Thesis for the Degree of Doctor of Philosophy

Conjugated Polymer-based Conductive Fibers for Smart Textile Applications

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ABSTRACT

Electrically conductive or electro-active fibers are the key components of smart and interactive textiles, which could be used in medical, sports, energy, and military applications in the near future. The functionalization of high-performance textile yarns/fibers with conjugated polymers can produce conductive fibers with better electro-mechanical properties, which is difficult with commonly used spinning techniques. In this thesis work, textile-based conductive yarns/fibers were prepared by coating viscose and polyester (PET) yarns with the conjugated polymer PEDOT. For coating purposes, an efficient technique called chemical vapor deposition (CVD) was used, which is a solventless technique and can produce PEDOT polymer layers with high conductivity values. The polymerization of EDOT monomer vapors and coating of oxidant− ($FeCl_3$ or Fe*p*TS) enriched viscose and PET yarns took place simultaneously. The PEDOT-coated viscose and polyester yarns showed relatively high conductivity values, which could be sufficient for many electronic applications.

The polymerization process and the quality of PEDOT polymer strongly depends on different reaction conditions. In this research work, the impact of most of these reaction parameters on the electrical, mechanical, and thermal properties of PEDOT-coated conductive yarns was considered separately. Under specific reaction conditions, it was found that viscose fibers were successfully coated with PEDOT polymer and showed rather high electrical conductivity ($\geq$ 15 S/cm). However, due to the acid hydrolysis of viscose fibers in $FeCl_3$ solutions, the mechanical properties were drastically reduced.

In order to improve the mechanical properties of conductive yarns, a relatively stable and chemical-resistant substrate (PET) was coated with PEDOT polymer. Comparative studies between PEDOT-coated viscose and PET conductive yarns showed that the electrical and mechanical properties were enhanced by changing the substrate material. Later on, PEDOT-coated conductive fibers were treated with silicone elastomer solution and due to the thin silicone layers, the hydrophobic properties, flexibility, and durability of coated yarns was improved. Furthermore, a novel electrical resistance-measuring setup was developed, which can be used not only for fibers but also for fabric structures. The electrical characterization of PEDOT-coated conductive yarns showed that it can be used effectively for sensitive fibers without damaging their surface morphology.

Finally, the use of conductive yarns as stretch sensors was evaluated. For this purpose, small rectangular knitted patches of conductive yarns were prepared and then the change in electrical resistance values at different extension percentages (5–50%) was investigated. The constant variations in electrical resistance values at different extension and relaxation cycles for longer periods of time revealed that the conductive yarns produced have the potential to be used as stretch sensors for monitoring of vital signs in medical and sports applications.

Keywords: *electro-active fibers, poly(3,4-ethylenedioxythiophene) (PEDOT), textile yarns, viscose, polyester, chemical vapor deposition (CVD) process, electrical characterizations, smart textiles, stretch sensor*

LIST OF PUBLICATIONS

This thesis is based on following papers:

Paper I

T. Bashir, M. Skrifvars, N.-K. Persson, “Production of highly conductive textile viscose yarns by chemical vapor deposition technique: A route to continuous process”, *Polymers for Advanced Technologies*, 22, 2214-2221, 2011.

Paper II

T. Bashir, M. Ali, S.-W. Cho, N.-K. Persson, M. Skrifvars, “OCVD polymerization of PEDOT: effects of pre-treatment steps on PEDOT-coated conductive fibers and a morphological study of PEDOT distribution on textile yarns”, *Polymers for Advanced Technologies*, 24, 210-219, 2013.

Paper III

T. Bashir, M. Skrifvars, N.-K. Persson, “Synthesis of high performance, conductive PEDOT-coated polyester yarns by OCVD technique”, *Polymers for Advanced Technologies,* 23, 611-617, 2012.

Paper IV

T. Bashir, M. Skrifvars, N.-K. Persson, “Surface modification of conductive PEDOT coated textile yarns with silicon resin”, *Materials Technology: Advanced Performance Materials,* 26 (3), 135-139, 2011.

Paper V

T. Bashir, L. Fast, M. Skrifvars, N.-K. Persson, “Electrical resistance measuring methods and electrical characterization of Poly(3,4-ethylenedioxythiophene) coated conductive fibers”, *Journal of Applied Polymer Science,* 124, 2954-2961, 2012.

Paper VI

T. Bashir, M. Ali, N.-K. Persson, S.K. Ramamoorthy, M. Skrifvars, “Stretch sensing properties of knitted structures made of PEDOT-coated conductive viscose and polyester yarns” Submitted to *Textile Research Journal.*

CONTRIBUTIONS OF THE AUTHOR

The author of this thesis, Tariq Bashir, was the main author of all the papers and did most of the planning, experimental work and writing in Paper I, II, III, IV, and V. The author also supervised one Master’s degree student Majid Ali, who performed most of the experimental work in Paper VI and few in Paper II but the interpretation of results and writing was done equally by the author and master student in Paper VI. Also, the resistance measuring setup in Paper V was provided by Lars Fast at SP Swedish Technical Research Institute, Sweden. The SEM analysis in Paper I and III was done by Anna Thorvaldsson at Swerea IVF, Sweden. In addition, the CT scanning analysis in Paper II was performed at GE Sensing & Inspection Technologies, Wunstorf Germany.

Conference Contributions

1. T. Bashir, M. Skrifvars, N.-K. Persson, "Oxidative chemical vapor deposition polymerization of Poly(3,4-ethylenedioxythiophene) on viscose yarns: a route to conductive textile structures", *47th Nordic Polymer Days*, Helsinki, Finland, 24-26 May, 2010. (Speaker)

2. T. Bashir, M. Skrifvars, N.-K. Persson, " Production of electroactive textile fibers by oxidative chemical vapor deposition polymerization of PEDOT on surface of viscose yarns", *4t Aachen-Dresden International Textile Conference*, Dresden, Germany, 25-26 November, 2010. (Speaker)

3. T. Bashir, M. Skrifvars, N.-K. Persson, "E-Textiles: a synergic combination of conjugated polymers and textile fibers, 49th Nordic Polymer Days, Copenhagen, Denmark, 29-31 May, 2012. (Speaker)

4. T. Bashir, M. Skrifvars, N.-K. Persson, "Functionalization of textile yarns by coating with conjugated polymer (PEDOT) for smart textile applications",10th IPF Colloquium on Functional Polymers and Composites for Application in Organic Electronics and Sensors, Dresden, Germany, 7-8 November, 2012. (Poster)

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APPENDIX

Abbreviations

ICPs	Intrinsically conductive polymers
PEDOT	Poly(3,4-ethylenedioxythiophene)
EDOT	3,4-ethylenedioxythiophene
PP	Polypropylene
PS	Polystyrene
PE	Polyethylene
PET	Polyethylene terephthalate
ESD	Electrostatic discharge
EMI	Electro-magnetic interference
LED	Light-emitting diode
OPV	Organic photovoltaic
CVD	Chemical vapor deposition
OCVD	Oxidative chemical vapor deposition
PACVD	Plasma assisted chemical vapor deposition
VPP	Vapor phase polymerization
Fe*p*TS	Ferric(III)*p*-toluenesulfonate
CPCs	Conductive polymer composites
CNT	Carbon nano-tubes
ECP	Extrinsically conductive polymer
PPy	Polypyrrole
EAPs	Electro-active polymers
PAN	Polyacrylonitrile
HWM	High wet modulus
HMW	High molecular weight
UHMW	Ultra high molecular weight
PES	Polyester
MEK	Methyl ethyl ketone
SEM	Scanning electron microscopy
CT	Computed tomography
TGA	Thermogravimeteric analysis
DSC	Differential scanning calorimeter

1. INTRODUCTION

1.1. Background

During the last few decades, the interest in electrically conductive fibers for medical, sports, military, and energy applications has increased markedly. This can be seen by the large number of publications and the broad spectrum of application areas investigated. These fibers have been featured extensively as power and signal transmitters for ECG measurement [2], strain sensors [3], motion-capture devices [4], devices for electrotherapy [5], pressure sensors [6], chemical sensors [7], and photovoltaic devices [8]. These multifunctional fibers could be a key component of the smart and interactive textiles that will be used in the future because of their attractive advantages, such as low cost, durability, and ease in adaptability. In order to use these conductive fibers in the above-mentioned applications, it is important that they should be strong, flexible, environmentally stable, and resistant to chemicals.

Different methods have been investigated for the production of conductive fibers, such as melt spinning, wet spinning, electrochemical processing, or coating of conventional insulating materials with conductive materials (metals, carbon black, and conjugated polymers).

Conductive polymer composites (CPCs) can be produced effectively by melt spinning of thermoplastic polymers– polyethylene (PE) or polystyrene (PS) with conductive fillers such as carbon nanotubes (CNT), metal powders, carbon black, or conjugated polymers but the conductivity levels obtained will be low [9]. A very limited conductivity values for CPCs have been reported so far. However, the mechanical performance is reduced when the concentration of conductive material is increased. Wet spinning of conductive polymers has also been described, but the involvement of large quantities of coagulation liquids and the removal of solvents after spinning limit the use of this process [10, 11].

In order to obtain better electro-mechanical properties, another interesting approach has been developed to transform the commercially available textile yarns or fibers into electrically conductive fibers. Textile fibers such as polyester, nylon, and viscose have good mechanical properties, and conductive fibers based on these textile fibers should also have enough electrical and mechanical properties that enable them to be used in real applications. Conductivity in textile fibers can be introduced either by incorporating metallic filaments in the yarns or by coating them with conductive materials. Metal content in material for clothing makes it difficult to process and also reduces the comfort of the final product. The coating of textile fibers with intrinsically conductive polymers (ICPs) is an interesting choice to overcome the above-mentioned difficulties, as the textile fiber will give the feel and processability required.

Intrinsically conductive polymers (ICPs), also known as conjugated polymers, are the class of polymeric materials that can conduct electricity. Since from the invention of poly(acetylene), $(-CH=CH-)_n$, in 1977 by Hideki Shirakawa, Alan J. Heeger, and Alan G. MacDiarmid, different types of conductive polymers such as poly(pyrrole), poly(aniline), poly(thiophene)and poly(3,4-ethylenedioxythiophene) (PEDOT) have been prepared with a broad range of conductivities i.e. from 10^{-10} to 10^{+5} S/cm [12]. Over the years, PEDOT has attracted a considerable amount of attention because of its high conductivity, good environmental stability, and its potential application in light-emitting diodes (LEDs) [13], organic photovoltaic (OPV) [14], EMI shielding [15], heat generation, and chemical sensors [16].

Conjugated polymers can be applied to the surface of various substrates using different techniques, such as inkjet printing, dip-coating, and solution casting. However, the deposition method of ICPs strongly affects the electrical properties of the final product. The coating of textile fibers with poly(pyrrole), poly(aniline), and PEDOT by solution process has been discussed extensively but low conductivity values (0.75 S/cm) have been reported [17, 18]. In order to get uniform, smooth, and continuous ICP coatings, showing higher electrical conductivities on the surface of different substrates, an efficient technique called chemical vapor deposition (CVD) was introduced. Winther-Jensen et al. reported that under controlled and specific reaction conditions, highly transparent and conductive PEDOT films (500–1,000 S/cm) can be produced by the CVD process [19, 20].

So, the deposition of highly conductive ICP (PEDOT) on the surface of textile fibers by oxidative chemical vapor deposition technique could be an efficient alternative for production of conductive fibers with better engineering properties. The fibers obtained could have possible application in the fields of medicine and energy generation, such as strain sensors, pressure sensors, and organic photovoltaic devices (OPVs).

In this thesis work, a number of studies have been carried out to produce textile-based conductive fibers by direct deposition of PEDOT on the surface of textile yarns with the CVD method. Regarding the electrical and mechanical properties, this technique has clear advantages over the other industrial processes for production of conductive fibers. Also, it should be possible to easily transform the conductive fibers obtained into different textile structures because of their high flexibility, comfort, and good weaving properties. However, large-scale production of CVD-coated fibers is still a challenge, although rather long electrically conductive yarns can be produced. This research work should make a considerable contribution in helping to commercialize the CVD process for the production of relatively highly conductive fibers.

2. LITERATURE REVIEW

2.1. Conjugated polymers

Polymers, either natural or synthetic, are large molecules (macromolecules) comprised of small building blocks or repeating units connected to each other by covalent bonds. These repeating units are called monomers. The polymeric materials are usually used as insulators because of their higher electrical resistance values (10^{-18} S/cm) [21]. However, after the revolutionary invention of poly(acetylene) as a highly conductive organic material in 1977 [22], a particular class of polymers called conjugated polymers or intrinsically conductive polymers could be differentiated from the rest. Later on, the Nobel Prize in Chemistry in the year 2000 was awarded to Hideki Shirakawa, Alan J. Heeger, and Alan MacDiarmid for their extraordinary breakthrough.

Conjugated polymers, also known as synthetic metals, can conduct electricity because of the presence of alternating carbon−carbon double bonds along the backbone structures of these polymers, which enable the overlapping of π-orbital along the molecule [23]. Due to their electron-transport characteristics, ICPs are regarded as semiconductors or even sometimes conductors.

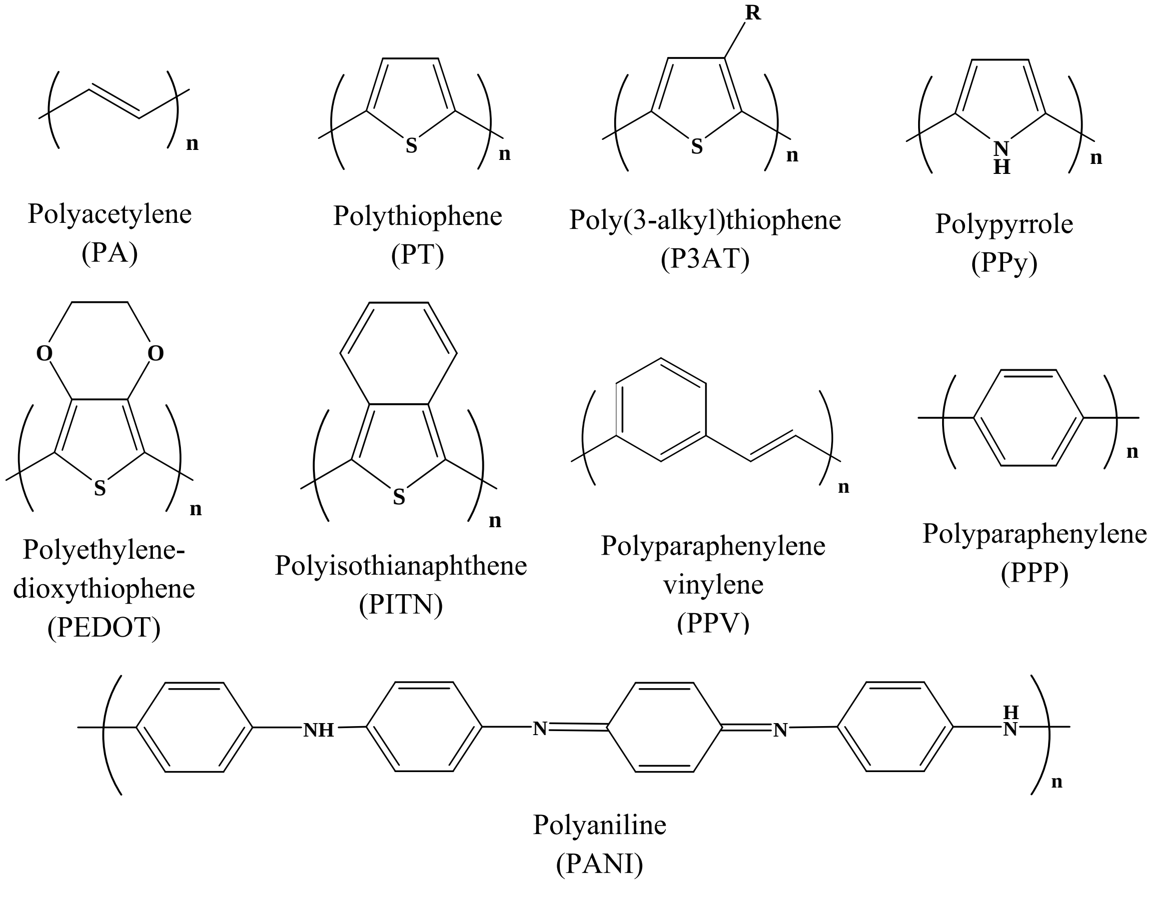


Figure 1: *Chemical structures of some commonly used ICPs*

During the last few decades, ICPs have attracted an overwhelming amount of interest around the world and considerable developments in this field have been made. Figure 1 shows the chemical structures of some of the most studied conjugated polymers. Intrinsically conductive polymers, because of their broad range of conductivities and possible uses in a number of electronics and optoelectronics applications, can replace the conventionally used metallic materials [24-32]. The range of conductivity values for the conjugated polymers known today is given in Figure 2.

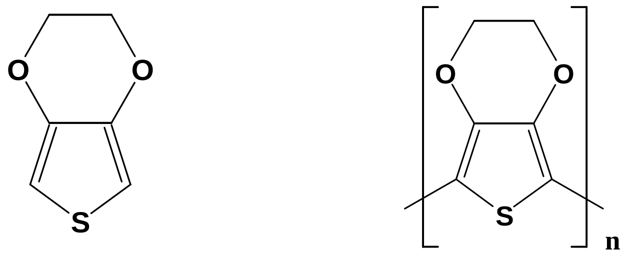
	Conductivity (S/cm)	**Materials**	**Conjugated polymers**	**Application areas w.r.t conductivity**
Conductors	10^6 10^4 10^2	Copper Iron Graphite Bismuth	10^5 S/cm ↕ 10^{-8} S/cm	Power cables Heating Sensors EMI shielding ESD applications Antistatics Insulation
Semiconductors	10^0 10^{-2} 10^{-4} 10^{-6} 10^{-8}	Indium/Antimony Gallium/Arsenic Germanium Silicon		
Insulators	10^{-10} 10^{-12} 10^{-14} 10^{-16} 10^{-18} 10^{-20}	Glass Diamond Polyethylene Polystyrene Quartz		

***Figure 2**: Comparison of the conductivity values of conjugated polymers with some common conductive materials*

2.1.1. Poly(3,4-ethylenedioxythiophene) (PEDOT)

The conductivity value of the *doped* poly(acetylene), i.e. 10^5 S/cm, is the highest conductivity achieved so far for any organic polymeric material. But due to its low stability outdoors and difficulties in processability, commercialization has not been possible [33]. Thus, many attempts have been made to establish new ICPs with good conductivity, long-term stability, and ease in processability so that they can be easily commercialized.

Among the wide range of conjugated polymers already developed, perhaps the diethoxy substituted thiophene poly(3,4-ethylenedioxythiophene) or PEDOT, also known under the trade name Baytron® or Clevios, is one of the most promising conducting polymer to date [34, 35]. It was synthesized by researchers at Bayer AG in Germany in 1988 with excellent conductivity (300 S/cm) [34, 36]. Since then, it has shown extraordinary scope for smart textiles, electronics, and optoelectronics applications [31]. PEDOT is highly conductive in its oxidized (doped) state, where the molecular backbone contains mobile carriers (holes). The chemical structures of 3,4-ethylenedioxythiophene (EDOT) monomer and PEDOT polymer are shown in Figure 3. The presence of only two reactive hydrogen atoms at the 2 and 5 positions on the EDOT monomer ring gives PEDOT a very regular molecular structure, which makes it a stable polymer [37, 38].



EDOT PEDOT

Figure 3: *Chemical structures of EDOT monomer and PEDOT polymer*

However, like other ICPs, PEDOT also has a stiff conjugated aromatic backbone structure, which makes it insoluble and infusible in most organic and inorganic solvents [39-41]. Bayer resolved this problem by introducing polystyrene sulfonic acid (PSS), a water-soluble polyanion, during the polymerization of PEDOT as a charge balancing dopant [42]. This water-soluble PEDOT:PSS complex, as a commercial product known as BAYTRON P^{TM}, has electrical and film-forming properties that somehow allow fairly stable, transparent conductive polymer coatings on a variety of substrates. However, PSS itself is a non-conducting material, which limits the conductivity of the PEDOT:PSS complex to the ~1–10 S/cm range [43].

2.1.2. Synthesizing routes of PEDOT

In order to use the conductive polymer PEDOT for electronics and optoelectronics applications, it should be applied or deposited as a thin film on the surface of different substrates. However, due to the lower solubility of PEDOT in most organic and inorganic solvents, the simplest coating techniques such as spray coating, spin casting, and solution casting are difficult to use with it.

Deposition of PEDOT polymer directly on the surface of desired substrates could therefore be an efficient way of obtaining highly conductive, flexible, and thin uniform films. The following are the most commonly used routes of synthesis of PEDOT films directly on different substrates [44]:

- Wet chemical oxidative polymerization
- Electrochemical polymerization
- Vapor-phase polymerization

Wet chemical oxidative polymerization involves the preparation of reactive solutions containing EDOT monomer and oxidants such as Fe(III)Cl$_3$ or Fe(III) p-toluenesulfonate [Fe(III) tosylate], and then application on the surface of different substrates [19]. The thin layer of PEDOT polymer can be obtained either by immersing the substrates in the reaction mixture directly or by spin casting the solution on a specific surface and then allow the solvent to evaporate [45, 46]. Although thin PEDOT films with good conductivity (300 S/cm) can be obtained by wet oxidative methods, but lack of reproducibility, limited pot-life of the reactive mixture, and difficult handling makes this process unsuitable [20].

Electrochemical polymerization produces highly conductive PEDOT films directly on the surface of the substrate. In this method, EDOT monomer is added in an electrolyte solution and then this solution is placed inside a cell containing three electrodes including conductive substrates. The polymerization reaction starts with the passage of periodic voltage cycles across the cell, and PEDOT is formed on the surface of the substrate material [47, 48]. Even for though higher conductivity value such as ~300 S/cm can be achieved, but the requirement of conductive substrate limits the applicability of this method [49].

Vapor-phase polymerization (VPP), also known as chemical vapor-phase deposition of PEDOT, is an efficient alternative to overcome most of the processability, performance, and pot-life related issues discussed for wet and electrochemical routes earlier [6, 50]. In this method, the polymerization and film formation of conjugated polymers occurs simultaneously on the surface of the substrate material [20]. This technique was first described by Mohammadi et al. in 1986 as the chemical vapor deposition (CVD) process. It was used for the polymerization of poly(pyrrole) (PPy) with $FeCl_3$ or H_2O_2 oxidants, and samples with conductivities ranging from 10^{-2} to 1 S/cm were produced [51].

VPP usually involves solution casting of oxidant on the substrate surface, which serves as polymerization agent and polymer dopant at the same time. For the polymerization step, the oxidant-coated substrates are then placed in the polymerization chamber where EDOT monomer is subsequently introduced through the vapor phase [52]. Under controlled reaction conditions, EDOT monomer vapors condense, polymerize, and create a homogenous and highly conductive coating of PEDOT on the substrate surface. As compared to the conventional wet polymerization route, VPP is a quick process: it takes only 10–30 minutes to achieve a homogenous and high-quality PEDOT coating [52].

For vapor-phase polymerization of PEDOT, Fe(III)Cl_3 and Fe(III) tosylate are the preferred oxidants. Kim et al. produced VPP PEDOT films by using $FeCl_3$ oxidant and the maximum conductivity obtained by this method was 70 S/cm [6]. Later on, Winther-Jensen et al. used Fe(III) tosylate instead of $FeCl_3$ as oxidant along with the alkaline inhibitor pyridine and improved the conductivity of PEDOT films to 1,025 S/cm [19, 53].

Analogous to vapor-phase polymerization, another process called ***oxidative chemical vapor deposition*** (oCVD) was developed by Gleason and co-workers [50, 54]. In this method, both the oxidant and commonly used monomers are delivered to the substrate inside the polymerization chamber through the vapor phase, which is the only difference between the VPP and oCVD processes. However, it is rather difficult to provide sufficient oxidant flux to the substrate for the oCVD process [55]. One way is to mount the oxidant-containing crucible inside the reaction chamber, as shown in Figure 4. As oxidants, solids with limited volatility, such as $FeCl_3$, are preferable for this method [50]. EDOT monomer vapors are provided by conventional means, whereas oxidant vapors are produced by heating the oxidant-containing crucible inside the reaction chamber. Under the controlled environment and reaction conditions, very smooth, homogenous and highly conductive PEDOT layers (>1,000 S/cm) have been achieved [56]. In this thesis work, the CVD process was used to produce the films of conductive PEDOT coating on the surface of textile fibers, as explained in section 3.2.

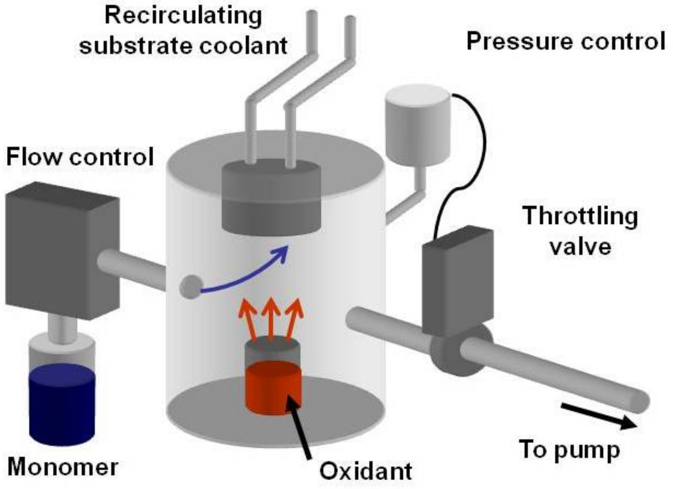
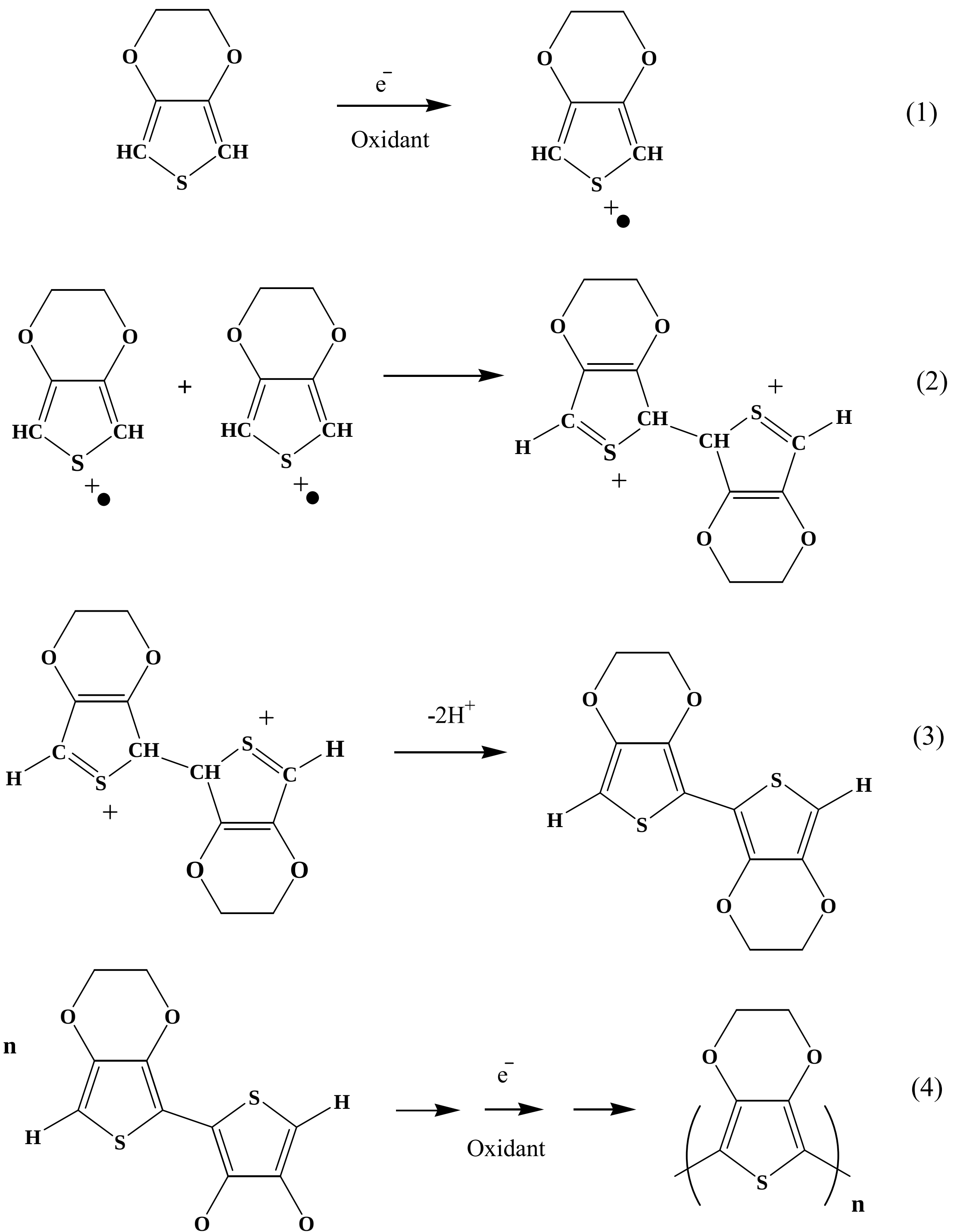


Figure 4: *Schematic diagram of the setup used for oCVD polymerization. Printed with the permission of K.K. Gleason, http://web.mit.edu/gleason-lab/research.htm [55]*

2.1.3. Mechanism for oxidative polymerization of EDOT to PEDOT

The stepwise reaction mechanism for oxidative polymerization of EDOT, which has been widely accepted [20, 50, 57], is shown in Figure. 5. In first step, the stoichiometric quantities of oxidant react with EDOT monomer, and after oxidation the EDOT cation radicals or polarons are generated (Fig. 5, eq.1). These cation radicals are then combine with each other in a second step, called dimerization, to form dimers (Fig. 5, eq.2). These can be stabilized by a subsequent deprotonation process (Fig. 5, eq.3). The presence of only two active hydrogen atoms at 2 and 5 positions blocks the β-coupling and new bonds can form only at available active sites of the EDOT monomer [38]. The further oxidation of dimers generates new positively charged cation radicals, which become transformed into conjugated PEDOT polymer after repeated coupling and deprotonation steps (Fig. 5, eq. 4) [50, 54]. The chain length of PEDOT polymer strongly depends on the availability of EDOT monomer vapor and on the oxidizing potential of used oxidant.

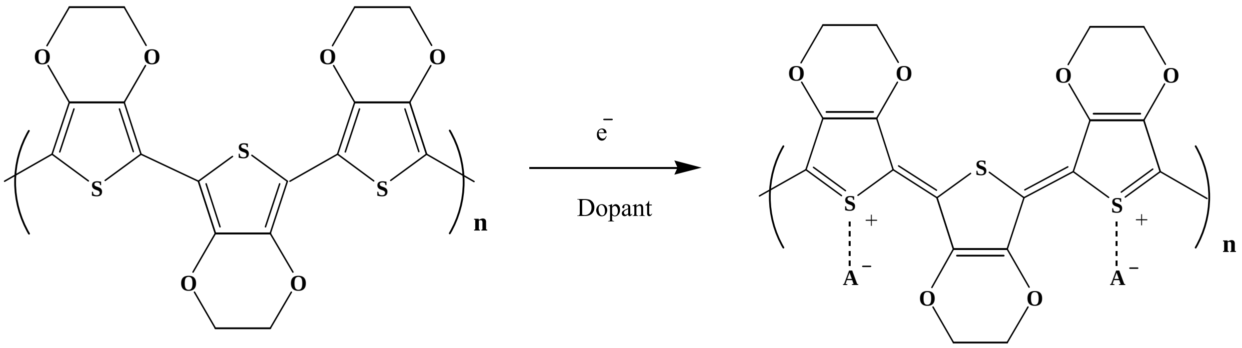


Oxidant should be $FeCl_3$ or Fe*p*TS

Figure 5: *Oxidative polymerization mechanism for PEDOT involving: (1) oxidation of EDOT; (2) dimerization; (3) deprotonation leading to stable dimer; (4) oxidation and coupling of dimers, forming the conjugated PEDOT polymer [54]*

Doping of PEDOT

The PEDOT polymer in its undoped form is usually non-conductive or shows very little conductivity [50]. Thus, in order to increase the conductivity, neutral PEDOT is further oxidized or reduced with a doping agent. This introduces positive charges along the backbone structure of PEDOT, as shown in Figure 6. Later on, these positive charges are balanced by the anions provided by the doping agent. The doped or oxidized form of PEDOT shows very high conductivity and reasonable chemical stability [37, 54].



A^{-} = $[FeCl_4]^{-}$ or Tos^{-} or Cl^{-}

Dopant could be $FeCl_3$ or Fe*p*TS

Figure 6: *Oxidation or doping of neutral PEDOT polymer*

2.2. Extrinsically conductive polymers

Conductive polymers can also be produced by physical blending of conductive materials such as carbon nanotubes [58, 59], carbon black [60, 61], conjugated polymers [9, 62, 63], or metallic fillers [64, 65] with inherently insulating thermoplastic polymers (PP, PE, PS). These are known as extrinsically conductive polymers (ECPs), conducting polymers (CPs), or conductive polymer composites (CPCs). However, the conductivity values for ECPs are much lower than the conductivity values of ICPs. This will be explained in detail in session 2.3.

2.3. Conductive fibers

2.3.1. Classification of conductive fibers

Generally, conductive fibers can be divided into two categories:

1) Naturally conductive fibers (Inherently conductive)

The fibers that can be produced purely from inherently conductive materials, such as metals, metal alloys, carbon sources, and conjugated polymers (ICPs), are associated with the class of naturally conductive fibers. In their pure form, these fibers have high conductivity values. A short description of each type is given below:

a) Metallic fibers

Metallic fibers, as suggested by the name, are the first man-made fibers to be developed from metals or metal alloys. These fibers have very thin metal filaments with diameter ranging from 1 to 80 μm, which can be produced by the bundle-drawing or shaving process [66]. Metallic fibers have very high conductivity (10^6 S/cm) with a wide range of mechanical properties [67]. Despite the fact that they have extraordinary electro-mechanical properties, metallic fibers have limited textile applications because of their low flexibility, stiffness, high weight, high cost, low compatibility with other materials, and poor weaving properties [66, 68].

b) Carbon fibers

Carbon fibers, which were invented by Edison in 1879, are used as the most demanding materials in high-tech industrial applications such as structural composites in aerospace, transportation, and defense-related products. Carbon fibers are petroleum-based products and they can be produced from petroleum pitch and polyacrylonitrile (PAN) [69]. The heat treatment of PAN, also called graphitization, strongly influences the electrical and mechanical properties of carbon fibers. Carbon fibers have graphite structure, which means that they have conductivity values similar to those of metals, i.e. 10^4–10^6 S/cm [70]. Carbon fiber composites are usually appropriate for structural applications when high strength, stiffness, lower weight, and extraordinary fatigue characteristics are required [71, 72]. For smart and interactive textile applications, carbon fibers cannot be easily integrated into knitted or weaved structures because of their high stiffness and brittleness. In addition, aesthetic considerations and health-related issues are also strong reasons for the use of carbon fibers being limited in the clothing industry.

c) Conjugated polymer fibers

As explained in section 2.1, conjugated polymers or ICPs are organic materials that conduct electricity. Due to their high conductivity, lower weight, and environmental stability, they have a very important place in the field of smart and interactive textiles. Several attempts have been made to produce conductive fibers that are wholly based on ICP. Pomfret et al. [73] and Okuzaki et al. [11] produced polyaniline and PEDOT:PSS fibers, respectively, by using a one-step wet spinning process. However, it is very difficult to use these fibers for interactive applications. The major reasons are poor mechanical strength, brittleness, a lower production rate, and difficult processing. The production of pure PEDOT fibers with high conductivity values, from 150 to 250 S/cm, by a chemical polymerization method has also been reported, but due to their micro-scale size and brittle nature, useful applications could not be found [74].

2) Treated conductive fibers (extrinsically conductive)

The conductive fibers that can be produced by the combination of two or more materials, such as non-conductive and conductive materials, are known as treated conductive fibers or extrinsically conductive fibers. Special treatments involve the mixing, blending, or coating of inherently insulating materials—such as polyethylene (PE), polypropylene (PP), polystyrene (PS), or textile fibers—with highly conductive materials such as metals, carbon black, or ICPs. The conductive fibers obtained, also known as conductive polymer composites (CPCs), can have a combination of the electrical and mechanical properties of the treated materials. These fibers can be classified further as:

a. *Conductive filled fibers*

Conductive filled fibers are a class of conductive fibers that can be produced by adding conductive fillers—such as metallic powder, carbon black, carbon nanotubes, or conjugated polymers—to non-conductive polymers such as PP, PS, or PE [59, 70, 75, 76]. Usually, melt spinning and solution spinning techniques are used to produce filled conductive fibers. However, in order to get homogenous distribution of conductive particles or ICPs in polymers, the parent materials are well mixed before the spinning process. However, the conductive fibers produced by the solution spinning process have better electrical properties than those produced by the melt spinning process, but the need for large quantities of solvents, their separation, and possible health hazards has made this process obsolete [22]. The electrical conductivity values of melt-spun conductive fibers strongly depend on two parameters: volume loading of filler and filler shape. The fibrous conductive filler can give higher conductivity in melt-spun fibers than irregular and spherical particulates [77]. The melt spinning process is the most economical and least complex process for the production of filled conductive fibers, but the lower electrical and mechanical properties of conductive fibers limit their use in smart and interactive textile applications.

b. *Conductive coated fibers*

The conductive fibers that can be produced by coating insulating materials with highly conductive materials, such as metals, metal alloys, carbon black, carbon nanotubes, and ICPs, are known as conductive coated fibers [7, 78-80]. With coating processes, not only can the highest conductivities be achieved but also the mechanical properties of conductive fibers can be enhanced. Depending on the type of conductive materials, different coating techniques can be used to transform polymeric or textile fibers into electro-active fibers. To apply metallic coatings, sputtering, vacuum deposition, electroless plating, carbonizing, and filling or loading fibers are the most extensively used methods [66, 81]. High conductivities similar to those of metals (10^6 S/cm) can be achieved with these methods, but high cost, stiffness, brittleness, high weight, and lower levels of comfort limit their application in the textile field.

Carbon black, carbon nanotubes, and ICPs can be applied as a thin layer to a fiber surface by the solution casting, inkjet printing, in-situ polymerization, VPP, CVD, or PACVD methods [45, 80, 82-84]. The thin layers of coating offer reasonably high conductivity and also preserve the flexibility and elasticity of substrate fibers [84]. However, the use of carbon black and carbon nanotubes for wearable applications is very limited because of health-hazard issues. On the other hand, due to their high conductivity, exceptional environmental stability, lower weight, and high compliance, ICPs are reasonable candidates for functionalization of different polymeric and textile materials. However, difficulty in processing, poor adhesion to substrate, and durability issues are some disadvantages of ICPs. By using suitable coating techniques and compatible substrates, these problems can be minimized [85].

Due to the technological advancements in the textile industry, a variety of textile fibers with extraordinary mechanical properties (shown in Table 1) have already been established. Coating of these high-strength fibers with ICPs can introduce multifunctionality in them without reducing the parent textile properties. Attempts have already been made to coat textile substrates such as viscose, PET, lyocell, nylon, cotton etc., with conductive polymers like poly(pyrrole), poly(aniline), and PEDOT [5, 27, 84, 86-88].

Table 1: *Mechanical properties of some well-known fibers [89]*

Fiber	**Strength (GPa)**	**Modulus (GPa)**
Polyester	0.4–1.3	10–16
Polyamide	0.4–1.0	0.6–6
Polypropylene	0.2–0.6	1–7
Polyacrylonitrile	0.4–0.6	6–9
Rayon (viscose)	0.3–0.4	8–13
Polyethylene (gel-spun)	2–3	120–170
p-Aramid	2–3	80–40
Carbon	3–4	200–400
Glass	3–5	70–90
Ceramic (Nicalon)	3	200

2.3.2. Different architectures of conductive fibers

Conductive fibers can either have homogenous (wholly conductive) or heterogeneous (bi-component) structures, as shown in Figure 7.

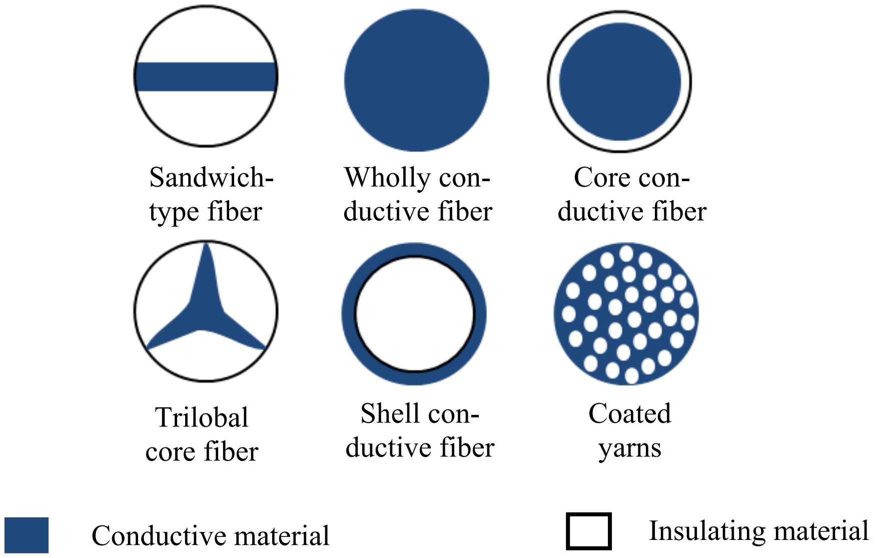


Figure 7: *Single and bi-component structures of commonly used conductive fibers*

The wholly conductive fibers can be obtained from inherently conductive materials such as metals, carbon compounds, and ICPs, and usually show the highest conductivity values. However, the bi-component fibers, which have a conductive core or shell, can have electrical and mechanical properties that are intermediate between those of the combined materials [90, 91]. Depending on their electrical conductivity values, i.e. from 10^{-8} S/cm to 10^{5} S/cm, electro-active fibers can have a wide range of applications [92, 93], as explained earlier.

2.4. Smart textiles or electronic textiles (e-textiles)

Today, people want to make their lives more comfortable and talk a lot about intelligent devices. An intelligent device means a system that can evaluate the environment and respond to the results of the evaluation [94, 95]. These systems can give us information we need in any particular situation and help us to plan our everyday lives [96]. In order to make human life healthier, more comfortable, and safer, intelligent devices are being brought one stage closer to the individual by means of easy-to-use wearable interfaces [1, 97, 98]. In this regard, the multifunctional fabrics commonly known as *smart textiles*, *electronic textiles (E-textiles)*, or *textronics* are good candidates for making our daily lives healthier, safer, and more comfortable [1].

The term *smart textiles* or *textronics* refers to interdisciplinary approaches in the process of producing and designing textile materials, which started about the year 2000 [99]. It is an emerging field of research that connects the textile industry with other disciplines such as information technology, micro-systems, and materials science with elements of automation and metrology, as shown in Figure 8 [99, 100].

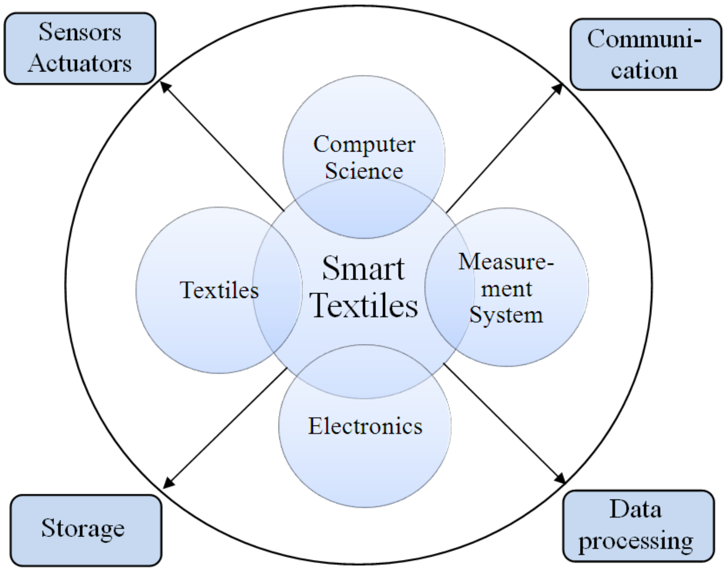


Figure 8: *The combination of different disciplines involved in smart textiles*

Smart textiles are defined as "*the synergic combination of electronic and conventionally used textile materials. They are able to sense the physical stimuli from the external environment and then perform some reactions against them*" [101]. These external stimuli and the reactions of smart textiles can be in the form of electrical, thermal, chemical or magnetic signals.

Smart textiles not only protect the human body from extreme environments, but can also monitor, do local computing, and communicate wirelessly [102]. E-textiles—because of their multifunctional interactivity in wearable devices that are adaptable, flexible, and conform to the human body—are successful promoters of better quality of life and progress in the field of biomedicine, as well as in several other health-based disciplines such as rehabilitation, telemedicine, ergonomics, tele-assistance, and sports medicine [1, 103-106].

During the last decade, apart from biomedical applications, smart and interactive textiles have been widely used (either in commercial or academic applications) in technical clothing [107], flexible solar cell panels [14, 108], protective garments for electromagnetic shielding and static charge dissipation [109], heating elements [16], fabrics for dust and germ-free clothes [110, 111], pressure sensors [105, 112], chemical sensors [7], power sources [113], and wireless devices [66].

2.4.1. Conductive polymers in smart textiles

Different functionalities can be introduced into wearable textiles and most of them have been done by incorporating (a) conventional off-the-shelf electronic devices to perform different tasks, and (b) metallic yarns for connections, power transfer, and data communication [114, 115]. By using this technology, a variety of products have been commercialized and are being widely used in smart garments for medical clothing, sports clothing, and protective clothing [100, 116-118]. But the integration of commonly used sensors, actuators, power sources, and electronic components in wearable garments reduces comfort, makes the process more complicated, increases the weight of the garment, and also increases the cost of the final product [1]. However, due to the promising developments in organic materials science and technology, today it is possible to make all-organic wearable devices for smart textile applications by incorporating ICPs or CPCs in fabrics. These ICPs and CPCs can introduce most of the necessary functionalities, such sensing, actuation, energy generation, computation, and energy storage in smart and interactive systems.

Textile-based wearable sensors, actuators, and computational devices can be obtained either by coating commercially available textile materials with ICPs or by mixing thermoplastics with conductive components, which was discussed previously. ICPs can be applied to the surfaces of textile materials homogenously or heterogeneously, as shown in Figure 9 [119].

Homogenous, untreated textile

Homogenous, coated textile

Conductive threads, grid

Conductive threads, monodirectional

Figure 9: *Homogenous and heterogeneous textile structures*

2.4.2. Wearable sensors

A sensor can be defined as "*a device which can identify or measure some conditions or properties, and can record, indicate, or otherwise react to the information received* [120]. So, sensors have the ability to transform external stimuli into a measured signal. For textile applications, sensors should have a fibrous shape and an electrical output, which give the advantages of flexibility, easy integration, and long sensing lines [99]. Depending on the electrical conductivity values (10^{-8} S/cm to 10^{5} S/cm), polymer-based electro-active fibers are being widely used as sensors to calculate humidity, temperature, pressure, the concentration of chemicals, and the intensity of light [79, 121].

Conductive fibers as wearable, sensitized systems can be classified in two categories: *active sensors* and *passive sensors*. ***Active sensors*** can intrinsically transform the input energy into a useful electrical potential difference. On the other hand, those sensors that convert the input signals into useable output signals, with the help of an external power source, are known as ***passive sensors***. They usually work according to the change in electrical properties in response to an applied stimulus [1].

In order to use the conductive fibers for biomedical applications, they can either be directly integrated into the wearable garments in fibrous form or a more flexible knitted or weaved structure can be made, as shown in Figure 10. A 1 × 1 rib-knit structure shows greater elasticity than other knitted patterns, such as plain and purl [122]. Thus, in this thesis work rib-knit structures were preferred in order to check the stretch-sensing properties of conductive yarns.

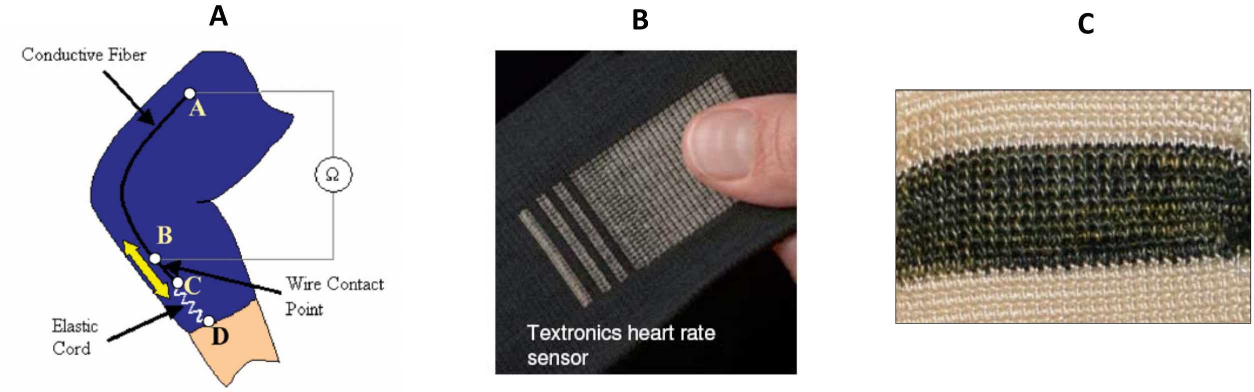


Figure 10: *Wearable stretch sensors: (A) single conductive thread sensor [123], (B) knitted heart-rate sensor [124], and (C) knitted vital-sign monitoring sensor (from Paper VI)*

These sensors can have the following physical effects: Piezoelectricity, thermoelectricity, pyroelectricity, and photoelectricity [1]. However, in the biomedical field, the more practical and efficient means of monitoring body signals and different variables are:

- Piezoresistive sensors
- Piezoelectric sensors

Piezoresistive sensors work according to piezoresistive effects, which can be described as the change in a material's electrical resistance in response to the external stress or material deformation applied [125].

Piezoelectric materials generate electrical signals due to the cross-coupling of mechanical and electrical energies. In piezoelectric sensors, when stress is applied to one of the main sides of the sensor, it generates charges that can be measured by applying a voltage across the sensor [125].

Continuous detection or monitoring of these effects is accepted as one of the main reasons for e-textiles being used in biomedicine and in health-based disciplines [1]. The devices (with fibrous or weaved/knitted structures) that allow sensing of elementary signals and variables related to mechanical or physiological activities of the human body (including vital signs) [1], are listed in Table 2.

Table 2: *Body signals measured by sensing devices/components, and their implementation as fabric in e-textiles [1]*

	Body signals or variables	**Sensing devices/components**	**Device implementation**
I.	Electrocardiogram (ECG)	Bioelectrodes	Woven or knitted metal electrodes
II.	Electromyogram (EMG)	Bioelectrodes	Woven or knitted metal electrodes
III.	Carotid pulse and radial artery pulse	Piezoelectric sensors	EAP-based textile fibers or small-size strips
IV.	Hear apex pulse (ballistocardiogram)	Piezoelectric sensors	EAP-based textile fibers or small-size strips
V.	Respiration (respitrace)	Piezoresistive sensors	EAP-based textile fibers or small-size strips
VI.	Articulation segment position and movements	Piezoresistive sensors	EAP-based textile fibers or small-size strips
VII.	Electrical Impedance of skin	Bioelectrodes	Woven metal electrodes
VIII.	Blood oxygenation (pulse oximetry)	Optical fibers	Optical fibers
IX.	Sound	Piezoelectric sensors (microphones)	EAP-based textile fibers or small-size strips
X.	Skin temperature	Thermoelectric sensors	EAP-based textile fibers or small-size strips

2.5. Aim of the work

The aim of the work described in this thesis was to produce electrically conductive fibers with better electrical and mechanical properties for smart and interactive textile applications. The textile substrates used, such as viscose and polyester (PET or PES) yarns, have good mechanical properties but they have no conductivity in their virgin form. On the other hand, PEDOT has better electrical properties. Polymerization of conductive polymer directly on the surface of textile fibers can generate multifunctional textile fibers with better electro-mechanical properties. In order to obtain better results, the CVD process was optimized by controlling the different pre- and post-polymerization reaction conditions. Attempts were made to determine the relationship between these reaction parameters and the electro-mechanical properties of the conductive fibers obtained. The purpose of Papers I, II, and III was to prepare PEDOT-coated conductive fibers (viscose and polyester) by using CVD technique and then to optimize the process by controlling the various reaction conditions. The perseverance of PEDOT layers by silicone coating was investigated in Paper IV, and the development of a new setup for the measurement of electrical resistance across the conductive fibers was studied in Paper V. Finally, the preparation of knitted structures with the PEDOT-coated conductive fibers obtained, and then their application as stretch sensors, was studied in Paper VI.

3. EXPERIMENTAL

3.1. Materials

3.1.1. Viscose yarns/fibers

Viscose or *viscose rayon*, with a chemical structure similar to that of cotton—which is almost pure cellulose—was the first man-made fiber to be produced from cellulose-based raw material derived from wood pulp. As it is obtained from naturally occurring resources, like most other man-made fibers it is not purely synthetic. Due to this dual character, it has properties that are more similar to cellulosic fibers than to petroleum-based synthetic fibers [126]. It is prepared by dissolving cellulose in sodium hydroxide (NaOH) to make alkali cellulose, which is later treated with carbon disulfide (CS_2) to give a solution of sodium cellulose xanthate. Finally, the rayon fibers or regenerated cellulose are obtained by spinning the sodium cellulose xanthate solution in a mineral acid, such as sulfuric acid [127].

Viscose has excellent properties: it is soft like cotton, smooth, strong like polyester, elastic, cool, comfortable, highly moisture-absorbent, and breathable. The modified forms of viscose, such as high-wet-modulus (HWM) rayon and high-tenacity (HT) rayon, can also be used for tire cord and for some high-tech industrial applications [126]. The filaments in viscose yarns vary from 80 to 980 filaments per yarn with a size ranging from 40 to 5,000 denier [128]. For this thesis work, viscose yarns (1,220 dtex; number of filaments 720, Z100 twist/m) commercially available as CORDENKA® 610F and purchased from CORDENKA® (Obemburg, Germany) were used. It has favorable properties such as good adhesion to plastics, high modulus, high dimensional stability, and high thermal and environmental stability. For most of the experimental work, viscose yarns were used without any surface modification, except in Papers III and VI.

3.1.2. Polyester/PET/PES yarns

Polyester is a common term used for the class of polymeric materials that contain the ester functional group (RCOOR) as a main constituent of the backbone structure [129]. Of the different types of polyesters, the most commonly used for fiber purposes is polyethylene terephthalate—or simply PET. Since the invention of PET in the 1940s [130], it has become the most developed and successful man-made fiber due to its excellent mechanical properties, high temperature resistance, economical and large-scale production, cheap and easy availability of raw materials, good chemical and abrasion resistance, and the possibility of recycling [131]. PET can be obtained either from naturally occurring chemicals such as cutin from plant cuticle, or by step-growth/condensation polymerization reaction of terephthalic acid [$C_6H_4(COOH)_2$] with ethylene glycol ($C_2H_6O_2$). Depending on the chemical structure, it could be a thermoplastic, such as PET, or a thermosetting material such as an unsaturated polyester [129, 132].

Table 3: *Comparative rating of cotton, viscose, and PET fibers [126]*

Parameters	Comparative rating		
	Cotton	**Viscose**	**Polyester**
Comfort			
Moisture Regain	Good	Very good	Poor
Thermal properties	Good	Very good	Poor
Air permeability	Very good	Good	Poor
Softness	Good	Very good	Poor
Smoothness	Poor	Good	Very good
Static dissipation	Good	Very good	Poor
Aesthetic			
Drape	Good	Very good	Poor
Luster	Poor	Very good	Poor
Crease recovery	Poor	Poor	Very good
Uniformity	Poor	Very good	Good
Utility preference			
Anti-pilling	Good	Very good	Poor
Wash and wear	Good	Poor	Very good

A variety of PET fibers—such as textile filaments, staple fibers, and industrial filaments—are being widely produced globally. Textile filaments are continuous fibers or yarns that are used to form knitted or woven fabrics. Staple PET fibers, with cut length (30–100 mm) and diameter (10–20 μm) similar to that of cotton or wool are spun into yarns and then fabric structures are produced. Industrial PET fibers, also known as HMW or UHMW PET fibers, are used as reinforcement in other composite materials, to make technical fabrics with high strength for use in car tires [133, 134]. In this thesis work, high-performance PET textile filament yarns (2,200 dtex; number of filaments 210, without twist) purchased from

Performance Fibers were selected. A comparative rating of viscose, polyester, and cotton fibers for smart and interactive textile applications is given in Table 3.

3.1.3. EDOT monomer

The chemical oxidation of 3,4-ethylenedioxythiophen (EDOT) monomer in the presence of suitable oxidant gives highly conductive PEDOT polymer, as explained in section 2.1.2. EDOT, which is commercially available with the trade name CLEVIOS M V2 (H.C. Starck, Germany), is not very resistant to oxidation and can decompose completely with very strong oxidants such as concentrated nitric acid. The derivatives of EDOT can even self-oxidize after a long period of time to make PEDOT with relatively good conductivity (80 S/cm) [21]. Some selected physical properties of EDOT monomer are listed in Table 4.

Table 4: *Selected physical properties of EDOT [21]*

Viscosity (20°C)	11 mPa.s
Density (20°C)	1.34 g/cm^3
Melting point	10.5°C
Boiling point (1,013 mbar)	225°C
Vapor pressure (20°C)	0.05 mbar
Vapor pressure (90°C)	10 mbar
Solubility in water (20°C)	2.1 g/l
Flash point	104°C
Ignition temperature	360°C

3.1.4. Oxidant solutions

The oxidation potential of any oxidant used for EDOT polymerization plays a very important role in obtaining smooth and highly conductive PEDOT layers. It should be high enough to start the polymerization reaction and low enough to avoid unwanted side reactions [50]. For the vapor-phase polymerization of PEDOT, the most often used oxidants are iron (III)-based salts, such as iron (III) chloride ($FeCl_3$) and iron (III) p-toluene sulfonate (Fe*p*TS) [135]. It has been reported that under controlled and specific reaction conditions, the highest conductivity of PEDOT films—up to 1,000 S/cm—can be achieved by using $FeCl_3$ and Fe*p*TS oxidants [6, 19]. Thus, in this thesis work the main focus was on the use of these two oxidant types for textile substrates and comparison of the results obtained. The $FeCl_3$ (98%) (Sigma-Aldrich, Germany) oxidant solutions were prepared in 1-butanol (Fisher Scientific) with concentrations varying from 3 to 15 wt.%. Another oxidant, Fe*p*TS (Clevios C-B 40 V2), was purchased from H.C. Starck, Germany, and it was used as received.

3.1.5. Silicone elastomer

Silicones are special reagents that are used to give special surface properties (such as softness, flexibility, bounciness, durability, and anti-wrinkle properties) to textile-related materials [136]. Surface treatment of wool and PET fabrics with silicone polymer has already been reported [137, 138]. In this research, thermoplastic silicone elastomer (Geniomer 80) was purchased from Wacker Chemie AG, Germany, for surface modification of PEDOT-coated conductive fibers. The solution of silicone elastomer at a concentration of 15 wt.% was prepared in methyl ethyl ketone (MEK) ($C_2H_5COCH_3$), and coated fibers were treated with silicone solution in order to obtain a smooth and thin protective layer.

3.1.6. Surface cleaning agents

The commercially available textiles yarns/fibers are usually lubricated with wax-like materials, which act as protective agents against biological and atmospheric influences. These finishing materials are necessary to speed up the processing of synthetic fibers on different weaving and knitting machines [139]. Consequently, the presence of these wax-like materials on the surface of textile substrates can affect the quality of deposited layers of conductive polymers. In order to study this effect, viscose fibers were treated with two well-known cleaning solvents, acetone and ethyl acetate (purchased from Fisher Scientific), before polymerization. Acetone and ethyl acetate were selected because these are the most commonly used solvents for removal of stains and wax-like materials from the surface of the fabrics. Also, they are not toxic and can easily evaporate even under ambient conditions. The surface treatment of different textile materials, such as wool, nylon, and cellulose, with acetone and ethyl acetate has already been reported extensively [140-142].

3.2. Process description

3.2.1. Chemical vapor deposition of PEDOT on textile yarns

As explained in section 2.1.2, chemical vapor deposition (CVD) or vapor-phase polymerization (VPP) is the most intensively used method to obtain highly conductive PEDOT layers on the surface of different substrates such as PET films, glass, silicon wafers, fabrics, and textile fibers. The direct deposition of ICPs on different substrates not only produces good-quality polymer layers but also minimizes the processing problems associated with the insoluble nature of conjugated polymers. In the CVD process, the oxidant-enriched substrate is usually exposed inside the reactor where the reacting monomers are provided in vapor form, which can readily oxidize and then polymerize on the surface of the substrate material.

The CVD polymerization of PEDOT usually consists of three steps:

a) Pretreatment of substrate with oxidant solution
b) Polymerization of EDOT to PEDOT
c) Doping of the PEDOT films produced

In order to follow these steps, the process scheme we used in this work is shown in Figure 11 and the setup that we developed for the polymerization step is shown in Figure 12. First of all, textile yarns (of viscose and polyester) were soaked with oxidant ($FeCl_3$, Fe*p*TS) solution for predefined intervals (1) and then after oxidant impregnation, the yarns were dried at different temperatures for variable times (2). Secondly, the oxidant-enriched yarns were inserted in a tubular reactor, which was flushed with EDOT monomer vapor (3). The EDOT monomer vapor was generated by heating the liquid EDOT monomer (at 70°C) in a separate flask and it was introduced into the tubular reactor along with the nitrogen gas. After exposure of oxidant-enriched textile yarns to the atmosphere containing EDOT monomer, the polymerization reaction started spontaneously and yarns were coated with a smooth, darkish-blue layer of PEDOT polymer. In order to avoid the discharge of excess monomer vapor to the outer environment, the end of the tubular reactor was capped with a flask and a reflux condenser. Thirdly, after polymerization, the PEDOT-coated textile yarns were treated with $FeCl_3$ solution again for doping purposes (4), and finally the coated yarns were rinsed several times with methanol in order to remove the unreacted monomer, by-products, and Fe (II) and Fe (III) salts (5).

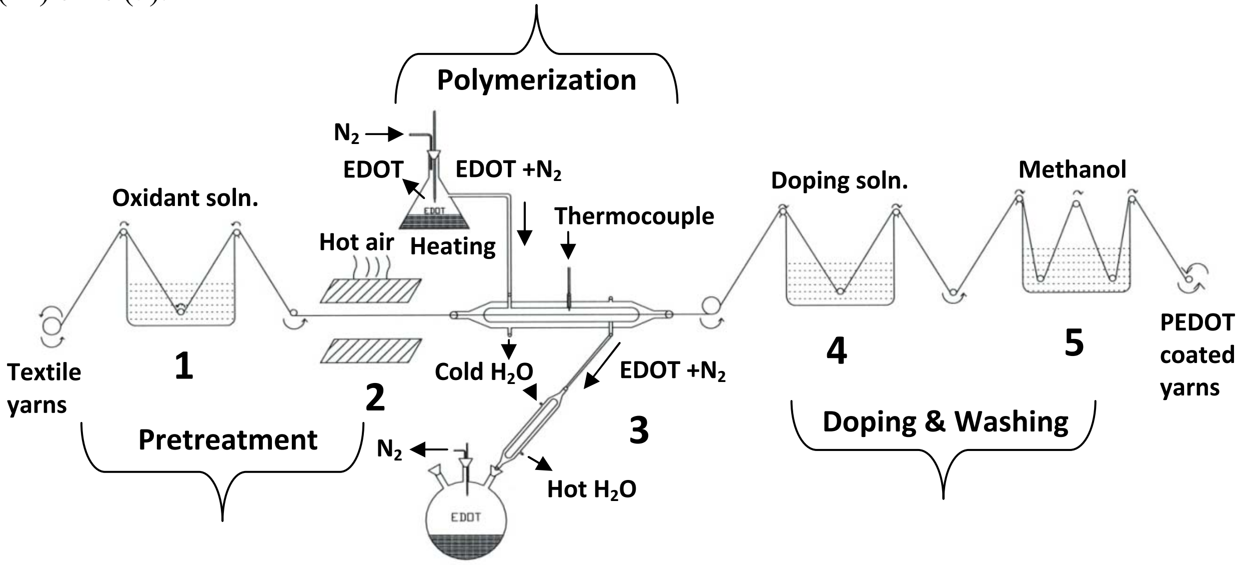


Figure 11: *Schematic diagram of the CVD process for the production of PEDOT-coated conductive yarns*

The CVD polymerization of PEDOT depends on several pre- and post-polymerization steps, such as oxidant concentration, dipping time of textile yarns in oxidant solutions, drying time and temperature, reaction time and temperature, concentration of dopant, etc. In this thesis work, it was tried to investigate the effects of all the possible parameters that can influence the deposition process. In order to obtain PEDOT-coated yarns with the desired properties, these parameters were optimized and finally the best reaction conditions were arrived at. A list of these reaction parameters, their values, and corresponding papers is given in Table 5.

The CVD process is usually a batch process and only small pieces of substrate can be coated in one batch. Thus, during the initial experiments, only coating of 15-cm long viscose fibers was tried in one batch and the most suitable reaction conditions investigated to obtain highly conductive PEDOT-coated yarns (Paper I). These reaction conditions were further optimized in order to minimize the overall reaction time for one batch process (Paper II). After getting very encouraging results with viscose yarns, another type of substrate yarn—polyester—was tried. The best reaction conditions, under which good electro-mechanical properties of

PEDOT-coated viscose were achieved were used to coat PET yarns, and then the results were compared with those for the conductive viscose yarns already produced (Paper III).

Later on, PEDOT-coated conductive viscose and PET yarns were produced in longer lengths, e.g. 15 meters long, using a special custom-made fiber-holding setup, which is explained in the next section. In order to protect the PEDOT coating on the surface of viscose yarns, a solution of thermoplastic silicone elastomer was prepared in MEK solvent and the PEDOT-coated yarns were treated with this solution. A thin, protective layer of silicone formed on the surface of PEDOT-coated fibers (Paper IV).

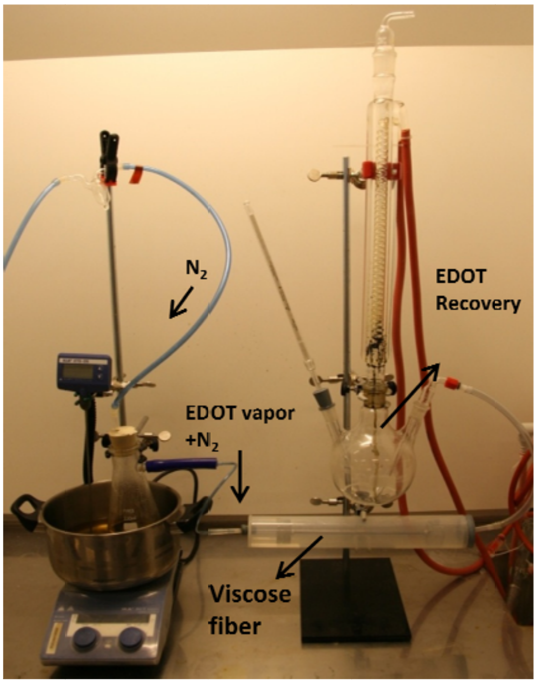


Figure 12: *The polymerization setup used in all experiments involving coating of textile yarns with PEDOT*

Table 5: *Reaction parameters studied in this thesis work*

Parameters	Values	Paper(s)
Oxidant concentration	3–15 wt.%	Paper I
Dipping time of textile yarns in oxidant solutions	3 min to 24 h	Paper I
Drying time of oxidant enriched yarns	3–60 min	Papers I & II
Drying temperature	25–60°C	Papers I & II
Reaction time	15–60 min	Paper I
Reaction temperature	25–50°C	Paper I
Oxidant type	$FeCl_3$ & Fe*p*TS	Paper II
Solvent treatment	Acetone & eth. acetate	Paper II
Substrate yarns	Viscose & polyester	Paper I–VI
Surface finishing	Silicone elastomer	Paper IV

Production of conductive fibers in longer length

Viscose and PET textile yarns were successfully coated using the CVD process, but in order to find useful applications for these electro-active fibers, it was necessary to produce them in reasonably long lengths. For this purpose, a 25-cm long fiber-holding setup, shown in Figure 13, was made. After impregnation with oxidant solution and subsequent drying, the textile yarns were wound over this setup and then placed inside the tubular reactor for the polymerization reaction. Later on, the maximum length achieved using the setup shown and the CVD process was 15 m (Paper VI).

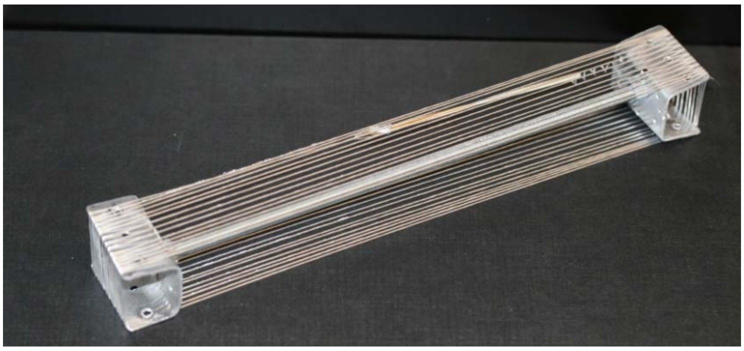


Figure 13: *Textile fibers wound over the fiber-holding setup. From Paper (VI)*

Preparation of knitted structure

In order to test some applications of PEDOT-coated conductive fibers, small rectangular knitted structures were prepared by using 15-m long conductive threads. For this purpose, a hand knitting machine (manufactured by Moretto, 8 gauges with latch-type needles made by Dubied) was used. The 1 × 1 rib-knit structure was preferred because of its good stretching properties and recovery of the structure after extension. The PEDOT-coated conductive fibers were integrated into the base fibers to give a rectangular structure with a total area 12 × 8 cm^2 containing a conductive portion of 12 × 2.5 cm^2. Later on, the stretch-sensing properties of these knitted structures were investigated on a cyclic tester.

3.3. Testing and characterization

3.3.1. Electrical properties

The term *volume resistivity (ρ)* is usually used to evaluate the electrical performance of a conductive material. It can be calculated by using the following mathematical expression:

$$\rho = \frac{R.A}{L} \qquad \text{eq. 1}$$

where *R (Ω)* is the measured resistance of the material along a specific length *L (m)*, with a particular cross-sectional area *A* (m^2). Thus, the standard SI units for volume resistivity are *(Ω.m)*. The reciprocal of resistivity is known as *conductivity* and it is used to measure the ability of any material to conduct electrons, with SI units Siemens per meter (S/m). Therefore, in order to calculate the conductivity, the exact dimensions of the sample and its resistance *(R)* should be known.

In the case of conductive fibers, it is always difficult to get exact information about the diameter of the fiber. For monofilaments it is rather easy, but for textile yarns with bundles of monofilaments—either twisted or untwisted—it is very difficult to measure the diameter by conventional methods. So, for textile yarns, another term known as mass-specific resistance, R_s, is used to better effect than using conventional electrical resistance [143]. The mass-specific resistance, R_s in Ω.g/cm^2, can be related to the commonly used volume resistivity *(ρ)* in Ω.cm by the mathematical expression:

$$R_s = \rho d \qquad \text{eq. 2}$$

In this mathematical relationship, d is the density of material in g/cm^3.

However, for conductive textile fibers and yarns, the term density in eq. 2 should be replaced by linear density and the modified mathematical expression for mass-specific resistance will be:

$$R_s = \frac{RNT}{L} \times 10^5 \qquad \text{eq. 3}$$

where R is the electrical resistance (Ω), L is the length of conductive yarn (cm), N is the number of ends of yarn or fiber, and T is the linear density of yarn or fiber (g/km). In order to calculate both the conductivity and the mass-specific resistance, the electrical resistance (R) should be known. Electrical resistance across conductive fibers or yarns can be measured by two methods: the two-probe method and four-probe method. Conventionally, the two-probe method with crocodile clips is used, but for very small resistance values (in the ohm range or even lower) the four-probe method gives more accurate results by eliminating the effect of the contact resistance [144]. In this thesis work, the electrical resistance across the conductive yarns was measured by the two-probe method, as shown in Figure 14.

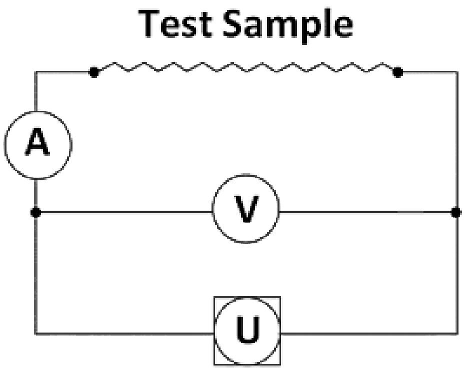


Figure 14: *Principle coupling scheme of the two-point resistance measurement setup. From Paper V*

For most of the experiments, the resistance along the coated fibers was measured using a Keithley 6000 picoammeter (Keithley; Cleveland, Ohio, USA) at a voltage sweep of 1–10 V by applying a constant current of 2.5 mA between two crocodile clips holding a 150-mm long fiber sample. However, later on a resistance-measuring setup was established, as discussed in section 4.3, which was used to investigate the electrical properties of fibers of longer length. All the electrical resistance values were measured under ambient conditions, such as 23 ± 2°C and 12 ± 5% RH. Each sample was tested 12 times and then average values were used.

For calculation of conductivity values, the diameter of coated yarn was determined by two methods: with a micrometer and with an optical microscope. Then the average diameter value was used to determine the cross-sectional area of conductive yarns. By putting the known values for electrical resistance (R), length (L), and cross-sectional area (A) into eq. 1, the electrical conductivity of coated yarns was calculated. Since textile yarns (viscose and PET) with a specific number of filaments were used as substrates, by using the linear density of coated yarn (T), the resistance (R), and the length (L), the mass-specific resistance was calculated using eq. 3.

3.3.2. Scanning electron microscopy (SEM)

Using the CVD process, PEDOT polymer was not only used successfully to coat the surface of textile yarns but it was also used to impregnate the yarns to some extent. The coating thickness and uniform distribution of PEDOT are very important factors; they can have a diverse effect on the properties of the conductive yarns obtained—and hence, on end-user applications. In this thesis work, the surface morphology of PEDO-coated conductive yarns was investigated by scanning electron microscopy. The SEM micrographs were prepared from gold-sputtered PEDOT-coated conductive samples using a JEOL JSM-840A scanning electron microscope at 10kV accelerated voltage. The experiments were performed in the laboratory of Swerea IVF, Sweden.

3.3.3. Computed tomography (CT) analysis

With SEM analysis, we obtained a better understanding of the surface appearance of PEDOT-coated conductive yarns, but the coating thickness and degree of impregnation of PEDOT inside the yarn was not investigated by SEM. It might be because of the involvement of several multifilaments in substrate yarns. In order to determine the three-dimensional distribution of PEDOT coating along the textile yarns, CT scanning was performed on the conductive samples obtained. CT scanning is a very effective technique for getting information about particle size, composition, internal distances, or internal wall thickness of very complex samples, which other commonly used optical scanners can never achieve [145]. For this purpose, a high-precision granite-based phoenix nanotom CT system (GE Sensing & Inspection Technologies, Wunstorf, Germany) with a 180-kV/15W high-power nanofocus tube with tungsten target was used. The tube offers a detection range from 200 to 300 nm (0.2–0.3 microns) depending on the sample size. For fast and more accurate acquisition of results, the datos|x, phoenix|x-rays proprietary software package was used. All the parameters used with the nanotom CT system are listed in Table 6.

Table 6: *The parameters used with the nanotom system for CT scanning. From Paper II*

Parameters	**Sample: PEDOT/viscose**
Magnification	83.4
Voxel size	0.6
FOD	2.4
FDD	199.9
No. of images	1,440
Image width	2,294 pixels
Image height	1,800 pixels
Scanning time	750 ms
Acceleration Voltage	70 kV
E-beam current	385 μA
Tube mode	3

3.3.4. Attenuated total-reflectance Fourier transform infrared spectroscopic (ATR-FTIR) analysis

Deposition of the PEDOT layer on viscose and PET yarns, the quality of the PEDOT film, chemical bonding between PEDOT and substrates, and variations in chemical structures of virgin substrate yarns were determined by using a Nicolet 6700 FT-IR spectrometer in ATR mode. IR spectra were acquired in the range of 4,000 to 400 cm^{-1}, with 32 scans and 4 cm^{-1} band resolution. On the other hand, in order to verify the PEDOT-coated layer and (to some extent) impregnated fibrils of the textile yarns, ATR-FT-IR imaging was performed using a Perkin-Elmer Spotlight 400 FT-IR coupled to the 400N FT-NIR imaging system. The samples were mounted on the X-Y stage of the FT-IR microscope and pressed against the ATR crystal via a force lever. The spectra were taken with an average of 2–8 scans between 4,000 cm^{-1} and 720 cm^{-1} and with a resolution of 6 cm^{-1}. The FT-IR imaging data were obtained with a linear array detector and a pixel size of $1.56 \times 1.56\ \mu m^2$. Other spectral data processing and image processing was carried out using Perkin-Elmer IMAGE software.

3.3.5. Tensile testing

The influence of different reaction conditions and PEDOT coatings on the mechanical properties of viscose and PET yarns was investigated using a Tinius-Olsen H10KT universal testing machine with a 250-N load cell and under a crosshead speed of 20 mm/min. The maximum force at break and the percentage elongation across the conductive fibers with a gauge length of 100 mm was measured. However, for textile fibers and yarns, the term that is usually used for mechanical strength is tenacity. Tenacity can be calculated by dividing the maximum force at break (in *N*) by the linear density of yarns or fibers (tex) in *g/km*. So, the tenacity of coated fibers—before and after PEDOT coating—was also measured in this thesis work. Tensile testing was performed on at least five samples of each type and then average values were taken. All readings were obtained under ambient conditions: at a temperature of 23 ± 2°C and with 12 ± 5% relative humidity.

3.3.6. Thermal characterization

The thermal properties of PEDOT-coated conductive yarns were investigated by TGA and DSC analysis. With TGA analysis, the amounts of PEDOT coatings and the thermal stabilities of PEDOT-coated yarns were estimated using a TA Instruments Q500 TGA apparatus at a heating rate of 10°C/min from 25°C to 600°C under nitrogen gas. For DSC analysis, the thermal properties of coated yarns were evaluated using a TA Instruments Q2000 DSC. The calorimeter cell was flushed with nitrogen at 100 ml/min, and about 3–6 mg of fiber sample was used in each test using an aluminum crucible. The temperature program was set in the range from 25°C to 400°C, at a heating rate of 10°C/min.

3.3.7. Stretch sensing characterization

In order to test the use of knitted structures made of PEDOT-coated yarns as stretch sensors, a self-designed cyclic testing setup attached to a Keithley 6000 picoammeter and an Agilent multimeter was used, as shown in Figure 15 (*right panel*). The knitted structure was fixed between two metallic clamps with two tight screws, as shown in Figure 15 (*left panel*). In order to establish a good contact between the knitted sample and the clamps, the inner walls of the clamps were coated with silver paint. The left-side clamp was fixed whereas the right-side clamp underwent to-and-fro motion in order to provide predefined stretching of the samples.

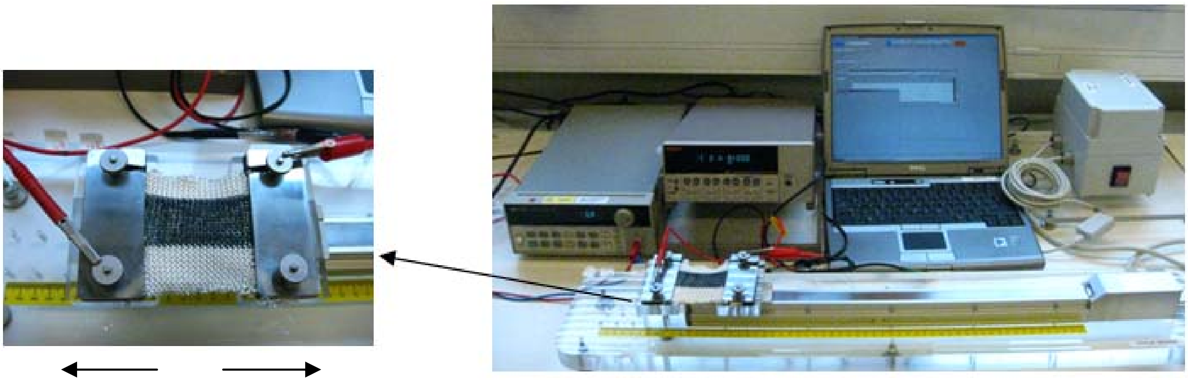


Figure 15: *The setup used to characterize the piezoresistive properties of knitted structures. From Paper VI*

In this thesis work, the experiments were performed at different degrees of stretching—from 5% to 50% of the original length of the samples—by adjusting the speed of the moving drive at 5 mm/s. The variation in electrical resistance values along the length of the knitted samples was measured at 25 mA and 10 V for a time period of 200 seconds. Stretching speed, stretching distance between two points, number of cycles, and current and voltage were controlled with LabVIEW software.

3.3.8. Washing test

To investigate the behavior of knitted structures, adhesion of PEDOT coatings, and the durability of fabric structures, two washing cycles were performed on PEDOT-coated knitted samples of viscose and PET. The washing cycles were performed in a laundry machine (*A type*) with a non-phosphate *ECE* detergent (type A without optical brightener) according to the *EN ISO-6330 standard* (domestic textile) washing and drying procedures for textile testing). Later on, the piezoresistive behavior of knitted structures, before and after washing, was evaluated with a cyclic tester and then the results were compared.

Overview of work done in each paper

In Paper I, PEDOT-coated conductive viscose fibers were produced by using the chemical vapor deposition technique. The effect of different reaction conditions, such as oxidant ($FeCl_3$) concentration (3−15 wt.%), soaking time of viscose fibers in oxidant solution (5 min to 24 h), drying time of oxidant-enriched fibers (5−120 min), and polymerization time (5−60 min) on the electrical, mechanical, morphological, and thermal properties of the fibers produced was investigated.

In Paper II, the CVD process was optimized further by controlling the various pretreatment steps, such as solvent treatment of viscose fibers before soaking with oxidant solution, oxidant types ($FeCl_3$, Fe*p*TS), drying of oxidant-enriched fibers at various temperatures (30−60°C), and time (3−10 min). The influence of these pretreatment steps on the electro-mechanical and thermal properties was studied. The distribution and degree of impregnation of PEDOT polymer along the viscose fibers was investigated by ATR-FTIR spectroscopic imaging and computed tomography (CT).

In Paper III, the best reaction conditions from Paper I at which maximum conductivity of PEDOT-coated viscose fibers was achieved were tried on polyester (PET) yarns in order to improve the mechanical properties of conductive fibers. The electrical, mechanical, morphological, and thermal characteristics of the PEDOT/PET fibers obtained were studied and then compared with those of previously prepared PEDOT/viscose fibers.

In Paper IV, the PEDOT-coated viscose fibers were prepared in longer length (5 m) and treated with silicone resin in order to improve the surface characteristics of the fibers obtained. The effect of silicone coating on the electrical, mechanical, and hygroscopic properties was investigated. The effects of washing on PEDOT-coated viscose fibers—before and after silicone treatment—were also studied.

In Paper V, electrical resistance measurements and electrical characterization of PEDOT-coated viscose fibers were carried out on a special type of custom-made setup with a Keithley picoammeter. The electrical resistance across the conductive fibers was measured by the two-point resistance method and then the results of the prepared setup and the conventionally used method were compared.

In Paper VI, the best reaction conditions from Papers I and III were used to produce PEDOT/viscose and PEDOT/PET conductive fibers of longer length i.e. 15 m. Knitted structures of PEDOT/viscose and PEDOT/PET fibers were prepared and then the stretch-sensing properties of knitted structures were investigated using a cyclic meter. Two washing cycles were performed on knitted structures in order to study the durability of a PEDOT coating on substrate fibers.

4. SUMMARY OF RESULTS

4.1. Synthesis of PEDOT-coated conductive textile yarns (Paper I–III)

When oxidant ($FeCl_3$) enriched textile yarns were exposed to EDOT monomer vapor, the polymerization reaction started very rapidly and a darkish-blue layer of PEDOT was formed on the surface of the oxidant-treated fibers. The amount of deposition of PEDOT on substrate fibers and the conductivity of the fibers obtained strongly depended on the reaction conditions. In Papers I–III, a number of reaction parameters were tried for two types of textile yarns (viscose and polyester) in order to determine the reaction conditions at which the optimum electro-mechanical properties of electro-active fibers could be achieved. The influence of these parameters on the electrical, mechanical, and thermal properties was investigated separately.

4.1.1. Influence of reaction parameters (Paper I)

In Paper I, small pieces of PEDOT-coated viscose fibers (150-mm long) were prepared under different reaction conditions. The purpose of this work was to investigate the possibility of using the CVD process to apply a PEDOT coating to viscose fibers. The relationship between the electro-mechanical properties and the reaction conditions was carefully evaluated. The mechanism of formation of PEDOT on the surface of viscose fibers and the step involving doping PEDOT polymer chains with $FeCl_3$ dopant are shown in Figure 16 (A→B and B→C, respectively).

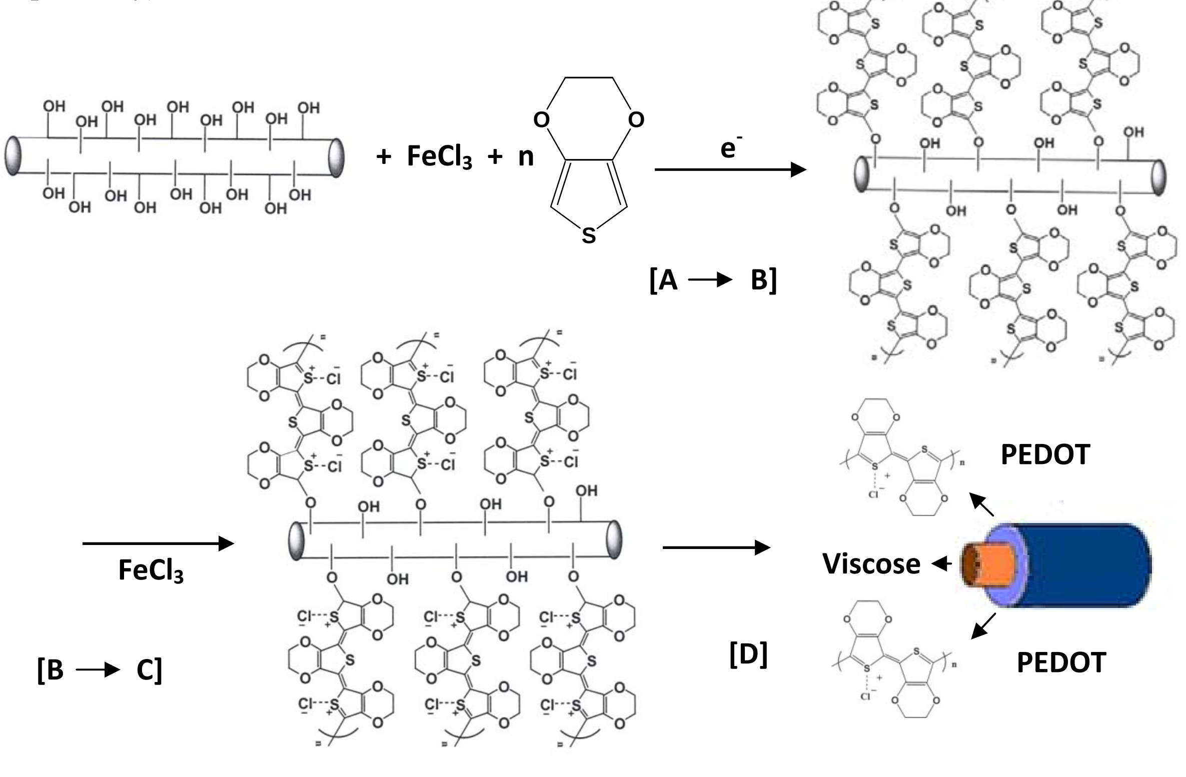


Figure 16: CVD-based mechanism for polymerization of PEDOT on the surface of viscose fibers (A→B) oxidation of EDOT monomer to PEDOT, (B→C) doping of PEDOT, (D) sketch of PEDOT-coated viscose fiber. From Paper II

The FTIR spectra of pure viscose and of PEDOT/viscose fibers are shown in Figure 17. The appearance of typical absorption peaks of PEDOT at 895, 1,208, 1,320, 1,521, and also 1,595 cm^{-1}, shown in Figure 17(b), revealed that the surfaces of viscose fibers had been successfully coated with PEDOT.

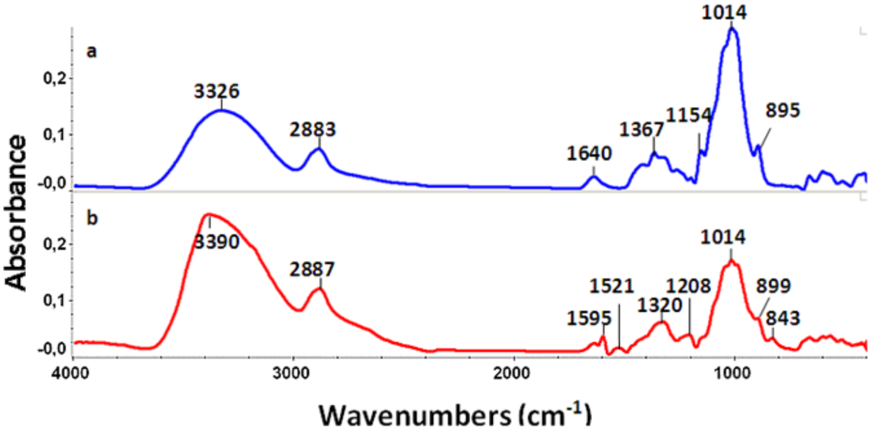


Figure 17: *FTIR spectra of (a) pure viscose fiber, and (b) PEDOT-coated viscose fiber. From Paper I*

The influence of oxidant ($FeCl_3$) concentration on the electrical and mechanical properties of the conductive fibers obtained is shown in Table 7. Percentage increase in oxidant concentration had inverse effects on the electrical and mechanical properties of PEDOT-coated fibers. The electrical conductivity was improved with increasing oxidant concentration from 3 to 15 wt.%, because the oxidation potential of oxidizing agent was also improved with increasing concentration, which initiated more EDOT monomer. However, the mechanical properties were reduced with increasing oxidant concentration, which may have been because of the acidic nature of $FeCl_3$ solution causing acid hydrolysis of viscose fibers.

Table 7: *The influence of oxidant concentration on the electrical and mechanical properties of PEDOT/viscose conductive fibers*

Oxidant conc. (wt. %)	**Max. force** (N)	**Elongation** (%)	**Tenacity** (N/tex)	**Resistance** (kΩ)
0	65.9 (± 3.3)	72.4 (± 4.4)	0.35	....
3	41.1 (± 1.4)	38.4 (± 1.2)	0.21	33.1
5	34.5 (± 1.3)	25.4 (± 1.3)	0.18	27.7
9	32.4 (± 1.9)	21.7 (± 2.4)	0.16	8.0
15	26.1 (± 2.1)	15.7 (± 1.9)	0.13	3.3

The surface morphology of conductive fibers has a significant effect on their end-use applications. The effect of oxidant concentration on the surface morphology of PEDOT-coated viscose fibers is shown in the SEM micrographs in Figure 18. A relatively smooth and thicker PEDOT polymer layer was deposited on the surface of viscose fibers with increasing oxidation concentration, from 3 to 9 wt.%.

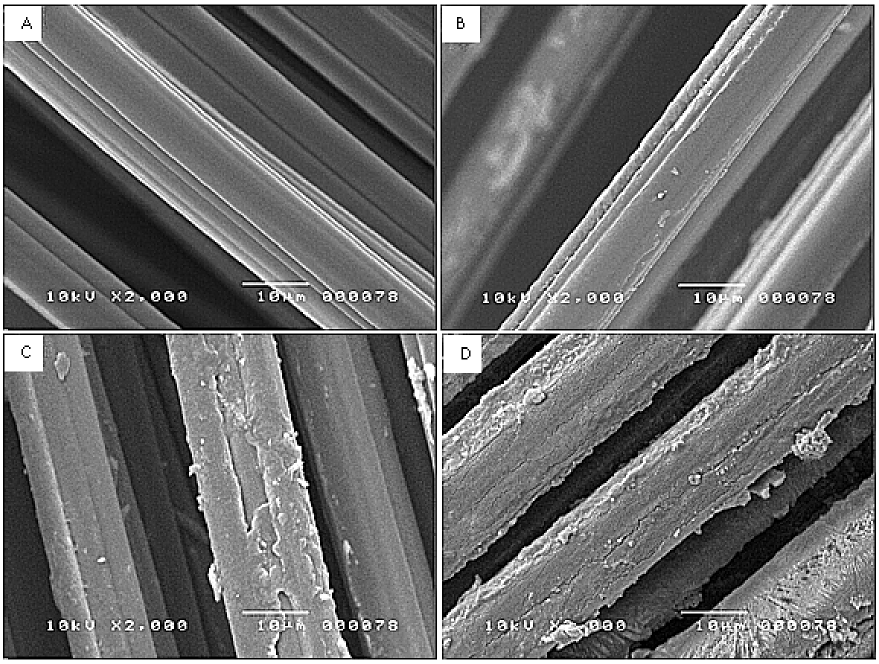


Figure 18: *SEM micrographs of PEDOT-coated viscose fibers impregnated with different concentration of* $FeCl_3$*: (A) 0 wt.%, (B) 3 wt.%, (C) 5 wt.%, (D) 9 wt.%. From Paper I*

The electrical properties of PEDOT-coated conductive fibers strongly depend on the amount and quality of PEDOT deposited or impregnated on the surface of substrate fibers. The effect of dipping time of viscose fibers in oxidant solution on the electrical properties is shown in Figure 19. With increasing soaking time up to 120 min, the electrical resistance was gradually reduced, but longer soaking time had an inverse effect on the electrical properties.

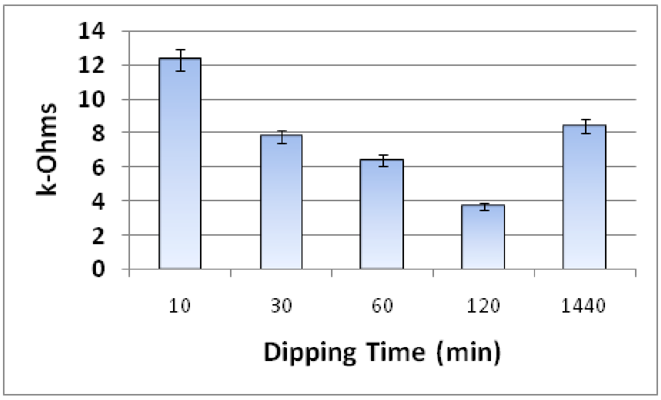


Figure 19: *Influence of dipping time of viscose fibers in* $FeCl_3$ *solution on the surface resistance of PEDOT-coated viscose fibers. Oxidant concentration was kept constant at 15 wt.%. From Paper I*

The impact of humidity on the polymerization of PEDOT has already been reported extensively in the literature. It should be at the optimum value to obtain maximum conductivity of PEDOT. Since viscose is hygroscopic in nature and can absorb moisture from the atmosphere, drying of oxidant-enriched viscose fibers plays a very important role in getting smooth and highly conductive PEDOT layers on the surface of viscose fibers. For the different oxidant concentrations shown in Figure 20, the electrical resistance became reduced until a specific time interval, after which it increased again. Depending on the properties required by the end-user, one can select a suitable drying time for a predefined oxidant concentration.

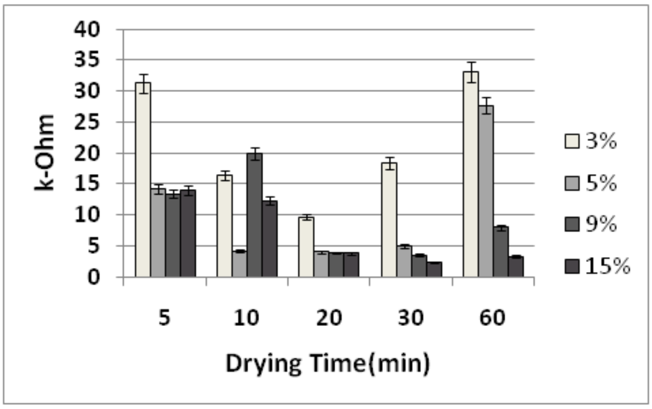


Figure 20: *Surface resistance of PEDOT-coated viscose fibers prepared at different drying times of oxidant impregnated fibers and at different oxidant concentrations. Other reaction conditions were kept constant: dipping time of the viscose fiber in oxidant solution (10 min), reaction time (15 min), and reaction temperature (50℃). From Paper I*

The influence of reaction time on the electrical properties of PEDOT-coated viscose fibers was investigated by keeping other parameters constant. The best reaction time at which minimum surface resistance was achieved, shown in Figure 21, was 15 min.

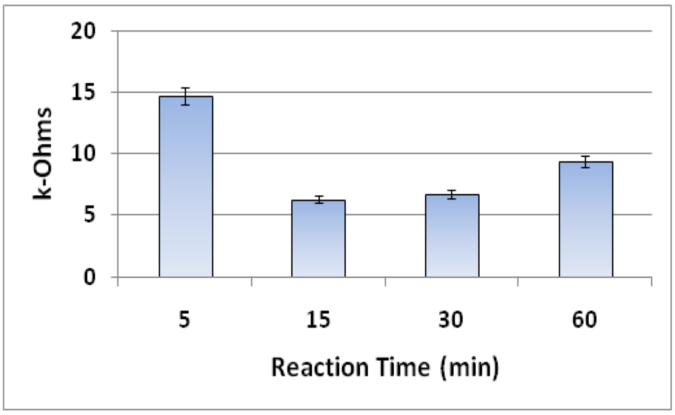


Figure 21: *Surface resistance of PEDOT-coated viscose fibers prepared at different reaction times. Oxidant concentration was kept constant at 15 wt.%. From Paper I*

Figure 22 illustrates the thermogravimetric analysis of viscose fibers before and after coating with PEDOT. By considering the extent of viscose decomposition at 400°C, it can be concluded that about 50% of the composite fiber consists of PEDOT polymer. The close resemblance of TGA thermograms with PEDOT and improved thermal stability of composite fibers shows that the viscose fibers were fully coated with PEDOT polymer and that a strong interaction between PEDOT polymer macromolecular chains and viscose fibers may have been established. After a series of experiments, the most suitable reaction conditions at which the highest electrical properties of PEDOT-coated viscose fibers were achieved were: an oxidant concentration of 15 wt.%, a dipping time of 10 min, a drying time of 30 min, and a reaction time of 15 min.

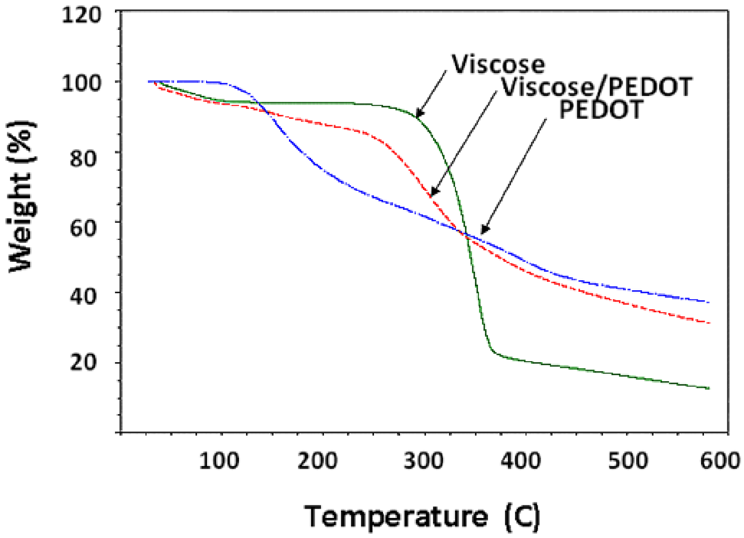


Figure 22: *TGA analysis of pure viscose, of pure PEDOT and of PEDOT-coated viscose fibers. From Paper I*

4.1.2. Optimization of the CVD process (Paper II)

It has already been found that a uniform layer of PEDOT with high conductivity can be obtained by the CVD process, but it is very difficult to make this process continuous. Only a small piece of substrate can be coated in one batch. Also, a number of steps are involved in successful coating of PEDOT; thus, the overall process time for one batch will be very high. For higher production, the process time should be minimized and this can be done by optimizing the different pre- and post-treatment steps involved in CVD-based polymerization of PEDOT.

On the other hand, commercially available textile fibers usually contain wax-like materials, which act as protective agents against biological and atmospheric influences. These lubricating substances are necessary to speed up the processing of synthetic fibers on different weaving and knitting machines. The presence of these coatings can also affect the polymerization of PEDOT. In this paper, the main focus was on pretreatment steps, which can not only minimize the overall process time required for the production of one batch of coated fibers, but also improve the engineering properties of the conductive fibers obtained. The pretreatment steps, including the surface treatment of viscose fibers with different solvents (acetone and ethyl acetate), two different types of oxidants ($FeCl_3$ and Fe*p*TS), and drying of oxidant-enriched fibers at different temperatures (30–60°C) for various times (3–10 min), were carefully evaluated. Also, the impact of these parameters on the electrical, mechanical, and thermal properties was investigated. The other reaction conditions were taken from a previous study in which maximum electrical properties were achieved. The optimum reaction conditions obtained for minimization of process time are shown in Table 8.

Table 8: *Reaction parameters for minimum process time and optimum properties of coated fibers. From Paper VI*

Fibers	Viscose, Polyester
Oxidant	15 wt.% $FeCl_3$
Soaking time in oxidant	10 min
Drying temperature of oxidant-treated fibers	60°C
Drying time of oxidant-treated fibers	10 min
Polymerization reaction time	15 min
Polymerization reaction temperature	50°C
Doping agent	3 wt.% $FeCl_3$

Surface treatment of viscose fibers with two well-known solvents, acetone and ethyl acetate, was done prior to the oxidant-enrichment and polymerization steps. The solvent-treated fibers were then carried through the polymerization steps and the electro-mechanical characteristics of PEDOT-coated fibers were studied. After solvent treatment, the electrical and mechanical properties of the coated fibers had changed, as shown in Figure 23. Acetone-treated fibers showed better electrical properties whereas better mechanical properties were achieved with ethyl acetate-treated viscose fibers.

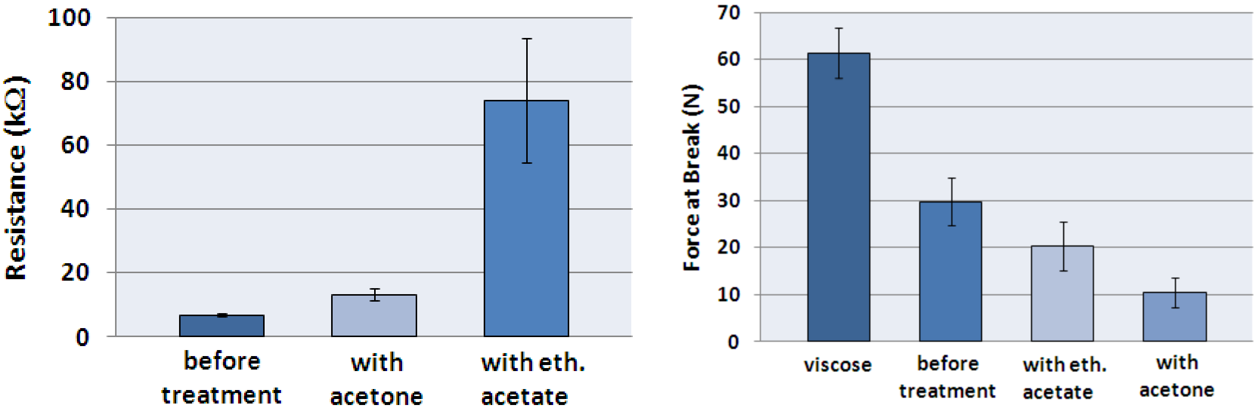


Figure 23: *Effect of surface treatment on the electrical (left panel) and mechanical (right panel) properties of PEDOT-coated viscose fibers. From Paper II*

In Paper I, the effect of drying time of oxidant-enriched viscose fibers under ambient conditions was investigated. It was concluded that 30 min of drying time gives better electro-mechanical properties. In order to minimize the overall process time, the oxidant-treated fibers were dried at different temperatures (30°C, 40°C, 50°C, and 60°C) for short time intervals and then the electro-mechanical characteristics of coated fibers were studied. The electrical properties of PEDOT-coated fibers obtained at different drying temperatures are shown in Figure 24. The minimum electrical resistance values of PEDOT-coated conductive fibers were obtained at 60°C with 10 min of drying time, i.e. (4 kΩ), which was almost the same as that from our previous results (i.e. 3.5 kΩ obtained at 30 min of drying). So, the overall process time can be significantly reduced by controlling the drying temperature and time.

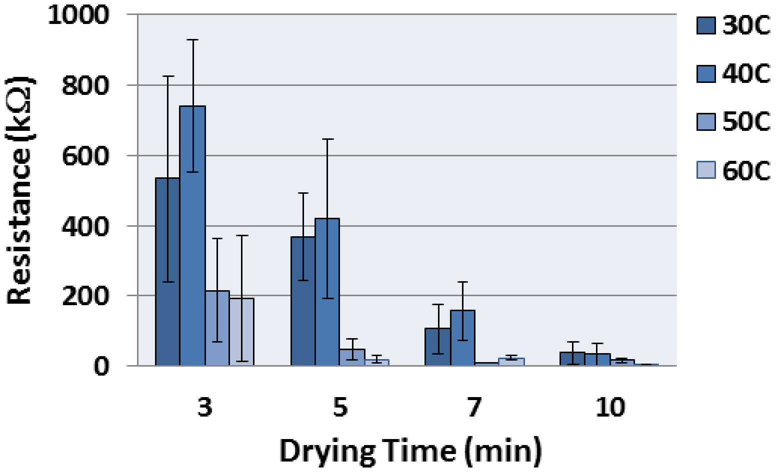


***Figure 24**: The electrical properties of PEDOT-coated viscose fibers produced with various drying times and temperatures. From Paper II*

The effect of drying conditions on the mechanical properties of the coated fibers produced is shown in Figure 25. The mechanical strength of PEDOT-coated viscose fibers was improved with increasing drying temperature up to 50°C and with a drying time of 7 min. Further drying of oxidant-treated fibers at higher temperature (60°C) for a longer time period (10 min) reduced the tensile strength of conductive fibers.

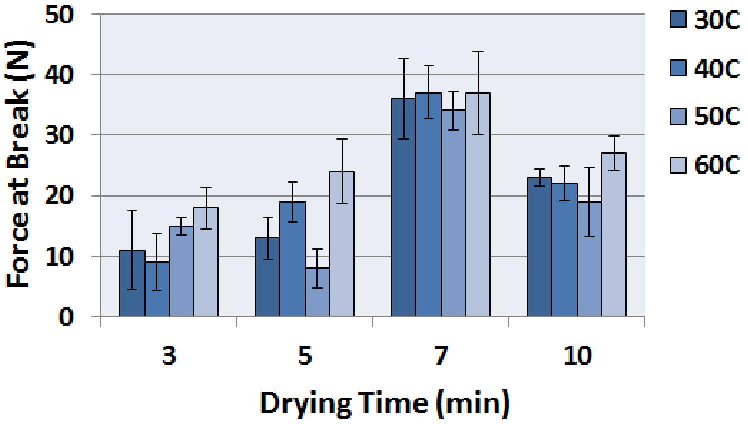


***Figure 25:** The mechanical properties of PEDOT-coated viscose fibers produced with various drying times and temperatures. From Paper II*

In order to improve the electro-mechanical properties of PEDOT-coated conductive fibers, $FeCl_3$ oxidant was tried along with another commonly used oxidant—Ferric(III)p-toluenesulfonate (Fe*p*TS)—and the results were compared. Light microscopic images of pure viscose and PEDOT-coated viscose prepared with either $FeCl_3$ or Fe*p*TS oxidant are shown in Figure 26. A relatively smooth and uniform PEDOT layer was formed on the surface of viscose fibers using $FeCl_3$ (Figure 26B), whereas the surface morphology of PEDOT-coated fibers with Fe*p*TS oxidant was very rough and brittle (Figure 26C). In the latter case, the handling of conductive fibers would be very difficult.

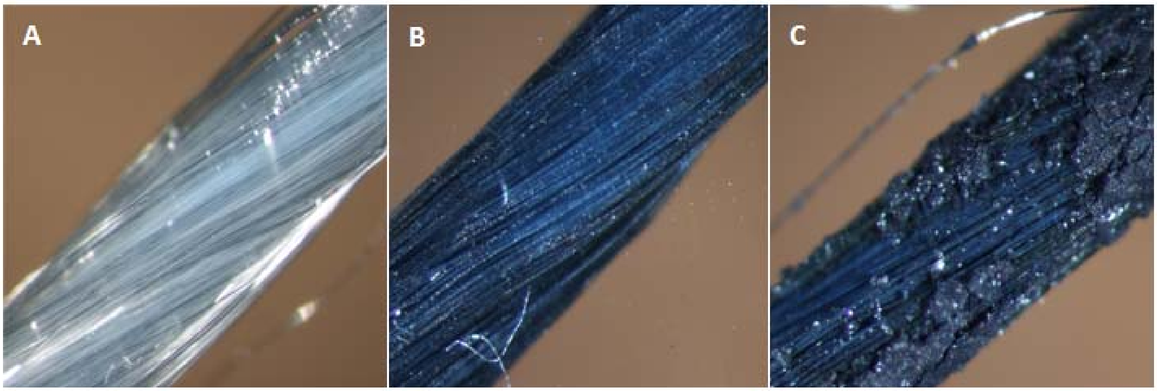


Figure 26: *Optical microscopic images of: (A) pure viscose, (B) PEDOT/viscose with* $FeCl_3$*, and (C) PEDOT/viscose with FepTS. From Paper II*

The electrical and mechanical properties of PEDOT-coated viscose fibers synthesized with $FeCl_3$ and Fe*p*TS oxidants are given in Table 9. The electrical resistance of PEDOT-coated conductive fibers prepared with $FeCl_3$ oxidant was considerably lower (6.8 kΩ) than that of PEDOT-coated conductive fibers produced with Fe*p*TS oxidant (54.5 kΩ). However, the mechanical properties of PEDOT-coated viscose fibers produced with $FeCl_3$ were inferior to those of the equivalent fibers produced with Fe*p*TS. So, better electrical properties can be achieved with $FeCl_3$ but better mechanical properties can be achieved with Fe*p*TS.

Table 9: *Electro-mechanical properties of PEDOT-coated conductive fibers produced with* $FeCl_3$ *and FepTS oxidants. From Paper II*

Sample type	**Resistance** (kΩ)	**Force at break** (N)	**Tenacity** (N/Tex)
Pure viscose	………..	61.3 (± 5.3)	0.32 (± 0.03)
$FeCl_3$	6.8 (± 0.7)	29.7 (± 5.0)	0.14 (± 0.05)
Fe*p*TS	54.5 (± 20)	40.8 (± 8.8)	0.16 (± 0.02)

The coating thickness of conjugated polymers on textile-based conductive fibers should be in the micro- or nano-scale range so that the original properties of textile substrates should not be disturbed. It has always been difficult to study the distribution of coating along textile yarns because a number of monofilaments are involved in a specific type of yarn. In this regard, highly sophisticated techniques—ATR-FTIR spectroscopic imaging and computed tomography (CT) analysis—were employed to investigate the distribution of PEDOT, and to some extent the extent of impregnation of PEDOT polymer, along the viscose fibers.

Figure 27 and Figure 28 are IR images of cross sections of viscose yarns before and after PEDOT coating, and IR spectra at different pixels. The distinctive absorption peaks related to cellulosic materials at 1,640, 1,365, 1,149, 1,014, and 895 cm^{-1} can be seen on the IR spectrum obtained at different points in Figure 27.

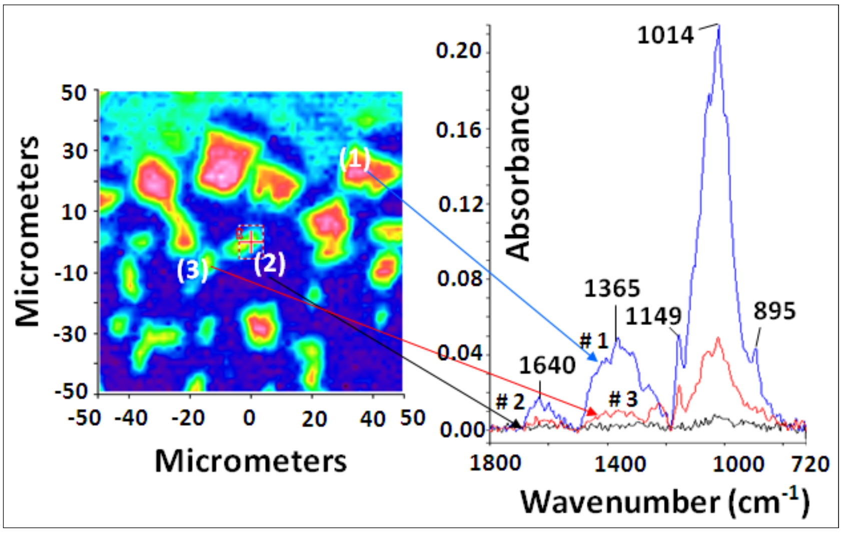


Figure 27: *ATR-FT-IR spectroscopic imaging analysis along neat viscose yarn fibers. From Paper II*

On the other hand, typical absorption peaks of PEDOT could be observed in some parts of viscose monofilament (Figure 28). Although, we could not investigate the coating thickness but the impregnation of PEDOT polymer along the viscose yarns had been justified.

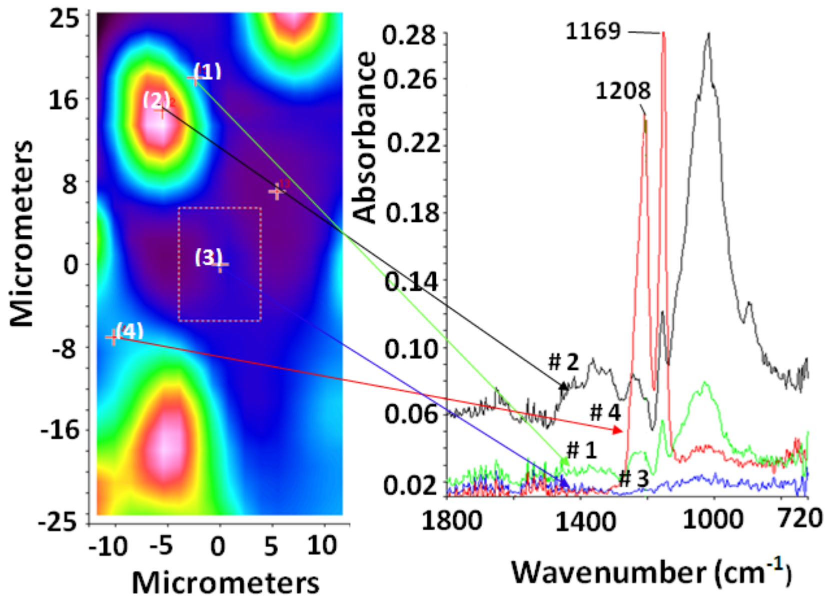


Figure 28: *ATR-FT-IR spectroscopic images and IR spectra of PEDOT-coated viscose fibers. From Paper II*

Computed tomography (CT) images of cross sections of PEDOT-coated viscose fibers, as shown in Figure 29, revealed that only some dense particles of PEDOT polymer could be seen on the outermost surface of conductive fibers. Due to several technical limitations, it was difficult to investigate the coating thickness using these sophisticated techniques.

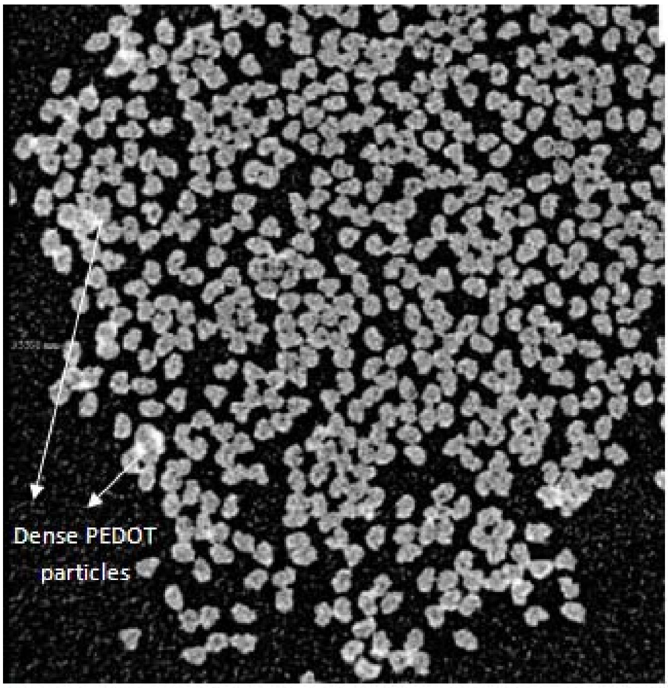


Figure 29: *Computed tomography scan of PEDOT-coated viscose fibers (cross sectional view). From Paper II*

4.1.3. Production of PEDOT-coated polyester yarns (Paper III)

In Paper I, we found that the viscose yarns were successfully coated with PEDOT polymer and that the electro-mechanical properties were strongly influenced by the reaction conditions. Under optimum reaction conditions, a relatively good electrical conductivity value of ≈15 S/cm was achieved, but at the same time the mechanical properties were considerably reduced because of acid hydrolysis of the viscose fibers by $FeCl_3$, which could limit the use of the conductive fibers produced.

In Paper III, another textile substrate—polyester yarn, with different chemical structure, good stability to chemicals, and better mechanical properties—was selected. For polymerization of PEDOT on the surface of polyester yarns, the same reaction conditions were used under which maximum electrical conductivity values were achieved in the previous paper. The electrical, mechanical, and morphological characteristics of PEDOT-coated polyester fibers were investigated and they were compared with those of the conductive fibers that had been previously produced.

In our previous studies, the electrical properties of conductive fibers were expressed in the form of surface resistance values, but it has been reported that mass-specific resistance (Ω g/cm^2) values give more appropriate results for textile fibers or yarns. The mass-specific resistance values of PEDOT/viscose and PEDOT/PET fibers were calculated at different voltage values (1–10 V) and a comparison between these values was made, which is presented in Table 10. The PEDOT-coated polyester fibers had lower mass-specific resistance values than the PEDOT-coated viscose fibers; thus, they were more conductive under the same reaction conditions.

Table 10: *Comparison of the surface resistance values (kΩ) and mass-specific resistance values (Ωg/cm^2) values of PEDOT-coated viscose and PET yarns. From Paper III*

	Viscose			**Polyester**		
	Resistance (kΩ)			Resistance (kΩ)		
Voltage (V)	Average	SD	**Specific resistance** (Ωg/cm^2)	Average	SD	**Specific resistance** (Ωg/cm^2)
1	2.501	± 0.18	224.98	1.301	± 0.85	41.82
2	2.336	± 0.22	210.14	1.263	± 0.82	40.59
3	2.259	± 0.23	203.21	1.230	± 0.79	39.54
4	2.218	± 0.23	199.50	1.187	± 0.75	38.16
5	2.192	± 0.22	197.18	1.162	± 0.72	37.36
6	2.160	± 0.23	194.28	1.142	± 0.71	36.69
7	2.131	± 0.23	191.68	1.128	± 0.70	36.27
8	2.105	± 0.23	189.37	1.117	± 0.70	35.91
9	2.082	± 0.23	187.24	1.105	± 0.69	35.50
10	2.060	± 0.23	185.27	1.088	± 0.67	34.98

The mechanical properties of PEDOT-coated polyester fibers compared to those of previously produced conductive fibers are illustrated in Figures 30 and 31. Virgin PET fibers had higher tensile strength than virgin viscose fibers but after CVD polymerization, the tensile strength of polyester fibers was not as reduced as that of viscose fibers, as shown in Figure 30.

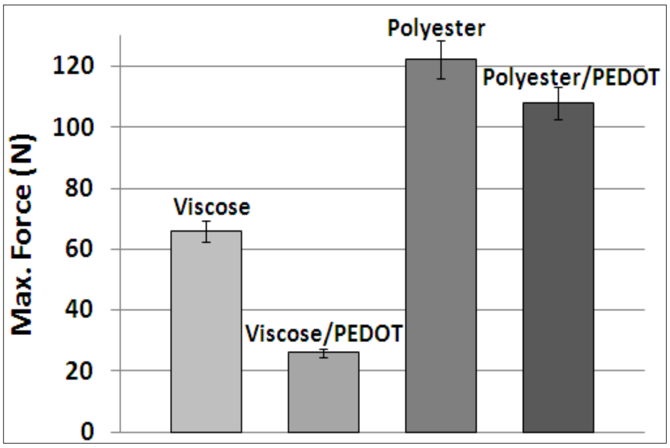


Figure 30: *Strength at break of viscose and polyester fibers before and after deposition of PEDOT coating. From Paper III*

On the other hand, the elongation of neat viscose fibers was higher than for polyester fibers, but after PEDOT coating, the elongation of viscose fibers was considerably reduced. For the PEDOT-coated polyester fibers, it remained almost same as it was before PEDOT coating.

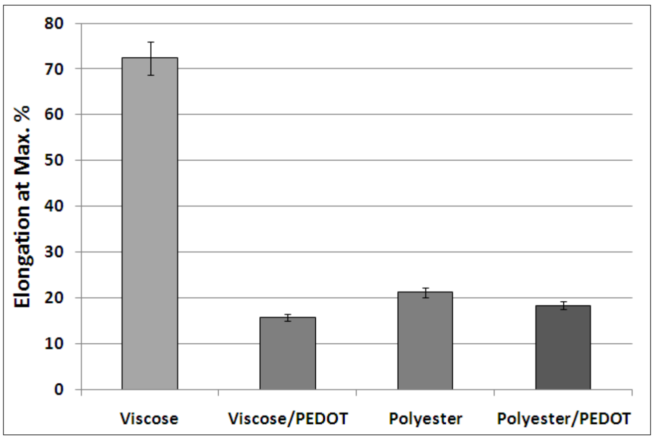


Figure 31*: Maximum percent elongation of fibers before and after polymerization of PEDOT. From Paper III*

The surface morphology of the conductive fibers produced was studied by SEM, as shown in Figure 32. After polymerization, a relatively smooth, thick, and uniform layer of PEDOT was deposited on the surface of PET fibers, as shown in Figure 32B, which was more even than the surface morphology of PEDOT-coated viscose fibers (see Figure 32C). This may have been due to a lower degree of oxidant ($FeCl_3$) impregnation of the PET fibers than of viscose fibers. An excess amount of oxidant might increase the rate of polymerization of PEDOT, and shorter polymer chains of PEDOT were produced on the surfaces of viscose fibers than on the surfaces of PET fibers, containing lower amounts of oxidant. This might be the reason for the surface roughness and the inferior electrical properties of PEDOT-coated viscose fibers.

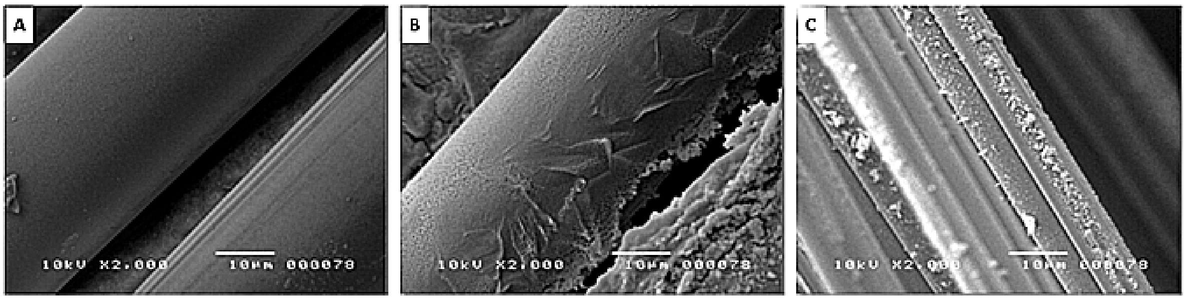


Figure 32: *SEM micrographs of: (A) neat PET fiber, (B) PEDOT-coated PET fiber, and (C) PEDOT-coated viscose fiber. From Paper III*

4.2. Surface modification of PEDOT-coated conductive fibers (Paper IV)

Viscose fibers were successfully coated with PEDOT polymer and a strong interaction between viscose and PEDOT polymer chains was to be expected, but excess amounts of PEDOT layer could easily be removed from the outer surface of coated fibers by rough handling. This could significantly reduce the electrical conductivity values. In order to preserve the electrical properties and to enhance the service life of the coated fibers produced, it is necessary to modify them with some suitable insulating materials.

In Paper IV, the PEDOT-coated viscose fibers were treated with a solution of silicone elastomer in methyl ethyl ketone (MEK) to form a protective layer on the outer surface of the conductive fibers. A schematic diagram of silicone-treated PEDOT-coated viscose fibers is presented in Figure 33. The silicone-treated conductive fibers were then characterized to investigate the impact of the protective layer on the electrical, mechanical, thermal, and hydrophobic properties. It was concluded that silicone coating can preserve the surface morphology of coated fibers, combine the monofilaments of yarns, improve the handling, and enhance the hydrophobic properties of PEDOT-coated viscose fibers.

In order to determine the amount of silicone elastomer deposited on the surface of conductive fibers, TGA analysis was performed on pure silicone, neat viscose, PEDOT/viscose, and PEDOT/viscose/silicone composite fibers, as shown in Figure 34.

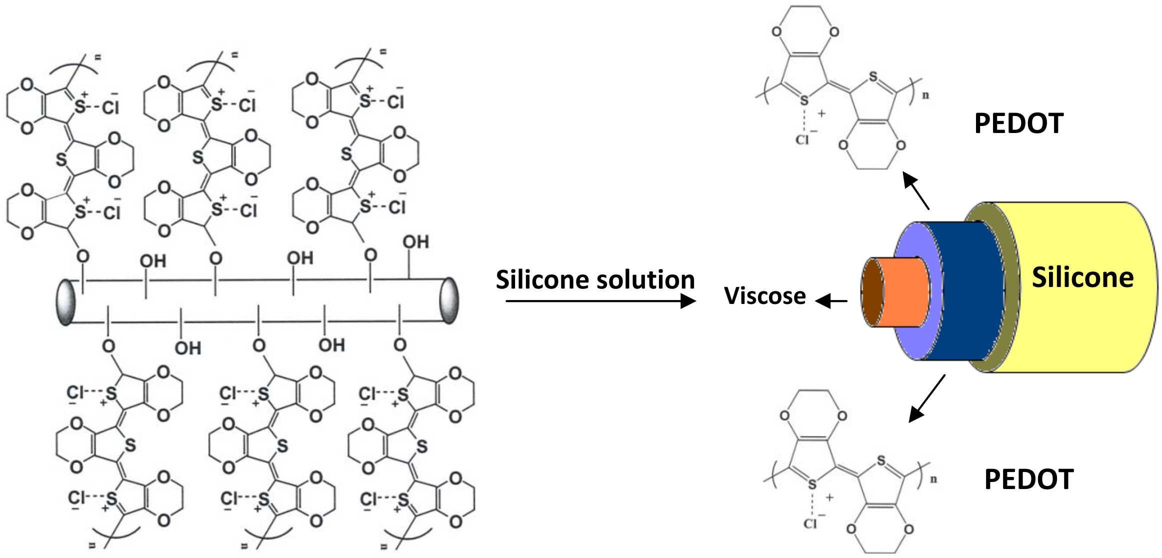


Figure 33: *Schematic diagram of conductive viscose yarn after silicone modification. From Paper IV*

It was found that the TGA trend of silicone-treated yarn was almost the same as that of PEDOT-coated viscose, and it was therefore concluded that a very thin layer of silicone was deposited on the surface of coated yarns and had no effect on the structural properties of PEDOT-coated viscose fibers.

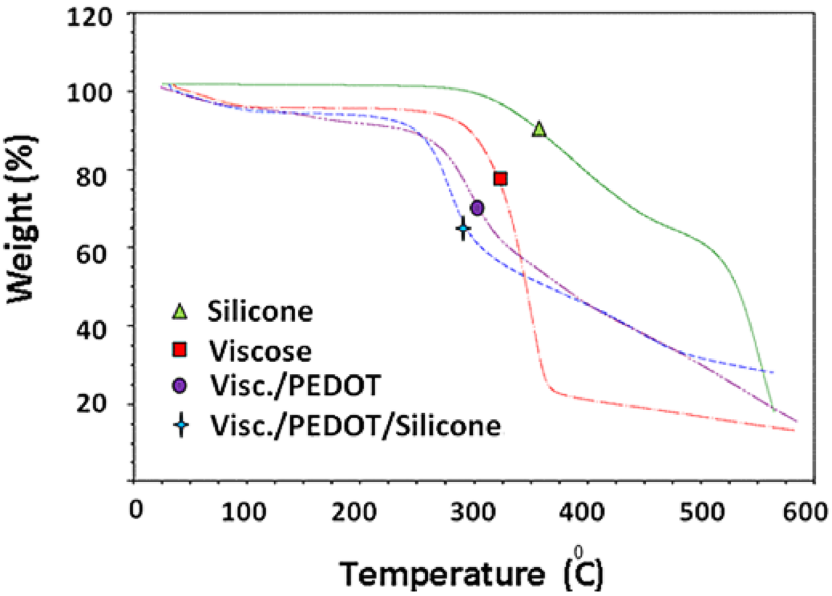


Figure 34: *TGA analysis of pure silicone resin, pure viscose, PEDOT-coated viscose, and silicone-treated conductive viscose. From Paper IV*

The electrical resistance values of PEDOT-coated viscose fibers were measured before and after silicone treatment. After coating with silicone, the electrical resistance of PEDOT-coated fibers had increased, as shown in Figure 35, but the fibers were still sufficiently conductive to transmit electrical signals. This might have been due to the thin layer of silicone coating on the surface of the fibers produced.

Viscose is hydrophilic in nature and can absorb moisture even from atmosphere. Thus, washing could destroy the parent properties of pure viscose fibers. In order to investigate the impact of silicone treatment on the hydrophobic properties of the conductive fibers produced, the silicone-treated fibers were dipped in water for 10 min and then the electrical properties were measured. Figure 35 shows a comparison of the electrical resistance values of viscose/PEDOT/silicone composite fibers before and after washing. A very negligible difference in electrical properties of silicone-treated conductive fibers was observed after tumbling with water, which shows the durability and ease of handling of these kinds of conductive fibers.

The mechanical properties of PEDOT-coated conductive fibers after silicone treatment were investigated, as shown in Figure 36. The tensile strength of the silicone-treated fibers remained almost the same, whereas the % elongation was slightly increased after surface modification. This may have been due to the elastic properties of silicone elastomer, absorbing part of the stress applied and then transferring that stress to PEDOT-coated viscose yarn, thus increasing the flexibility of the silicone-treated yarn.

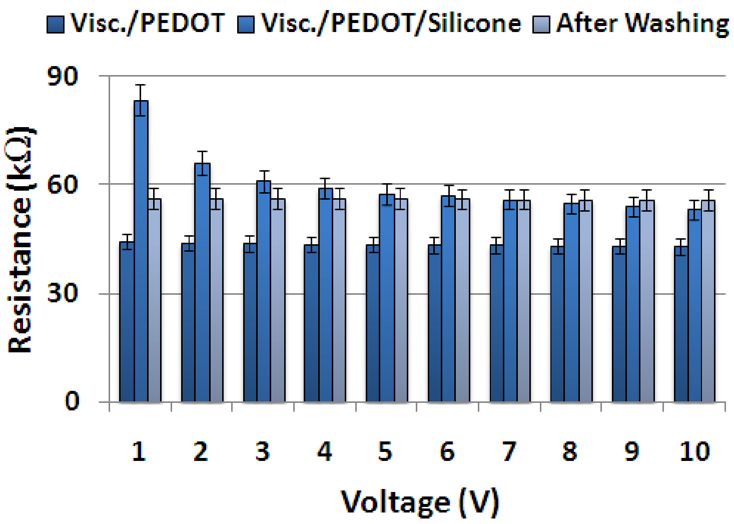


Figure 35: *Surface resistance values of PEDOT-coated viscose fibers and silicone-treated conductive viscose fibers before and after dipping in water. From Paper IV*

Although the electrical properties of the silicone-treated conductive fibers were reduced, the service life of PEDOT-coated fibers was improved. By increasing the coating thickness of silicone elastomer, textile-based electrical cables for smart textile applications can also be produced.

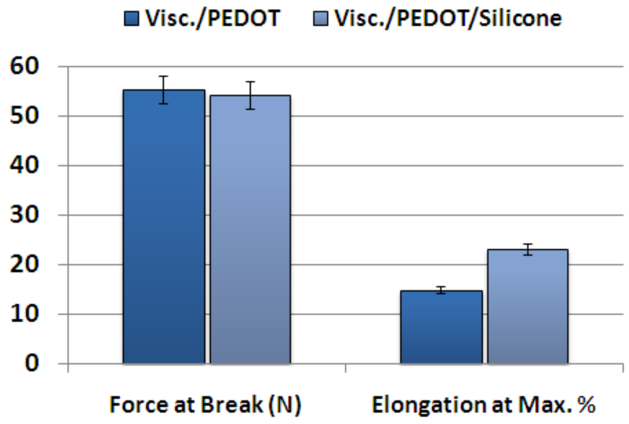


Figure 36: *Effect of surface modification on the mechanical properties of PEDOT-coated viscose fibers. From Paper IV*

4.3. Setup for electrical resistance measurements on conductive fibers (Paper V)

In Paper V, the main interest was measurement of the electrical resistance of fibrous structures. For the measurement of electrical resistance of conductive fibers, crocodile clips are usually used to hold the samples, but these could destroy the surface morphology of samples—especially coated samples; thus, accurate electrical resistance values might not be obtained. For this purpose, a fiber-holding setup was constructed, as shown in Figure 37. This could be used not only for conductive threads but also for fabric structures of specific dimensions. It could also be used to monitor the electrical properties of conductive fibers during continuous production.

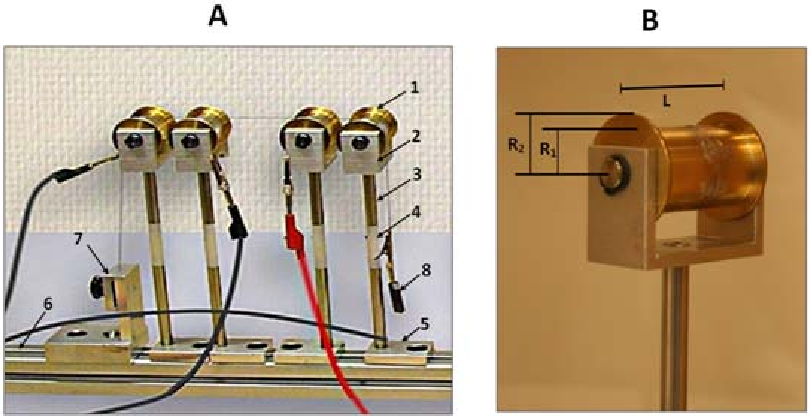


Figure 37: *Sample-holding unit: (A) Different parts of the setup, and (B) the dimensions of a single brass wheel. From Paper V*

The sample holder had four identical units to support the test object (Figure 37A), which could be a single thread or a piece of fabric. The wheels were made of brass, with dimensions R_1 = 30 mm, R_2 = 40 mm, and L = 50 mm (Figure 37B). The test object need only have surface contact with the sample holder, which preserves the surface morphology of samples. Figure 37A shows how the conductive thread can be held by the setup.

For measurement of electrical resistance, the sample-holding unit was connected to a Keithley picoammeter 6000 and a computer, as shown in Figure 38. The whole setup was controlled by the LabVIEW program. By using this setup, we could determine electrical resistance of the samples either by the two-point method or by the four-point method.

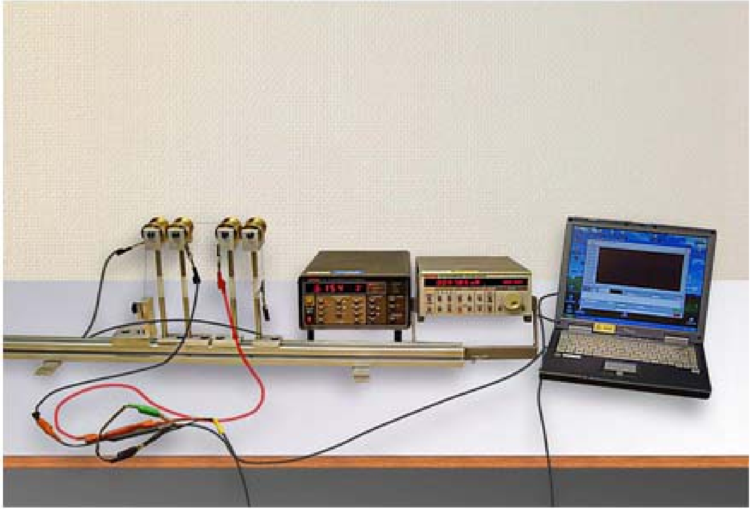


Figure 38: *Electrical resistance-measuring setup used for electrical characterization of PEDOT-coated viscose fibers. From Paper V*

Models for the two-point and four-point resistance measurements used are shown in the left panel and the right panel, respectively, of Figure 39. However, only two-point resistance measurement was used to investigate the electrical properties of conductive threads, and the results were compared with the results of the traditionally used method. Electrical resistance measurements and electrical characterization of previously produced PEDOT-coated viscose fibers were performed on the newly designed setup.

For standardization of the new setup, a conductive yarn of carbon fibers with known resistance (885 Ω/m) was used and we measured the surface resistance values from crocodile clips and from the new setup. For both methods, the same length of yarn was used. It was found that the surface resistance values measured with the new setup were approximately 1.5 (± 0.3) times higher than the resistance values measured with crocodile clips. Although the resistance values obtained with the new setup were slightly higher than with the crocodile-clip method, the results could be reproduced without affecting the outer surface of the conductive fibers—something that was difficult to achieve with crocodile clips.

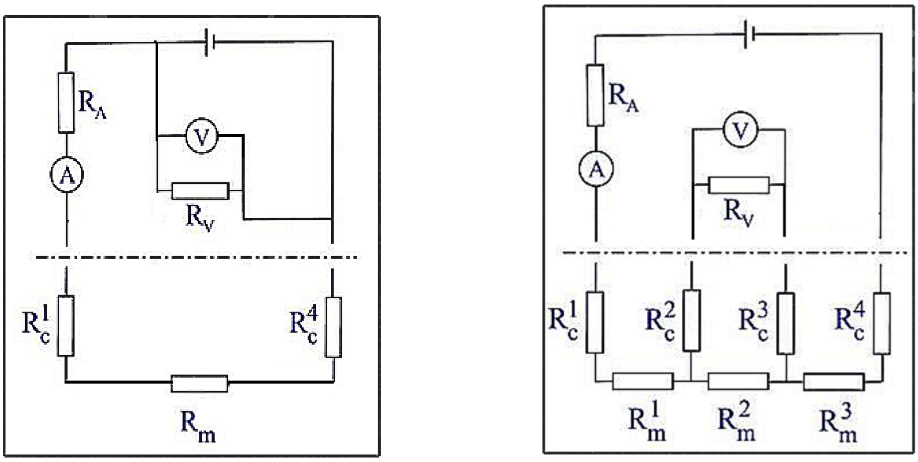


Figure 39: *Two-point (left) and four-point (right) resistance measurement models used with the newly designed setup. From Paper V*

Electrical characterization of previously produced PEDOT-coated conductive fibers under different reaction conditions was then performed on the manufactured sample-holding unit. Most of the characterization results are summarized in Figure 40.

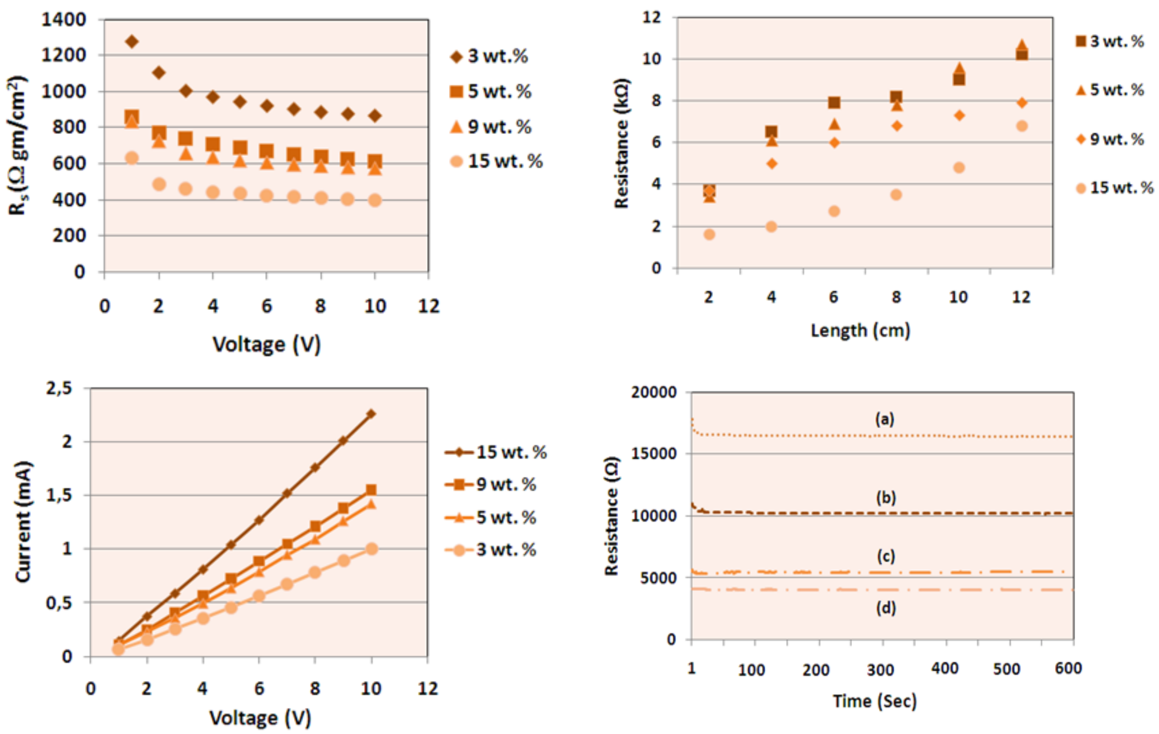


Figure 40: *Results of electrical characterization of PEDOT-coated viscose fibers, obtained with the newly designed setup. From Paper V*

4.4. Stretch-sensing properties of PEDOT-coated conductive fibers (Paper VI)

The possible applications of PEDOT-coated conductive fibers as stretch sensors were studied in Paper VI. For this purpose, PEDOT-coated viscose and polyester fibers were produced in longer length, i.e. 15 m, by using the optimum reaction conditions achieved in Paper II. These reaction conditions are listed in Table 8.

The rectangular rib-knit structures/patches were prepared by incorporating the conductive fibers with parent viscose and PES fibers, as shown in Figure 41. These patches were then mounted on the cyclic tester, as explained in section 3.3.7, and piezoresistive responses to the degree of extension—from 5% to 50%—were investigated.

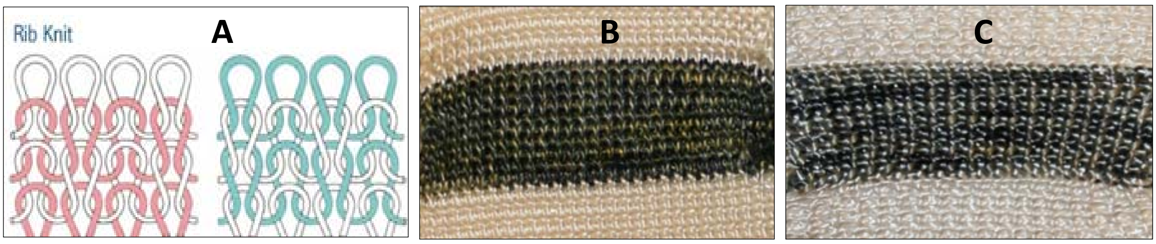


Figure 41: *Rib-knit structures: (A) schematic diagram, (B) viscose/PEDOT, and (C) PES/PEDOT. From Paper VI*

It was apparent that electrical resistance values of knitted structures at the relaxed position were higher than the values at the stretched position. This variation in electrical resistance values could be used to monitor vital signs such as joint movements, breathing rate etc. The change in electrical resistance values of knitted viscose- and PES structures with different stretching and relaxing cycles are shown in Figure 42 and Figure 43, respectively.

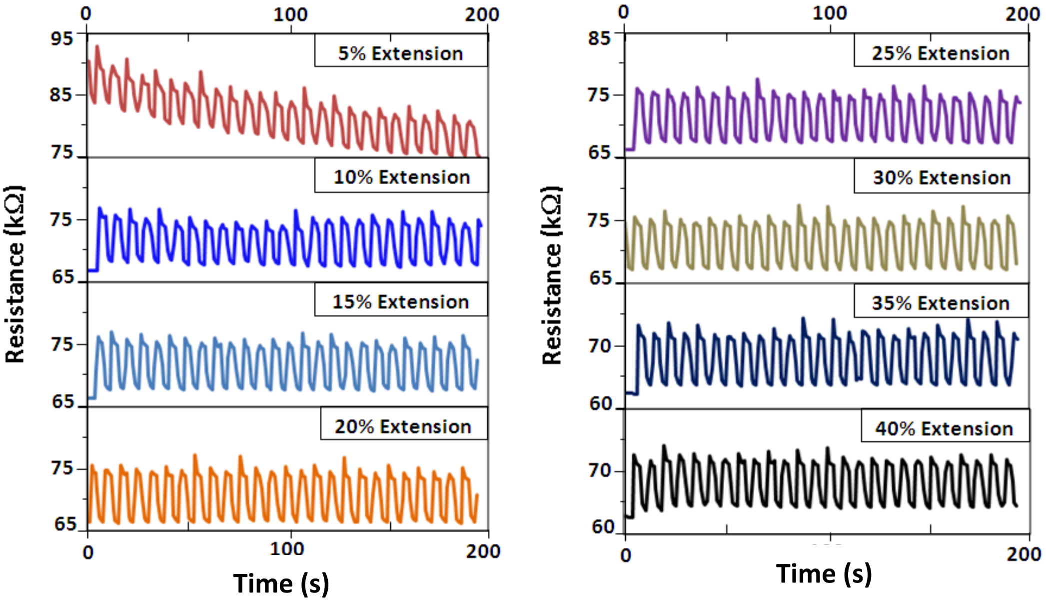


***Figure 42**: Piezoresistive response of knitted viscose structures at different degrees of extension (5–40%) and before washing. From Paper VI*

It can be seen that the knitted structures showed approximately steady behavior and excellent stretch recovery for almost all degrees of extension, even after cycles of extension/relaxation for a reasonable period of time.

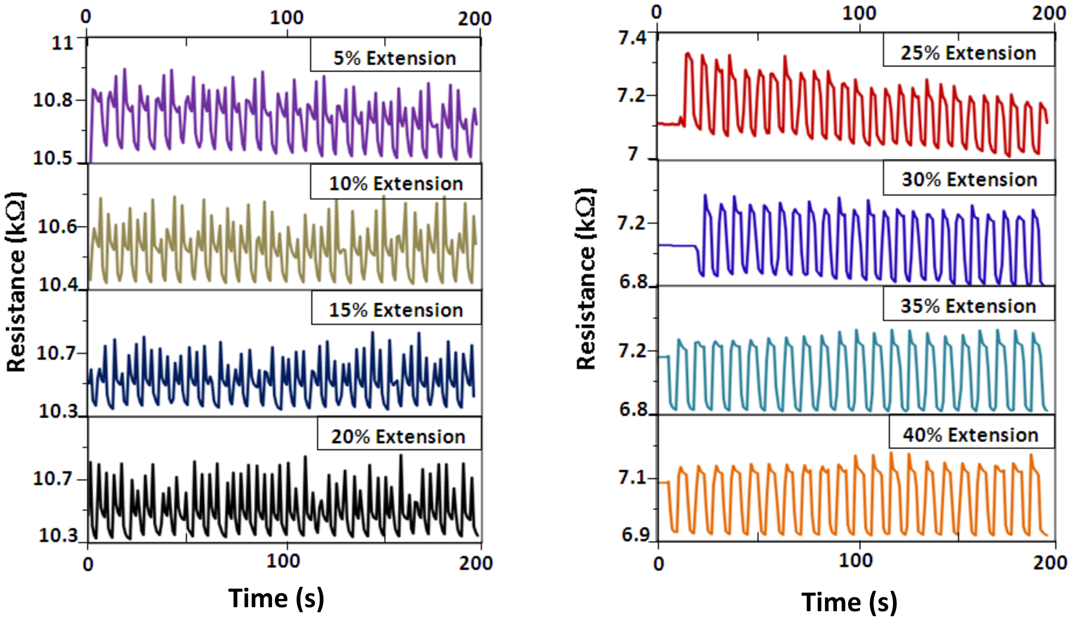


***Figure 43:** Piezoresistive response of knitted polyester structures at different degrees of extension (5–50%) and before washing. From Paper VI*

The significant variation in electrical properties and exceptional stretch recovery are the necessary characteristics of a stretch sensor, and knitted structures with PEDOT-coated viscose and polyester had these characteristics, which is rather unusual with most of the other stretch sensors that have been prepared from other conductive threads.

Washing effects

The piezoresistive responses of knitted PEDOT-coated viscose and polyester structures after two washing cycles are illustrated in Figure 44 and Figure 45, respectively. The increase in electrical resistance values, at particular extension percentages for both of the knitted viscose and PES structures, revealed that the PEDOT coating was significantly removed from the surface of the coated yarns. In the case of knitted viscose structures, this increment was much higher than for the knitted PES structures, which may have been because of the hydrophilic nature of the viscose. However, despite a reduction in the PEDOT coating to some extent, the knitted structures showed exceptional piezoresistive characteristics. It is worth nothing that these structures still had acceptable conductivity values to transmit electrical signals to the output interfaces, and also reasonable stretch recovery, even after two washing cycles.

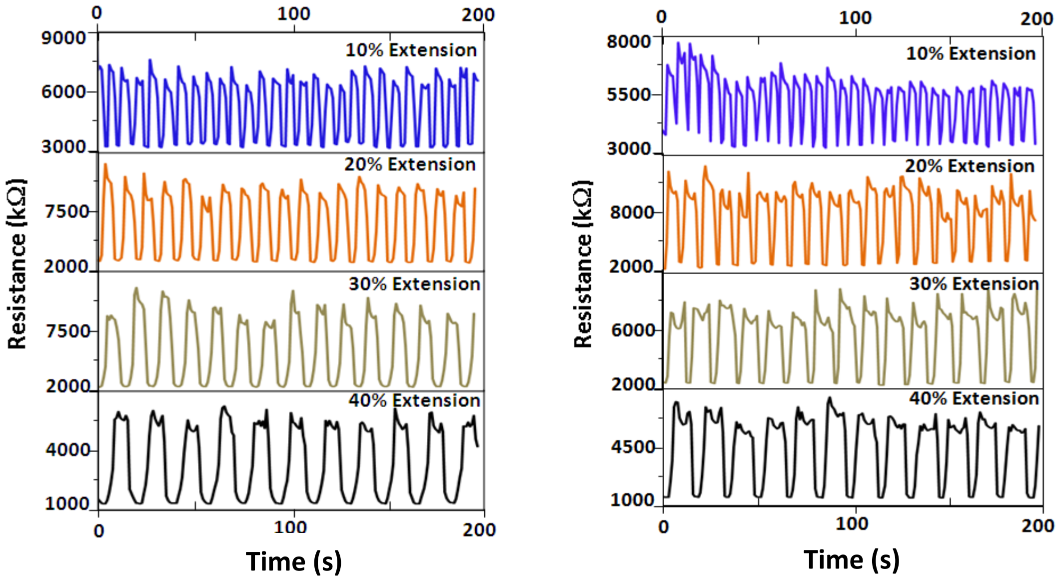


Figure 44: *Influence of first (left) and second (right) washing cycles on stretch sensing properties of PEDOT-coated viscose knitted structures. From Paper VI*

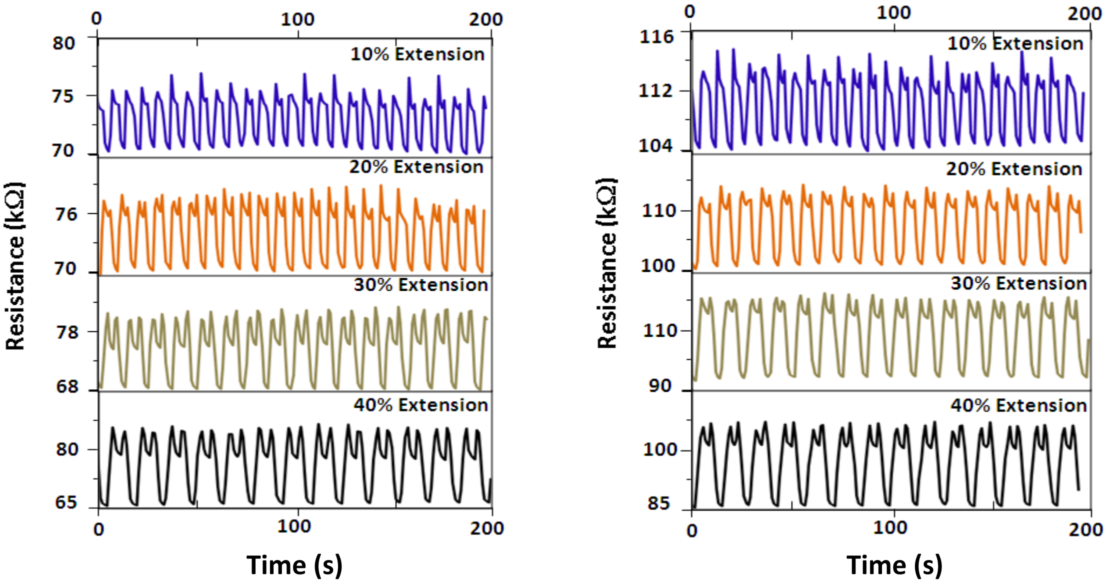


Figure 45: *Influence of first (left) and second (right) washing cycles on the stretch-sensing properties of knitted PEDOT-coated polyester structures. From Paper VI*

The variation in electrical resistance for the knitted viscose and PES structures, depending on the degree of extension (from 5% to 50%) and before and after cycles of washing, is shown in Figure 46 and Figure 47, respectively.

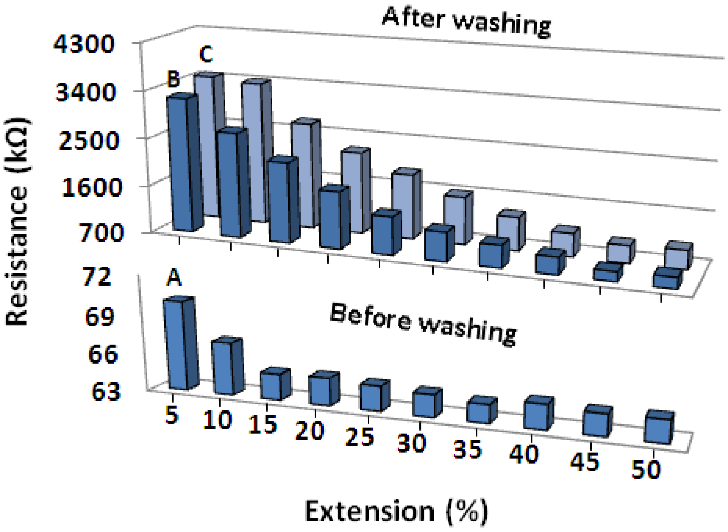


Figure 46: *Resistance of knitted PEDOT-coated viscose structure at 5–50% extension: (A) before wash, (B) after the first wash, and (C) after the second wash. From Paper VI*

The decreasing trend in electrical resistance values, before and after washing, with an increasing degree of extension shows that these knitted structures might be used to monitor vital signs in medical and sports applications, where different degrees of extension are required, such as during joint movement and breathing.

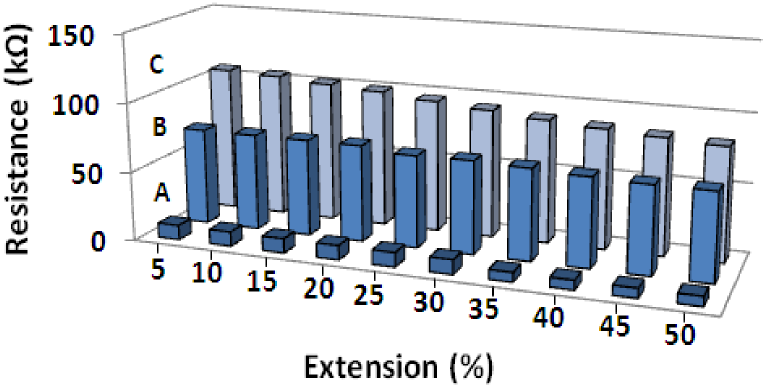


Figure 47: *Resistance of knitted PEDOT-coated polyester structure at 5–50% extension: (A) before washing, (B) after the first wash, and (C) after the second wash. From Paper VI*

5. CONCLUSIONS

In this thesis work, attempts were made to produce relatively highly conductive fibers with good mechanical and thermal properties. The commercially available high-performance yarns, viscose and polyester, were successfully transformed into electro-active fibers by coating them with conjugated polymer, PEDOT. An efficient coating technique called chemical vapor deposition (CVD) was used to polymerize the PEDOT polymer directly on the surface of textile yarns. The impact of different reaction conditions such as type of oxidant, concentration of oxidant, time of pretreatment of textile yarns with oxidant solution, drying time and temperature of oxidant-impregnated yarns, reaction time and temperature, and pretreatment of textile yarns with different solvents, on the electrical and mechanical properties of the PEDOT-coated fibers obtained was investigated separately.

For viscose/PEDOT composite fibers, the results showed that with increasing oxidant ($FeCl_3$) concentration, from 3 wt.% to 15 wt.%, the thickness of the PEDOT coating was substantially increased, and thus the electrical properties were also significantly improved. However, the mechanical properties were considerably reduced, which was apparently due to the acid hydrolysis of viscose fibers in acidic solutions of $FeCl_3$. The electrical characterization of viscose/PEDOT composite fibers produced with variable soaking time in $FeCl_3$ solution, drying time, polymerization time, and temperature revealed that electro-active fibers with a broad range of conductivity values can be obtained by controlling reaction conditions. Moreover, the thermal stability of viscose yarns was also improved after using PEDOT coating as a protective layer.

Since the CVD method is a batch process consisting of various steps, to produce conductive coatings on textile yarns the overall reaction time required for one batch was optimized by controlling other pre-polymerization parameters. The pretreatment steps involving surface modification of viscose yarns with organic solvents (acetone and ethyl acetate), oxidant type ($FeCl_3$ and Fe*p*TS), and the drying temperature of oxidant-enriched yarns played a critical role in determining overall reaction time. Of the two types of oxidants, better electrical properties were achieved with $FeCl_3$, whereas acceptable mechanical properties were obtained with Fe*p*TS. The solvent treatment of viscose yarns produced inverse effects on electrical and mechanical properties. This might be due to the removal of wax-like protective coatings from the surface of viscose yarns, which would increase the absorbability of oxidant; thus, the acid hydrolysis was also accelerated. However, the overall reaction time for one batch of the CVD process was significantly minimized by reducing the drying time of oxidant-impregnated viscose yarns at relatively high temperatures. Also, the rate of production of conductive fibers and the electrical and mechanical properties were also improved by adjusting the pretreatment steps.

For polyester/PEDOT composite yarns, it was found that by selecting an appropriate substrate material, the electro-mechanical properties can be improved. The results showed that the mass-specific resistance values of viscose/PEDOT fibers were higher than the mass-specific resistance values of polyester/PEDOT fibers, so the former showed lower electrical conductivity. TGA analysis of polyester/PEDOT composite fibers indicated that there was no significant change in the parent properties of polyester fibers.

In order to preserve the PEDOT layers on the surface of textile fibers, a thermoplastic silicone elastomer was used to protect the PEDOT-coated conductive fibers obtained. A very thin layer of silicone elastomer was deposited on the surface of viscose/PEDOT composite fibers by a dip-coating process. The results showed that the mechanical and hydrophobic properties of the viscose/PEDOT fibers were improved after application of the protective layer of silicone. On the other hand, the electrical properties of the conductive fibers were reduced significantly, as was expected, but the thin layer of silicone did not eliminate the electrical conductivity completely.

A novel setup for the measurement of electrical resistance values across the fibrous structures was designed, constructed, and tested. The PEDOT-coated conductive fibers obtained were characterized by using this new setup and also the conventional crocodile-clip method, and then a comparative study was done. It was found that the new setup can be used effectively for coated samples in order to get consistent results, which is almost impossible with crocodile-clip method.

In order to explore the possibility of using the PEDOT-coated conductive fibers for smart textile applications, small knitted structures were prepared on hand knitting machines and then the piezoresistive response was determined at different degrees of extension. The consistent electrical resistance values obtained during stretching and relaxing cycles for relatively long periods of time showed that these knitted structures could be used as stretch sensors to monitor joint movements and breathing rate in medical and sports applications. Furthermore, cycles of washing were performed on these knitted structures and it was found that the piezoresistive character remained almost the same even after removal of some of the PEDOT coating.

In summary, a different method was used to produce conductive fibers with better electrical and mechanical properties. All the results obtained and the assessments made in this thesis work can be used for commercialization of the CVD process for continuous production of ICP-coated conductive yarns.

6. FUTURE WORK

Production of conductive fibers with even better electrical and mechanical properties might be possible by changing the substrate materials, conjugated polymer, and by controlling other parameters such as humidity, the pH of the oxidant solution, and the pressure of EDOT monomer vapors inside the reactor. This can also be achieved by using different oxidant solutions in a variety of solvents. Different textile structures, either weaved or knitted, can also be made from coated yarns and then tried as sensors in the sports and medical fields. The large-scale production of PEDOT-coated conductive fibers might also be possible by designing a special setup on a laboratory scale or even on an industrial scale.

Furthermore, PEDOT-coated conductive yarns can also be used as an active substrate for the deposition of multiple layers of different materials, which could lead to the production of fibrous solar cell panels, pressure sensors, and actuators.

The possibility of using textile-based conductive fibers in the field of thermal electricity can also be investigated, which would open the new doors for the continuous production of sustainable energy.

The CVD process can also be used to coat different woven or non-woven fabric structures with conjugated polymers for the production of conductive membranes. These conductive membranes could be used as anti-static air filters and substrates for organic fuel cells and organic batteries.

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