fibers doped with benzene phosphinic acid (BPA) had conductivities around 1 S/cm, tensile strength of ~14 MPa, Young’s modulus of ~0.5 GPa and elongation at break of 8%. By applying a 4x hot-stretch, the electrical conductivity increased to 10 S/cm, the tensile strength to 60 MPa, the Young’s modulus to 2.15 GPa and the elongation at break decreased to 6%. Later, Pomfret et al. [31] extruded mixtures of PANi, 2-acrylamido-2-methyl-1-propanesulfonic acid and dichloroacetic acid into acetone and obtained as-spun fibers with conductivities of 100 S/cm, that increased to ~1000 S/cm after drawing. The drawn fibers had a tensile strength of 97 MPa and Young’s modulus of 2 GPa.

Shortly after the first reports of wet spun PANi fibers, Moulton et al. [32,33] investigated the wet spinning of poly(3-alkyl-thiophenes) (P3ATs) including poly(3-octylthiophene) (P3OT) and P3HT. The P3ATs were dissolved in chloroform and then wet
spun using an acetone coagulation bath. Young’s modulus of ~ 4.5 GPa, tensile strength of 120 MPa and electrical conductivity of 160 S/cm were achieved for wet spun and drawn P3HT fibers. More recently, Fanous et al. [34] reported the fabrication of conductive P3HT fibers using melt spinning by extruding the polymer melt at 260 °C. The extruded filaments were subsequently drawn with a drawing ratio of 2 at 150 °C. After doping with a FeCl₃ solution in nitromethane, the drawn P3HT fibers showed a high electrical conductivity of 350 S/cm.

Foroughi et al. [35] have investigated the wet spinning of PPy. When PPy is synthesized by incorporating di-(2-ethylhexyl) sulfosuccinate (DEHS) as the dopant anion, the resulting doped PPy is soluble in various organic solvents such as NMP, DMSO, or DMF. Foroughi et al. dissolved PPy:DEHS in dichloroacetic acid to form a dope that was subsequently extruded into a DMF/water coagulation bath. The tensile strength, Young’s modulus and elongation at break of the obtained fibers were 25 MPa, 1.5 GPa and 2%, respectively, with an electrical conductivity of around 3 S/cm. Later, by increasing the molecular weight of the PPy used, the mechanical properties were improved, obtaining values of tensile strength, Young’s modulus and elongation at break of 136 MPa, 4.2 GPa and 5%, respectively [36].

Lastly, Okuzaki et al. reported in 2003 the first study on wet spinning of conducting PEDOT:PSS fibers [37]. In this study, aqueous solutions of PEDOT:PSS were extruded through a single-hole spinneret into an acetone coagulation bath. The formed fibers were continuously taken up on a winding spool and dried under vacuum. They reported that as soon as the spinneret end was submerged into the acetone bath, the PEDOT:PSS solution was spontaneously extruded by the effect of gravity. They studied
the electrical and mechanical properties of the fibers as a function of spinneret diameter and PEDOT:PSS dope concentration. No difference in electrical conductivity and mechanical properties was found at the different conditions studied, which they explained by the lack of orientation of the polymer chains. Indeed, the electrical conductivity of the fibers, \( \sim 0.1 \text{ S/cm} \), was in the same order as that of a cast film using the spinning dope, \( 0.8 \text{ S/cm} \). The Young’s modulus and tensile strength of the film were also superior to those of the fibers (1.8 GPa and 42.8 MPa, respectively, for the films versus 1.1 GPa and 17.2 MPa, for the fibers). They attributed this to defects in the fibers, in the form of microvoids and microfractures, created due to the rapid dehydration of the dope in acetone.

Later, in 2009, Okuzaki et al. \cite{38} reported the effect of including an EG post treatment to their previous PEDOT:PSS wet-spinning process. The as-spun PEDOT:PSS fibers were dipped in EG, which induced secondary doping. The dip-treatment enhanced electrical conductivity and mechanical properties. They reported an electrical conductivity of 467 S/cm, Young’s modulus of 4 GPa and tensile strength of 130 MPa.

In 2011, Jalili et al. \cite{39} reported the one-step fabrication of PEDOT:PSS fibers with electrical conductivities of up to 264 S/cm by addition of poly(ethyleneglycol) (PEG) to the PEDOT:PSS dope, which eliminated the need for a post-treatment with EG. PEG had been previously reported to be an effective secondary dopant for PEDOT:PSS thin films \cite{40}. In this study, they also investigated the use of isopropyl alcohol (IPA) in the coagulation bath instead of acetone. It was found that IPA dehydrated the forming filament at a slower rate, yielding denser filaments with superior electrical and mechanical properties as compared to the filaments spun into acetone.
In 2015, Zhou et al. [41] reported a two-step method to fabricate even higher conductivity PEDOT:PSS fibers with electrical conductivities of up to 2804 S/cm. The fabrication process consisted of wet spinning of the fibers using a 50:50 by volume mixture of acetone:IPA as coagulation bath followed by drying the fiber at 90 °C in air before take-up. After this, secondary doping with EG was performed by immersing the fibers in an EG bath for 1 hour. The superior electrical conductivity compared to previous reports was due to the increased molecular alignment of the polymer chains in the fiber direction. Moreover, mechanical properties were also superior. They reported a Young’s modulus of 8.3 GPa and tensile strength of 410 MPa with an elongation at break of 21%.

Finally, Zhang et al. [42] published in 2019 the continuous fabrication of PEDOT:PSS fibers with conductivities of up to 3828 S/cm, the highest yet reported, by switching the coagulation bath from IPA to concentrated sulfuric acid and keeping a residence time of the fiber in the coagulation bath of 10 min. They attributed the enormous increase in electrical conductivity to the very effective removal of excess PSS in the concentrated sulfuric acid bath. The Young’s modulus, tensile strength and elongation at break of these sulfuric acid spun fibers were 3.9 GPa, 425 MPa and 36%, respectively.

The field of conjugated polymer fibers is still in its infancy when compared to other well-established fiber fields such as wet-spinning of polyacrylonitrile fibers or melt-spinning of polyethylene. At the beginning of this dissertation a continuous process for the fabrication of highly conductive and mechanically robust PEDOT:PSS fibers had not been reported. Additionally, all of the previously mentioned reports on wet-spun PEDOT:PSS fibers focused on the removal of PSS in order to increase the electrical properties of the fibers with characteristic wet-spinning steps such as drawing being only briefly mentioned.
A detailed study on the effect of varying the applied draw on the properties of the resultant PEDOT:PSS fibers did not exist in the literature.

Drawing or stretching is a characteristic step of every fiber fabrication process. Drawing induces preferential orientation of the polymer chains in the fiber-axis direction, enhancing the mechanical properties of the fiber. Moreover, increased electrical conductivity with increasing draw has been previously reported for other conducting polymer fibers, such as P3AT [32,33] and PANi [31] fibers. In addition to the mechanical properties and electrical conductivity, other transport properties such as the thermal conductivity and Seebeck coefficient are also of great interest for electronic textiles and can also be affected by the preferential orientation of the polymer chains. For instance, the thermal conductivity at room temperature of an oriented polyacetylene film was measured to be $\sim 13 \text{ Wm}^{-1}\text{K}^{-1}$ [43], while oriented polyethylene nanofibers achieved values as high as 104 Wm$^{-1}$K$^{-1}$ [44]. On the other hand, the effect of orientation on the Seebeck coefficient is less clear and it has been reported to decrease [45,46], remain the same [47], or increase [48] with increasing orientation in conjugated polymer films. PEDOT:PSS is a promising candidate to be used in future fiber-based devices and, therefore, the study of electrical, thermoelectric and mechanical properties in its fiber geometry has great scientific value.

Motivated by this, in this dissertation, a continuous wet-spinning process for the fabrication of oriented, highly conductive and mechanically robust PEDOT:PSS fibers was developed. Furthermore, the process-structure-property relationships of the final fibers were investigated with special emphasis on the effect that applied draw has on the electrical, thermoelectric and mechanical properties of the fibers.
4.2 Experimental details on the wet-spinning setup

4.2.1 Materials

PEDOT:PSS water dispersion was purchased from Heraeus (PH1000; PEDOT:PSS weight ratio of 1:2.5 (28.57 wt.% PEDOT) solid content 1.3 wt.%). DMSO and IPA were purchased from VWR.

4.2.2 Dope preparation

The PEDOT:PSS dispersion was placed on a hot plate at 90 °C while magnetically stirring and the mass of evaporated water was monitored until the solid concentration reached 2.5 wt.%. The viscosity of this dispersion is estimated around 140 mPa·s from reference [49]. Afterward, 5 wt.% of DMSO was added (with respect to the total solution) and the dope was further stirred for 2 h at room temperature. Then, the dope was bath sonicated for 30 min and finally degassed in a vacuum oven for 5 min at room temperature.

4.2.3 Wet-spinning setup

Figure 4.2 shows a scheme of the continuous wet-spinning setup used. First, the degassed PEDOT:PSS dope was transferred carefully to a 5 mL syringe and placed on a syringe pump (KD Scientific) that allowed precise control of the flow rate. A constant flow rate of 0.25 mL/h was used in all cases. The dope passed through a sintered metal disk, with an average pore size of 5 μm, before exiting through a 100 μm diameter capillary spinneret (length to diameter of the capillary, L/D = 5) into the coagulation bath. Two coagulation baths were investigated, pure IPA and 10 vol.% DMSO in IPA. After coagulation, the fiber was dried by passing through a heater, which kept the air temperature around 120 °C, before reaching the first roller. Coagulation bath fiber samples were taken from this first powered roller directly onto a spool. Otherwise, after the first roller, the fiber entered a pure DMSO draw bath (kept at room temperature) followed by another drying
step in a keyhole-cylinder-shaped oven with a maximum air temperature inside the oven of 170 °C. After the oven, drawn and dried fiber could be continuously taken-up on a spool with no interfilament fusion. Typical linear speeds of the fibers at take up range between 0.8 to 2 m/min. Note that the samples measured in this study were collected over the course of several spin runs with dopes made from scratch for each spin run. Independent characterization data is reported for each sample. That is, two samples may have the same processing conditions, but may be from different spin runs and they are presented as separate data points. This reveals insight into the reproducibility of the data.

**Figure 4.2.** Scheme of the continuous wet-spinning process for the fabrication of PEDOT:PSS fibers. Insets are (a) image of the fiber formation in the coagulation bath (scale bar is 10 mm); (b) image of dried fiber before entering the DMSO draw bath (scale bar is 2 mm); (c) image of the same fiber as in panel b visibly swollen by DMSO after exiting the DMSO draw bath (scale bar is 2 mm); (d) image of a fiber on a PTFE spool of 26 mm diameter.

### 4.3 Results and discussion

#### 4.3.1 Wet-spinning process

**Figure 4.2** shows a scheme of the wet-spinning setup used. The PEDOT:PSS dope had to be carefully transferred to the syringe avoiding suction of air, as that would have resulted in entrapped air bubbles. If air bubbles were entrapped during transfer, they could be released during the spinning process, resulting in breakage of the fiber in the coagulation bath. Once the dope was in the syringe, it was pumped out through a 5 μm syringe filter.
Initial tests without filtration were performed but frequent breakage of the filaments occurred in the coagulation bath. After careful observation of the breakage events, it was determined that particulates, which were unable to stretch at the same rate that the rest of the jet, were the cause of the frequent breakages. A sintered disk to filter particles down to 5 µm was included in the setup and continuous spinning without breakage was achieved. **Figure 4.2a** shows an image of the polymer jet exiting the spinneret in the coagulation bath and forming a solid fiber that can then be taken out of the coagulation bath by a rotating roller. IPA was chosen as coagulation bath since it has been previously reported that fibers coagulated in IPA were less porous than fibers coagulated in acetone and thus had superior electrical and mechanical properties [39]. When the PEDOT:PSS dope enters the coagulation bath, water diffuses from the nascent fiber into the coagulation bath and IPA diffuses into it. This causes a fast destabilization of the dispersion as PSS loses its surfactant effect, resulting in the formation of a solid filament. Additionally, a coagulation bath with 10 vol.% DMSO in IPA was also investigated. Following the coagulation bath, the fiber was dried in-line by a vertical heater. Initial tests did not include a heater at this point. However, when the wet fiber touched the first roller, the surface tension between the IPA and the roller stuck the fiber to the roller and breakage would occur in any attempt to take the fiber further down the spinning line. Thus, completely drying the filament before touching the first roller was necessary. After drying, the filament (see **Figure 4.2b**) entered the draw bath. DMSO is a polar solvent that can screen to some extent the Coulombic interactions between PEDOT and PSS, leading to an enhancement in the local order of PEDOT chains and partial removal of excess PSS [50,51]. With this screening effect in mind, we decided to test DMSO as the media to further draw the fibers. In the draw bath,
DMSO rapidly swelled the fiber, which was clearly visible by the increase in size of the filament (Figure 4.2c). DMSO acted as a plasticizer allowing for the application of higher draw to the fiber than would have otherwise been possible. Afterward, the filament was taken out of the DMSO bath by the second powered roller. At this point, the filament was strong enough to release from the roller without breakage and, therefore, drying the fiber between the DMSO bath and the second roller was not necessary. Finally, the filament was dried by passing through a keyhole-cylinder-shaped oven before being taken-up on a spool (Figure 4.2d).

4.3.2 Critical draw ratios

The ratio between the first roller linear speed, $v_1$, and the dope velocity, $v_{dope}$, is called the coagulation bath draw.

$$DR_{Coag} = \frac{v_1}{v_{dope}}$$  \hspace{1cm} \text{eq. 4.1}

The ratio between the take-up speed, $v_{take-up}$, and $v_1$ is the DMSO bath draw ratio.

$$DR_{DMSO} = \frac{v_{take-up}}{v_1}$$  \hspace{1cm} \text{eq. 4.2}

The total draw ratio is then defined as the ratio between $v_{take-up}$ and $v_{dope}$.

$$DR_{Total} = \frac{v_{take-up}}{v_{dope}} = DR_{Coag} \cdot DR_{DMSO}$$  \hspace{1cm} \text{eq. 4.3}

In this work, critical draw ratios were defined as the maximum draw ratios at which spinning was stable without fiber breakage for at least 20 min. The critical draw ratios are presented in Figure 4.3. The critical $DR_{Coag}$ was found to be around 3-3.5 in both IPA and 10 vol. % DMSO in IPA coagulation baths. The critical $DR_{DMSO}$ decreased from
around 1.6 to 1.1 with increasing $\text{DR}_{\text{Coag}}$ from 1.5 to 3 while the critical $\text{DR}_{\text{Total}}$ increased from around 2.4 to 3.3.

![Critical draw ratios as a function of the coagulation bath draw ratio.](image)

**Figure 4.3.** Critical draw ratios as a function of the coagulation bath draw ratio.

### 4.3.3 Diameter and geometry of the fibers

**Figure 4.4a** shows the diameters of the fibers as a function of total draw. As expected, the diameter of the fibers decreased with increasing draw. The diameter of coagulation bath fibers decreased from 9.5-11 µm to 6.4-7 µm at the highest applied draw. Similarly, the diameter of DMSO drawn fibers also decreased from 7.7-8.3 µm (at the lowest draw) to 5.4-6 µm (at the highest draw). It must be noted that these diameters were measured in vacuum (from SEM imaging), and thus, the fibers were presumably dehydrated. Since ambient atmospheric diameters are unknown, it has been assumed that the change in diameter because of dehydration is negligible. No difference in diameter was observed between the fibers spun into IPA and 10 vol. % DMSO in IPA. However, a difference in the cross-sectional shape of the fibers was observed. Fibers spun into a pure IPA coagulation bath showed a noncircular cross-section, while fibers spun into 10 vol.% DMSO in IPA were all circular (see **Figure 4.4b** and **c**). Our group has investigated, in the past, the change from noncircular to circular cross-section of wet-spun polyacrylonitrile...
precursor fibers [52]. It was found that in coagulation baths with high nonsolvent concentrations (in this case IPA), the coagulation rate is high and a dense skin forms in the outer perimeter of the filament impeding diffusion in and out of the fiber, which subsequently collapses locking-in the circumference of the dense skin layer, causing noncircular cross sections. However, diluting the coagulation bath (in this case by adding 10 vol.% DMSO) decreases the coagulation rate, and little or no skin is formed, resulting in circular-shaped cross sections. Additionally, the addition of DMSO to the isopropanol bath changes the surface tension, which could also affect the shape of the cross-sections of the fibers. Figure 4.4d-f shows SEM images of fibers spun into 10 vol.% DMSO in IPA and taken at different total draw ratios through DMSO draw bath. The smooth surface and cylindrical shape of the fibers can be observed. In all cases, high quality fibers with the absence of voids could be spun for hours without breakage.
Figure 4.4. (a) Diameter versus total draw ratio of the PEDOT:PSS fibers. Plotted values are average values of 50-75 diameter measurements performed on 5 different specimens (10-15 per specimen) and error bars represent the standard deviation within specimens of the same sample. (b and c) SEM cross-section image of fibers spun into a coagulation bath of IPA and 10 vol.% DMSO in IPA, respectively, and stretched through DMSO for a total draw ratio of 1.67. Insets are close-ups to one of the fibers. (d-f) SEM images of fibers spun into 10 vol.% DMSO in IPA and further stretched through DMSO with total draw ratios of 1.58, 1.97, and 2.36, respectively. Scale bars are 10 µm except in insets that are 3 µm.

4.3.4 Linear density and removal of PSS from the fibers in the DMSO bath

In Figure 4.4a it can be observed that DMSO drawn fibers are smaller in diameter compared to coagulation bath fibers given that they have been stretched to the same draw ratio. This suggests that either DMSO drawn fibers are significantly denser or that there is polymer mass lost into the DMSO bath. The linear densities of the fibers were measured using the single-filament test system FAVIMAT+ from Textechno (see Chapter 3, section 5 for more details). The linear density, $LD$, is related to the bulk density of the fiber, $\rho_{fiber}$, by:

$$LD = \rho_{fiber} \cdot A$$  \hspace{1cm} \text{eq. 4.4}$$

where $A$ is the cross-sectional area of the fibers. Thus, a plot $LD$ versus $A$ should result in a straight line with $\rho_{fiber}$ as its slope. As can be observed in Figure 4.5, both coagulation bath samples and DMSO drawn samples lay in the same line regardless of the coagulation
bath employed. This suggests that all fibers have a similar bulk density (of around 1.61 g/cm$^3$) and that the differences observed in the diameters must stem from mass loss in the DMSO bath.

![Figure 4.5](image.png)

**Figure 4.5.** Linear density versus the cross-sectional area for all samples.

Post-treatment of PEDOT:PSS films to remove excess PSS is a common practice in the literature. In fact, as discussed in the introduction, most strategies to improve the electrical conductivity of PEDOT:PSS fibers involve removing excess PSS. DMSO has been widely used in the literature for this purpose. Thus, we studied the possible removal of PSS from the fiber in the short time (around 5 seconds) that the fibers spent in the DMSO bath during fabrication.

The linear density of the fibers can reflect the removal of PSS. The linear density of the fibers can be found by applying a mass balance to the wet-spinning system with respect to PEDOT:

$$
\dot{M}_{PEDOT,dope} = \dot{M}_{PEDOT,washed} + \dot{M}_{PEDOT,fiber}
$$

where $\dot{M}_{PEDOT,dope}$ is the mass flow of PEDOT entering the coagulation bath from the syringe, $\dot{M}_{PEDOT,washed}$ is the mass flow of PEDOT being washed off in the DMSO bath.
and $\dot{M}_{PEDOT,fiber}$ is the mass flow of PEDOT being taken up as a fiber. We will assume that only PSS is being washed off in the DMSO bath and, thus, $\dot{M}_{PEDOT,washed} = 0$. Additionally, for $\dot{M}_{PEDOT,dope}$ and $\dot{M}_{PEDOT,fiber}$ we have:

$$\dot{M}_{PEDOT,dope} = \dot{Q} \cdot \rho_{dope} \cdot C_{PEDOT:PSS,dope} \cdot \text{wt. \% PEDOT}_{dope} \quad \text{eq. 4.6}$$

$$\dot{M}_{PEDOT,fiber} = LD \cdot v_{take-up} \cdot \text{wt. \% PEDOT}_{fiber} \quad \text{eq. 4.7}$$

where $\dot{Q}$ is the flow rate (constant at 0.25 mL/h), $\rho_{dope}$ is the dope density (assumed to be $\sim 1 \text{ g/cm}^3$), $C_{PEDOT:PSS,dope}$ is the concentration of PEDOT:PSS in the dope (2.5 wt.% in this work) and wt. \% $PEDOT_t$ is the weight percentage of PEDOT with respect to PSS (28.57 wt.% for the dope). Using eqs. 4.3, 4.5, 4.6 and 4.7, the linear density can be expressed as:

$$LD = A_{spinneret} \cdot \rho_{dope} \cdot C_{PEDOT:PSS,dope} \frac{\text{wt. \% PEDOT}_{dope}}{\text{wt. \% PEDOT}_{fiber}} \quad \text{eq. 4.8}$$

where $A_{spinneret}$ is the cross-sectional area of the spinneret orifice. Using eq. 4.8, the linear density of the fibers can be calculated as a function of total draw for a given weight percentage of PEDOT in the final fiber.

**Figure 4.6** plots the linear density of the fibers as function of total draw where the dotted curves represent the calculated linear densities using eq. 4.8 using the noted weight percentage of PEDOT in the final fiber (28.57, 35 and 40%). On one hand, the linear density of coagulation bath samples follows closely the 28.57 wt.% PEDOT curve, which assumes no mass loss of PSS (therefore equal wt.% of PEDOT in dope and fiber). On the other hand, DMSO drawn fibers lay in between the 35 wt.% and 40 wt.% PEDOT curves, which suggests that there was removal of PSS in the DMSO bath such that the PEDOT content of the fibers was effectively enriched from 28.57 wt.% to 35-40 wt.\%.
Figure 4.6. Linear density as a function of total draw ratio. Linear density is given in denier (grams of fiber per 9000 meter of fiber). The dotted curves are calculated using eq. 4.8 using varying weight percentages of PEDOT in the final fiber.

Additionally, XPS of a bundle of coagulation bath fibers and a bundle of DMSO drawn fibers was performed. Figure 4.7 shows the XPS sulfur signal (S2p). The S2p XPS signal of PEDOT:PSS is typically separated in two doublets corresponding to the two distinct chemical states of sulfur encountered in PEDOT:PSS, i.e. thiophene and sulfonate. The thiophene signal (from PEDOT) appears at ~163.6 and 164.7 eV while the sulfonate component (from PSS) is found at binding energies, around 168 eV. An increase in relative intensity of the peaks corresponding to PEDOT at the filament surface can be observed, indicating partial removal of PSS in the DMSO bath. The wt.% of PEDOT in the surface of DMSO drawn fibers is estimated at 33.9 wt.% from these XPS results, which is close to the values estimated using the linear densities.
Figure 4.7. XPS S2p of coagulation bath fibers and DMSO drawn fibers. Intensities normalized to the PSS peak.

4.3.5 **Wide-angle X-ray scattering (WAXS)**

Figure 4.8a-c show the 2D WAXS patterns of a PEDOT:PSS film, coagulation bath fibers spun into 10 vol.% DMSO in IPA and fibers stretched through the DMSO bath (draw ratio of 2.36). The 2D WAXS pattern of the PEDOT:PSS film shows homogeneous intensity through the azimuthal angle, not showing any signs of preferred orientation, indicating random orientation of the PEDOT crystallites. However, in the 2D WAXS patterns of the fibers, the characteristic arcs indicating preferred orientation of crystalline planes can be observed and become more evident at higher draw ratios (see marked arcs in Figure 4.8c). Since the fibers were aligned vertically for the WAXS characterization, the appearance of horizontal arcs indicated preferred orientation of crystal planes parallel to the fiber axis direction. The integrated intensity versus 2\( \theta \) is presented in Figure 4.8d. One broad hump and two peaks are observed for all samples. The broad hump peaking at 17.7\(^\circ\) is attributed to amorphous and randomly oriented PSS [53,54]. The peak that appears at 4.8\(^\circ\) for the film sample shifted to 3.4\(^\circ\) for all the fiber samples, which corresponds to a shift in \(d\)-spacings from 18.4 to 26.3 Å. This peak corresponds to the (100) lamella stacking
of alternating PEDOT and PSS. In Figure 4.8e, the exact positions of the PSS chains are not drawn and are represented instead with a blank box, but this does not affect the analysis [55]. The two different \( d \)-spacings for the lamella stacking of PEDOT and PSS have been previously reported by other authors and are attributed to two different alternate orders of PEDOT and PSS [56,57]. The (100) peak for the coagulation bath fiber spun into pure IPA increases in intensity with respect to the film, indicating that higher crystalline order was induced during fiber formation. Additionally, adding 10 vol.% DMSO to the coagulation bath further increases the intensity of this peak. The screening effects of DMSO diminished the strong Coulombic interactions between PEDOT and PSS and allowed for a better organization of the polymer chains. The intensity increases even further at higher draw ratios, which could be indicative of drawing-induced ordering of the polymer chains [34,58], but it is also most likely related to the removal of PSS in the DMSO bath.

A peak also appears at 25.8\(^\circ\) for the PEDOT:PSS film and the coagulation bath fibers spun into pure IPA, which shifts to 26.2\(^\circ\) for the fibers spun into a coagulation bath that contains DMSO and the fibers stretched through the DMSO bath regardless of the coagulation bath. This peak is assigned to the (020) reflection, which corresponds to the \( \pi-\pi \) stacking of PEDOT chains [55]. As shown in Figure 4.8e, PEDOT chains crystallize stacking face-to-face by overlapping the \( \pi \)-orbitals and keeping a planar structure [53]. The observed shift corresponds to a reduction in the \( \pi-\pi \) stacking distance from 3.5 to 3.4 \( \text{Å} \). The shorter distance indicates stronger \( \pi-\pi \) overlap between PEDOT chains which should translate into enhanced interchain charge transport in the \( b \)-axis direction. A \( \pi-\pi \) stacking distance of 3.4 \( \text{Å} \) has been previously reported for PEDOT:tosylate crystals [55] and PEDOT:PSS crystals [53,57,59].
Figure 4.8f and g present the intensity along the azimuthal angle for the (100) and (020) reflection, respectively. The film sample shows flat patterns in both cases indicating no preferential orientation. The fiber samples, however, present peaks at 0° and 180° indicating preferential orientation of these planes parallel to the fiber axis direction. The peaks also increase in intensity as the drawing increases indicating a more pronounced orientation at higher applied draws. The fact that both the (100) and (020) planes are oriented parallel to the fiber axis direction means that the PEDOT backbones are also oriented in the fiber axis direction (c-direction in Figure 4.8e).
Figure 4.8. WAXS analysis of wet-spun PEDOT:PSS fibers. 2D WAXS pattern of (a) PEDOT:PSS film, (b) coagulation bath fibers spun into 10 vol.% DMSO in IPA (draw 1.58) and (c) fibers spun into 10 vol.% DMSO in IPA and drawn through a DMSO bath at 2.36 draw ratio. (d) Normalized intensity (with respect to the PSS broad hump) versus $2\theta$. (e) Scheme of the PEDOT:PSS crystal structure. Intensity as a function of azimuthal angle for (f) (100) reflections and (g) (020) reflections.
4.3.6 *Electrical conductivity*

Figure 4.9 shows the electrical conductivity as a function of the total draw ratio. Adding 10 vol.% DMSO to the coagulation bath, while keeping all else equal increased the electrical conductivity of the coagulation bath fibers by an order of magnitude from ~125 to ~1030 S/cm. This increase in electrical conductivity is attributed to the secondary doping effect of DMSO in PEDOT:PSS. As discussed in WAXS analysis, DMSO induced stronger \( \pi-\pi \) interactions between PEDOT chains, which resulted in enhanced interchain transport in the \( b \)-axis direction, leading to an overall increase in the electrical conductivity. On the other hand, increasing the coagulation bath draw slightly increased the electrical conductivity, which reached ~1200 S/cm at an applied draw of 3.34. However, drawing the fiber through a DMSO bath had a greater impact on the electrical properties. The electrical conductivity of the fibers increased with increasing draw through the DMSO bath and saturated around 2000 S/cm, with some samples reaching values as high as 2250 S/cm. For these fibers the \( \pi-\pi \) stacking distance remained constant at 3.4 Å; thus, the increase in electrical conductivity is not due to a stronger orbital overlap between PEDOT stacks. Instead, the increase in electrical conductivity can be attributed to the drawing-induced orientation of (100) and (020) planes combined with the partial removal of PSS in the DMSO bath. Charge transport is likely to be the fastest along the conjugated polymer backbone [55], thus aligning the chains improves the charge carrier transport in the fiber axis direction (\( c \)-direction). On the other hand, the DMSO-induced stronger \( \pi-\pi \) interactions greatly improved charge transport in the \( b \)-axis direction. This resulted in a synergistic effect where the charge-carrier transport is improved in both parallel and perpendicular directions with respect to the fiber axis yielding the high electrical
conductivities observed. Similar trends showing an increase in electrical conductivity with increasing draw have been previously reported for other conducting polymer fibers, such as P3ATs [32,33] and PANi [31] fibers.

**Figure 4.9.** Electrical conductivity of PEDOT:PSS fibers as a function of total draw.

To test the possibility of the increase in electrical conductivity observed being solely due to removal of PSS, coagulation bath samples were washed in DMSO without applying any tension (for different washing times from 1 to 60 min). **Figure 4.10a** shows the electrical conductivity of the washed fibers compared to the coagulation bath fibers and DMSO drawn fibers. The electrical conductivity of the washed fibers was found to be similar to that of the coagulation bath fibers. This result contrasts with the increase in electrical conductivity observed when the fibers where drawn through the DMSO bath and supports the conclusion that the increase in electrical conductivity is not solely due to PSS removal. Moreover, the electrical conductivity as a function of strain for a coagulation bath sample is presented in **Figure 4.10b.** The electrical conductivity increased with strain up to +13% at failure. This increase in electrical conductivity must be purely associated with induced chain orientation since the tests were made in air without any PSS removal or
secondary doping. Nevertheless, much larger increases in electrical conductivity were observed by drawing the fibers through DMSO. Neither DMSO washing nor pure stretching seem to achieve such enhancement by themselves which indicates the synergistic effect of secondary doping and simultaneous drawing.

![Figure 4.10](image)

**Figure 4.10.** (a) Electrical conductivity as a function of total draw of fibers spun into 10 vol.% DMSO in IPA including DMSO-washed coagulation bath samples which are plotted at 1.5 total draw instead 1.58 to avoid overlap of the symbols and improve clarity. (b) Electrical conductivity (standardized to the initial electrical conductivity) as a function of strain for a coagulation bath sample spun into 10 vol.% DMSO in IPA. For this test the resistance as a function of strain was measured, and then, the electrical conductivity at each strain was calculated assuming constant specimen volume. Values presented are average of 3 specimens.

The charge carrier transport mechanism of the fibers was also investigated. **Figure 4.11** shows a typical temperature dependence of the resistance for fibers spun into 10 vol.% DMSO in IPA. The temperature dependence was similar for all samples at all the different draw ratios studied, with $R(78K)/R(300K)$ varying between 1.32 and 1.38 in all cases. The temperature dependence was fitted using a 1D-VRH model (eq. 2.18). We obtained a value for $T_0$ of 32 K, which is two orders of magnitude smaller than the value obtained for pristine PEDOT:PSS films (1901 K) [60], one order of magnitude smaller than the value obtained for EG-treated PEDOT:PSS films (360 K) [61] and similar to the value obtained
for sulfuric acid treated PEDOT:PSS films (29 K) [62]. This low value for $T_0$ implies a low energy barrier for hopping between conducting grains. The weak overall temperature dependence suggests that the charge carrier transport mechanism, for these PEDOT:PSS fibers, is dominantly metallic conductivity in the heavily doped, crystalline PEDOT domains moderated by hopping between domains through thin insulating PSS barriers [62,63].

\[ \text{Figure 4.11. Typical temperature dependence of the resistance normalized to its (vacuum) room temperature value (blue crosses) and fit to 1D-VRH with hopping parameter } T_0 = 32 \, K \text{(red curve).} \]

4.3.7 Thermoelectric properties

**Figure 4.12a** shows the Seebeck coefficient as a function of total draw for the different fiber samples. The Seebeck coefficient remained practically constant at around 15 $\mu$V/K across all the samples studied. Thus, drawing the polymer chains resulting in preferred orientation of crystal planes seemed to have little to no effect on the Seebeck coefficient. The Seebeck coefficient depends strongly on the charge carrier concentration, decreasing, in general, with increasing doping [64]. Therefore, the drawing process seems to increase the electrical conductivity mainly by improving the charge carrier mobility and not by affecting the charge carrier concentration. As a result of the constant Seebeck coefficient, the thermoelectric power factor, $\alpha^2 \sigma$, increased following the same trend.
observed for the electrical conductivity and yielded maximum power factors in the range of 40-50 µW/K²m (see Figure 4.12b).

![Figure 4.12](image.png)

**Figure 4.12.** (a) Seebeck coefficient as a function of total draw. (b) Thermoelectric power factor as a function of total draw. Seebeck coefficients are the average of 3 specimens per sample. The power factor was calculated using the average values of electrical conductivity and Seebeck coefficient. The error bars represent standard deviation between specimens within the same sample.

The thermal conductivity of the fibers spun into 10 vol.% DMSO in IPA was also investigated. Determining the thermal conductivity of fibers with diameters of 10 µm or less is challenging. Here, in collaboration with Prof. J. Brill’s group in University of Kentucky Department of Physics, a self-heating technique [65,66] that takes advantage of the electrically conductive nature of the fibers to determine the thermal conductivity was used (more details about the technique are given in Chapter 3). **Figure 4.13a** shows the thermal conductivity of the fibers at liquid nitrogen temperature, as a function of total draw. Here, the error bars include uncertainties due to thermal radiation and length uncertainties (~ ±10%) but are dominated by deviation from specimens within the same sample. The most likely cause of these deviations are damages in the specimens caused during mounting, in which case the largest value (i.e., ~ top of the error bar) for each sample may
be the best estimate. Like the electrical conductivities, the coagulation bath sample had the lowest thermal conductivity (~ 2.4 W/mK), while the drawn fibers all had thermal conductivities between 3 and 6 W/mK (at 78 K). Moreover, the temperature dependence of the thermal conductivity is shown in Figure 4.13b for one of the specimens. The trend seems to indicate an increase in thermal conductivity with increasing temperature. Here, the increasing deviation between the thermal conductivities obtained assuming emissivity of 0 or 1 is due to thermal radiation being more important at higher temperatures. In any case the value obtained assuming emissivity of 1 is most likely closer to the real thermal conductivity. Unlike crystalline materials, the thermal conductivity of amorphous and semicrystalline polymers increases with increasing temperature, similar to inorganic glasses [67]. In fact, similar trends of increasing thermal conductivity with increasing temperature have been previously reported for PEDOT:Tos thin films [68], although with lower absolute values. On this note, the measured thermal conductivities of the fiber samples are one to two orders of magnitude larger than conventionally found for PEDOT:PSS films (typically between 0.2 and 0.6 W/mK) [50,69-71]. This reflects the preferred orientation of both PEDOT and PSS chains in the fiber axis direction as opposed to the random orientation typically found in films since aligned polymer chains offer lower thermal resistance in the orientation direction.

It must be noted that for all samples, the measured total thermal conductivity was about a factor of 20 larger than the electronic contribution to the thermal conductivity as calculated using the Wiedemann-Franz law taking the Sommerfeld value for $L_0$ (eq. 2.14 and 2.15). This could be indicative of the lattice thermal conductivity dominating over the electronic thermal conductivity despite the large electrical conductivities observed.
However, there are precedents where the Lorenz value $L$ deviates from $L_0$ for PEDOT samples [68], and therefore, whether the thermal conductivity observed is dominated by phonon or electronic transport is still unclear and is under further investigation.

![Figure 4.13](image.png)

**Figure 4.13.** (a) Average values of the calculated thermal conductivity from samples spun into 10 vol.% DMSO in IPA at different total draws and $T = 78$ K. (b) Temperature dependence of thermal conductivity for a sample with total draw ratio of 2.36.

### 4.3.8 Mechanical properties

The mechanical properties of the fibers in uniaxial tension were also investigated. To fully understand the behavior observed in the mechanical properties, the difference in molecular weights between PEDOT and PSS must be considered. In the commercial product used in this dissertation, the molecular weight of PEDOT ranges between 1000 and 2500 and the molecular weight of PSS is approximately 400000 [53,72]. Moreover, the content of PEDOT in the fibers is estimated to be around 28.5 wt.% for coagulation bath samples and ~34 wt.% for DMSO drawn fibers (Figure 4.6 and Figure 4.7). Since PSS chains are much longer than PEDOT chains and the fibers are also richer in PSS than in PEDOT, we believe that PSS bears an immensely larger fraction of the applied mechanical stress. Having these facts in mind, we can proceed to analyze the mechanical
behavior of the fibers. Typical stress-strain curves of the fibers at different draw ratios are presented in Figure 4.14.

![Stress-strain curves](image)

**Figure 4.14.** Typical stress-strain curves in uniaxial tension of fibers spun into 10 vol.% DMSO in IPA at different draw ratios from 1.58 to 2.36.

In general, the Young’s modulus of the fibers and the break stress increased as the total draw increased while the elongation at break decreased. Figure 4.15a-c presents these trends in more detail. The coagulation bath samples had Young’s moduli between 4-6 GPa, regardless of whether DMSO was present or not in the coagulation bath. Applying draw in the coagulation bath had little effect on the Young’s modulus of the fibers. However, applying draw through the DMSO bath increased the Young’s modulus of the fibers, reaching values as high as 16 GPa. The DMSO-assisted drawing induced orientation of the PEDOT and PSS backbones along the fiber axis direction, which in turn resulted in the high observed values of Young’s modulus. These values are higher than those of all the previously reported wet-spun PEDOT:PSS fibers [41,42] and to the best of our knowledge, represent the highest Young’s modulus reported for a PEDOT:PSS material. The increase in Young’s modulus came accompanied by the characteristic decrease in elongation at break that is usually observed for oriented polymer materials. The break stress followed a
similar trend to that of the Young’s modulus, reaching values as high as 450 MPa, however with a larger dispersion (see Figure 4.15c). The break stress is a function of both Young’s modulus and elongation at break and, thus, the dispersion in the latter properties gets magnified in the break stress.

Figure 4.15. Single-filament tensile properties of PEDOT:PSS fibers as a function of total draw: (a) Young’s modulus, (b) elongation at break, and (c) break stress. Values are average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample.

Interestingly, applying draw through the coagulation bath had little effect on either the electrical or mechanical properties of the fibers, suggesting that coagulation bath draw is not as effective as DMSO drawing on inducing preferential orientation of the polymer chains. Additionally, both Young’s modulus and electrical conductivity seem to follow a very similar trend with increasing applied draw through the DMSO bath (compare Figure 4.9a and Figure 4.15a). This is not a coincidence, since electrical conductivity and mechanical properties are strongly correlated in conducting polymers because they both are affected by inter- and intrachain interactions [33]. In general, the mechanical properties of polymeric materials are highest along the polymer backbone, while in conducting polymers, the electrical conductivity is also the highest along the polymer backbone. Thus, alignment of the polymer chains along the axis of the fiber benefits both electrical and mechanical properties [12].

90
In this study, the applied draw resulted in the orientation of (100) and (020) planes parallel to the axis of the fiber, thus aligning both PEDOT and PSS backbones in the fiber axis direction. To quantify the degree of orientation introduced by drawing the fibers through the DMSO bath and correlate it to the mechanical and electrical properties, the Hermans orientation factors [73] for the (100) reflection were calculated using eq. 3.9 and 3.10. As was expected from simple observation of Figure 4.8a, the PEDOT:PSS film showed no orientation, with a calculated $f_{100}$ value of -0.01, while all fiber samples had some degree of orientation, with values ranging from 0.30 to 0.70. Figure 4.16a and b show the electrical conductivity and Young’s modulus as a function of $f_{100}$. On one hand, the DMSO-induced shortening of the $\pi-\pi$ stacking distance of PEDOT increased the electrical conductivity but did not increase orientation in the coagulation bath samples, as demonstrated by the constant (and even smaller) values of $f_{100}$ (see bottom left corner in Figure 4.16a). On the other hand, the drawing-induced orientation effectively aligned both PEDOT and PSS chains along the fiber axis, resulting in a rather linear increase of both electrical conductivity and Young’s modulus. It must be noted that the increase in Young’s modulus seems purely due to the drawing-induced alignment of the polymer chains as can be inferred from the absence of a step in Figure 4.16b as compared to Figure 4.16a where the enhanced $\pi-\pi$ interactions caused a step jump in electrical conductivity. This interesting result supports the idea that the larger molecular weight PSS chains bear practically all the mechanical stress of the fibers.
Figure 4.16. Correlation between polymer chain orientation and electrical and mechanical properties. (a) Electrical conductivity versus (100) Hermans orientation factor, $f_{100}$, and (b) Young’s modulus versus $f_{100}$. Values are the average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample.

All the previous analyses are very well summarized in Figure 4.17, which plots the electrical conductivity versus the Young’s modulus. Adding DMSO to the coagulation bath, increased the electrical conductivity while keeping the Young’s modulus constant due to enhanced $\pi-\pi$ interactions. Drawing through the DMSO bath increased both the electrical conductivity and Young’s modulus due to preferred orientation of the polymer chains in the fiber axis direction and, in general, the highest conducting fibers were also the stiffest in tension. Notice, however, the two distinct trends observed that are encircled as “summer season” and “winter season” in Figure 4.17. These correspond to samples whose properties were measured during summer and winter, respectively. The difference between these samples stems from the difference in ambient humidity between the seasons. During summer, ambient air is more humid (40-60% relative humidity during summer, and typically < 20% during winter) and the water uptake by the fibers is higher. It has been
observed the electrical conductivity of the fibers increases with increased humidity while the Young’s modulus decreases, as can be inferred from Figure 4.17.

![Figure 4.17](image)

**Figure 4.17.** Electrical conductivity versus Young’s modulus. Values are the average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample. Data encircled as “summer season” or “winter season” are samples that were measured during summer or winter, respectively.

### 4.4 Conclusions

The field of conducting polymer fibers is still in its infancy when compared to the established fields of textile fibers or carbon fibers. There are currently very few papers reporting the wet-spinning of conducting fibers from conjugated polymers. However, electrically conducting and mechanically robust fibers and yarns are needed as building blocks in next generation electronic textiles. In this chapter, a continuous wet-spinning process to produce PEDOT:PSS fibers has been described. The PEDOT:PSS fibers produced by this method have high electrical conductivity, high thermal conductivity, excellent mechanical properties, and moderate thermoelectric performance. Drawing the fibers through DMSO was shown to be key to achieve such optimal properties. DMSO
induced stronger $\pi-\pi$ interaction between PEDOT chains while facilitating the application of high draws that effectively aligned the backbones of both PEDOT and PSS along the fiber axis direction. This synergistic effect resulted in room temperature electrical conductivities of around 2000 S/cm and Young’s moduli as high as 16 GPa. In fact, to the best of our knowledge, these Young’s moduli are the highest reported to date for a PEDOT:PSS material. Furthermore, the structure of the fibers was investigated using WAXS and a strong correlation between the orientation of the polymer chains along the fiber axis and the trends observed in the fibers’ properties was found. In general, the fibers with the highest degree of orientation were also the stiffest and the most conducting fibers. These are important steps toward the continuous fabrication of high performance PEDOT:PSS fibers to be used as fundamental building blocks in future electronic textiles.
4.5 References


Semi-metallic, strong and stretchable wet-spun conjugated polymer microfibers. 


CHAPTER 5. ENHANCING THE ELECTRICAL CONDUCTIVITY OF PEDOT:PSS FIBERS BY SULFURIC ACID DRAWING

This chapter briefly discusses the current literature related to the acid treatment of PEDOT:PSS to improve its electrical conductivity. It then describes two experimental approaches used to perform sulfuric acid treatments on the PEDOT:PSS fibers. Finally, the properties of the sulfuric acid treated fibers are reported and discussed.

5.1 Introduction

In Chapter 4 a process was described to obtain highly conductive and mechanically robust wet-spun PEDOT:PSS fibers by stretching the fibers in a DMSO bath. The excellent properties obtained were mainly attributed to the preferred orientation of the polymer chains parallel to the fiber axis direction that was induced during stretching. Preferred orientation of polymer chains is a characteristic feature of almost every polymer fiber. In contrast, in the field of polymeric thin films, inducing orientation of the polymer chains in a particular direction is not a trivial task. Therefore, in PEDOT:PSS thin film studies, the focus to enhance the electrical conductivity of the material has been to improve crystallinity and reduce the amount of excess PSS present in the material. This has been mainly achieved by using secondary dopants such as DMSO or EG. Indeed, the fibers fabricated in this work also experienced secondary doping by DMSO, as was demonstrated by the stronger $\pi-\pi$ interactions between PEDOT stacks after adding DMSO to the coagulation bath and the loss of excess PSS to the DMSO drawing bath.

More recently, the use of acids has been proven more effective on enhancing the electrical conductivity of PEDOT:PSS thin films than the use of traditional secondary dopants (DMSO, EG). Xia et al. [1] were the first to report the use of acids to increase the electrical conductivity of PEDOT:PSS films. They studied the post-treatment of
PEDOT:PSS films with acetic acid, propionic acid, butyric acid, oxalic acid, sulfurous acid, and hydrochloric acid. The post-treatment consisted on dropping 100 µL of the acid aqueous solution on the PEDOT:PSS films while they were placed on a hot plate at 140 °C, followed by drying, water rinsing and further drying at 140 °C. The electrical conductivity of the PEDOT:PSS films was significantly enhanced in all cases and was found to be dependent on the type of acid, acid concentration and treatment temperature. In all cases, the increase in electrical conductivity was attributed to the removal of PSS from the PEDOT:PSS films and to conformational changes within the PEDOT chains. The mechanism suggested for this enhancement was that the small dissociated anions from the acids could penetrate the PEDOT:PSS structure and temporarily substitute the PSS as counterions, allowing the PSS chains to leave the structure and the PEDOT chains to reorganize. Xia et al. reported, however, that the acid anions did not remain in the PEDOT:PSS film after the treatment [1]. The same group later reported the use of dilute sulfuric acid (~1 M) to increase the electrical conductivity of PEDOT:PSS films to values between 2200-2500 S/cm [2]. The increase was attributed to similar effects as the previous study with the other acids. Nevertheless, in this case, Xia et al. reported FTIR data suggesting the presence of sulfate ions in the structure of the sulfuric acid treated PEDOT:PSS films, which could indicate the partial substitution of PSS with HSO₄⁻ or SO₄²⁻ as counterions.

Kim et al. [3] used concentrated sulfuric acid (instead of dilute) to post-treat PEDOT:PSS films and obtained electrical conductivity values as high as 4300 S/cm. This value of electrical conductivity is the highest ever reported to date for a PEDOT:PSS film. They attributed the increase in electrical conductivity to the very efficient removal of PSS.
from the film and a reorganization of the PEDOT chains into a more crystalline nanofibrillar structure. However, as opposed to Xia et al., they ruled out the possibility of sulfuric acid acting as a dopant or counterion and indicated that it only served as a very good solvent for PSS.

Similarly, Gueye et al. [4] deposited thin films of PEDOT with the very small counterion trifluoromethanesulfonate (OTf), which showed conductivities as high as 5400 S/cm after being post-treated with sulfuric acid. But in that report, they concluded that the sulfuric acid treatment induced further oxidation (but not overoxidation) of the PEDOT chains, increasing the charge carrier concentration (i.e. primary doping) and also reported XPS data that indicated the presence of sulfate anions in the post-treated films, which suggested substitution of some of the OTf by HSO$_4^-$ as counterion.

Khan et al. [5] studied the treatment of PEDOT:Tos films with hydrochloric acid (HCl). The electrical conductivity increased with the HCl treatment and was attributed to the substitution of tosylate anions with Cl$^-$ as counterion, accompanied by further oxidation of the PEDOT chains (doping).

Zhang et al. [6] wet-spun PEDOT:PSS fibers using a concentrated sulfuric acid coagulation bath. The fibers had conductivities as high as 3800 S/cm when the residence time in the coagulation bath was 10 min. This is the highest electrical conductivity reported to date for a PEDOT:PSS fiber. The high electrical conductivity was attributed to the very effective removal of PSS in the sulfuric acid coagulation bath while the fibers were forming. However, the question of whether the sulfuric acid induced further doping or remained in the structure as a counterion was not mentioned.
As can be inferred, acid treatment of the various PEDOT-based films is an effective method to increase their conductivity. Nevertheless, the exact mechanism by which this increase occurs is still a topic under discussion. In the particular case of PEDOT:PSS, most of the authors agree on the effectiveness of these acid treatments (particularly concentrated sulfuric acid treatments) to remove excess PSS. However, it is not clear whether the acid anions (such as sulfate) partially substitute PSS as counterions and/or if the acid treatment induces primary doping of the PEDOT chains, increasing the charge carrier concentration.

Motivated by this, in this dissertation, we decided to explore the use of sulfuric acid treatments to further increase the electrical conductivity of the PEDOT:PSS fibers. First, simple experiments where the fibers’ spools where immersed in sulfuric acid where carried out. Then, a modification of the PEDOT:PSS continuous wet-spinning process was done to include a sulfuric acid draw bath. The effect that the sulfuric acid drawing had on the electrical and mechanical properties of the fibers was investigated. Moreover, the structure of the fibers after sulfuric acid drawing was studied using WAXS and XPS, in order to correlate changes in the structure with the changes observed in the fiber properties.

5.2 Experimental details on the sulfuric acid treatment setups

5.2.1 Immersion post-treatment in sulfuric acid

PTFE spools with coagulation bath (10 vol.% DMSO in IPA) PEDOT:PSS fibers wound on them were immersed in 93 wt.% sulfuric acid such that all the fibers were covered with the sulfuric acid solution. The fibers were left immersed for different periods of time (1, 5, 10, 30 and 60 min) at room temperature. Then, they were transferred to a deionized water bath where they were left immersed for 10 min in order to wash off the
sulfuric acid from the fibers. Lastly, the washed spools were transferred to an oven where they were dried at 140 °C for 10 min.

5.2.2 Sulfuric acid drawing process

A scheme of the in-line sulfuric acid drawing process is shown in Figure 5.1. Typically, a spool of fiber fabricated using the setup described in Chapter 4 was placed on the first roller, rotating at a speed, $v_1$. The fiber was unwound from the spool and passed through a PTFE container filled with 93 wt.% sulfuric acid. The fiber speed was adjusted such that the residence time of the fiber in the sulfuric acid bath was approximately 1 min. The fiber was taken out of the sulfuric acid bath by a second powered roller with speed, $v_2$. The sulfuric acid draw ratio was defined as

$$DR_{Sulf} = \frac{v_2}{v_1}$$

and was typically kept between 1.05-1.20.

After the sulfuric acid bath, the fibers entered a deionized water wash bath to remove sulfuric acid from the fibers. The fibers were taken from the wash bath at speed $v_3$, and the water wash draw ratio was defined as

$$DR_{Wash} = \frac{v_3}{v_2}$$

and was typically kept around 0.90-1.02.

In some cases, the fibers were collected on a spool directly after the water wash and, therefore, $v_3$ was the final take-up speed. Alternatively, the fibers could undergo a final drying step by passing through a keyhole-cylinder-shaped oven before collection. In those cases, the oven draw ratio was
\[ DR_{Oven} = \frac{v_{\text{take-up}}}{v_3} \]  

and was typically kept around 0.95-1.02.

The total draw ratio for these fibers is still the ratio between take-up and dope velocities. However, because of the additional processing steps, eq. 4.3. had to be modified to

\[ DR_{Total} = \frac{v_{\text{take-up}}}{v_{\text{dope}}} = DR_{\text{Coag}} \cdot DR_{DMSO} \cdot DR_{Sulf} \cdot DR_{Wash} \cdot DR_{Oven} \]  

**5.3 Results and discussion**

**5.3.1 Immersion post-treatment in sulfuric acid**

**Figure 5.2a** shows the change in diameter versus immersion time in the sulfuric acid bath for two coagulation bath samples at total draws of 1.58 and 3.34. In both cases, after only one minute of treatment, there was a reduction in diameter from ~10 to ~6 \(\mu\)m and from ~7 to ~4 \(\mu\)m for a total draw of 1.58 and 3.34, respectively. Moreover, the diameter was rather constant with increasing treatment time after that first drop. The linear densities of the sulfuric acid treated fibers are plotted in **Figure 5.2b** together with the linear densities of coagulation bath fibers and DMSO drawn fibers as a function of total draw. Calculated linear density curves using eq. 4.8 are also included for different PEDOT wt.% in the final fiber (28.57, 35, 40, 60 and 70 wt.%). As discussed in Chapter 4,
coagulation bath fibers closely follow the 28.57 wt.% curve, which assumes no loss of PSS. Additionally, the linear density of the DMSO drawn fibers lies in between the 35 and 40 wt.% curves, indicating removal of PSS by the DMSO draw bath. Nevertheless, a much larger decrease in linear density was observed for the fibers that were immersed in sulfuric acid. For these samples the linear density lies closer to the 60-70 wt.% curves. Figure 5.2c and d show SEM images of a fiber before and after being treated with sulfuric acid. The decrease in diameter is evidently observed. These results suggest that sulfuric acid is much more efficient in removing excess PSS from the fibers than DMSO, which is in line with results obtained by other authors [2,3]. It must be noted, that after the sulfuric acid immersion treatment, pronounced fusion between fibers was observed. Figure 5.2e shows an image of fibers with several fusion points and in Figure 5.2f the point where two fused fibers are undergoing separation, leaving visible tear marks behind. The interfilament fusion made it very difficult to obtain long single-filament specimens, as frequent breakage of the fibers would occur when attempting to unwind a single-filament from the spool.
Figure 5.2. (a) Diameter as a function of sulfuric acid immersion treatment time. (b) Linear density of coagulation bath, DMSO drawn and sulfuric acid treated fibers versus total draw. (c) SEM image of a coagulation bath fiber. (d) SEM image of a sulfuric acid treated fiber. (e) SEM images showing several fusion points between fibers after sulfuric acid treatment. (f) Close up image of a fusion point.

The electrical conductivity of the sulfuric acid treated fibers is shown in Figure 5.3. For both samples, the electrical conductivity increased with increasing treatment time until it saturated after 30 min of treatment at values around 3200-3500 S/cm. This is more than a 3-fold increase in electrical conductivity with respect to the untreated coagulation bath samples. Interestingly, the trend observed for the electrical conductivity is different to that observed for the diameters and linear density (Figure 5.2a and b). While the decrease in linear density and diameter of the treated fibers was immediate and remained constant with increasing treatment time, the increase in electrical conductivity had first a sharp increase at the 1 min mark and then a more gradual increase until saturating after 30 min. This result suggests that the mechanism by which sulfuric acid increases the electrical conductivity is not simply by removal of PSS since, in that case, the increase in electrical conductivity...
conductivity would have been immediate and constant with further increase in treatment time.

Figure 5.3. Electrical conductivity as a function of sulfuric acid immersion treatment time for coagulation samples with total draw of 1.58 and 3.34.

5.3.2 Sulfuric acid drawing process

In view of the positive results obtained from the sulfuric acid immersion treatments, it was decided to design an in-line sulfuric acid drawing step (see Figure 5.1). The hypothesis was that higher electrical conductivity would be attained by performing the sulfuric acid treatment while keeping tension on the fiber (similar to the results obtained in Chapter 3 with the DMSO treatment). Additionally, the in-line treatment would allow us to obtain non-fused sulfuric acid treated fibers which could be unwound into long single-filament specimens without breakage. Indeed, tens of meter-long spools of sulfuric acid treated fiber could be obtained using this method. Moreover, the fiber could be completely unspooled if desired, without breaking.
5.3.2.1  *Linear density of sulfuric acid drawn fibers*

The sulfuric acid drawing step was designed such that the residence time of the fibers in the sulfuric acid bath was around 1 min. Ideally, the residence time would be equal to the time required to obtain maximum electrical conductivity per the immersion tests (30 min). However, attaining this residence time would have required extremely slow spinning speeds, an extremely long sulfuric acid bath, or a far more complex spinning setup than the one here, such that the fiber could reenter the same bath several times. Considering these limitations, a residence time of 1 min was chosen as a compromise. Nevertheless, for comparison purposes, a sulfuric acid stretched fiber was also subjected to sulfuric acid immersion for 30 min. It must be noted here that all sulfuric acid treatments in this dissertation were performed at room temperature. The effect on the fibers’ electrical conductivity of increasing the treatment temperature is not known and it is an interesting area to explore in the future since it might result in shorter treatment times.

In **Figure 5.4** the linear density of coagulation bath fibers, DMSO drawn fibers, sulfuric acid immersed fibers and sulfuric acid drawn fibers is shown as a function of total draw. As can be observed, the linear density of the sulfuric acid drawn fibers is close to the 60 and 70 wt.% PEDOT calculated curves. These results are in good agreement with the sulfuric acid immersion tests, where 1 min was sufficient residence time to decrease the linear density of the fibers to those values.
Figure 5.4. Linear density of coagulation bath fibers, DMSO drawn fibers, sulfuric acid immersed fibers and sulfuric acid drawn fibers. Dotted curves represent the linear density of the fibers as calculated with eq. 4.8 using the noted wt.% of PEDOT in the final fiber.

5.3.2.2 XPS analysis

To gain insight into the compositional changes occurring in the fibers as a result of the sulfuric acid treatments, XPS was performed on bundles of coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers, and a sample of sulfuric acid drawn fibers that was in addition immersed in sulfuric acid for 30 min.

On one hand, Figure 5.5a shows the C1s XPS scans of the four samples. The curves can be deconvoluted into three components. The sp³ and sp² carbon-carbon bonding appear at ~284.8 eV, the carbon-oxygen and carbon-sulfur bonds appear as a broader peak at ~286 eV, and the carbon-oxygen double bonds appear around 289 eV [7,8]. The intensity of the C-O/C-S peak slightly increases after the DMSO drawing and increases more notably after the sulfuric acid treatments. The area ratio between the C-O/C-S peak and the C-C/C=C peak is 0.44 for the coagulation bath fibers, 0.55 for the DMSO drawn fibers, 1.08 for the sulfuric acid drawn fibers and 1.11 for the fibers that were immersed in sulfuric acid after also being stretched. If we consider the chemical structures of PEDOT and PSS (see
Figure 2.6), the ratio of C-O/C-S bonds to C-C/C=C bonds for PEDOT and PSS is 1.33 and 0.11, respectively. Therefore, the increase of this ratio indicates an increase in the concentration of PEDOT with respect to PSS (due to loss of PSS in DMSO and acid treatments). The increase in PEDOT concentration is larger in the sulfuric acid treatments, which is consistent with the linear density results. The small peak at 289 eV could be stemming from the C=O bonds present in some of the resonance structures of PEDOT (see Figure 2.13), which explains its increase with increasing PEDOT concentration.

On the other hand, the S2p XPS scans for the same samples are presented in Figure 5.5b. The S2p line of PEDOT:PSS is typically deconvoluted into two doublets (Sp1/2,3/2) corresponding to the two distinct chemical states of sulfur encountered in PEDOT:PSS, i.e. thiophene and sulfonate. The thiophene doublet appears at ~163.6 and 164.7 eV [4,8-10] with an asymmetric tail that extends into higher binding energies due to the positive charge in the oxidized PEDOT chain that gets partially localized in the sulfur atoms [9,11]. The sulfonate component is found at higher binding energies, around 168 eV [9,12]. The intensity of the thiophene doublet increases with respect to the sulfonate doublet after drawing the fibers through DMSO. This result was already discussed in Chapter 4 (see Figure 4.7) and it is consistent with partial removal of PSS from the fibers in the DMSO bath. Nevertheless, the increase in intensity of the thiophene doublet is more pronounced after drawing the fibers through sulfuric acid. This is reminiscent of the results obtained from the C1s scans and suggests that sulfuric acid drawing is more effective at removing PSS from the fibers than DMSO drawing, which also agrees well with the linear density results. In addition to the increase in intensity of the thiophene doublet, the sulfonate doublet shifts slightly towards lower binding energies. The sulfonate signal
actually has two components (and could be split into two doublets, but it would unnecessarily complicate the deconvolution). One component is the sulfonic acid group \( \text{SO}_3\text{H}^+ \) and the other is the sulfonate group acting as counterion \( \text{SO}_3\text{PEDOT}^+ \) [9]. The sulfonic acid component appears at higher binding energies, therefore, the shift towards lower binding energy indicates a decrease of this component with respect to the sulfonates acting as counterions. The PEDOT:PSS commercial dispersion used in this work contains excess PSS (PEDOT:PSS weight ratio 1:2.5). Therefore, in the coagulation bath fibers, most of the sulfonate groups are in the \( \text{SO}_3\text{H}^+ \) form. DMSO is not very effective at removing PSS and, thus, the \( \text{SO}_3\text{H}^+ \) form remains as the majority after the DMSO draw. However, upon treatment with sulfuric acid, the excess PSS is washed off and the sulfonate groups acting as counterion become the majority, shifting the signal towards lower binding energies. Moreover, after sulfuric acid drawing, an additional doublet appears at higher binding energies (168.8 eV), and increases in intensity upon further immersing the fibers in sulfuric acid for 30 min. This doublet indicates the presence of sulfates in the fibers after sulfuric acid treatment [4,8,10]. Therefore, the sulfuric acid treatment not only removes excess PSS from the fibers, but it also leads to partial substitution of PSS with sulfates as counterions. This statement contrasts with the report from Kim et al. [3] that affirmed that the sulfuric acid did not remain in the PEDOT structure after treatment. However, it is in line with the results of other authors [2,4] that also observed indications of sulfate groups remaining in the structure after sulfuric acid treatment.
Figure 5.5. XPS spectra of coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers and sulfuric acid drawn fibers that were also immersed in sulfuric acid for 30 min. (a) C1s scan and (b) S2p scan. Intensities are normalized to the maximum intensity.

5.3.2.3 WAXS analysis

Figure 5.6a-d show the 2D WAXS patterns of coagulation bath PEDOT:PSS fibers, DMSO drawn fibers, sulfuric acid drawn fibers, and fibers that were sulfuric acid drawn and additionally immersed in sulfuric acid for 30 min, respectively. In all cases, the characteristic arcs indicating the preferential orientation of the polymer chains in the fiber axis directions are observed. Moreover, the PSS amorphous halo practically disappears from the 2D patterns of the sulfuric acid treated samples (compare Figure 5.6a and b with Figure 5.6c and d), indicating the effectiveness of the sulfuric acid treatments on removing the excess PSS from the fibers and supporting the XPS and linear density results that were discussed above.
Figure 5.6. WAXS analysis of PEDOT:PSS fibers. 2D WAXS patterns of (a) coagulation bath fibers, (b) DMSO drawn fibers, (c) sulfuric acid drawn fibers and (d) sulfuric acid drawn fibers that were then immersed in sulfuric acid for 30 min. (e) Integrated intensity (normalized to the maximum intensity) versus $2\theta$. (f) Scheme of the PEDOT crystal structure.

The integrated intensity versus $2\theta$ is presented in Figure 5.6e. Three distinct features can be differentiated for all samples. Firstly, the broad hump that is found around $18^\circ$ is attributed to amorphous and randomly oriented PSS [13,14]. This PSS broad hump decreases in intensity after the fibers have been drawn through DMSO and is practically non-existent for the fibers that have been treated with sulfuric acid, due to the removal of PSS. Secondly, the peak that is found around $26.2^\circ$ is assigned to the (020) reflection, corresponding to the $\pi-\pi$ stacking of PEDOT chains with a $\pi-\pi$ stacking distance of 3.4 Å [15]. Finally, the feature appearing at small angles between $3^\circ$ and $8^\circ$ is assigned to the (100) reflection, which corresponds to the lamella stacking of PEDOT and counterion. In the case of coagulation bath fibers and DMSO drawn fibers, the (100) peak is found at $3.7^\circ$ which corresponds to a $d$-spacing of 23.6 Å. This peak shifts toward larger angles and splits into two peaks after the fibers have been drawn in sulfuric acid. In that case, the two peaks
are found at 4.8° and 6.6°, which corresponds to \(d\)-spacings of 18.6 and 13.4 Å, respectively. Lastly, when the sulfuric acid drawn fibers are additionally immersed in sulfuric acid for 30 min, the peak at 4.8° disappears and only the peak at 6.6° is observed. The shifts in \(2\theta\) of the (100) peak indicate changes in the crystal structure of PEDOT and must be related to changes in the way PEDOT and counterions (blank box in Figure 5.6f) stack.

A scheme with the proposed structural changes is shown in Figure 5.7. In the case of the coagulation bath fibers and DMSO drawn fibers, the \(d\)-spacing of 23.6 Å is close to the sum of the theoretical widths of PEDOT and PSS (7.5 Å and 15.5 Å), and it corresponds to the alternate stacking of PEDOT and PSS, where PSS has its sulfonate groups oriented in the a-direction (Figure 5.7a) [16]. The reduction of the (100) \(d\)-spacing from 23.6 Å to 18.6 Å in the sulfuric acid drawn fibers could be related to a change in how PSS is accommodated in the structure, for example, with the sulfonate groups oriented in the b-direction instead of the a-direction as shown in Figure 5.7b. This structure is similar to the stacking of PEDOT and tosylate anions (edge to edge) with a (100) \(d\)-spacing of ~14 Å [15], however, the bulkiness of the PSS counterion results in a larger distance in this case. Furthermore, the appearance of a second peak with (100) \(d\)-spacing of 13.4 Å after the sulfuric acid treatment is very interesting because similar values of \(d\)-spacing have been reported before for PEDOT with sulfate as the counterion [4,10,17,18]. Therefore, the appearance of this peak is in line with some PSS being substituted by sulfate as counterion (Figure 5.7c). Thus, the sulfuric drawn fibers show a mix of PEDOT-PSS and PEDOT-sulfate lamella stacking, yielding the split peak observed in the WAXS pattern. Further treating the fibers by immersing them in sulfuric acid for 30 min, promotes the
reorganization of the remaining PEDOT chains still stacked with PSS to stack with sulfate anions instead, resulting in the disappearance of the peak at 4.8° and the increase in intensity of the peak at 6.6°. These results are also in line with the increase in the intensity of the sulfate doublet relative to the sulfonate doublet in the XPS S2p scan (Figure 5.5b).

Figure 5.7. Scheme showing the different proposed changes in the (100) lamella stacking of PEDOT and counterions upon sulfuric acid treatment. Insets show the (100) peaks in the intensity versus 2θ plots.

The crystallite size along the a and b directions was also calculated using the Scherrer’s equation:

$$L_Z = \frac{K\lambda}{\beta \cos\theta}$$

where $L_Z$ is the crystallite size along a direction Z, $K$ is a dimensionless shape factor (value of 0.9 used in this work), $\lambda$ is the X-ray wavelength (1.54189 Å in this work) and $\beta$ is the full width at half maximum (FWHM) of the corresponding peak in radians. The values
obtained are listed in Table 5.1. $L_a$ is found to be the same (around 35 Å) for both coagulation bath fibers and DMSO drawn fibers. In the case of the sulfuric acid drawn fibers, the crystallite size calculated from the (100) lamella stacking of PEDOT and PSS, $L_{a,PSS}$, decreases to 27 Å, however, the size calculated using the (100) lamella stacking of PEDOT and sulfates, $L_{a,sulfate}$, has a higher value of 40 Å. Moreover, after immersing the fiber in sulfuric acid for 30 min, the peak corresponding to the lamella stacking of PEDOT and PSS disappears, and $L_{a,sulfate}$ increases to 48 Å. On the other hand, $L_b$ calculated from the (020) reflection is found to increase from 18 Å to 22 Å after DMSO drawing or sulfuric acid drawing, and further increase to 25 Å after being sulfuric acid drawn and immersed in sulfuric acid for 30 min. Therefore, the substitution of PSS by sulfate as counterion seems to promote a more crystalline structure, given the increased crystallite sizes observed in both the a and b directions. This is likely due to reduced steric effects imposed in the structure by the smaller size sulfate counterions as opposed to the bulky PSS polymer chains.

Additionally, the degree of crystallinity, $\chi_c$, was also calculated for the different samples. For this purpose, the (100) and (020) peaks in 2D WAXS patterns were considered as the signal for the crystalline regions, while the peak corresponding to the PSS halo was considered amorphous signal. $\chi_c$ was then calculated using the following equation:

$$
\chi_c = \frac{A_{(100)} + A_{(020)}}{A_{(100)} + A_{(020)} + A_{PSS}} \cdot 100
$$

where $A_Z$ is the area of the 2D WAXS peak corresponding to the Z reflection. As can be observed in Table 5.1, the crystallinity of the samples increased from 49% to 56% after DMO drawing. Nevertheless, a much higher increase in the degree of crystallinity occurs upon treating the fibers with sulfuric acid, reaching values in the range of 83-86%. These
results are in line with the removal of the amorphous PSS phase from the fibers, leaving behind a crystalline phase of PEDOT.

**Table 5.1.** Crystallite size in the a and b directions, and degree of crystallinity for the different fiber samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$L_a_{PSS}$ (Å)</th>
<th>$L_{a,sulfate}$ (Å)</th>
<th>$L_b$ (Å)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulation bath fibers</td>
<td>35</td>
<td>-</td>
<td>18</td>
<td>49</td>
</tr>
<tr>
<td>DMSO drawn fibers</td>
<td>35</td>
<td>-</td>
<td>18</td>
<td>49</td>
</tr>
<tr>
<td>Sulfuric acid drawn fibers</td>
<td>27</td>
<td>40</td>
<td>22</td>
<td>56</td>
</tr>
<tr>
<td>Sulfuric acid drawn + immersed fibers</td>
<td>-</td>
<td>48</td>
<td>25</td>
<td>83</td>
</tr>
</tbody>
</table>

5.3.2.4 *Electrical conductivity*

**Figure 5.8** shows the electrical conductivity of coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers, and sulfuric acid drawn fibers that have additionally been immersed in sulfuric acid for 30 min, as a function of the draw ratio. The electrical conductivity of the sulfuric acid treated fibers was always found to be higher than the electrical conductivity of coagulation bath or DMSO drawn fibers, in agreement with the previous results obtained from the immersion of spools in sulfuric acid (**Figure 5.3**). Moreover, the fibers that were further immersed in sulfuric acid for 30 min present the highest electrical conductivity, reaching a value as high as 4039 S/cm. This value is the highest reported to date for a PEDOT:PSS fiber and is very close to the highest reported for a PEDOT:PSS film (4200 S/cm) [3], which demonstrates the effectiveness of the treatments here developed. Additionally, as it was hypothesized, the drawing in sulfuric acid was more effective in enhancing the electrical conductivity of the fibers than the immersion method. With 1 min residence time, the sulfuric acid drawn fibers reached conductivities in the range between 3000-3500 S/cm, while the fibers that were immersed in sulfuric acid (not drawn) for 1 min only reached conductivities around 2250 S/cm. The immersion time has to be increased to 30 min to obtain values of conductivity similar to
those obtained with the drawing process. These results suggest that if the residence time of the fibers in the sulfuric acid bath during the drawing step was increased to 30 min, the electrical conductivity would be enhanced to even larger values than those here reported.

For reference, electrical conductivity values as high as 5400 S/cm have been previously reported for PEDOT:sulfate thin films [4]. Moreover, a record value of 8797 S/cm has been reported for single-crystal PEDOT nanowires obtained by templated vapor phase polymerization [19], which shows that there is still room to improve the electrical conductivity of the fibers even further.

![Graph showing electrical conductivity as a function of draw ratio](image)

**Figure 5.8.** Electrical conductivity as a function of draw ratio for coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers and sulfuric acid drawn fibers that have additionally been immersed in sulfuric acid for 30 min. Values are the average of five specimens and error bars represent the standard deviation between specimens within the same sample.

Considering the results obtained from linear density (**Figure 5.4**), XPS (**Figure 5.5**), and WAXS (**Figure 5.6**) characterizations, we can re-examine the mechanism by which the electrical conductivity of the fibers is enhanced, as observed in Figure 5.3 and Figure 5.8. When the fibers are treated with sulfuric acid, most of the excess PSS is immediately (within 1 min) removed from the fibers, leading to a decrease in the linear
density of the fibers and in the sulfonate XPS signal. Additionally, as evidenced by XPS results, sulfate ions partially substitute PSS as counterions. The removal of PSS and substitution of sulfate promotes a structural reorganization of the lamella stacking of PEDOT and counterions, as proposed in Figure 5.7. The reorganization results in the shortening of the (100) lamella stacking distance and induces crystallization, as evidenced by the larger crystallite size in the a-direction (Table 5.1). Both the shortening of the (100) stacking distance and the improved crystallinity enhance the transport of charge carriers by promoting charge-carrier delocalization and increasing their mean free path, thus, increasing their mobility and, therefore, the electrical conductivity. Indeed, Petsagkourakis et al. [20] recently reported an almost linear increase in charge carrier mobility with increasing crystallinity in PEDOT:Tosylate thin films.

Furthermore, increasing the length of the sulfuric acid treatment (i.e. immersing the fibers for 30 min), promotes further substitution of sulfates as counterions as evidenced by the increased sulfate XPS signal, and allows for further structural reorganization to take place. The shortest (100) lamella stacking distance seems to be favored while improved crystallinity in both a and b directions is also observed. Thus, the charge carrier transport is further enhanced, and the highest electrical conductivity is attained.

It seems, then, that while the removal of excess PSS by sulfuric acid treatment is almost immediate, the structural reorganization of the PEDOT crystal structure that occurs with it, and involves substitution of sulfates for PSS as counterions, is kinetically limited and requires longer processing times. This would explain the immediate decrease in linear density and diameters observed during the immersion tests (see Figure 5.2) as opposed to
the gradual increase in electrical conductivity observed with increasing immersion time (see Figure 5.3).

4.3.2.5 Thermoelectric properties

The thermoelectric properties of coagulation bath fibers, DMSO drawn fibers, and sulfuric acid drawn fibers are shown in Figure 5.9. The Seebeck coefficient of the fibers slightly increased from ~15-16 μV/K to ~18-19 μV/K after the sulfuric acid treatment. This result is very interesting because typically an enhancement in electrical conductivity is accompanied by a decrease in the Seebeck coefficient since they are anticorrelated. It must be noted, however, that this anticorrelation stems from their dependence on the charge carrier concentration. As discussed in Chapter 2, the electrical conductivity increases as the charge carrier concentration increases, while the Seebeck coefficient typically decreases. Nevertheless, the electrical conductivity is also directly proportional to the charge carrier mobility (eq. 2.6) while the impact of mobility on the Seebeck coefficient is less clear. Nevertheless, a weak increase in the Seebeck coefficient with increasing mobility at constant charge carrier concentration for PEDOT:Tosylate films has been previously reported [20]. Thus, the slight increase in the Seebeck coefficient of the fibers could be related to the increase in charge carrier mobility induced by the sulfuric acid treatment. Moreover, the increased structural order promoted by the sulfuric acid treatment could have reduced the tail of localized states extending into the bandgap typically found in disordered polymers. A reduction of these localized states would result in an increase of the asymmetry of the density of states at the Fermi level, thus increasing the Seebeck coefficient (see discussion of eq. 2.10 and Figure 2.5 in Chapter 2). Indeed, Bubnova et al. [21] studied the Seebeck coefficient of PEDOT:PSS and PEDOT:Tosylate films and found
that PEDOT:Tosylate films formed more crystalline structures and the density of states had a sharper asymmetry near the Fermi level compared to disordered PEDOT:PSS films. In that study, the PEDOT:Tosylate films had Seebeck coefficients between 30-50 μV/K and were more conductive than the PEDOT:PSS films that had Seebeck coefficients around 10-15 μV/K.

The slight increase in the Seebeck coefficient together with the increase in the electrical conductivity observed in the sulfuric acid drawn fibers yielded a thermoelectric power factor of 115 μW/K²m, which is almost a 5-fold increase with respect to the coagulation bath fibers and a ~3-fold increase with respect to the DMSO drawn fibers. To the best of our knowledge, this power factor is the highest reported for a PEDOT:PSS fiber.

![Seebeck coefficient and thermoelectric power factor of coagulation bath fibers, DMSO drawn fibers, and sulfuric acid drawn fibers.](image)

**Figure 5.9.** Seebeck coefficient and thermoelectric power factor of coagulation bath fibers, DMSO drawn fibers, and sulfuric acid drawn fibers.

### 5.3.2.6 Mechanical properties

**Figure 5.10** shows characteristic stress-elongation curves of four representative fibers and **Figure 5.11a-c** show the elongation at break, break stress, and Young’s modulus as a function of total draw. Coagulation bath fibers have the largest elongations at break
and lowest modulus, characteristic of a poorly oriented polymeric material. The Young’s modulus increases as the fibers are drawn in DMSO (as discussed in Chapter 4), however, the increase is larger when the fibers are drawn in sulfuric acid. Interestingly, the elongation at break of DMSO drawn and sulfuric acid drawn fibers is similar, which suggests that the increase in Young’s modulus is not due to increased preferred orientation. Instead, as the excess PSS is removed from the fibers, the amorphous phase of the fiber is also removed (as clearly observed in the 2D WAXS patterns in Figure 5.6a-d) and so, the remaining phase is more highly oriented. Moreover, the concentration of PEDOT in the fibers increases as PSS is removed, which could shift the mechanical stress bearing towards the PEDOT chains, which are stiffer than the PSS chains due to their conjugated nature. The higher Young’s moduli combined with the similar elongations at break, results in sulfuric acid drawn fibers having the highest break stresses with values as high as 550 MPa, which is the highest reported to date for a PEDOT:PSS fiber. It must be noted that the fibers that were immersed in sulfuric acid after being drawn still showed interfilament fusion and breakage of the fibers while unwinding still occurred. In fact, this sample (shown in green in Figure 5.10) showed the lowest elongation at break among all the sulfuric acid treated samples and the lowest Young’s modulus and break stress (with a rather large standard deviation), which is most likely stemming from existing tearing damage on the tested specimens caused when the fused filaments were separated.
Figure 5.10. Typical stress-elongation curves in uniaxial tension of coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers and sulfuric acid drawn fibers that were additionally immersed in sulfuric acid for 30 min.

Figure 5.11. Single-filament tensile properties of PEDOT:PSS coagulation bath fibers, DMSO drawn fibers, sulfuric acid drawn fibers, and sulfuric acid drawn fibers that were additionally immersed in sulfuric acid for 30 min. (a) Elongation at break, (b) break stress and (c) Young’s modulus. Values are the average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample.

5.3.2.7 Color change after sulfuric acid treatment

After performing the sulfuric acid treatment, a change in the color of the light reflected by the fibers was observed. On one hand, Figure 5.12a shows a photograph of as spun PEDOT:PSS fibers being collected on a spool. The fibers look black to the naked eye, while reflected light is white as can be seen in the inset (which is saturated to emphasize
colors). On the other hand, Figure 5.12b shows a photograph of sulfuric acid drawn fibers being collected on a spool right after the water wash bath. The fibers also look black to the naked eye, however, the reflected light looks orange-red. This change in color occurred for all sulfuric acid treated fibers. It has been hypothesized that the change in color is related to the structural reorganization and change in $d$-spacing occurring in the crystal structure of the fibers after sulfuric acid treatment. UV-vis characterization of the fibers is planned to be done in the future to better understand and explain these observations.

![Image](image1.png)

**Figure 5.12.** Photographs of (a) as-spun PEDOT:PSS fibers and (b) sulfuric acid drawn PEDOT:PSS fibers both being collected into a PTFE spool. Insets are artificially saturated enlargements of the marked area to emphasize the change in color.

### 5.3.2.8 Correlation between electrical conductivity and Young’s modulus

Figure 5.13 plots the electrical conductivity versus the Young’s modulus of the fibers. The coagulation bath fibers have both the lowest electrical conductivity and lowest Young’s modulus. Coagulation bath fibers have the lowest concentration of PEDOT of all the samples (around 28 wt.%) and are also weakly oriented because they had not been stretched, with a Hermans orientation factor, $f_{100}$, around 0.30. After drawing the fibers in DMSO, significant preferred orientation of the crystal planes is induced in the fiber axis direction, and $f_{100}$ increases to values around 0.60-0.70. Additionally, some PSS is removed from the fibers, slightly increasing the PEDOT concentration of the fibers to
values around 35 wt.%. The higher state of orientation and the increase in PEDOT concentration leads to an increase in both the electrical conductivity and the Young’s modulus of the fibers. Nevertheless, the highest electrical conductivities and Young’s moduli are obtained if the fibers are drawn in sulfuric acid instead of DMSO. The state of orientation induced in the fibers by sulfuric acid drawing is similar to the DMSO drawing with $f_{100}$ around 0.70. However, a large quantity of PSS is removed from the fibers and the PEDOT concentration with respect to PSS is greatly increased, to values around 60-70 wt.%. After the removal of the amorphous PSS phase, the fiber is mainly composed of a highly oriented and crystalline PEDOT phase, leading to the increased conductivity and stiffness observed. In Chapter 4, a correlation between electrical conductivity and the mechanical properties was found. In general, the stiffest fibers were also the most conductive. As can be observed, the correlation still holds true after the sulfuric acid treatments.
5.13. Electrical conductivity versus Young’s modulus. Values are average of 5 specimens per sample. The error bars represent standard deviation between specimens within the same sample.

5.4 Conclusions

Acid treatments of PEDOT:PSS films are common in the literature with the objective of increasing its electrical properties. Concentrated sulfuric acid treatments have been the most effective so far, however, the mechanism by which the electrical properties are enhanced is still a topic of debate. Furthermore, few reports exist that discuss the effect of these treatments on the mechanical properties of the material. In this chapter, the drawing of PEDOT:PSS fibers in sulfuric acid was described. The sulfuric acid drawn PEDOT:PSS fibers showed outstanding electrical conductivities with values as high as 4039 S/cm, which is the highest reported to date for a PEDOT:PSS fiber. The mechanical properties of the fibers were also enhanced, with Young’s modulus and break stress values of approximately 20 GPa and 550 MPa, respectively. These values are the highest reported to date for a PEDOT:PSS fiber and, to the best of our knowledge, for any PEDOT:PSS material. Additionally, XPS and WAXS characterizations of the fibers were performed. It
was found that the sulfuric acid treatment effectively removed excess PSS from the fibers and promoted the substitution of PSS by sulfate as counterion. Moreover, these compositional changes were accompanied by a structural reorganization of the crystal structure of PEDOT, increasing the crystallinity and effectively reducing the (100) \(d\)-spacing that corresponds with the lamella stacking distance of PEDOT and counterion. The improvement of the electrical and mechanical properties was correlated with the changes in the composition and structure observed in the fibers after the sulfuric acid treatment. These results provide insight into the mechanism by which the sulfuric acid treatments enhance both the electrical and the mechanical properties of PEDOT:PSS while also lead the way in the fabrication of high performance PEDOT:PSS fibers for future electronic textiles.
5.5 References


CHAPTER 6. APPLICATIONS OF PEDOT:PSS FIBERS

This chapter first provides a comparison between the properties of the PEDOT:PSS fibers, traditional fibers, such as textile fibers and carbon fibers, and metals. Additionally, the stability of the electrical conductivity of the PEDOT:PSS fibers with respect to time and humidity is presented. Finally, several potential applications are discussed while providing preliminary results and proof of concept demonstrations of the use of the fibers in such applications.

6.1 Comparison between PEDOT:PSS fibers, textile and carbon fibers, and metals

Fibers are unique forms of matter characterized by having a large aspect ratio and, generally, a high level of anisotropy in their properties between the radial and axis directions. In terms of mechanics, whether we consider cotton apparel or carbon fiber reinforced composites, fibers are very often used to support tensile loads. The study of the mechanical properties of fibers in tension is, therefore, important. Not only because of their end use application, but also because fibers are typically processed into textiles by weaving, knitting, sewing, or other processes that require a certain level of robustness, sometimes higher than the end use application. Table 6.1 shows the mechanical and electrical properties of some common metals and fibers, including the properties of the PEDOT:PSS fibers fabricated in this work. The mechanical properties of the PEDOT:PSS fibers are very similar to those of some natural fibers such as cotton or silk. Additionally, the PEDOT:PSS fibers have electrical conductivities that rival carbon fibers. Cotton textiles are ubiquitous; however, cotton is an electrically insulating material. On the other hand, carbon fibers have good electrical properties but are too brittle to be considered for textile applications.
PEDOT:PSS fibers bridge the gap between these two: a fiber with the mechanical properties of cotton fibers but with the electrical conductivity of carbon fibers.
Table 6.1. Mechanical and electrical properties of common metals and fibers.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density</th>
<th>Young’s modulus</th>
<th>Specific Young’s modulus</th>
<th>Tensile strength</th>
<th>Strain to failure</th>
<th>Electrical conductivity</th>
<th>Specific electrical conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/cm³</td>
<td>GPa</td>
<td>GPa/(g/cm³)</td>
<td>MPa</td>
<td>%</td>
<td>S/cm</td>
<td>S/cm/(g/cm³)</td>
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<td><strong>Metals</strong></td>
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<td></td>
<td></td>
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<tr>
<td>Steel</td>
<td>7.90</td>
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<td>25.3</td>
<td>-</td>
<td>-</td>
<td>14500</td>
<td>1800</td>
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<tr>
<td>Aluminum</td>
<td>2.70</td>
<td>76</td>
<td>28.1</td>
<td>-</td>
<td>-</td>
<td>377000</td>
<td>139600</td>
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<tr>
<td>Titanium</td>
<td>4.50</td>
<td>116</td>
<td>25.7</td>
<td>-</td>
<td>-</td>
<td>23800</td>
<td>5300</td>
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<tr>
<td>Copper</td>
<td>8.96</td>
<td>128</td>
<td>14.2</td>
<td>-</td>
<td>-</td>
<td>596000</td>
<td>66500</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Cotton</td>
<td>1.54</td>
<td>8</td>
<td>5.2</td>
<td>600</td>
<td>7</td>
<td>-</td>
<td>-</td>
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<td>Wool</td>
<td>1.30</td>
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<td>1.5</td>
<td>170</td>
<td>35</td>
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<td>-</td>
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<tr>
<td>Silk (silk worm)</td>
<td>1.40</td>
<td>8</td>
<td>5.7</td>
<td>400</td>
<td>25</td>
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<tr>
<td>Silk (spider)</td>
<td>1.40</td>
<td>12</td>
<td>8.6</td>
<td>600</td>
<td>25</td>
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<td><strong>Organic synthetic fibers</strong></td>
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</tr>
<tr>
<td>Polyamide 66</td>
<td>1.2</td>
<td>&lt; 5</td>
<td>&lt; 4.2</td>
<td>1000</td>
<td>20</td>
<td>-</td>
<td>-</td>
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<td>Polyester</td>
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<td>11</td>
<td>800</td>
<td>15</td>
<td>-</td>
<td>-</td>
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<td>Kevlar 49</td>
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<td>93</td>
<td>3000</td>
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<td>-</td>
<td>-</td>
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<td>122</td>
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<td><strong>Carbon fibers from pitch</strong></td>
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<td>3800</td>
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<td>1400</td>
<td>0.5</td>
<td>1170</td>
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<tr>
<td><strong>Carbon fibers from PAN</strong></td>
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<td>Toray T1000</td>
<td>1.80</td>
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<td>7060</td>
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<td>Toray M60J</td>
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<td>305</td>
<td>3920</td>
<td>0.7</td>
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<td>740</td>
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<tr>
<td><strong>PEDOT:PSS fibers in this work</strong></td>
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<td></td>
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<tr>
<td>Coagulation bath</td>
<td>1.61</td>
<td>5</td>
<td>3.1</td>
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<td>20</td>
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<tr>
<td>DMSO drawn</td>
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<td>8</td>
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<td>Sulfuric acid drawn</td>
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<td>11</td>
<td>525</td>
<td>8</td>
<td>3500</td>
<td>2170</td>
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</table>

Metals properties extracted from [www.engineeringtoolbox.com](http://www.engineeringtoolbox.com), natural and synthetic fibers properties from reference [1] and carbon fiber properties from reference [2].
6.2 Stability of the electrical properties of PEDOT:PSS fibers

Another important aspect to consider from the applicability perspective of the fibers is the stability of their electrical properties. For the purposes of studying the stability, specimens of fiber were mounted in 2-probe configuration to measure their resistance using silver paint (methyl isobutyl ketone based, Electron Microscopy Sciences) to make the electrical contacts. Some specimens were kept in laboratory atmosphere (T ~ 22 °C and non-controlled relative humidity that ranged between 10-50%) while others were kept in a controlled atmosphere (T ~ 21 °C and 0.5% relative humidity). The results are shown in Figure 6.1a-b in terms of resistance, R, divided by the initial resistance at day 0, R₀. On one hand, in the laboratory atmosphere, the resistance of coagulation bath fibers continuously increased by a factor of 3.2 after 89 days, while the resistance of both DMSO drawn and sulfuric acid drawn fibers increased at a slower pace and seemed to equilibrate at approximately R/R₀ = 1.6 after 89 days. On the other hand, in a controlled atmosphere, the resistance of both coagulation bath fibers and DMSO drawn fibers barely changed (R/R₀ ~ 0.98 after 99 days) while the sulfuric acid drawn fibers had a resistance 1.16 times higher after 99 days. Clearly, humidity played a role in the degradation of the electrical conductivity of these specimens. All specimens showed an increase in resistance when kept in a laboratory atmosphere with variable humidity while the increase in resistance was non-existent or relatively small when kept in a controlled atmosphere at 0.5% relative humidity.
In order to elucidate if the degradation in the electrical properties observed in laboratory atmosphere were due to degradation of the electrical contacts or degradation of the fibers, ‘fresh’ fiber specimens from the spool were measured on different days after fabrication. The spools were kept in the laboratory atmosphere. In this case, each measurement of electrical conductivity was done with new specimens recently cut from the spool and with new electrical contacts made with silver paint, thus, avoiding any contact degradation. **Figure 6.2** shows the values of electrical conductivity measured as a function of time. The electrical conductivity of coagulation bath fibers and DMSO drawn fibers decreased very slightly after 194 and 142 days since fabrication, respectively. $R/R_0$ for coagulation bath fibers was 1.16 after 194 days, contrasting the value of 3.2 obtained during the stability experiment in **Figure 6.1a**. Similarly, $R/R_0$ for DMSO drawn fibers was 1.06 after 142 days as opposed to 1.6 during the stability experiment in **Figure 6.1a**. However, the sulfuric acid drawn fibers experienced higher degradation, with a value of $R/R_0$ of 1.37 after 135 days since fabrication. In fact, the electrical conductivity of the sulfuric acid drawn fibers approaches that of the DMSO drawn fibers after 135 days.
In view of these results, we can conclude that coagulation bath fibers and DMSO drawn fibers present good stability, even in the presence of humidity with only a slight decrease in electrical conductivity after fabrication. This decrease seems to happen on the first few days after fabrication since the electrical conductivity measured after day 0 is rather constant. However, the electrical contacts (at least when contacting with silver paint), degrade in the presence of humidity but are quite stable in the absence of it. Our hypothesis is that the fibers uptake water from the environment and some of this water ends up forming a layer at the fiber-contact interface, however, we do not have enough information to corroborate this hypothesis at this moment.

On the other hand, the sulfuric acid fibers experienced degradation in all the cases studied. We believe that, in addition to the contact degradation, sulfuric acid drawn fibers experience other degradation mechanisms not occurring in the coagulation bath or DMSO drawn fibers. Some of our hypotheses include corrosion of contacts and/or increased hygroscopicity due to sulfuric acid remaining in the fibers after treatment or the possibility that the changes in the PEDOT structure after the sulfuric acid treatment are metastable. As in the previous case, we do not have enough information to corroborate any of these hypotheses at this moment.
Figure 6.2. Electrical conductivity versus time of specimens cut from the spool with new electrical contacts.

6.3 PEDOT:PSS fibers as flexible textile interconnections

Nowadays, electric power and electronic devices are ubiquitous. The transmission lines that constitute the power grid, the insulated cables of home appliances or the channels in printed circuit boards, all serve the purpose of transporting electricity. Developing flexible textile interconnections is a cornerstone to advance the field of electronic textiles. Imagine a future textile device that can sense a wearer’s blood pressure and send an alert if it is too low or too high. The device may be composed of a pressure sensor, a signal amplifier, a controller, an energy harvester and two LEDs. All those components have to be interconnected somehow such that electrons can be transported from one component to another. Electrically conductive fibers such as the PEDOT:PSS fibers developed in this dissertation could serve that purpose.

An important characteristic to consider for an interconnection is the maximum current carrying capacity or ampacity. How to define ampacity is sometimes ambiguous. In the scientific literature, the most used definition is the maximum current density that causes the immediate electrical failure of the conductor and it is often called the failure
current density (FCD) [3]. However, copper cables, for instance, must operate below a certain temperature to avoid damage to their insulating material. In this case, the ampacity is defined as the maximum current density that does not exceed the temperature rating of the insulating material and is called the continuous current rating (CCR) [3]. In this dissertation, the FCD definition of ampacity is used.

**Figure 6.3a** shows the resistance divided by the initial resistance, $R/R_0$, as a function of current density for coagulation bath fiber samples. To obtain these curves, fiber specimens were mounted in 2-probe configuration and the voltage was swept at rates between 0.1 mV/s to 1000 mV/s while measuring the current until electrical failure of the fiber occurred. The resistance of the fiber at each I-V point was then calculated using Ohm’s law. The maximum current density value of each of the curves corresponds to the maximum current density at which the electrical failure, as observed as the onset of a steep increase in resistance, started, and the fiber’s resistance increased irreversibly until breakdown. As can be observed, the value of maximum current density depends on the voltage sweep rate. At high sweep rates, the maximum current is achieved in a short period of time ($< 3$ s), and the process largely occurs with the fiber not being at thermal equilibrium. At low sweep rate, the maximum current is achieved in a long period of time ($> 5$ h) and the fiber can be largely considered to be at thermal equilibrium at each given point. An ampacity of 16.2 kA/cm² can be extracted from the 1000 mV/s curve but it is only valid for peaks of current that last very short period of times ($< 3$ s). A more practical value of 11.3 kA/cm² can be extracted from the 0.1 mV/s curve, which is valid for continuous operation. Indeed, **Figure 6.3b** shows the change in resistance with time of coagulation bath fiber specimens kept at a certain current density for 60 min. The fibers
kept at 12 kA/cm\(^2\) and 11.5 kA/cm\(^2\) broke after 7.4 min and 56.4 min of operation, respectively, while the fiber kept at 11 kA/cm\(^2\) did not break. This suggest that the ampacity for continuous operation is between 11 and 11.5 kA/cm\(^2\), which is in good agreement with the value of 11.3 kA/cm\(^2\) obtained from Figure 6.3a at a voltage sweep rate of 0.1 mV/s.

![Figure 6.3](image)

**Figure 6.3.** (a) Resistance (standardized to the initial resistance) of coagulation bath fibers versus increasing current density at different voltage sweep rates until electrical failure. (b) Change in resistance (standardized to the initial resistance) of coagulation bath fibers with time at different constant current densities.

Similarly, R/R\(_0\) versus current density curves at different voltage sweep rates were obtained for DMSO drawn fibers and sulfuric acid drawn fibers. Figure 6.4a shows the curves at a voltage sweep rate of 0.1 mV/s while Figure 6.4b shows the values of ampacity for the three types of fiber as a function of the voltage sweep rate. The ampacity of DMSO drawn fibers is higher than coagulation bath fibers and further increases for sulfuric acid drawn fibers. The continuous operating ampacities taken from Figure 6.4a are 18.1 kA/cm\(^2\) for DMSO drawn fibers and 21.1 kA/cm\(^2\) for sulfuric acid drawn fibers. A similar value of ampacity (18 kA/cm\(^2\)) has been reported by Zhou et al.[4] for PEDOT:PSS fibers fabricated by a two-step wet-spinning process where the fibers were first spun into an isopropanol/acetone coagulation bath and then immersed for 1 h in ethylene glycol. Otley
et al. [5] fabricated textile interconnections by coating polyester fabrics with PEDOT:PSS. However, the ampacity was only 1.09 kA/cm$^2$ due to the low electrical conductivity of the coated textile. Moreover, it is worth mentioning that the ampcities of the PEDOT:PSS fibers fabricated in this work are in the same range of typical ampacity values obtained for oriented carbon nanotube yarns (10-100 kA/cm$^2$) [6,7].

![Figure 6.4](image)

**Figure 6.4.** (a) Resistance (standardized to the initial resistance) of the three types of fibers versus increasing current density at 0.1 mV/s voltage sweep rates until electrical failure. (b) Ampacity as a function of the voltage sweep rate.

These results indicate that the PEDOT:PSS fibers are strong candidates to be used as electrical interconnections. As a proof of concept, two bundles of 3 DMSO drawn fibers were sewed to a cotton cloth and connected to a red LED. As shown in Figure 6.5a, the LED could be lit by passing 1 mA of current through the PEDOT:PSS interconnections. Moreover, the interconnections remained functional even after continuous manipulation and bending (Figure 6.5b-c).
Figure 6.5. (a) Photograph showing a red LED being lit by passing 1 mA through PEDOT:PSS fiber interconnections sewed to cotton cloth. Inset shows an enlargement of the PEDOT:PSS fibers. (b-c) Photographs showing functional interconnections even after bending the cotton cloth.

6.4 PEDOT:PSS fibers as heating elements

The electrical failure studied in the last section is caused by overheating of the fiber due to the Joule effect. When an electric field is created by applying a voltage difference between two points of a conductor, charge carriers are accelerated in the direction of the electric field. However, the charge carriers frequently collide with atoms (scattering), and some of their kinetic energy is transferred to the atoms, increasing their vibrational motion, or in other words, kinetic energy is converted into thermal energy.

In this section, the Joule heating characteristics of DMSO drawn PEDOT:PSS fibers are presented. An infrared camera (FLIR i60) was used to record videos of fiber specimens while passing current through them and temperature versus time plots were extracted from them. Figure 6.6a shows the temperature of the fiber\(^2\) versus time while the

\(^{2}\) The temperature here referred as “temperature of the fiber” is the temperature as obtained from the infrared camera. However, the resolution of the camera was not sufficient to properly capture the single filaments due to their small diameter. To work around this, the fibers were mounted on paper substrates with low thermal conductivity. The temperature recorded is, therefore, the temperature of the area around the contact between the fiber and paper. The actual temperature of the fiber is unknown and likely to be higher.
current was increased in steps of 0.5 mA each 30 seconds until the electrical failure of the fiber occurred. The temperature of the fiber reached around 80 ºC before thermal runaway occurred followed by electrical failure. The temperature of the fiber increased parabolically with the current density (Figure 6.6b) and had a linear relationship with the power dissipated in the fiber (see inset of Figure 6.6b). The corresponding energy balance is written in eq. 6.1. The energy dissipated must be equal to the energy used to raise the temperature of the fiber, the energy loss by convection and the energy loss by radiation.

\[
P dt = C dT + h_c S (T - T_{amb}) dt + E_R \tag{6.1}
\]

where \(P\) is the power dissipated by the fiber, \(C\) is the heat capacity, \(h_c\) is the convective heat transfer coefficient, \(S\) is the surface area of the fiber, \(T\) is the temperature of the fiber, \(T_{amb}\) is the ambient temperature and \(E_R\) is the energy loss due to radiation. The energy loss by radiation is given by the Stefan-Boltzmann equation:

\[
E_R = \varepsilon s S (T^4 - T_{amb}^4) \tag{6.2}
\]

where \(\varepsilon\) is the emissivity of the fibers and \(s\) is the Stefan-Boltzmann constant.

Eq. 6.2 can be rewritten using a temperature-related radiation heat transfer coefficient, \(h_R\) [8].

\[
E_R = \varepsilon s S (T^4 - T_{amb}^4) = \varepsilon s S (T^2 + T_{amb}^2) (T + T_{amb}) (T - T_{amb}) = Sh_R (T - T_{amb}) \tag{6.3}
\]

Using eq. 6.3, eq. 6.1 can be rewritten as:

\[
C dT = P dt - h S (T - T_{amb}) \tag{6.4}
\]

where \(h\) (\(h = h_c + h_R\)) is the global heat transfer coefficient. If we assume that the variations with temperature of \(C\), \(h_c\) and \(h_R\) are negligible considering the small range of temperatures (20-80 ºC), then eq. 6.4 has the following solution [8]:
\[ T = T_{amb} + \frac{P}{hS} \left( 1 - e^{-\frac{t}{\tau}} \right) \]  
\text{eq. 6.5}

where \( \tau \) is the first-order time constant given by \( \tau = \frac{C}{hS} \). The maximum temperature, \( T_{max} \), is found at sufficiently large time when the term within the brackets in eq. 6.5 tends to 1. Therefore:

\[ T_{max} = T_{amb} + \frac{P}{hS} \]  
\text{eq. 6.6}

Eq. 6.6 predicts a linear relationship between the electrical power dissipated in the fiber and the temperature of the fiber, in good agreement with the trend observed in the inset of Figure 6.6b.

**Figure 5.6.** (a) Temperature of a fiber versus time while increasing the current by 0.5 mA each 30 s. (b) Temperature of the fibers as a function of the current density (inset: temperature as a function of power dissipated).

The first-order time constant, \( \tau \), is an important parameter since it is an indicator of how fast the material heats up due to a step change in the applied power. The time constant represents how much time the fiber would have taken to heat up to the equilibrium temperature if the heating rate stayed constant at the initial rate, \((dT/dt)_{max}\). However, because the heating rate decreases as the fiber heats up, the actual increase in temperature at \( t = \tau \) is around 63.2\% \((1 - 1/e)\) of the equilibrium value. A fit to eq. 6.5 of the
temperature response of the fibers after a step change in current is shown in Figure 6.7a. The time constant is 0.87 s, the maximum heating rate is 36 °C/s and $h_S$ takes a value of 0.00125 W/K. Figure 6.7b shows heating-cooling cycles of the fibers at different frequencies. Each cycle is composed of a period of time where the current (15 kA/cm$^2$) is turned on and an equal period of time where the current is turned off. For instance, a cycle with 5 s on and 5 s off has a total duration of 10 s and a frequency of 1 cycle per each 10 s or 0.1 Hz. As can be observed, the fibers perform well, heating up to the maximum temperature and cooling down to ambient temperature, when the frequency of the cycles is 0.1 Hz or lower. However, increasing the frequency beyond that resulted in incomplete heating and cooling. First-order systems reach 99.3% of their final value when the time elapsed is equal to five time constants which, in this case, is 4.35 s. Since each cycle is composed of a heating and a cooling portion then the minimum cycle time to achieve (almost) complete heating and cooling is 8.7 s per cycle or 0.11 Hz, which is in good agreement with the results observed in Figure 6.7b.
Figure 6.7. (a) Temperature response to a step change in current fitted to eq. 5.5. (b) Temperature response to step changes in current (ON: 15 kA/cm$^2$, OFF: 0) at different cycle frequencies between 0.017 and 1 Hz.

In view of these results, the PEDOT:PSS fibers are good candidates to be used as heating elements in textile heaters. Additionally, a perhaps less evident potential application is in thermochromic textiles. Thermochromism is the property of changing color due to a change in temperature. Thermochromic pigments are typically made of molecules with a weak bond such that when the temperature is increased the weak bond breaks and the molecules undergo a structural reorganization resulting in a color change. Rubacha et al. [9] prepared thermochromic cellulose fibers by including thermochromic substances in the dope, followed by wet-spinning. Similarly, Zhang et al. [10] fabricated polypropylene thermochromic fibers by mixing polypropylene and thermochromic substances followed by melt-spinning. However, these fibers only react to changes in the ambient temperature and their color cannot be changed on demand. Laforgue et al. [11] fabricated thermochromic electrospun polyvinylpyrrolidone/PEDOT non-woven mats. The color of the mat could be switched by passing a current through the mat using the Joule effect. Inspired by this, the PEDOT:PSS fibers fabricated in this work were used to fabricate a thermochromic fiber bundle as a proof of concept. The thermochromic bundle
was fabricated by coating it with a thermochromic paint\(^3\) that changes color from blue to white at 31 °C. Figure 6.8a and b show the bundle sewed to a cotton cloth in its OFF and ON state, respectively, where the color change from blue to white is clear. The temperature response of the bundle to the step change in current is presented in Figure 6.8c. These results demonstrate the potential of the PEDOT:PSS fibers to be used in on-demand color-changing clothing for fashion, camouflage purposes or even visual communication systems.

![Thermochromic PEDOT:PSS fiber bundle](image)

**Figure 6.8.** Thermochromic PEDOT:PSS fiber bundle sewed on a cotton cloth in its (a) OFF (blue) and (b) ON (white) state. (c) Temperature response of the bundle to a step change in current (inset: infrared image of the thermochromic bundle in its ON state.).

### 6.5 PEDOT:PSS fibers as p-type legs in textile thermoelectric generators

PEDOT-based materials have shown the most promising thermoelectric performance among polymer-based flexible thermoelectric materials [12,13]. Therefore, PEDOT:PSS fibers are ideal candidates as p-type legs in future textile thermoelectric generators. A thermoelectric generator is composed of several thermoelectric couples,

\(^3\) A turquoise blue to clear thermochromatic pigment with a switching temperature of 31 °C was purchased from Uniglow Products. The pigment was mixed with titanium white acrylic paint from Artist’s Loft to obtain a thermochromic acrylic based paint that changes from blue to white at 31 °C.
which are made of n-type and p-type legs connected electrically in series but thermally in parallel (Figure 6.9a). A thermoelectric generator can be modelled as a voltage source connected in series with a resistor that represents the internal resistance of the device, $R_i$, as shown in Figure 6.9b.

**Figure 6.9.** (a) Scheme of a thermoelectric generator showing p-n couples connected electrically in series but thermally in parallel. (b) Equivalent electrical circuit of a thermoelectric generator.

Ohm’s law applied to the circuit in Figure 6.9b gives:

$$V_{OC} = I(R_i + R_L)$$

\[ eq. 6.7 \]

where $V_{OC}$ is the open circuit voltage $I$ is the current and $R_L$ is the load resistance.

$V_{OC}$ is simply the thermoelectric voltage produced due to the temperature difference, $\Delta T$:

$$V_{OC} = N(\alpha_p - \alpha_n)\Delta T$$

\[ eq. 6.8 \]

where $N$ is the number of couples connected in series in the device and $\alpha_p$ and $\alpha_n$ are the Seebeck coefficients of the $p$ and $n$-type materials, respectively.

The short circuit current, $I_{SC}$, can be extracted from eq. 6.7 by simply substituting $R_L = 0$.

$$I_{SC} = \frac{V_{OC}}{R_i}$$

\[ eq. 6.9 \]

The electrical power, $P$, delivered to the load is given by:
\[ P = I^2 R_L = \frac{V_{OC}^2 R_L}{(R_i + R_L)^2} \]  \hspace{1cm} \text{eq. 6.10}

The maximum power, \( P_{\text{max}} \), from eq. 6.10 is obtained when the load resistance matches the internal resistance of the thermoelectric generator \( (R_L = R_i) \) and can be written in terms of \( V_{OC} \) and \( I_{SC} \):

\[ P_{\text{max}} = \frac{V_{OC}^2}{4R_i} = \frac{I_{SC}^2 R_i}{4} = \frac{V_{OC}I_{SC}}{4} \]  \hspace{1cm} \text{eq. 6.11}

Eq. 6.11 provides a very interesting result since it basically states that to characterize the maximum power output of a thermoelectric device at any given temperature only two measurements are needed (any pair between \( V_{OC}, I_{SC} \) and \( R_i \)).

Moreover, using eqs. 3.2, 6.8 and 6.11, we can express the maximum output power as a function of the thermoelectric properties of the \( p \) and \( n \)-type materials, the geometry of the device and the temperature difference as follows:

\[ P_{\text{max}} = \frac{NA}{4L} \left( \frac{\alpha_p - \alpha_n}{\sigma_p - \sigma_n} \right)^2 \Delta T^2 \]  \hspace{1cm} \text{eq. 6.12}

where it has been assumed that both \( p \) and \( n \)-type legs have the same length, \( L \), and cross-sectional area, \( A \). The first term in the right side of the equality in eq. 6.12 can be understood as a geometric component involving the number of couples and their geometry. Interestingly, the second term is purely related to the thermoelectric properties of the components and it is reminiscent of the thermoelectric power factor, \( \alpha^2 \sigma \), widely used to assess the thermoelectric performance of materials, and, thus, it could be understood as a device power factor.

In this work, a thermoelectric textile device was built by sewing PEDOT:PSS fiber bundles in a cotton cloth as \( p \)-type legs while using alumel wire as \( n \)-type legs (see Figure...
The textile device was composed of 20 thermoelectric couples and had an internal resistance of \( \sim 200 \, \Omega \). The output characteristics of the fabricated textile device were measured by placing one side of the device on a Peltier heater and increasing the temperature of that side while connecting different resistors to the device. Moreover, the experimental results were fitted by using the equations presented above. Figure 6.10b shows the output voltage and output power as a function of the output current of the device at \( \Delta T \) of 84 °C. The experimental data agrees well with the fit to the model. \( V_{OC} \) was 45.9 mV while \( P_{max} \) was 2.82 \( \mu W \) at \( \Delta T \) of 84 °C. Additionally, the output power is plotted as a function of \( \Delta T \) in Figure 6.10c. The output power follows a parabolic trend with increasing \( \Delta T \) in accordance with eq.6.12. For comparison, several parameters from textile thermoelectric generators previously reported in the literature are listed in Table 6.2. The textile thermoelectric generator fabricated in this work compares very positively, having one of the highest power outputs reported for a textile thermoelectric device. This is mainly due to the high power factor of the PEDOT:PSS fibers (p-type material) compared to the other PEDOT:PSS-based materials, which is only second to carbon nanotube-based materials. It is clearly observed that the devices fabricated from coated fibers perform 2 to 3 orders of magnitude worse, which is attributed to the low bulk electrical conductivity of the coated fibers. Moreover, the performance of the PEDOT:PSS-based device is on the same order as the textile thermoelectric devices fabricated from carbon nanotube fibers or layers, which shows the great potential of the PEDOT:PSS fibers to be used as the p-type component in future textile thermoelectric generators.
Figure 6.10. (a) Photograph of the textile thermoelectric device fabricated by sewing PEDOT:PSS fiber bundles and alumel wire to a cotton cloth. (b) Output voltage and output power of the device as a function of output current at $\Delta T = 84^\circ$C. (c) Output power of the device as a function of $\Delta T$. The dotted curves in (a) and (b) represent the theoretical fit to eqs. 6.7-6.12.
# Table 6.2. Performance parameters of previously reported textile thermoelectric devices.

<table>
<thead>
<tr>
<th>Materials</th>
<th>σ&lt;sub&gt;p&lt;/sub&gt;</th>
<th>α&lt;sub&gt;p&lt;/sub&gt;&lt;sup&gt;2&lt;/sup&gt;σ&lt;sub&gt;p&lt;/sub&gt;</th>
<th># of couples</th>
<th>ΔT</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt;</th>
<th>P&lt;sub&gt;max&lt;/sub&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-type</td>
<td>n-type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEDOT:PSS coated nylon fibers</td>
<td>S/cm</td>
<td>μW/K²m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEDOT:PSS coated polyester fabric</td>
<td>Silver wires</td>
<td></td>
<td></td>
<td>4</td>
<td>20</td>
<td>3.5</td>
<td>[14]</td>
</tr>
<tr>
<td>PEDOT:PSS dyed silk yarns</td>
<td>Silver wires</td>
<td>3</td>
<td>5</td>
<td>75.2</td>
<td>4.3</td>
<td>0.005</td>
<td>[15]</td>
</tr>
<tr>
<td>PEDOT:PSS dyed silk yarns</td>
<td>PVP/MWCNT</td>
<td>14</td>
<td>38</td>
<td>80</td>
<td>98.4</td>
<td>0.007</td>
<td>[17]</td>
</tr>
<tr>
<td>PEDOT:PSS hydrogel fibers</td>
<td>PEI/SWCNT</td>
<td>173</td>
<td>5</td>
<td>60</td>
<td>20.7</td>
<td>0.43</td>
<td>[18]</td>
</tr>
<tr>
<td>Wet-spun PEDOT:PSS fibers</td>
<td>Ag-plated nylon yarns</td>
<td>830</td>
<td>10</td>
<td>40</td>
<td>7.9</td>
<td>0.003</td>
<td>[19]</td>
</tr>
<tr>
<td>CNT/PVDF layers</td>
<td>CNT/PVDF layers</td>
<td>4.8</td>
<td>72</td>
<td>50</td>
<td>26</td>
<td>0.13</td>
<td>[20]</td>
</tr>
<tr>
<td>SDBS/CNT layers</td>
<td>PEI/CNT layers</td>
<td>110</td>
<td>72</td>
<td>32</td>
<td>150</td>
<td>1.80</td>
<td>[21]</td>
</tr>
<tr>
<td>CNT/PEDOT:PSS-Hydrazine fibers</td>
<td>CNT/PEDOT:PSS-Hydrazine fibers</td>
<td>1000</td>
<td>12</td>
<td>10</td>
<td>8</td>
<td>0.43</td>
<td>[22]</td>
</tr>
<tr>
<td>Wet-spun PEDOT:PSS fibers</td>
<td>Alumel wires</td>
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<td>20</td>
<td>84</td>
<td>45.9</td>
<td>2.82</td>
<td>This work</td>
</tr>
</tbody>
</table>

## 6.6 PEDOT:PSS fibers as channels in organic electrochemical transistors

Organic electrochemical transistors (OECTs) are transistors with an organic semiconductor material acting as a channel separating the source and drain electrodes and an electrolyte separating the channel and the gate electrode. They are similar to organic
field-effect transistors (OFETs) with the only difference being that in OFETs the channel and the gate electrode are separated by a standard dielectric material rather than an electrolyte. **Figure 6.11** shows a scheme of both configurations.

![Diagram of electrochemical and field-effect transistors](image)

**Figure 6.11.** Scheme of (a) electrochemical transistor and (b) field-effect transistor, both with a positive gate voltage applied.

When a drain voltage, $V_D$, is applied, a current, $I_D$, flows between the source and the drain electrodes. This current can be modulated by applying a gate voltage, $V_G$. The modulation occurs because the voltage applied to the gate electrode creates an electric field that injects ions from the electrolyte into the organic semiconductor channel. These ions interact with the organic semiconductor material changing its redox state (doping or de-doping it depending on the semiconductor type and voltage applied) [23]. For instance, in a p-type channel (such as one made with PEDOT:PSS) applying a positive gate voltage attracts the anions from the electrolyte to the gate electrode and injects the cations into the channel. The cations neutralize the negative charges of the counterion (PSS in this case) and the p-type organic semiconductor is de-doped, resulting in the reduction of the channel electrical conductivity, effectively decreasing the drain current. Thus, PEDOT:PSS-based OECTs are conductive when $V_G = 0$ and become less conductive at positive non-zero gate voltages. Because of this, PEDOT:PSS-based OECTs are classified as p-type, depletion-mode OECTs.
Electrochemical transistors have been used in multiple applications including biosensors [24,25] and integrated circuits [26,27]. PEDOT:PSS is one of the most used channel materials for OECTs due to its high electrical conductivity, mixed electronic/ionic conduction and biocompatibility [28,29]. In the developing field of electronic textiles, OECTs could play an important role similar to how the invention of the transistor flourished the era of microelectronics. For example, Hamedi et al. [30] used PEDOT:PSS coated nylon fibers to fabricate textile-based logic circuits by using the fibers as both channel and gate electrodes in OECTs. Additionally, fiber-based OECTs can also be used as biosensors. For instance, Kim et al. [31] used wet-spun PEDOT:PSS fibers to fabricate a fiber-based wearable OECT that could be attached to the skin and be used as a sweat sensor to measure ion concentration.

In this work, an OECT was fabricated using one DMSO drawn PEDOT:PSS fiber as the channel material and copper wire as the gate. Moreover, a solid polymer electrolyte was used instead of a liquid one to obtain an all-solid state OECT, which is more practical for textile applications. To fabricate the solid polymer electrolyte, 5 g of polyvinyl alcohol (PVA) (avg. molecular weight 95000, Acros Organics) and 5.88 g of 85% phosphoric acid (H₃PO₄) were added to 40 g of water and stirred on a hotplate at 90 °C until a clear solution was obtained. Then, a drop of the solution was placed on top of the copper wire and PEDOT:PSS fiber and left to dry overnight. Figure 6.12a shows an image of the OECT with 1 cm fiber channel length. The output curves of the device are presented in Figure 6.12b. At low values of $V_D$, the current shows a linear dependence on $V_D$, however, it saturates at higher voltages. Additionally, as $V_G$ is increased the PEDOT:PSS fiber channel is dedoped and the drain current decreases. Effectively, the OECT behaves as a
variable resistor or switch from the point of view of an electronic circuit, where the resistance of the PEDOT:PSS fiber acting as the channel can be varied by applying a gate voltage.

![Image of PEDOT:PSS fiber-based OECT](image)

**Figure 6.12.** (a) Image of the PEDOT:PSS fiber-based OECT. (b) Output curves showing the dependence of $I_D$ on $V_D$ at different $V_G$ from 0 to 0.7 with $\Delta V_G$ of 0.1 V and channel length of 1 cm.

To demonstrate some of the capabilities of the PEDOT:PSS fiber-based OECTs, a dimmer was built for an LED that was attached to a cotton cloth with the electrical interconnections made of PEDOT:PSS fibers. The dimmer was simply made by attaching copper wire to the cotton cloth and depositing PVA/H$_3$PO$_4$ solid electrolyte covering part of the copper wire (gate) and a section of the PEDOT:PSS fiber interconnection. That section of the PEDOT:PSS interconnection acted as the OECT channel and its resistance could be modulated by applying a voltage to the gate, effectively modulating the current applied to the LED. **Figure 6.13a** shows a photograph of the OECT dimmer, LED, and interconnections on the cotton cloth, including a schematic representation of the applied voltages. **Figure 6.13b** shows the LED emitting light at different intensities from more intense at $V_G = 0$ V to completely off at $V_G = 1$ V while applying a constant drain voltage of -3.3 V.
Figure 6.13. (a) Photograph of an LED attached to a cotton cloth with PEDOT:PSS sewn fiber interconnections with dimming capabilities by including a PEDOT:PSS fiber-based OECT. (b) Photographs showing the LED emitting at different intensities by changing the gate voltage from 0 V to 1 V while applying a constant drain voltage of -3.3 V.

OECTs can also be used as signal amplifiers, whereby small input signals (gate voltage) are transduced into large changes in an output signal (drain current). This is one of the reasons OECTs are widely used as biosensors, where input signals can be in the order of mV or µV [32]. The signal transduction is characterized by the transfer curves that describe the dependence of $I_D$ on $V_G$. Figure 6.14a shows the transfer curves of the PEDOT:PSS fiber-based OECT. For a constant value of $V_D$, the drain current decreases as $V_G$ increases, consistent with the behavior of a p-type depletion-mode OECT. The transduction efficiency is usually calculated using the first derivative of the transfer curves and it is called transconductance, $g_m$ [29]:

$$g_m = \frac{\partial I_D}{\partial V_G} \quad \text{eq. 6.13}$$

Per eq. 6.13, if an OECT has a large transconductance, small changes in the gate voltage will result in large changes in the drain current, effectively amplifying the input signal. The transconductance of the PEDOT:PSS fiber-based OECT as a function of $V_G$ at different constant $V_D$ are presented in Figure 6.14b. The transconductance is higher at
low values of $V_G$ (good for amplifying small signals) while operating near the saturation regime ($V_D = -0.6$ V).

![Figure 6.14](image)

**Figure 6.14.** (a) Transfer curves showing the dependence of $I_D$ on $V_G$ and (b) transconductance as a function of $V_G$. Both (a) and (b) at different values of $V_D$ from 0 V to -0.6 V with $\Delta V_D$ of -0.1 V and channel length of 1 cm. Solid lines connecting the data points are guides to the eye.

Typical values of transconductance for OECTs in film geometry are in the order of mS, which is significantly higher than OFETs that have transconductances in the order of $\mu$S [29]. The OECT fabricated here, using only 1 fiber as the channel, had a maximum transconductance of 314 $\mu$S, which is around 1 order of magnitude lower than typical PEDOT:PSS-based OECTs in the film geometry. Nevertheless, the transconductance can be increased by fabricating OECTs with more fibers connected in parallel acting as the channel. **Figure 6.15a** shows the transconductance curves as a function of $V_G$ and at constant $V_D = -0.6$ V for OECTs fabricated using 1, 2, 5 and 10 fibers as channel. The transconductance increases as the number of fibers is increased, reaching values around 4 mS when using a bundle of 10 PEDOT:PSS fibers as the channel. Bernards and Malliaras [33] have developed OECT models by considering the ionic and electronic nature of these
devices. According to their model the following expression can be used to calculate the transconductance for OECTs in film geometry:

\[ g_m = \frac{Wd}{L} \mu C^*(V_{th} - V_G) \]  

where \( W, d \) and \( L \) are the width, thickness and length of the channel, respectively. Here, \( \mu \) is the charge carrier mobility, \( C^* \) is the volumetric capacitance and \( V_{th} \) is the threshold voltage. Eq. 6.14 is only valid for channels with film geometry. However, a similar expression can be obtained if the channel has cylindrical geometry, as in a fiber:

\[ g_m = N \frac{\pi D^2}{4L} \mu C^*(V_{th} - V_G) \]  

where \( N \) is the number of fibers acting as the channel and \( D \) is the diameter of the fibers. According to eq. 6.15, \( g_m \) should scale linearly with the number of fibers acting as the channel if the length of the channel is kept constant. Indeed, a linear relationship between these two parameters can be observed in Figure 6.15b where the maximum transconductance (at \( V_D = -0.6 \) V and \( V_G = 0.2 \) V) of the PEDOT:PSS fiber-based OECTs is plotted against the number of fibers acting as the channel. In these devices the channel length was kept constant at 1 cm.
Figure 6.15. (a) Transconductance as a function of gate voltage and number of fibers acting as channel. Here $V_D$ was kept constant at -0.6 V and the channel length was 1 cm. (b) Transconductance at $V_D = -0.6$ V and $V_G = 0.2$ V as a function of the number of fibers acting as channel (1 cm) showing the linear relationship between these two parameters per eq. 6.15.

Per eq. 6.15, the transconductance of the PEDOT:PSS fiber-based OECTs could be further increased by using bundles with even more fibers or by reducing the channel length. Nevertheless, the values reported here are already in the same order as those of typical OECTs in the film geometry. For instance, Rivnay et al. [34] used OECTs with $g_m$ ranging between 3 and 6 mS as amplifiers to record electroencephalograms from a human volunteer using the brain as the supply of gate voltage. While Braendlein et al. [32] constructed a voltage amplifier using an OECT with $g_m$ around 9 mS and used it to record electrocardiograms. In a similar way, textile PEDOT:PSS fiber-based OECTs could be used in the future to record biological signals, such as heart or brain activity, in wearable health monitoring textile devices.

6.7 Conclusions

In this chapter, first, the electrical and mechanical properties of the fibers were compared to traditional textile fibers and carbon fibers. The PEDOT:PSS fibers have electrical conductivities that rival carbon fibers while having mechanical properties similar
to cotton. Additionally, the electrical conductivity of coagulation bath and DMSO drawn fibers have good ambient stability while the sulfuric acid drawn fibers seem to degrade with time even in the near-absence of humidity.

The ampacity of the fibers was also probed, obtaining values of 11.3 kA/cm², 18.1 kA/cm² and 21.1 kA/cm² for coagulation bath, DMSO drawn, and sulfuric acid drawn fibers, respectively. These values of ampacity are high enough to withstand the typical current requirements of small electronic textile devices. As a proof of concept, PEDOT:PSS fibers were sewn to a cotton cloth and used as interconnections to light up an LED. The PEDOT:PSS fiber interconnections were flexible and remained functional even after substantial bending of the textile.

The Joule heating characteristic of the PEDOT:PSS fibers were also explored. The temperature of the fibers increased linearly with the applied power, reaching temperatures as high as 80 ºC. The fibers showed fast heating-cooling response times and could be heated to 55 ºC and cooled down to ambient temperature at frequencies as high as 0.1 Hz. Moreover, a thermochromic fiber bundle was built by coating a PEDOT:PSS fiber bundle with a thermochromic paint. The bundle changed color from blue to white when the temperature reached 31 ºC. The bundle could be heated above this temperature by simply passing a current through the PEDOT:PSS fibers, providing an on-demand method to switch colors, opening the door towards on-demand color-switching textiles.

The thermoelectric capabilities of the fibers were also demonstrated by using the PEDOT:PSS fibers as p-type legs in a textile thermoelectric generator (using alumel wire as n-type legs). The device had an output power as high as 2.82 µW at ∆T of 84 ºC and its performance compared very positively with other devices reported in the literature.
Finally, the use of the PEDOT:PSS fibers in OECTs was also explored. The electrical conductivity of the fibers can be modulated by using them as channels in OECTs, which could be used to design logic circuits in future electronic textile devices. As a proof of concept, dimming capabilities were demonstrated on an LED attached to a cotton cloth using PEDOT:PSS fibers as interconnections and including a fiber-based OECT. Moreover, the transconductance of the PEDOT:PSS fiber-based OECTs is high enough to potentially use them as amplifiers to record biological signals, opening possibilities to use the fibers in future health monitoring textiles, for instance to monitor heart or brain activity.
6.8 References


CHAPTER 7. CONCLUSIONS AND FUTURE WORK

This chapter brings this dissertation to an end by presenting a summary of the conclusions obtained during this work. Additionally, a section of future work is also included, discussing potential future research directions in terms of unanswered questions or further development needed before the use of PEDOT:PSS fibers becomes widespread in the emerging field of electronic textiles.

7.1 Conclusions

Conjugated polymer fibers are promising candidates for use as building blocks in the emerging field of electronic textiles. However, the field of conjugated polymer fibers is still in its infancy when compared to other well-established fiber fields such as wet-spinning of polyacrylonitrile fibers or melt-spinning of polyethylene. At the beginning of this dissertation a continuous process for the fabrication of highly conductive and mechanically robust PEDOT:PSS fibers had not been reported.

In Chapter 4 of this dissertation, a continuous wet-spinning process for the fabrication of oriented, highly conductive and mechanically robust PEDOT:PSS fibers was described. Initially, wet-spinning by simply extruding an aqueous PEDOT:PSS dope into an isopropanol coagulation bath resulted in fibers with electrical conductivities of approximately 100 S/cm. By adding 10 vol.% DMSO into the coagulation bath, the electrical conductivity of the fibers increased by one order of magnitude due to stronger $\pi$-$\pi$ interactions between PEDOT chains (secondary doping) induced by the DMSO. However, including a drawing step through DMSO was proven to be key to achieve even higher electrical conductivities while also improving the mechanical properties of the fibers. The DMSO drawing step facilitated the application of high draws, that effectively
aligned the backbones of both PEDOT and PSS chains in the fiber axis direction while also removing some of the excess PSS. This synergistic effect resulted in room temperature electrical conductivities of around 2000 S/cm and Young’s moduli as high as 16 GPa. By investigating the structure of the fibers, a strong correlation between the orientation of the polymer chains along the fiber axis and the trends observed in the fiber’s properties was found. In general, the fibers with the highest degree of orientation were also the stiffest and the most highly conducting fibers.

In Chapter 5, we explored the use of sulfuric acid to further increase the properties of the PEDOT:PSS fibers. In this chapter, a modification of the PEDOT:PSS continuous wet-spinning process to include a sulfuric acid draw bath was detailed. Sulfuric acid was proven very effective at improving the PEDOT:PSS fibers’ properties. Sulfuric acid drawn PEDOT:PSS fibers showed outstanding electrical conductivities with values as high as 4039 S/cm, which is the highest reported to date for a PEDOT:PSS fiber. The mechanical properties of the fibers were also enhanced, with Young’s modulus and break stress values of approximately 20 GPa and 550 MPa, respectively. These values are the highest reported to date for a PEDOT:PSS fiber and, to the best of the author’s knowledge, for any PEDOT:PSS material (film or fiber). The improvement of the electrical and mechanical properties was correlated with changes in the composition and structure of the fibers after the sulfuric acid treatment. The sulfuric acid drawing step removed excess PSS from the fibers while also promoting the ion exchange of sulfates in place of PSS as counterions. This change in composition was accompanied by a structural reorganization of the crystal structure of PEDOT, increasing the crystallinity and reducing the (100) lamella stacking distance, which resulted in enhanced carrier transport.
Chapter 6 was the most application focused chapter of the dissertation. In this chapter, the electrical and mechanical properties of the fibers were compared to traditional textile fibers and carbon fibers. The PEDOT:PSS fibers have similar mechanical properties to cotton or silk. However, while cotton and silk are insulating materials, these PEDOT:PSS fibers have electrical conductivities that rival carbon fibers. The electrical stability of the fibers was also investigated. Coagulation bath fibers and DMSO drawn fibers have good ambient stability, however, sulfuric acid drawn fibers seem to degrade even in the near-absence of humidity.

Additionally, the use of the fibers in multiple applications was demonstrated. The PEDOT:PSS fibers have values of ampacity as high as 21.1 kA/cm², which is enough to withstand the typical current requirements of small electronic textile devices. As a proof of concept, PEDOT:PSS fibers were sewn to a cotton cloth and used as flexible interconnections to light up an LED.

The Joule heating characteristics of the PEDOT:PSS fibers were also explored. The fibers could be heated to temperatures up to 80 ºC by applying electrical power. Moreover, the fibers had fast heating-cooling response times, allowing complete heating-cooling to be achieved when cycling at frequencies below 0.1 Hz. By using the Joule heating effect of the fibers, a thermochromic fiber bundle was constructed. The bundle changed color from blue to white by passing a current through the fibers, opening the door towards on-demand color-switching textiles.

Future wearable electronic textiles will require power to function. Textile energy harvesters are, therefore, interesting from this perspective. Here, a textile thermoelectric

\footnote{As measured by IR camera (see Chapter 6 footnote 1)}
generator was built by using the PEDOT:PSS fibers as p-type legs. The device had an output power of 2.82 μW at ΔΤ of 84 °C. Further miniaturization and optimization should lead to increases in the output power while decreasing the temperature gradient required.

Finally, the use of the PEDOT:PSS fibers in OECTs was also explored. The electrical conductivity of the fibers can be modulated by using them as channels in OECTs, which could be used to design logic circuits in future electronic textile devices. As a proof of concept, dimming capabilities were demonstrated on an LED attached to a cotton cloth using PEDOT:PSS fibers as interconnections and including a fiber-based OECT. Moreover, the transconductance of the PEDOT:PSS fiber-based OECTs is high enough to potentially use them as amplifiers to record biological signals, opening possibilities to use the fibers in future health monitoring textiles, for instance to monitor heart or brain activity.

In summary, this work has presented a detailed process to fabricate high performance PEDOT:PSS fibers while seeking structure-process-property relationships to gain a better understanding of the fibers’ properties and their trends. Furthermore, the versatility of the fibers has been demonstrated by providing preliminary data and proof of concept demonstrations of the uses of the fibers in different applications. The PEDOT:PSS fibers fabricated in this work are a unique type of material with the potential of becoming a cornerstone in the emerging field of electronic textiles.

7.2 Future work

Probably, the most central question in terms of future work, will be whether it is possible to scale up the fabrication process of PEDOT:PSS fibers to meaningful quantities for widespread use in the fabrication of electronic textiles. The first step towards scaling up the fabrication process is to demonstrate multifilament spinning of PEDOT:PSS fibers
to obtain electrically conductive fiber bundles (typically referred as to ‘tows’). The main problem that could be encountered is interfilament fusion during processing, resulting in a tow of fused filaments instead of a tow formed by separable individual filaments. It must be noted that, from a purely electrical conductivity point of view, a tow of fused filaments could even be desirable since it would improve electrical connectivity between filaments. However unfused filaments would be preferred for textiles and other applications. In practice, whether a tow of fused filaments or a tow of unfused filaments is preferred is most likely going to depend on the final applications and, thus, the fabrication process should be engineered to be able to obtain both kind of tows on-demand.

Another question central to the application of the fibers is that of the stability of the sulfuric acid drawn fibers. In Chapter 6, it was observed that the conductivity of the sulfuric acid drawn fibers degrades even in near-absence of humidity. The sulfuric acid drawn fibers have the highest initial electrical conductivity, however, with time the electrical conductivity degrades to values similar to the DMSO drawn fibers. Future work should focus on studying and understanding the degradation mechanism, maybe by investigating possible changes in composition and structure of the fibers over time while coming up with ideas and methods to make the fibers stable at their highest conductivity.

Related to stability is also the topic of making electrical contacts to the fibers. In the stability studies of Chapter 6, it was observed that silver paint contacts seem to be unstable in ambient humidity conditions. The exact mechanism by which the contacts degrade is unknown and could be the topic of study in the future. Additionally, future work could also focus on finding new contact materials that form stable contacts with the fibers while being convenient for textile applications.
A wide area to explore in the future is finding new applications for the fibers. PEDOT:PSS is one of the most used polymers in organic electronics and is used in a vast array of different applications in the film geometry that could serve as inspiration. Here, the challenge lies in how to adapt and reconfigure the devices that are typically in a thin film geometry to a fiber or textile geometry. Additionally, unique applications made only possible by having the PEDOT in a fiber form should also be sought and explored.

Last, but not least, the fabrication process itself still has room for improvement, optimization, and exploration. For instance, investigating new coagulation bath or draw bath chemistries, using higher temperatures in the drawing baths or including new steps to modify the fibers, for example with an insulating protective coating.

This dissertation covers, in-depth, the wet-spinning of high performance PEDOT:PSS fibers, relations between their structure and properties, and presents some specific applications. The summary in this chapter highlights just a few of the future directions that could advance the field. But that is another research work and shall be told in another dissertation².

² Modified from the closing sentence of “The Neverending Story”, a fantasy novel by Michael Ende.


171


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Publications


**Patents**
