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PEDOT Coated Viscose Fibers by Optimized OCVD Process: Washing and Stretch Sensing Properties

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This thesis comprises 22.5 ECTS credits and was a compulsory part in the fulfillment of the Master in Textile Technology 60 ECTS (Report # 2011.7.6)

PEDOT Coated Viscose Fibers by Optimized OCVD Process: Washing and Stretch Sensing Properties

Master Thesis

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Preface

It can be observed from modern age that revolution in technology comes every twenty years. Smart textile are in the same phase where computer was fifteen years ago. One can predict by viewing ongoing research on smart textile that it will not take too long when ordinary textiles not only serve the basic necessity but to offer integration, functionality and portability. This thesis is a small effort towards the desire of such functional textiles.

Majid Ali

Acknowledgments

I wish to convey my deepest gratitude and cordial thanks to my supervisor Tariq Bashir for his valuable suggestions, beneficial advices and moral support throughout this work. He was always available when I need him.

I feel extremely indebted to my examiner Nils-Krister Persson, he was more than examiner in this work and he was always available when I tried to reach him.

I would like to express my special thanks to Mikael Skrifvars for giving me a chance to do my master thesis on this top.

Last but not least, my special thanks to Heike Hilke (incharge polymer lab), Maria Persson for the preparation of knitted structures, Johnas Hanson (incharge chemistry lab) and to all who helped in the completion of this work.

Abstract

Electroactive textile fibers are key components in smart and interactive textile applications. In previous research on textile base conductive fibers, viscose fibers were coated with poly (3,4-ethylenedioxythiophene) (PEDOT) using oxidative chemical vapor deposition (oCVD) technique[1]. Ferric chloride was used as oxidant and reaction conditions were optimized at which better electrical as well as mechanical properties of conductive viscose fibers could be achieved. In this thesis work, effect of new parameters such as pretreatment of viscose fibers with solvents, drying of oxidant treated viscose fibers at different time and temperature and comparison of two different oxidants have been tried. One new and important oxidant, ferric (III) *p*-toluene sulfonate or ferric (III) tosylate, used to prepare PEDOT coated viscose fibers and then compared with PEDOT coated viscose fibers prepared using oxidant ferric (III) chloride. Viscose fibers have been treated with two well know solvents, acetone and ethyl acetate before soaking in oxidant solution. Oxidant enriched fibers dried at different temperature for variable time prior to polymerization step. Knitted structures of conductive viscose fibers have been prepared. Hand washing of PEDOT coated viscose fibers with tap water and machine washing of knitted structures according to the international standard ISO EN-6330 have been performed and washing effects were investigated. Effects of all of the above mentioned variables on electromechanical properties of PEDOT coated viscose fibers were studied by using tensile testing, TGA analysis, FTIR spectra and conductivity measurements. Stretch sensing properties of knitted structures; before and after washing, were determined on cyclic tester. The purpose of this study is to enhance the properties of PEDOT-coated viscose fibers by controlling different parameters and to evaluate their usage as stretch sensors as well as to check the washability of PEDOT coated viscose fibers and knitted structures. Better electromechanical properties were achieved on new parameters and PEDOT coated viscose fibers were successfully utilized as stretch sensors.

PEDOT coated viscose fibers could have potential to apply in areas such as, military textiles, medical textiles and sensors.

Keywords: Viscose yarn, conductive polymers, PEDOT, ferric (III) chloride, ferric tosylate (*p*-toluene sulfonate), stretch sensors

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1 Introduction

Electroactive textiles also refer to smart textile or e-textile getting more and more interest of the researchers in this era due to their low cost, durability, flexibility, adaptability and portability. Due to the conductive fibers, it became easier to develop smart garments which can be used in military and health care applications[2]. Smart textile as wearable textile system also comprises components, like sensors to detect body and environmental parameters, actuators that can give signal to the wearer and interconnection of different components. Electrically conductive yarns and fabrics have high importance in the manufacturing of filters, electrostatic discharge, plastic welds, electromagnetic interface shielding, and data transfer in clothing etc[3]. Conductive polymers not only in the form of conductive fibers but also their coating on the textile substrates, are playing an important role in the development of these smart textiles due to their broad range of applications such as, power and signal transmitter, sensors, light emitting devices (LEDs), actuators and controlling units[1]. One of the astonishing applications of conductive textiles could be in the field of stretch sensors which could be used to determine and monitor the joint and muscle moment[2, 4, 5]. Textile base stretch sensor could be conductive fiber or in the shape of weaving and knitting structure.

Textile fibers can be made conductive by incorporating metal filament into yarns or producing metallic yarns. Conductive fibers can be produced directly from conductive polymers by melt or wet spinning processes but cost and solvent recovery issues limit their production via these techniques. Another way to make textile fibres conductive is to coat them with carbon black, metal powders and conductive polymers such as polypyrrol, polyaniline, poly (3, 4-ethylenedioxythiophene) PEDOT, polycarbazoles and polymethylene blue[1]. PEDOT is a very promising conductive polymer due its versatility and stability and can give high conductivity up to 1000S/cm depending upon the manufacturing and application areas. There have been a number of conductive polymers that reported to be used for coating of conventional non-conductive textile fiber with ICPs. Yang et al.[6], Xue et al.[7], Zou et al.[8], Tonin et al.[9], Bashir et al.[1, 10] produced PPy and PEDOT-coated PET, PA6, Lycra, viscose and polyester conductive fibers by chemical vapor deposition (CVD) technique. Out of other coating techniques, oCVD has been reported as highly ranked process in many publications due to the achievement of highly conductive polymer coating on any rigid and flexible substrates[1, 11, 12].

Knitting structure as stretch sensors could be produced from metallic fibers, but non-flexible rigid structure is the drawback of these structures. It is more interesting approach to prepare knitting structures from traditional textile fibers such as viscose coated with conductive polymers, which gives properties of both, the original fiber and electrical conductivity.

Research on preparing conductive textile substrates by coating them with PEDOT using OCVD process is already carried out in University of Boras. This work is the extension of ongoing research work to find out the factors that influence the electromechanical properties of PEDOT

coated viscose fibers and to prepare knitting structures of PEDOT coated viscose fibers as well as to check the washability of both, the fibers and the knitting structures. Previously, viscose fibers were coated with PEDOT by using ferric (III) chloride as oxidant. This time one new oxidant, ferric (III) tosylate has been tried and compared with previously produce PEDOT coated viscose fibers. Drying process of oxidant treated viscose fibers is very important with respect to electrical and mechanical properties. In previous research, Bashir et al[1] studied the behavior of drying time (at room temperature) of oxidant treated viscose fibers on electromechanical properties of PEDOT coated viscose fibers and found out that best electromechanical properties can be achieved by drying oxidant treated viscose fibers for 30min. As we know that atmospheric conditions such as relative humidity do not remain same at different places, therefore, to get similar results at every place, oxidant treated viscose fibers were dried at different time and temperature rather than drying at room temperature. Effect of drying time and temperature of oxidant treated viscose fibers were evaluated and results have been compared to PEDOT coated viscose fibers produced by drying at ambient temperature for 30 min. Two different organic solvents, acetone and ethylacetate were tried for surface cleaning of viscose fibers. Effect of these solvents has been determined by comparing the results with previously prepared PEDOT coated viscose fibers. PEDOT coated viscose fibers were hand washed to determine the washing effects on electrical and mechanical properties of the coated fibers. Rib knit structure of PEDOT coated viscose fibers was prepared and investigated the behavior of knitted structures as stretch sensors. Prepared knitted structures were washed with international standard EN-ISO 6330 and effects of washing on stretch sensing properties were determined.

1.1 Background

Advancement in technologies makes human life not only faster but much more comfortable ever before. Therefore it increased the desires and demand of making textile which are not only integrated with functionalities but also offer wear comfort to the end user. Research on conductive textile fibers which provide not only the conductivity but, also contain inherent properties of the original fibers is already getting more interest. There are several methods to make textiles electrically conductive such as incorporating conductive wires during weaving process or more precisely manufacture a textile with electrically conductive yarn. Less flexibility, brittleness and wearing comfort are the major drawbacks of incorporating conductive wires in fabrics. Therefore, the importance of inherently conductive yarns has been increased. Conductive fibres can be directly produced from conjugated polymers using wet and melt spinning but there are some limitation and drawbacks such as usage of high amount of expansive conjugated polymer in melt spinning, solvent recovery in wet spinning and low conductivity of fibers. Another method is the blending of conventional nonconductive textile fibres with conductive polymeric fibre. Although advantage of this method is that the conductive yarns have the same mechanical properties as yarn fabricated from pure non-conductive fibres but gives poor electrical conductivity. Oxidative chemical vapor deposition is a technique which is used to coat films and fibers with conjugated polymers like PEDOT. Coating of textile fibers with

conjugated polymers using oxidative chemical vapor deposition technique not only gives high conductivity but also the inherent properties of textiles fibers could be present after coating.

1.2 Purpose

The purpose of the thesis has been summarized as follow:

To reduce the time required in the preparation of PEDOT coated viscose fibers by oCVD process to make this process more attractive and efficient for the production point of view. To get the same electromechanical result from oCVD process at every place. Strength of PEDOT coated viscose fibers prepared with oxidant ferric (III) chloride is very low as compared to original viscose fibers. Therefore a new famous oxidant ferric (III) tosylate is tried.

Below are the main points which were considered and evaluated in this thesis work,

- How the electromechanical properties of conductive viscose fibers will be affected by surface treatment of fibres with organic solvents and to compare the results achieved before and after surface treatment.
- Determination of the effects of drying temperature and time on electromechanical properties of PEDOT viscose fibers.
- Determination of hand washing effect on viscose conductive fibres.
- Preparation of knitting structures of the conductive fibers and then evaluation of these structures as stretch sensors.
- To check the washing effects on fibers and knitted structures

1.3 Delimitations

The boundaries of the thesis work can be described by the following points.

- Different kind of organic solvents are available, out of them acetone and ethylacetate used for surface cleaning of the viscose fibers, which then be coated with PEDOT by oCVD process
- Oxidants, Ferric (III) chloride and ferric (III) tosylate, were used. Although there are more oxidants available but these two oxidants are more famous and widely used.
- Conductive viscose fibers hand washed using tap water two times with intense and normal stirring. .
- Washing on knitted structure prepared from PEDOT coated viscose fibers was performed according to ISO EN-6330.
- Only one type of knitted structures prepared.

2 Methodology

Chemical vapor deposition (CVD) process can produce highly conductive PEDOT layers on many materials like silicon wafers or glass[13]. Oxidative chemical vapor deposition (oCVD) method is an oxidant initiated process and can be used to polymerize PEDOT and provide good electrical properties. Therefore oCVD process is used to coat viscose fibers with PEDOT. To prepare reference samples, viscose fibers were dipped in oxidant ferric (III) chloride solution then dried at room temperature. Dried oxidant treated viscose fibers then placed in a tubular reactor where vapors of EDOT monomers supplied by heating EDOT monomer in a flask. EDOT monomers were readily polymerized and deposited on the viscose fibers. After polymerization, the PEDOT coated viscose fibers doped with oxidant ferric (III) chloride and washed with methanol to remove the byproducts and unreacted EDOT monomers[1]. Effects of changing parameters determined step by step. Experimental samples on different parameters of the process such as drying time and temperature, oxidant type, solvent treatment for surface cleaning were prepared separately. Maximum no of samples were prepared for characterization in order to enhance the reliability of the results.

Washing of the PEDOT coated viscose fibers were performed by hands, using the tap water by putting samples in a beaker and with consistence stirring.

Knitted structures of the PEDOT coated viscose fibers were prepared on a hand knitting machine (8 gauge needle bed with leach type needles by Moretto) and their stretch sensing properties were investigated on a cyclic tester. Washing on knitted samples was performed according to international standard EN-ISO-6330 on type A machine with non phosphate ECE reference detergent A (without optical brightener).

Surface resistance of the PEDOT coated viscose fibers were measured using Keithly 6000 picoammeter. Thermal behavior of the PEDOT coated viscose fibers prepared by using different oxidants, organic solvents and after washing was determined with TA instrument Q500. Tensile testing for mechanical properties was performed on Tinius Olsen 10KN universal testing machine. To evaluate the PEDOT deposition on viscose fibers Nicolet 6700 FT-IR spectrometer in the ATR mood was used. Cyclic tester was used to find out the resistance of knitted samples at extension and relaxation.

3 Surface engineering

To change the properties of the surface and region near to the surface in a desired way is called surface engineering. Surface engineering process changes the properties of the substrate. Surface of substrate (underlying material) may be completely covered or part of it still present on the surface depending upon the process adopted[14]. In table.1, different processes for surface engineering are mentioned.

Table 1: Processes for Surface Engineering [6]

Atomistic/Molecular Deposition	<i>Chemical Solution</i>	<ul style="list-style-type: none"> ○ Wet chemical solution (dispersion & layered) ○ Gaseous (thermal) ○ Plasma (thermal) <i>Electrolytic Environment</i> <ul style="list-style-type: none"> ○ Anodizing ○ Ion substitution <i>Mechanical</i> <ul style="list-style-type: none"> ○ Shot peening ○ Work hardening <i>Thermal Treatment</i> <ul style="list-style-type: none"> ○ Thermal stressing <i>Ion Implantation</i> <ul style="list-style-type: none"> ○ Ion beam ○ Plasma immersion ion implantation <i>Roughening and Smoothing</i> <ul style="list-style-type: none"> ○ Chemical ○ Mechanical ○ Chemical-mechanical polishing ○ Sputter texturing <i>Enrichment and Depletion</i> <ul style="list-style-type: none"> ○ Thermal ○ Chemical 		
<i>Electrolytic Environment</i> <ul style="list-style-type: none"> ○ Electroplating ○ Electroless plating ○ Displacement plating ○ Electrophoretic deposition <i>Vacuum Environment</i> <ul style="list-style-type: none"> ○ Vacuum evaporation ○ Ion beam sputter deposition ○ Ion beam assisted deposition <i>(IBAD)</i> <ul style="list-style-type: none"> ○ Laser vaporization ○ Hot-wire and low pressure CVD ○ Jet vapor deposition ○ Ionized cluster beam deposition <i>Plasma Environment</i> <ul style="list-style-type: none"> ○ Sputter deposition ○ Arc vaporization ○ Ion Plating ○ Plasma enhanced (PE)CVD ○ Plasma polymerization <i>Chemical Vapor Environment</i> <ul style="list-style-type: none"> ○ Chemical vapor deposition (CVD) Pack cementation	<ul style="list-style-type: none"> ○ Spray pyrolysis ○ Chemical reduction 			
	Particulate Deposition		<ul style="list-style-type: none"> ○ Thermal Spray ○ Flame Spray ○ Arc-wire spray ○ Plasma spraying ○ D-gun ○ High-vel-oxygen-fuel (HVOF) 	
	<i>Impact Plating</i>		Bulk Coatings	
	<i>Wetting Processes</i>		<ul style="list-style-type: none"> ○ Dip coating ○ Spin coating ○ Painting 	
			<i>Fusion Coatings</i>	<ul style="list-style-type: none"> ○ Thick films ○ Enameling ○ Sol-gel coatings ○ Weld overlay
	<i>Solid Coating</i>		<ul style="list-style-type: none"> ○ Cladding ○ Gilding 	
			Surface Modification	
			<i>Chemical Conversion</i>	

3.1 Vapor Transfer Processes

The processes in which deposition species are atoms or molecules or combination of both, and materials in vapor state are condensed through condensation, chemical reaction or conversion to form a solid material[15]. There are two major categories of vapor depositions process discussed and compared usually.

- Physical vapor deposition (PVD)
- Chemical vapor deposition (CVD)

As CVD process is used in the thesis work therefore this process has discussed in detail.

3.1.1 Physical vapor deposition

PVD process is similar to CVD process except raw material/ precursors i.e. the material which is going to be deposited starts in the form of solid which, in the case of CVD, introduce into the chamber in gaseous form. In PVD processes, also called thin layer processes, material is vaporized in the form of atom or molecule from a solid or liquid source with the help of high energy source such as beam of electrons or ions, traveled in the form of vapor through vacuum or plasma environment and deposited on the substrate where it condenses. The advantage of this process is, as it is atomistic deposition processes therefore the film thickness on the substrate can be achieved from few nanometers to thousand of nanometers as well as multilayer coating can also be achieved. Vacuum evaporation, sputter deposition and ion plating are the main categories of PVD processing[14].

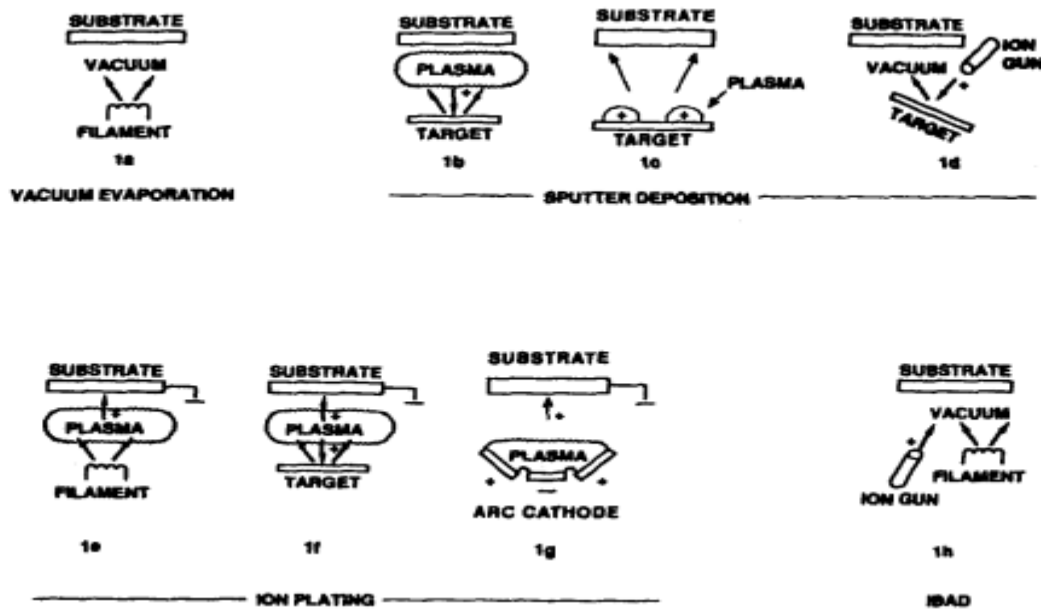


Figure 1: Diagrammatic explanation of PVD processes (1a) vacuum evaporation, (1b & 1c) sputter deposition in a plasma environment, (1d) sputter deposition in a vacuum, (1e) ion plating in a plasma environment with a thermal evaporation source, (1f) ion

Below are some advantages and disadvantages of PVD processes.

Advantages

- Improved properties of material can be deposited as compared to the substrate material.
- Mostly all inorganic as well as some kind of organic materials can be used.
- PVD process is more environmental friendly[16].

Disadvantages

- High capital cost
- Specially skilled operator required to run the process
- Low rate of coating deposition[16].

3.1.2 Chemical Vapor Deposition (CVD)

A synthesis process includes chemical constituents react in the vapor phase near or on a heated substrate to form a solid deposit is called chemical vapor deposition[15]. In general narration, CVD process includes a precursor gas into a chamber where subject is place that has to be coated which may or may not be heated depending upon the chosen process. Broadly speaking, CVD processes can be categorized by following types:

- i. Application,
- ii. Process and reactor used,
- iii. Precursor and chemical reaction used[15].

Due to the surface tension effects, textile, membranes and other substrate having three dimensional surfaces cannot be coated uniformly by solution-phase methods such as spin coating, spray coating and dip coating. CVD process can coat three dimensional surfaces uniformly and it is more environmental friendly process because no organic solvents used[17]. CVD process is complex process and to get reproducibility, a number of aspects should be in consideration. Fig. 2 depicts the fundamental aspects of the CVD processes.

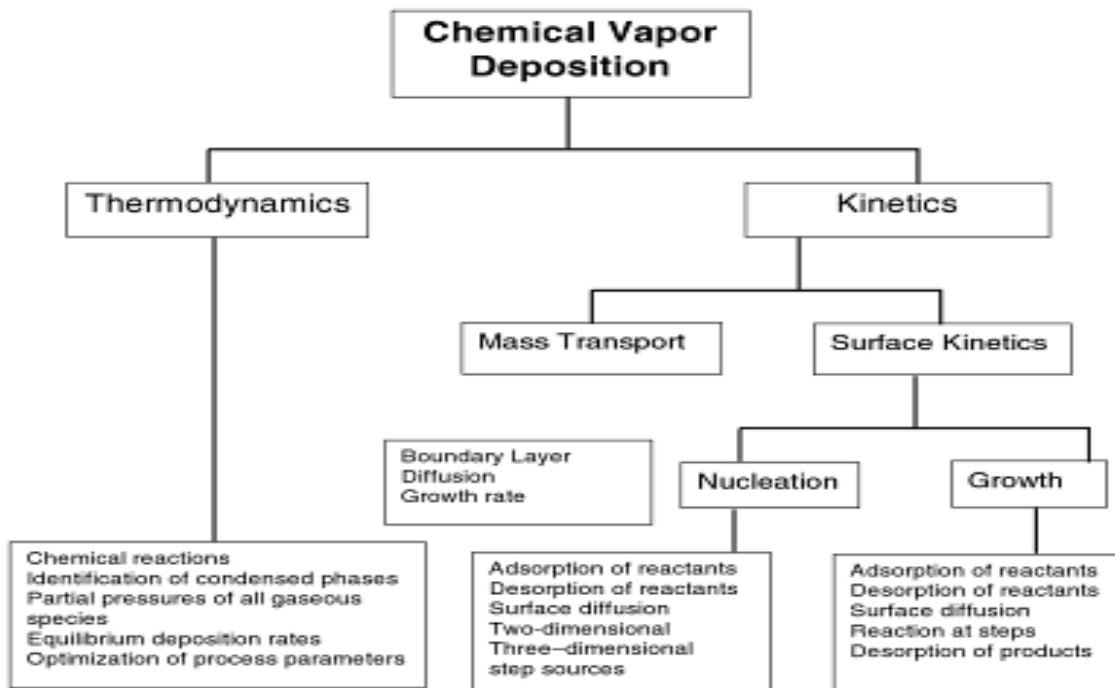


Figure 2: Various fundamental aspects involved in the general chemical vapor deposition process [7]

Mechanistic steps involved in CVD process are shown in the fig. 3

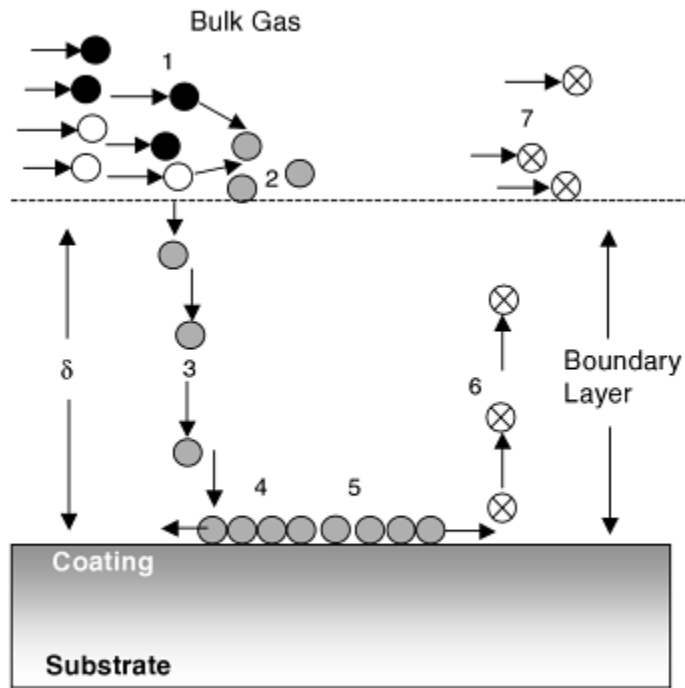


Figure 3: (1) Transport of the gases into the reaction chamber, (2) intermediate reactants gases, (3) diffusion of reactants gases through gaseous boundary to the substrate, (4) absorption of gases onto the substrate surface, (5) single or multi step reactions at the substrate surface, (6) desorption of products from the substrate surface, (7) transport of products away from the reaction chamber

There are several other modified methods of CVD processes such as vapor deposition polymerization (VDP), plasma enhanced chemical vapor deposition (PECVD), initiated chemical vapor deposition (iCVD), oxidative chemical vapor deposition (oCVD) and combustion chemical vapor deposition process (CCVD)[15, 17] etc. CVD process has a wide areas of applications such as diamond films in tribological applications, ceramic materials, semiconductors, electronic applications (conductor and insulator etc), in optoelectronic and ferroelectric, optical applications, wear and corrosion resistance application, cutting tools application, fiber, powder and monolithic applications and for polymer (including conjugated polymers)[15, 18].

4. Conjugated polymers

Since their discovery back in 1970[19] due to their vast potential application in diversified areas such as light emitting diodes (LEDs), photovoltaic, transistors, biosensors, memory devices, nanoswitches, optical modulators, imaging materials and nonlinear optical devices, extensive research has been motivated on conjugated polymers[20]. Conjugated polymers induced conductivity as a result of the formation of charge carriers upon oxidation or reduction of their conjugated backbone. Most conducting polymers have π -conjugation as opposite to σ -

conjugation and electron delocalization occurs from the resonance resulting from alternating single and double bonds[20]. Figure 7 shows the conductivity rang for insulators, semi-conductors and metallic conductors.

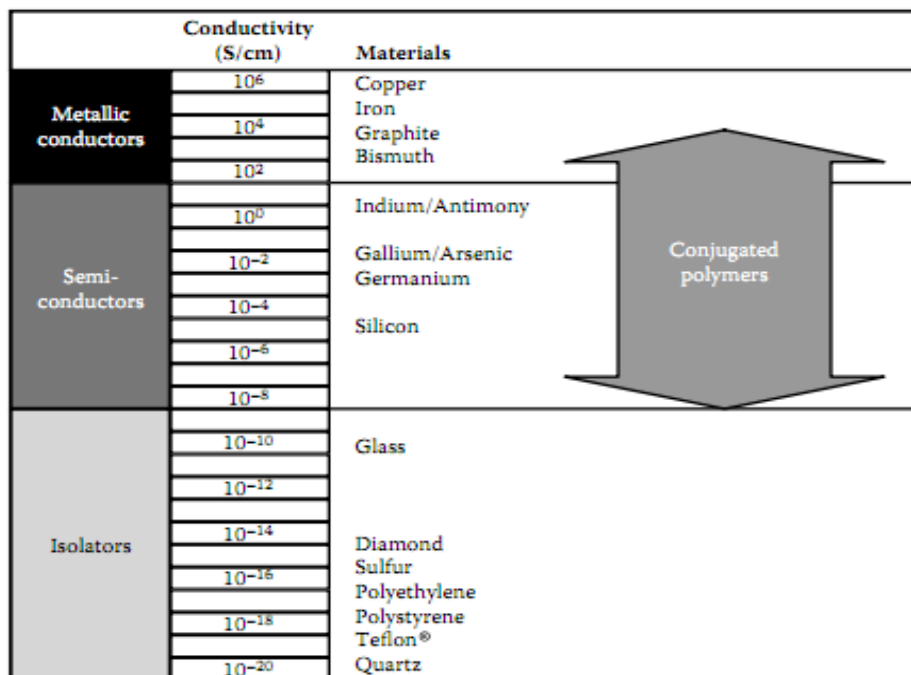


Figure 4: Electrical conductivity of insulators, semiconductors and conductive materials [29]

There are four major types of conductive polymers: filled polymers, ionically conducting polymers, charge transfer polymers and electrically active polymers (EAPs). EAPs include intrinsically conductive polymers/electrically conductive polymers (ICP/ECP).

ICP are either semi conductor or insulator in undoped form which can be converted into electrically conductive by oxidation or reduction reactions which form delocalized charge carriers. An opposite charge ion is required to maintain charge balance in such systems. EAPs are either n-doped or p-doped. Oxidized (p-doped) EAPs have had an electron removed from the backbone, resulting in delocalized polymer cation formation whereas reduced (n-doped) EAPs have had electrons added to the backbone, resulting in polymer anion formation. Polyacetylene, poly (para-phenylene), polyheterocycles (includes Polypyrrole, polythiophenes, polyfurans, poly (phenylene vinylene) and polyanilines are examples of EAPs[21]. Fig. 5 shows structures of some conductive polymers.

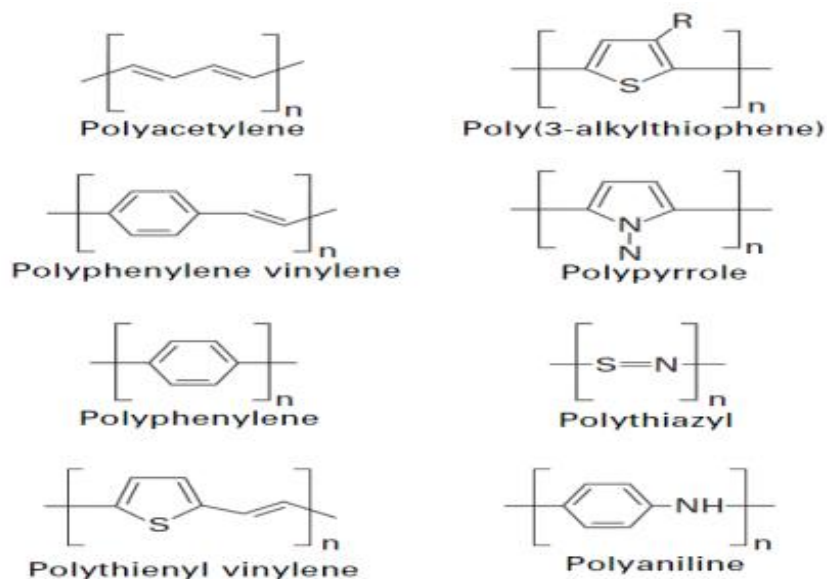


Figure 5: Chemical structures of conductive polymers[21]

PEDOT is most promising conducting polymer due to its versatility[22]. In PEDOT, 3- and 4-positions of the thiophene ring are block by oxygen due to which chance of unwanted polymerization on these two β -carbon sites reduced which also lowering down the oxidation potential of polymer. Also oxygen acts as electron donating group increasing the electron density of the thiophene ring due to which conjugated polythiophene ring can easily be charged positively by the anion dopants. The ethylene moiety caps the opposite sides of the oxygen atoms form a stable six-member ring. Unwanted polymerization reaction branched from 3-and/ or 4-position is minimized by this back bone ring. Fig 6 and fig 7 shows proposed polymerization mechanism of PEDOT and its reaction with cellulose respectively. It is supposed that PEDOT have good bonding with cellulose due to the presence of excess numbers of OH groups. PEDOT is commercially available under the trade name of Baytron®. PEDOT give high conductive values upto 1000S/cm depending upon the manufacturing and application areas. PEDOT have vide application areas such as EMI shielding[23], light emitting diodes (LEDs)[24], heat generation[6] and chemical sensors[25].

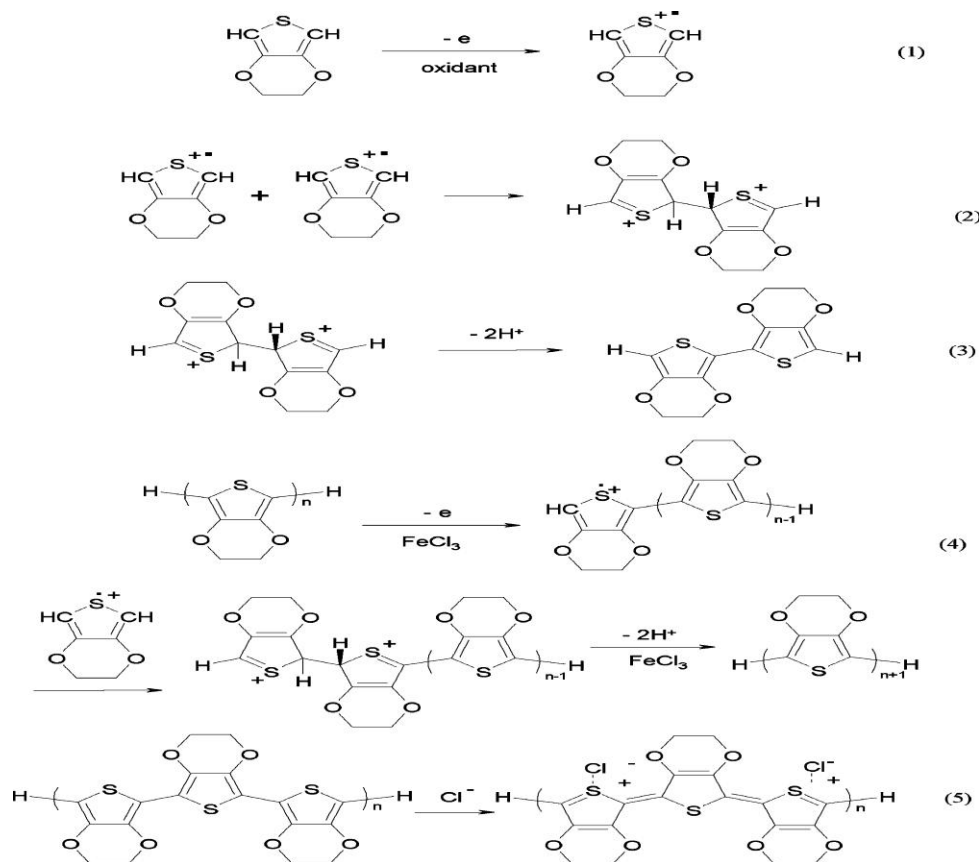


Figure 6: (1) oxidation of EDOT to form cation radical; (2) dimerization of cation radical; (3) deprotonation to form conjugation; (4) further polymerization from n-mer to (n+1)-mer; (5) doping process of PEDOT[21]

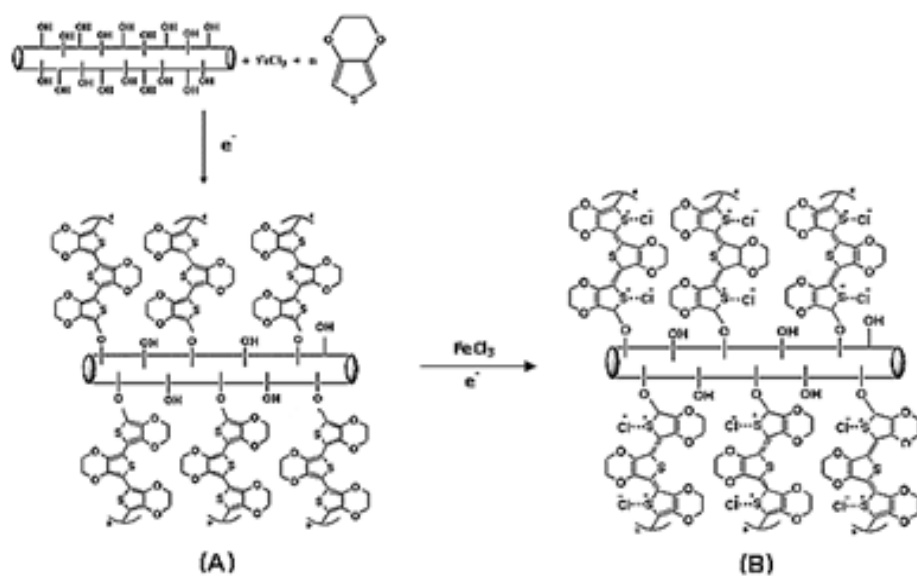


Figure 7: (A) Undoped PEDOT attached with cellulose (B) After doping[2]

5 Synthesis of conjugated polymers by CVD processes

CVD for conjugated polymers are motivated due to difficulties in synthesis for conjugated polymers as they are insoluble because of the rigid backbone chain[21]. They become crystallized readily overcoming the resultant heat of crystallization makes them difficult to dissolved[26]. CVD for polymers also called sometime chemical vapor polymerization (CVP) or vapor deposition polymerization (VPD) used for thin film deposition have several applications in microelectronics, optical devises, biomedical industry, corrosion resistance and protective coatings. CVD technique for thin film deposition of polymers provides unique advantages on other solution based synthesis such as excellent film uniformity, high purity (no solvent retention and contamination), ease of deposition over large substrates, ease of fabrication of multilayered and heterojunction films etc[18]. Fig. 8 shows the steps for the formation of growth of film on underlying substrate.

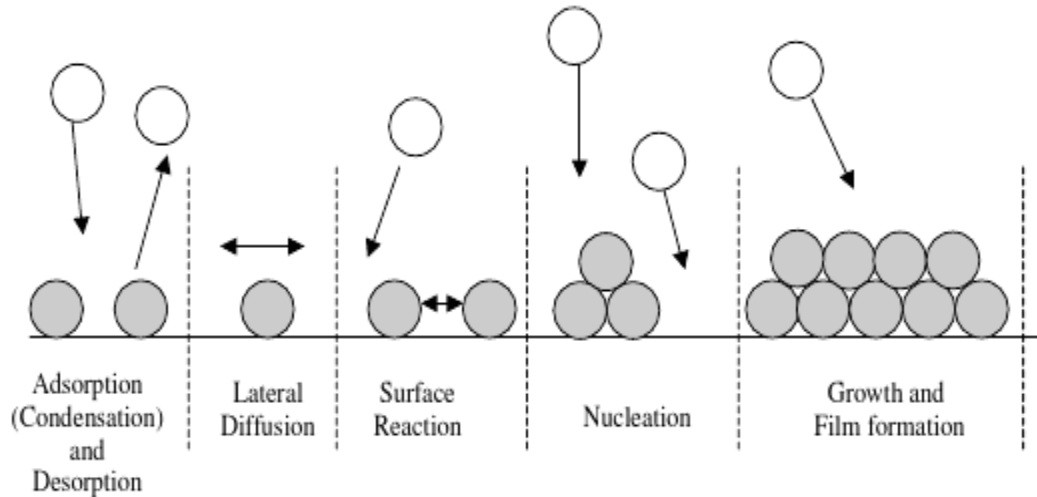


Figure 8: Underlying processes involved in typical thin film deposition by CVD[10]

There are four main approaches for the synthesis of conductive polymers to form conductive coating on a substrate via oxidative polymerization[27]: immersing a substrate in a solution of monomer and oxidants during polymerization, electropolymerization of monomers at electrodes, casting a solution of monomers on a surface and allowing the solvents to evaporate and chemical oxidation of a monomer directly on a substrate that already has been enriched with an oxidant. The last approach has been used in the thesis experimentation therefore it is will discuss in details.

5.1 Initiative chemical vapor deposition (iCVD)

Initiative chemical vapor deposition enable to synthesize polymers from vapor phase which are difficult to synthesize by solution based processes. It is a free radical polymer synthesis

technique and substrate temperature often less than 150°C or some time at ambient temperature depending upon the material due to which it enables compatibility with any kind of material including paper, plastic, conductive polymers etc[28]. Monomers in iCVD remain intact without degradation of their organic functional groups, which happens in plasma assisted CVD processes[29]. A volatile initiator molecule is required in iCVD process which entered into the vacuum chamber along with single or multiple type of polymeric monomers. With the introduction of initiator molecule, the deposition rate of the polymeric film increased drastically. Perfluorooctane sulfonyl fluoride, triethylamine, tert-butyl peroxide and benzophenone are some initiators used for different polymer film deposition by iCVD process[28, 30]. Propargyl methacrylate, glycidyl methacrylate, furfuryl methacrylate, vinyl pyrrolidone and 4-aminostyrene are examples of some monomers that can be polymerized into film via iCVD process[29]. Table 2 shows some advantages of iCVD and oCVD processes

Table 2: Advantages of iCVD and oCVD processes[29]

Process Characteristic	Advantage
Solvent-free	Easy stacking of polymeric films Limited damage to the substrate Copolymerization with immiscible monomers Reduced waste generation
Vapor-phase	Conformal coverage One-step film formation Extremely low level of impurities Tunable film properties
Uniqueness of iCVD/oCVD	Retention of organic functionality Applicability of various monomers Scalable Mild, low power processes
Use of polymeric materials	Low cost Flexible Wide variety of functional groups Well-known structure-property relationships

5.2 Oxidative chemical vapor deposition (oCVD)

Solution base synthesis of conjugated polymers such as PEDOT is limited due to the rigid nature of the conjugated backbone as described before[26]. Due to this reason spin casting from solution and melt processing cannot be used. Although, electropolymerization gives high conductive polymer thin film of numerous conjugated polymers but this process is not suited for large scale application. Winther et al[31] have used iron (III) sulfonates to prepare the coating of polypyrrole, polybithiophene and polyterthiophene using vapor phase polymerization and showed

that the same level of conductivities can be achieved by using vapor phase deposition as compared to electropolymerization. Also, PEDOT could be synthesized with electropolymerization and oxidative polymerization providing highly conductive thin film but, requirement of conductive substrate and reproducibility issues respectively are major drawback in these processes[11, 32-34]. PEDOT, polypyrrole (PPy), poly(thiophene-3-acetic acid) (PTAA), copolymer such as poly (EDOT-*co*-TAA) and poly (pyrrole-*co*-TAA) can be synthesis with oCVD process[28, 35], [36],[12],[37],[30],[38]. Difference between iCVD and oCVD is, the requirement of initiator in iCVD process which is not required in case of oCVD process. Oxidant and monomers are provided simultaneously to the substrate which means to be coated in the vacuum chamber through vapor phase[37]. The in-situ vapor-phase delivery of oxidant to substrate makes this process different from the rest of the vapor phase polymerization processes. Oxidant and monomer both provided to the substrate in the vapor phase. Polymerization is initiated with oxidant and any substrate such as rigid, flexible, porous and 3D structure can be coated[11, 12, 28]. Polymerization and growth of coating both occur simultaneously[38]. Fig. 9 shows process design for oCVD.

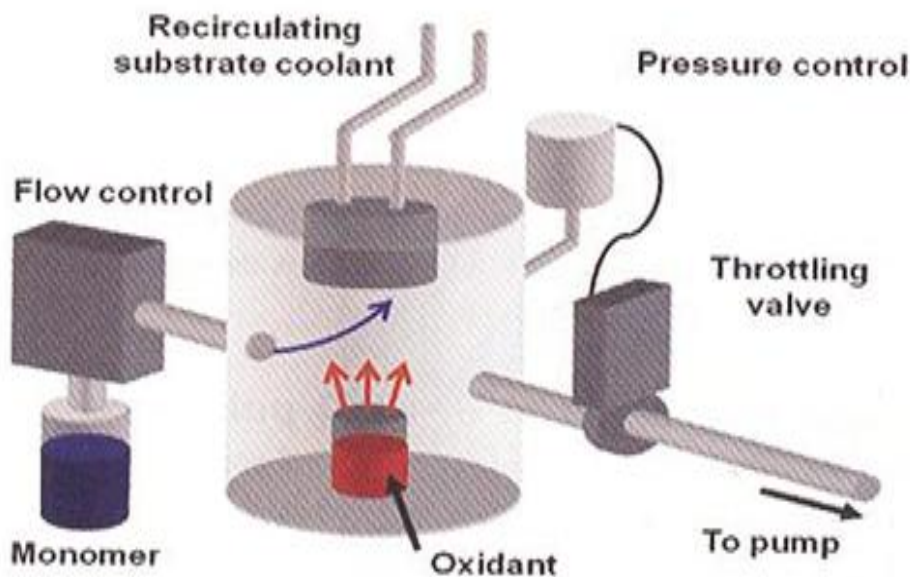


Figure 9: Oxidative chemical vapor deposition of conjugated polymers[17]

5.2.1 Oxidative Chemical Vapor Deposition of PEDOT

Like other conjugated polymers that contain very rigid conformation in order to maintain electron orbital along the backbone, PEDOT also found insoluble[39]. Although Bayer AG under the commercial name of Baytron PTM developed PEDOT doped with polystyrene sulfonic acid (PSS) water emulsion, but the conductivity of the film made with this emulsion is very low as compared to the film prepared with original PEDOT. Coating of thiophene and its derivative like

PEDOT achieved with PECVD have very low to no conductivity due to loss of aromatic structure[40]. This is also one of the reasons to motivate the synthesis of PEDOT with oCVD process[37]. J.P. Lock et al developed oCVD process for PEDOT synthesis on idea to introduce EDOT monomer from the vapor phase[12].

5.2.2 Oxidant in oCVD of Conjugated Polymers

Oxidants such as ferric (III) chloride, ferric (III) tosylate, in case of oCVD process provide the covalent grafting of the PEDOT to the underlying substrate. If underlying substrate contain aromatic group no linker molecule such as silane and thiol compounds or specific surface treatment (for the bonding point of view between conjugated polymer and the underlying substrate) is required. Great adhesion can be achieved with inherently grafted PEDOT[38]. The mechanism of the grafting PEDOT can be described with Kovacic's report which indicate that benzene could be polymerized using Friedel-Craft catalyst such as FeCl_3 , CuCl_2 , MoCl_5 and AlCl_3 [41]. The formation of radical cations from benzene, toluene, chlorobenzene, phenol, biphenyl and naphthalene facilitate with Friedel-Craft catalysts also which is similar to the proposed mechanism for oxidative polymerization of PPy, polythiophene and PEDOT[38]. The formation of radical cation site on an aromatic ring subsequently participates in reactions to form brushes comprised of chains of conducting polymers. Fig. 10 shows reactions mechanism involved in the grafting of PEDOT on aromatic substrates.

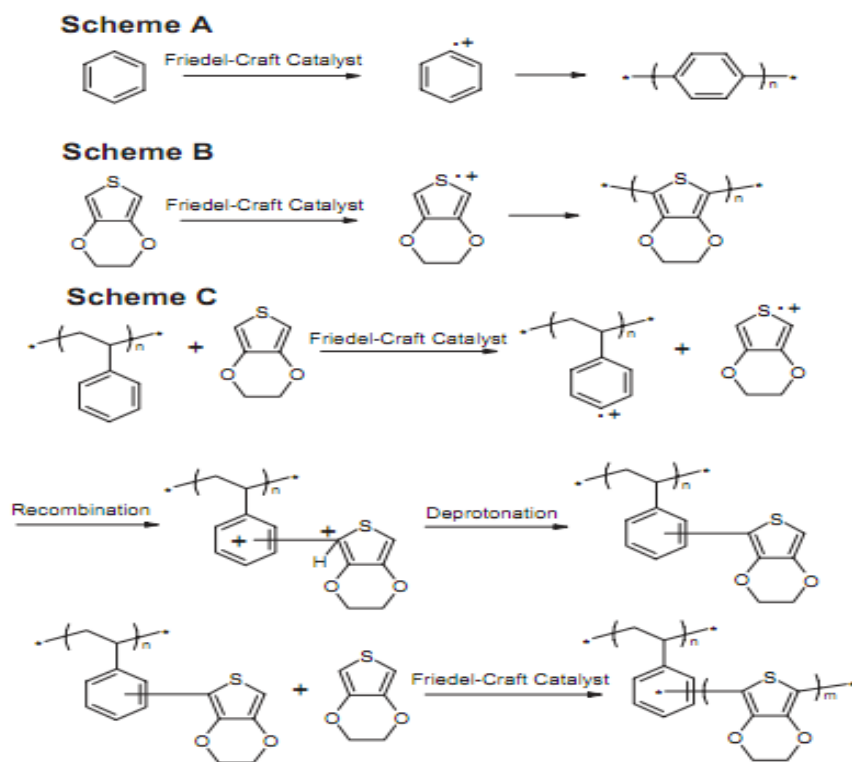


Figure 10: Schematic representation of the reaction mechanism involved in the grafting PEDOT on aromatic substrates [23]

6 Smart textiles

Few years ago textile entered into a new era, the era of smart textile. These textiles can sense stimuli from the environment react and adapt to them by integration of functionalities in the textile structures. Five basic functions of these textiles are: sensors, data processing, actuators, storage and communication[42]. Smart textile could be used to measure number of characteristics such as physiological characteristics, by incorporating wearable electronics in the textile structures[43], or physical integration of microelectronics with textile and clothing construction[44] and/or produce them directly from technical yarns[3]

6.1 Electroactive textiles

Electroactive textiles enhance the possibility of making human life healthier, comfortable and safer by bringing the technological advances closer to the people through the use of easy-to-use interface between the humans measuring devices and actuators. There are two kind of electroactive textile which can be described as follow.

- *Passive textiles*: Do not required energy source, and can be used to prevent the static electricity and electrostatic discharge. EMI/RFI shielding, carpets, antistatic clothing and medical, are some application areas.
- *Active textiles*: Equipped with an energy source, electronic sensors and actuators. Mostly used to create heat, transport signals and connect electronic components. Medical health monitoring, sports and leisure and personal protection are some examples of application areas.

This is near to possible with recent development in material processing to make all components of interactive electromechanical systems such as sensors, actuators, electronics and power source from polymeric materials that can be woven or knit directly onto fabrics or printed/coated or applied onto the fabrics. Electroactive polymers due to their properties such as intrinsic sensing, dielectric or conductive, compliance and flexibility become potentially suitable for the realization of such systems[45, 46].

6.2 Textile based sensors

One important application of electroactive smart textile would be as sensors. These sensors work according to two principles;

- *Piezoresistive effect*: describe the change of material electrical resistance owing to external stress or deformation.
- *Piezoelectric effect*: piezoelectricity produced to certain materials with the cross-coupling of mechanical and electrical energy.

In piezoresistive sensors, a voltage source is applied across the sensors to measure the strain whereas, when piezoelectric device used as sensors it actively generate charges in response to the external load.

There are several ways to produce textile sensors such as by incorporating metallic fibres into the textile structure[47], making textile structures from conductive polymeric fibers or conductive polymers (EAP) coated fibers used to prepare these sensors[48-50]. By printing the sensing lines of conductive polymers on the fabrics also prepare textile sensor[4]. Textile based sensors can be used as strain sensors, pressure sensors and fiber optics sensors[51, 52].

6.2.1 Fabric base pressure sensors

Textile pressure sensors are used in health care and sports application. A typical pressure sensor is shown in fig. 11.

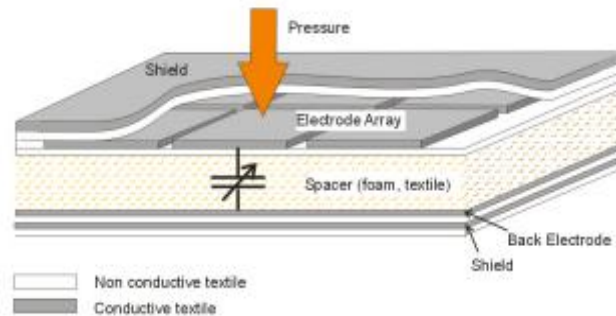


Figure 11: Textile pressure sensor[53]

It consist of two layers of conductive fabric separated by non-conductive layer of textile fabric, when pressure is applied on it, conductive layers get into contact and signal is detected on the monitor screen.

6.2.2 Textile strain sensors

A strain sensor can be prepared in several ways such as using thick film strain gauge into the fabric, printing conductive polymer composite filled with carbon black powder to nylon fabric or simply attaching fiber-shaped sensor to the textile structure. It may be consist of carbon based piezoresistive layers terminated with silver conducting lines[54].

6.2.3 Piezoresistive based yarn and knitted Sensors

Knitted fabrics made from the conductive yarn, which can be used as sensors based on their loop configuration, is a novel application of the conventional knitted fabrics[47]. These conductive textile structures based on the electrical resistance could respond to the external elements such as deformation, chemicals, humidity and temperature[55]. Dimensional changes in knitted structure

results the change in resistance of knitted sensors which can be detected. Huang et al.[56] reported yarn based piezoresistive sensor, that can be used to monitor the joint and muscle movements.

7 Experimental

7.1. Materials Used

For experimentations, viscose fibers (1220 dtex, number of filaments 720, Z100 twist/meter) provided by CORDENKA[®], EDOT monomer (CLEVIOUS[®] M V2), FeCl₃ (Sigma-Aldrich, 98%), Ferric (III) Tosylate 40% (Clevios C-B 40 V2), C₄H₉OH (Aldrich, 99%), Acetone (Fisher Scientific), Ethylacetate (Fisher Scientific) have been used without any further modifications and purifications..

7.2 Process

Preparation of conductive fibers with oCVD process involves three steps

- i. Impregnation of fiber in oxidant solution followed by subsequent drying
- ii. Oxidant enrich fibers expose to EDOT monomer vapors
- iii. PEDOT-coated fibers doped with oxidant followed by subsequent washing with methanol to remove the by-products and unreacted monomers

In previous studies, reaction parameters have been optimized at which maximum conductivity achieved. Table 3 indicates these parameters.

Table 3: Parameters for the preparation of PEDOT coated fibers with oCVD

Oxidant Conc.	Soaking Time in oxidant	Drying Time at ambient conditions	Reaction Time	Reaction Temperature	Doping oxidant Conc.
Wt. %	(min)	(min)	(min)	°C	%
15	10	30	15	50	3

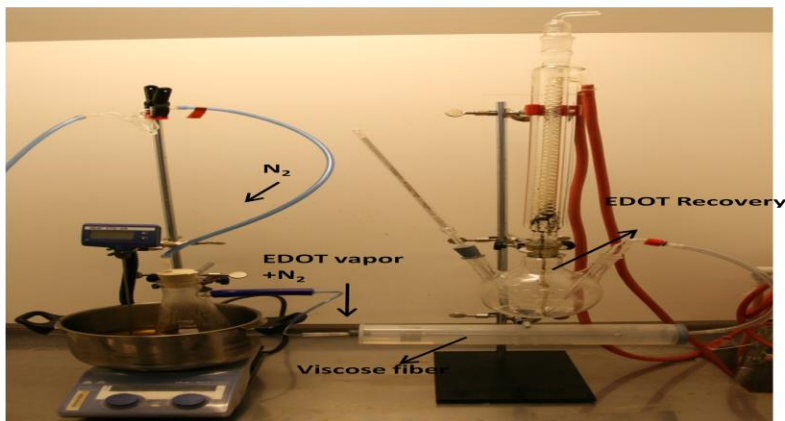


Figure 12: Apparatus designed for the production of PEDOT coated fibers

Apparatus designed for the preparation of PEDOT coated fibers shown in fig. 12. By heating flask contains EDOT solution EDOT monomer obtained which travels to the tubular reactor with nitrogen gas. Oxidant treated viscose fibers wound on frame, placed in the tubular reactor. EDOT monomers react with oxidant treated viscose fibers in the tubular reactor, polymerization of EDOT and coating occurs simultaneously. Unreacted EDOT monomers travel to the recovery channel where they condensed and recovered. PEDOT coated viscose fibers removed from the tubular reactor and doped with oxidant solution. Finally, PEDOT coated viscose fibers washed several times with methanol solution.

Experimental work was divided into following three major categories:

- 1) Preparation of PEDOT coated viscose fibers at different parameters
- 2) Preparation of knitted structures of the produced PEDOT coated viscose fibers
- 3) Washing of viscose fibers and knitted structures

7.2.1 Preparation of PEDOT coated viscose fibers at different parameters

Below are the parameters which have been tried for the preparation of PEDOT coated viscose fibers.

- Pretreatment of viscose fibers with solvents for cleaning surface cleaning
- Changing drying time and temperature of the oxidant treated viscose fibers prior to the polymerization step
- Using two different oxidants ferric (III) tosylate and ferric (III) chloride

Fibers were pretreated with two different solvents acetone and ethylacetate separately for surface cleaning of the fibers. Table 4 indicates the parameters used for solvent treatment.

Table 4: Parameters used in solvents treatment

Type of Solvent	Treated Time	Drying Time	Drying Temperature
	(min)	(min)	°C
Acetone	10	5	50
Ethylacetate	10	5	50

These pretreated fibers were then polymerized at reaction conditions mentioned in table 3 without any further changes in the process. Five to Seven samples for each type of solvent were prepared and tested accordingly.

Viscose fibers were treated with oxidant 15 wt. % FeCl_3 for 10 min, after that these oxidant treated fibers were dried at different temperatures for different time periods. Table 5 indicates the drying time and temperature at which fibers were dried

Table 5: Drying time and temperature of oxidant treated fibers

Set of Samples	Drying Temperature	Drying Time (min)			
	°C	3	5	7	10
1	30	3	5	7	10
2	40	3	5	7	10
3	50	3	5	7	10
4	60	3	5	7	10

These dried viscose fibers at different parameters were then polymerized at 50°C for 15 min and rest of the process remains same. Five to Seven samples for each set of drying time and temperature were prepared Oxidant type is very important with respect to electromechanical properties. Many oxidants are available which can be used in oCVD process. In this thesis work ferric (III) tosylate and ferric (III) chloride were used as oxidants.

In previous study, Bashir et al[1] found that good electromechanical properties can be achieved by using 15 wt. % of ferric (III) chloride, therefore initially 15 wt. % of ferric (III) tosylate was used. But, viscose fibers were not coated with PEDOT using 15 wt. % of ferric (III) tosylate. Therefore, 40 wt. % concentrated ferric (III) tosylate used as oxidant instead of 15 wt % concentration. Ferric (III) tosylate treated viscose fibers then polymerized with regular process according to the parameters described in table 3 except the concentration of oxidant used in doping step, which changed to 40 wt. % instead of 3 wt. %. PEDOT coated viscose fibers were

also prepared using 15 wt % of ferric (III) chloride according parameters of table 3. Ten to twelve samples were prepared for each type of oxidants and tested.

7.2.2 Preparation of knitted structures of the produced PEDOT coated viscose fibers

Knitted structures were prepared on a hand knitting machine. PEDOT coated fibers were produced according to the parameters described in table 6 and then used to prepare knitted structures. 15-20 meter length of the viscose yarn was coated successfully with PEDOT and utilized in the preparation of knitted structures.

Table 6: Parameters used to prepare PEDOT coated fibers for knitting samples

Fibers	Viscose
Oxidant	15 wt. % FeCl ₃
Soaking time in oxidant	10min
Drying temperature of oxidant treated fibers	60°C
Drying time of oxidant treated fibers	10min
Polymerization reaction time	15min
Polymerization reaction temperature	50°C
Doping oxidant	3 wt. % FeCl ₃

Rib knitting structure chosen for knitted structures. Fig. 13 (a) shows rib knit structure and fig. 13 (b) shows the prepared knitted sample.

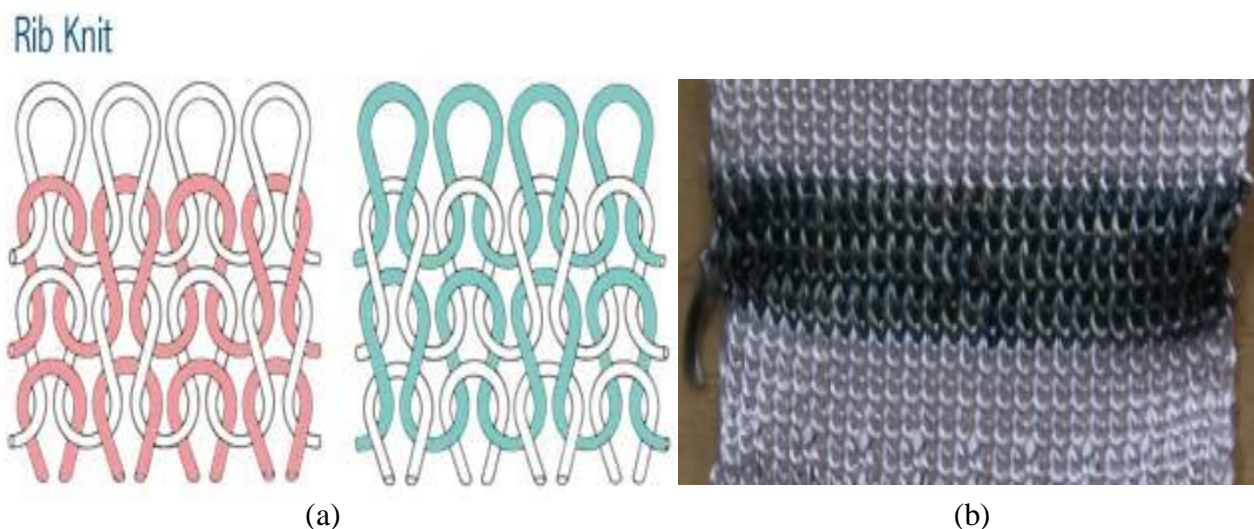


Figure 13: a) Rib knit structure; b) knitted samples prepared from PEDOT coated viscose fibers

7.2.3 Washing of viscose fibers and knitted structures

Fiber: PEDOT coated viscose fiber (prepared according to the parameters of table 3) were hand washed two times with tap water for 10min using normal and intensive stirring.

Knitting Structures: Washing was performed according to *EN ISO-6330* (Textiles-Domestic washing and drying procedures for textile texting) with non phosphate ECE detergent A (without optical brightener) on a type A washer-front loading horizontal drum, shown in fig. 14, and flat drying process was adopted for drying. Procedure of adopted standard is available in Appendix A.



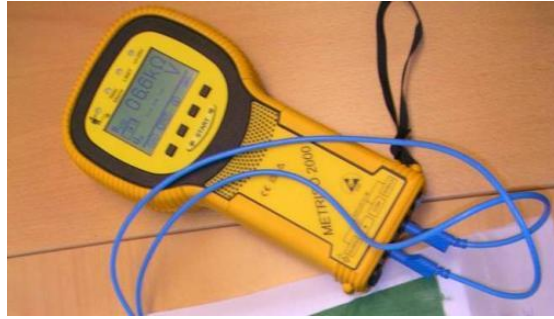
Figure 14: Type A washer- Front loading, horizontal drum Type

7.3 Testing techniques

Different testing techniques were used to determine the electromechanical properties of PEDOT coated viscose fibers and for knitted structures.

7.3.1 Resistance measurement

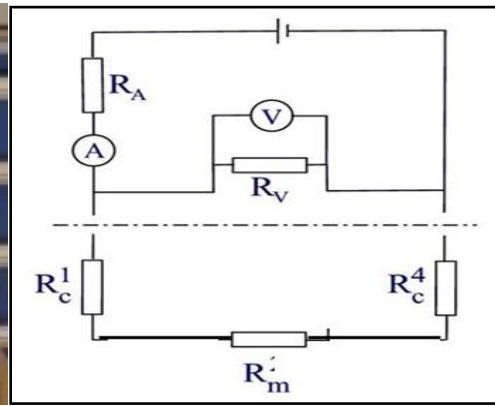
Two different instruments were used to measure the surface resistance along the conductive fibers, as shown in fig. 15 .Metriso 2000 is handheld meter for initial readings with specific voltage setting 10V, 100V and 250V. Keithly 6000 picoammeter, high voltage meter with voltage sweep capability 0.1 to 500. Resistance was measure at 10V, 2.5mA current and at room temperature on 150 mm long fibers holding between two crocodile clips. Each fiber was tested from six different places and then average of these reading was taken and used. Two point resistance measurement systems were used as shown in fig 15c.



(a)



(b)



(c)

Figure 15: (a) Metriso 2000, (b) Keithly 6000 picoammeter, (c) 2 points resistance measurement system

7.3.2 Cyclic testing for knitted structures

Cyclic tester was used to find out the resistance of the knitted structures at stretch and relax positions. Knitted structure holds at two points as shown in fig. 16. Measurements were taken with 20mm/sec speed using 25mA current and 10V voltage at 50% and 100% stretch of the original length of the knitted structures

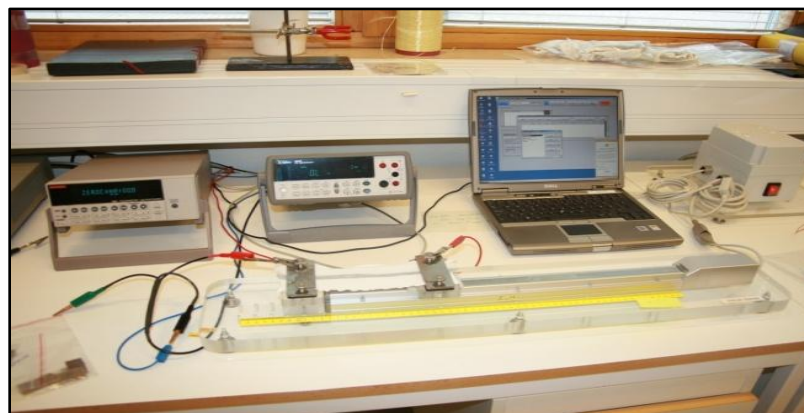


Figure 16: Cyclic tester

7.3.3 Attenuated total reflection-fourier transforms infrared spectra (ATR-FTIR)

Deposition of PEDOT on the viscose fiber was characterized by using a Nicolet 6700 FT-IR spectrometer in ATR mode. IR spectra were acquired in the range from 4000 to 400 cm^{-1} , with 32 scans and 3 cm^{-1} of band resolution. Apparatus is shown in fig.17.



Figure 17: Nicolet 6700 FTIR spectrometer

7.3.4 Thermogravimetric analysis (TGA)

TGA analysis was performed on TA instrument Q500 TGA apparatus at a heating of 10°C/min from 25 to 600 °C under nitrogen gas to get the information about the thermal stability of prepared samples. TGA apparatus is shown in fig.18.



Figure 18: TA instrument Q500 TGA apparatus

7.3.5 Tensile testing

Tinius Olsen 10kN universal testing machine used to analyze the tensile properties of viscose fibers at a crosshead speed of 20mm/min. Maximum force, liner density and tenacity value have been determined. Maximum samples were tested to get more reliable results. Fig. 19 shows the apparatus used.

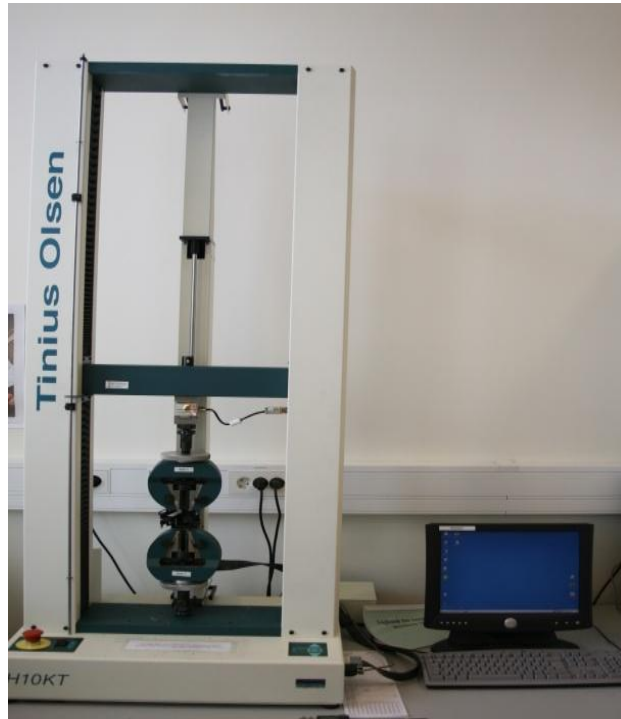


Figure 19: Tinius Olsen 19KN universal testing

8 Results and discussion

8.1 Surface Treatment of fibers with solvents

Mechanical Properties:

Fibers strengths decreased when viscose fibers were treated with solvents. Fig. 22 shows that pure viscose fiber have highest strength of almost 65N. PEDOT coated viscose fibers which are not treated with solvents have strength around 30N but it changes drastically in case of the fibers which were pretreated with ethylacetate and acetone and decreased to 20 N and 12 N respectively. After surface treatment, waxes and other chemicals such as starch which used to give strength to fibers, removed and fibers become more absorbent. Due to this fact, absorbency of the viscose fiber increased and high amount of oxidant absorbed to the fiber. It has been reported by Bashir et al[1] that higher wt. % of oxidant reduce the fibers strength. The excess amount of oxidant might increase the acid hydrolysis of the cellulose base viscose fiber which results in decrease in the fiber strength.

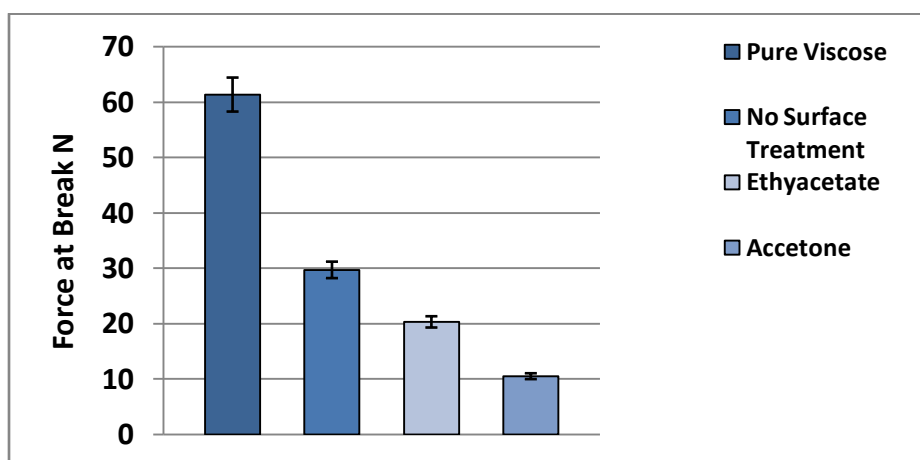


Figure 20: Tensile testing of the surface treated PEDOT coated viscose fibers

Thermogravimetric Analysis (TGA):

TGA results have been shown in fig. 23. The weight loss of pure viscose fiber fig. 23(a) starts at about 300°C and nearly 80% decomposed until 400°C and 90% was decomposed at 600°C. Weight loss in viscose fiber appears 5 wt% at 100°C due to moisture evaporation. In case of pure PEDOT fig. 23(e), weight loss appears very rapidly till 140°C and continuous upto 600°C but still 40% remains at 600°C. Pure viscose fiber shows more stability as compare to pure PEDOT below 330°C but PEDOT has more stability between 330-600°C. In case of PEDOT coated viscose fiber without surface treatment fig. 23(b), thermal stability is in between pure viscose fibers and pure PEDOT above 330°C to 400°C and still almost 30 wt. % remain at 600 °C, which is more than pure viscose fibers and less than pure PEDOT. Decomposition of ethyl

acetate pretreated PEDOT coated viscose fibers fig. 23(c) start similar to that of untreated PEDOT coated viscose fibers until 150°C, but after that weight loss is more upto 300°C. After 350°C, weight loss and stability of the ethyl acetate pretreated fibers become same as that of untreated viscose fibers. In case of acetone pretreated PEDOT coated viscose fiber fig.23 (d), weight loss is same as that of pure viscose, untreated and ethyl acetate pretreated viscose fiber upto 150°C, but after that it decreases more as compare to above mention fibers until 350°C. From 350 °C to 600°C, thermal stability and weight loss of acetone pretreated PEDOT coated viscose fiber is same as for that of pure viscose, untreated and ethylacetate treated PEDOT coated viscose fibers. Results show that, more PEDOT is deposited on viscose fibers that are pretreated with ethyl acetate and acetone because of the thermal degradation of these coated fibers are more near to that of pure PEDOT as compare to pure viscose and untreated PEDOT coated viscose fibers which indicate the presence of more PEDOT.

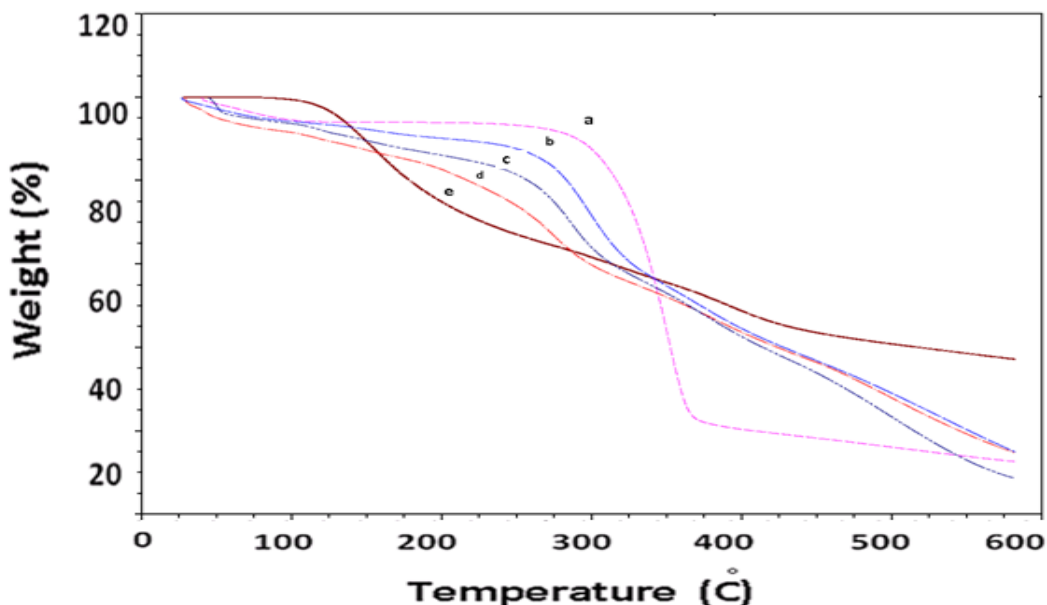


Figure 21: TGA analysis of (a) Pure viscose, (b) without surface treatment PEDOT viscose fibers (c) ethylacetate treated PEDOT coated viscose fiber, (d) acetone treated PEDOT coated viscose fiber, (e) pure PEDOT

Surface Resistance:

Electrical properties of the untreated, acetone pretreated and ethylacetate pretreated PEDOT coated viscose fibers shown in fig. 24. Untreated PEDOT coated viscose has resistance less than 10 kΩ. Acetone pretreated viscose fibers show increase in resistance but ethylacetate treated PEDOT coated viscose fibers have maximum resistance which is more than 70 KΩ. The increase in resistance might be due to the over oxidation of the PEDOT due to presence of excess amount

of oxidant in pretreated PEDOT coated viscose fibers. When cellulose fibers treated with oxidant (FeCl_3), it absorbed easily onto fibers and higher amount of FeCl_3 causes higher rate of polymerization of PEDOT but the length of polymer chain decreases hence PEDOT obtained has lower conductivity[10]. Zykwinska et al[57] reported over oxidation of polymer chain result in decrease in the conjugated length of the polymer's delocalized π -bond through cross linking of the polymer chains. After pretreatment with solvents for cleaning purpose, absorbency of the viscose fibers increases due to which more oxidant absorbed to the fibers. These could be one of the reasons of increase in the resistance of the acetone and ethylacetate pretreated PEDOT viscose fibers as compare to untreated PEDOT coated viscose fibers.

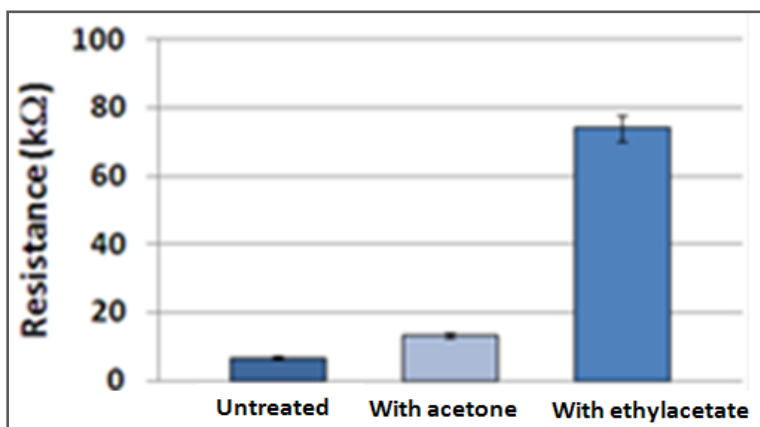


Figure 22: Electrical properties of untreated, acetone pretreated and ethylacetate pretreated PEDOT coated viscose fiber

8.1 Effect of drying time and temperature

Surface Resistance:

Resistance values of PEDOT coated viscose fibers dried at different time periods and temperatures after dipping in oxidant (FeCl_3) and prior to the polymerization step shown in fig. 20. Graph clearly shows that surface resistance decrease as drying time and temperature increases. Resistance values are maximum when temperature is low such as from 30°C to 40°C . But with the increase of drying time even at low temperature decreases the resistance values. Minimum resistance achieved by drying at 60°C for 10min. Stabilization of Cl^- active anions is also important, which take part in the oxidation of EDOT monomer with $(-\text{Na}^+\text{S})$ and $(-\text{OCS})$ functional group of viscose fibers[1]. As drying time and temperature increases, excess amount of oxidant dried or become inactive that could take part in over oxidation of the PEDOT resulting in high surface resistance of viscose fibers coated with PEDOT. It might be possible that the stabilization of Cl^- active anions occur at higher temperature due to which resistance decreases. Or, Inactivation or removal of excess amount of oxidant at higher temperature might be one of the reasons of the decrease in resistance values with increase in drying time and temperature.

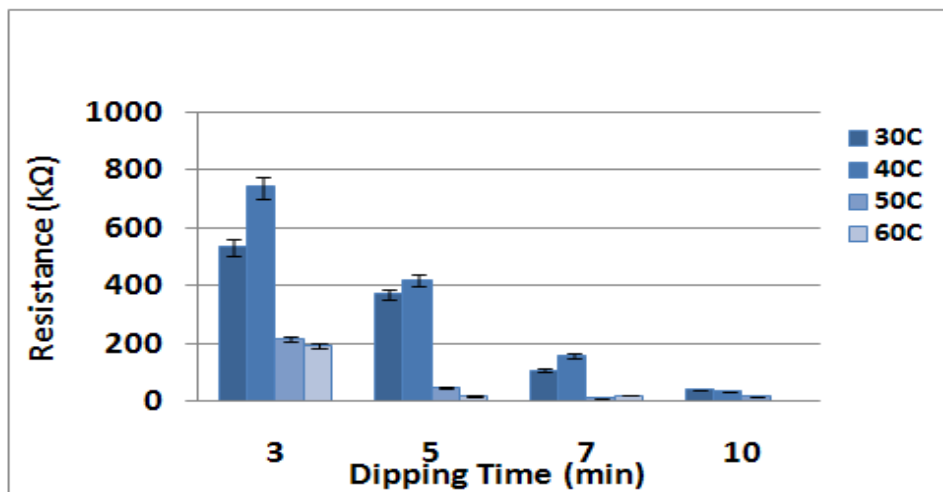


Figure 23: Effect of drying time and temperature on electrical resistance of PEDOT coated viscose fibers

Mechanical Properties:

The effect of drying time and temperature on mechanical properties of PEDOT coated viscose fibers shown in fig. 21. Fibers strength is very low at low temperature but it is clear from the graph that increase in drying time improves fibers strength. Fibers have very low strength at temperature 30-40°C but increase in drying time at this time range also increase fibers strength. At 50°C, fibers show maximum strength which is around 30-35 N. Again, at high temperature, excess amount of oxidant that absorbed to the viscose fibers dried which could take part in acid hydrolysis of viscose fibers. Further increase in temperature to 60°C decreases the fibers strength to 20-25N. At higher temperature internal surface of the cellulose base fibers decreases due to which fibers shrink which creates core to sheath difference[58]. It can be hypothesized that at high temperature viscose fiber shrinks and become brittle which results in decrease in mechanical properties.

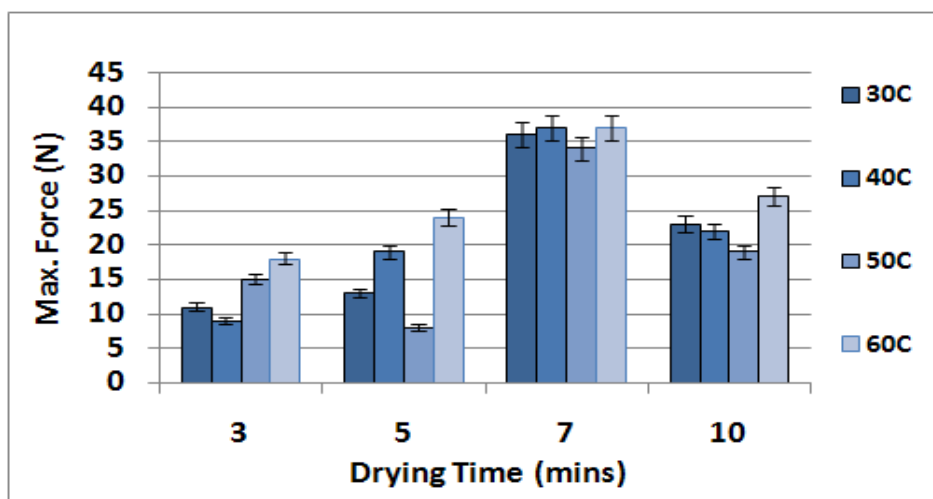


Figure 24: Effect of drying time and temperature on mechanical properties of the PEDOT coated viscose fibers

8.3 Effect of oxidant types and their comparison

Electromechanical properties:

Table 7 shows that by using ferric (III) chloride, surface resistance of PEDOT coated fibers is $6.8\text{k}\Omega$, which is almost 10 times less than that in the case of ferric (III) tosylate which is $54.5\text{k}\Omega$. It shows that by using ferric chloride as oxidant, low surface resistance of PEDOT coated viscose fibers can be achieved. It was observed that coating was very brittle in case of ferric (III) tosylate as compare to coating with ferric (III) chloride. Table 7 also shows that good strength of PEDOT coated viscose fiber can be achieved with ferric tosylate as compared to ferric chloride. Acid hydrolysis of viscose with ferric (III) chloride is reported[59]. In case of ferric (III) chloride, (Cl^-) ion might be responsible for the acid hydrolysis of viscose fibers which is not present in case of ferric (III) tosylate. Therefore it might be one of the reasons of the higher fiber strength with of ferric (III) tosylate. Ferric (III) tosylate has high acidity and when solvent evaporate acid concentration increased which is favorable for the reactions resulting in byproducts which cannot be oxidized and react to PEDOT giving impurities rather than taking part in oxidation of PEDOT[60, 61], It can illustrated that ferric (III) tosylate do not provide the medium which is favorable for the formation of highly conductive PEDOT. This might be one of the reasons to the high resistance of PEDOT coated viscose fiber with ferric (III) tosylate. It is also reported that atmospheric water vapor plays important role in PEDOT coating with ferric (III) tosylate and by controlling humidity good electrical properties of PEDOT can be achieved[62]. The humidity factor was not considered in experimentations therefore, humidity might be causing decrease in electrical properties of PEDOT with ferric (III) tosylate.

Table 7: Comparison of electro-mechanical properties of oxidant ferric (III) chloride and ferric (III) tosylate

Sample Type	Resistance (k Ω)	Force at Break (N)	Tenacity (N/Text)
Pure viscose	61.3 (± 5.3)	0.32 (± 0.03)
Ferric (III) Chloride	6.8 (± 0.7)	29.7 (± 5.0)	0.14 (± 0.05)
Ferric (III) Tosylate	54.5 (± 20)	40.8 (± 8.8)	0.16 (± 0.02)

Thermogravimetric Analysis (TGA:)

Fig.24 shows TGA analysis of pure viscose fig. 24(a), PEDOT coated viscose fiber prepared with ferric (III) chloride fig. 24(b), ferric (III) tosylate fig. 24(c) and pure PEDOT fig. 24(d). Thermogram of ferric (III) tosylate shows that the thermal degradation starts similar to pure viscose and ferric (III) chloride and remains same upto 200°C. From 200-300 °C weight lost is much higher in case of ferric (III) tosylate as compare to pure viscose and ferric (III) chloride. Then, after 400-600°C thermal stability of ferric (III) tosylate is almost same with ferric chloride except the remaining wt. % at 600°C is 25% which is in the case of ferric chloride is nearly 15%. This shows the presence of higher amount of PEDOT in case of ferric (III) tosylate because PEDOT is more stable at higher temperature. Also higher weight lost from 200-300 °C in case of ferric (III) tosylate as compare to ferric (III) chloride shows the presence of higher amount of PEDOT because weight loss in PEDOT is higher in this temperature range.

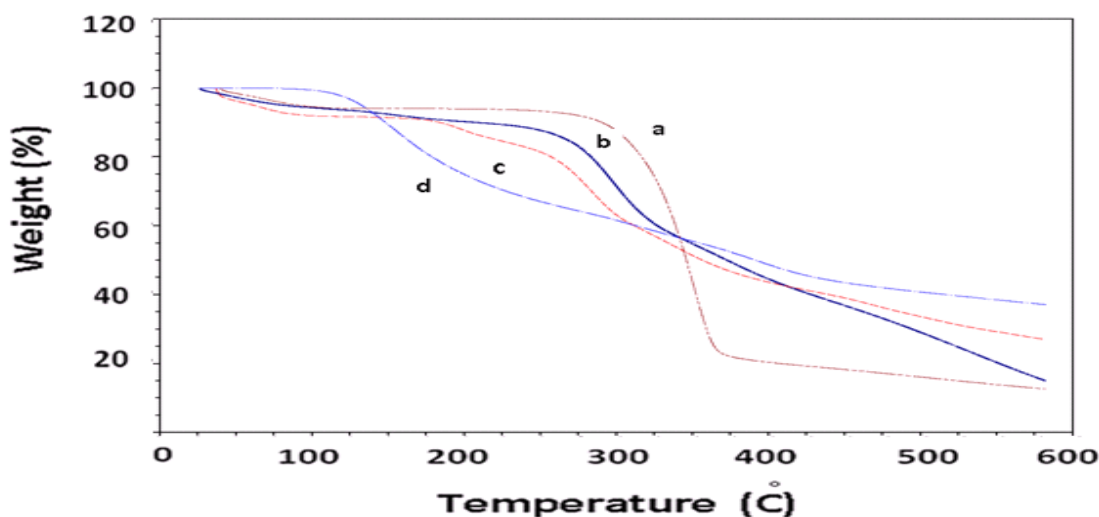


Figure 25: TGA analysis of (a) pure viscose, (b) PEDOT coated viscose fiber with oxidant ferric (III) chloride, (c) PEDOT coated viscose fiber with oxidant ferric (III) tosylate, (d) Pure PEDOT

FTIR analysis:

Deposition of PEDOT coating on viscose fibers with ferric (III) chloride and ferric (III) tosylate oxidants was studied with FTIR spectroscopy. IR spectrum of pure viscose fig. 26(a) shows the presence of cellulose because of the broad peaks at 2889 cm^{-1} and at 3326 cm^{-1} . These peaks are due to the $(\text{C-H})_{\text{str}}$ and $(\text{O-H})_{\text{str}}$ respectively. Peaks at 835 cm^{-1} , 1011 cm^{-1} and 1366 cm^{-1} shows the presence of $(\text{C-C})_{\text{str}}$, $(\text{C-O})_{\text{str}}$, and (C-O-C) functional groups[1]. Natural aging of cellulose (due to partial oxidation of hydroxyl groups to carbonyl group) can be seen at peak 1643 cm^{-1} [9]. IR Spectrum of pure PEDOT shows in fig. 26(c). PEDOT characteristic absorption peaks between 1187 cm^{-1} and 1489 cm^{-1} can be observed. IR spectrum of PEDOT coated viscose fibers with oxidant ferric (III) chloride fig. 26(a) shows the presence of typical peaks between 1019 cm^{-1} and 1315 cm^{-1} . Sharp peaks between 1037 and 1383 in IR spectrum of PEDOT coated viscose fibers with ferric (III) tosylate fig. 26(b) shows the presence of more PEDOT as compared to PEDOT coated viscose fibers with oxidant ferric tosylate. Also typical peak of cellulose at around 3326 cm^{-1} absent in case of PEDOT coated viscose fibers with oxidant ferric (III) tosylate showing that surface of viscose is completely coated and covered with PEDOT. In case of PEDOT coated viscose fiber with oxidant ferric (III) chloride, presence of peak at 3319 cm^{-1} indicate the presence of cellulose on the surface. It shows either viscose fibers are not fully covered with PEDOT coating or might be the thickness of the coating is not enough due to which underlying cellulose is detected.

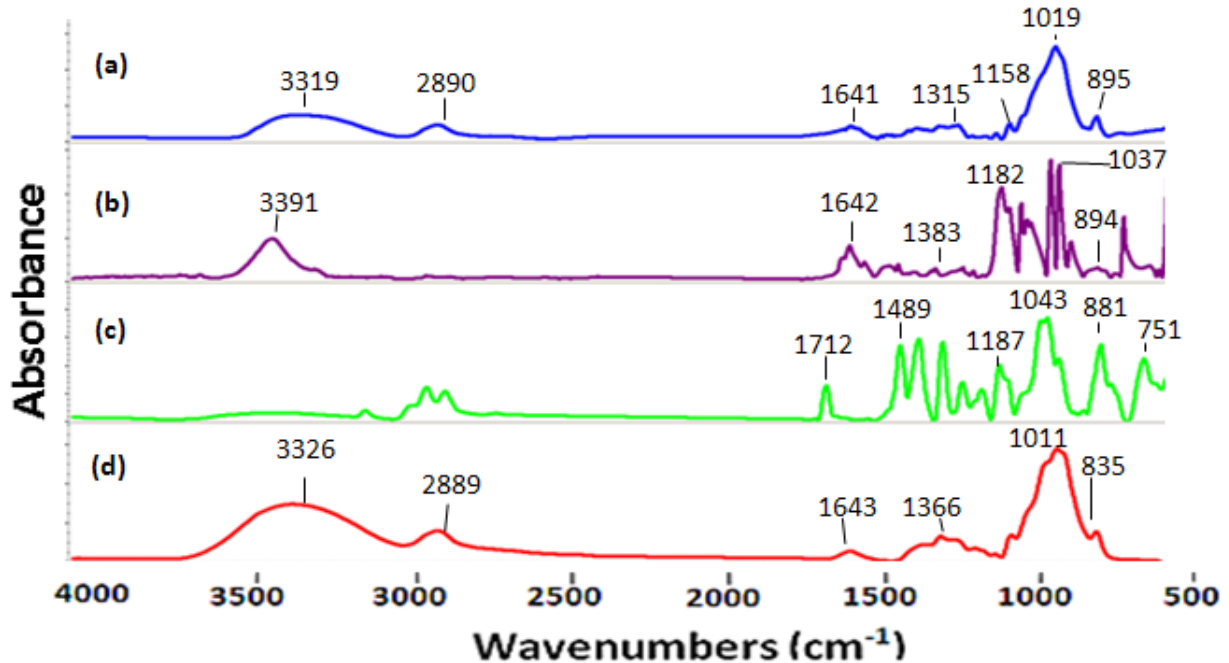


Figure 26: FTIR spectra of (a) PEDOT coated viscose fiber with ferric (III) chloride, (b) PEDOT coated viscose fibers with ferric (III) tosylate, (c) pure PEDOT, and (d) pure viscose

8.4 Stretch sensing properties

Knitted structures of PEDOT coated viscose fibers were tested on a cyclic tester. Due to piezoresistive properties, resistance values vary when dimension of the knitted structures changes from stretch to relaxed position and vice versa. 50%-100% stretch of the original length of the samples was applied to the knitted structures and resistance values were checked.

8.4.1 Resistance measurements at 50% stretch

Initially, 50% stretch of the original length of the knitted sample was applied. Fig. 27 shows that during extension, the resistance value drops to almost 30 k Ω and it increase to almost 44 k Ω at relaxation point of the knitted sample. This trend of drop and increase in resistance at extension and relaxation points of knitted sample remain almost same for 600sec. When knitted sample is at extension point, the loops become straighter which allow the current to pass through more easy and resistance decreases. Whereas at relaxation point, loops become more entangle which increase resistance values of knitted samples.

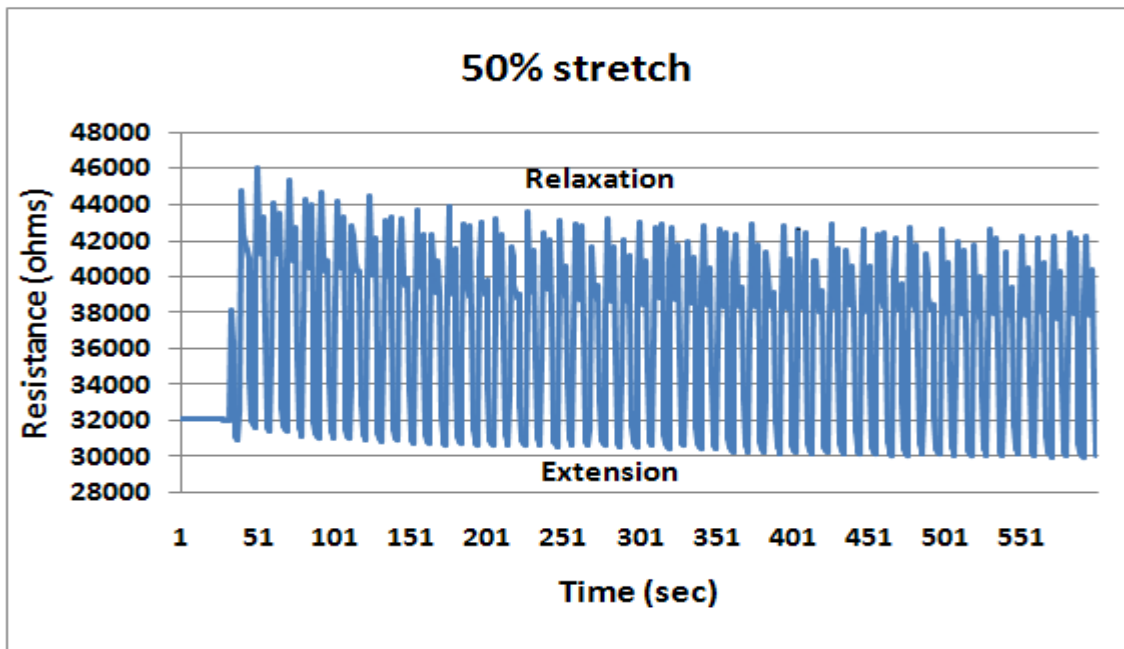


Figure 27: Resistance values at stretch and relax position of knitting samples of PEDOT coated viscose fiber at 50% stretch of samples for 600 sec (20 cycles)

8.4.2 Resistance measurements at 100% stretch

Knitted samples were stretched to 100% of the original length of the knitted samples. Fig. 28 shows that at 100% stretching, resistance of knitted structure has been dropped up to 23k Ω which was 30 k Ω in the case of 50 % stretching. Resistance values at relaxation increased as compare to 50% stretch and it reach to between 45-47 k Ω which was in between 42-45 k Ω in

case of 50% stretching. It was observed that after 100% stretching, stretch recovery of the knitted samples reduced to some extent and shape of the knitted structure impaired which could be one of the reasons of increase in resistance at relaxation of knitted samples. At extension point, because 100% stretching is applied therefore loops become straighter then with 50% stretching. Therefore, resistance values decreases further more. Overall trend of the experiment shows that resistance values at extension and relaxation points remains almost same for 600 sec even when 100% stretch was applied.

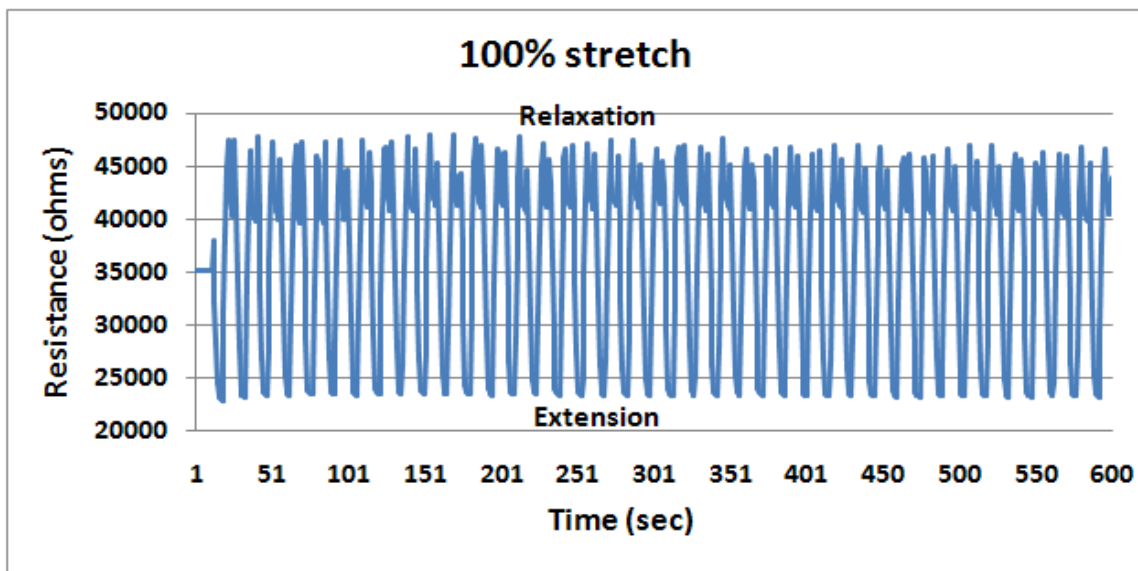


Figure 28: Resistance values at stretch and relax position of knitting samples of PEDOT coated viscose fiber at 100% stretch of samples for 600 sec (20 cycles)

8.5 Washing effects

Washing have been performed on knitted samples and PEDOT coated viscose fibers separately.

8.5.1 Knitted samples

Washing of knitted samples was performed on A type washing machine using gentle wash operational mode. Although, PEDOT is insoluble in water but due to the mechanical forces in washing some of the PEDOT coating removed from fibers but it do not removed completely from the fibers. Fig. 29(a) shows the picture of knitted structures of PEDOT coated viscose fibers before washing and fig 29 (b) shows picture of knitted sample after washing. Presence of dark blue color on fibers in fig. 29 (b) shows that after washing PEDOT is still present on fibers.

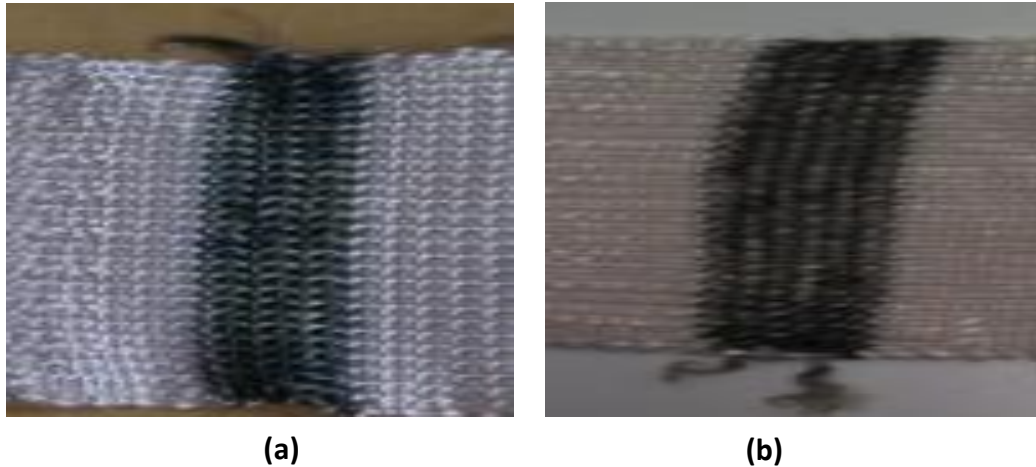


Figure 29: Knitting samples (a) before washing, (b) after washing

Fig. 30 and 31 shows that resistance values increased a lot after washing but resistance behavior of the knitted structures remain same at extension and relaxation points. It was observed that after washing stretch recovery of the knitted structures of PEDOT coated viscose fiber were decreased. Fig. 30 shows result taken at 50% stretch was applied to the original length of the knitted samples. Resistance values of the knitted sample increased and reached to nearly 2500 k Ω at relaxation point and decreased to below 500 k Ω at extension point. The difference of resistance at extension and relaxation point is quite high as compared to the before washing measurements.

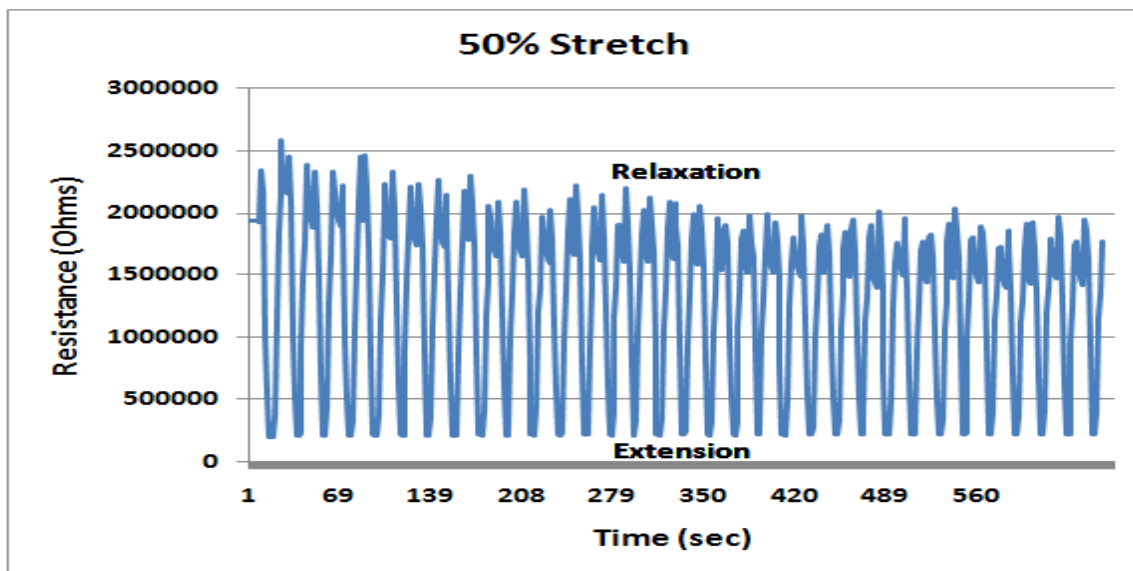


Figure 30: After washing resistance measurement at stretch and relax position of knitted structure of PEDOT coated viscose fiber max. 50% of samples for 600 sec (20 cycles)

In fig. 31 it can be illustrated that when 100% stretching applied to washed knitted samples, resistance of knitted structures start from very high values at relaxation point, but after one cycle it decreased and become steady. It can also be seen from the fig. 31 that resistance values do not decrease as much at extension point as compared to 50% stretching. As at 100% stretching, loops become straighter therefore resistance should decrease but because of the removal of PEDOT coating, aligned loops might be do not have the continuity of PEDOT coating therefore resistance increased. High difference in resistance values at extension and relaxation of knitted structure can also be seen from the graphs. It was observed that stretch recovery of the knitted structures was poor after washing especially when 100% stretch was applied.

This huge difference in resistance values at relaxation and extension of knitted structures shows the existence of stretch sensors properties even after washing.

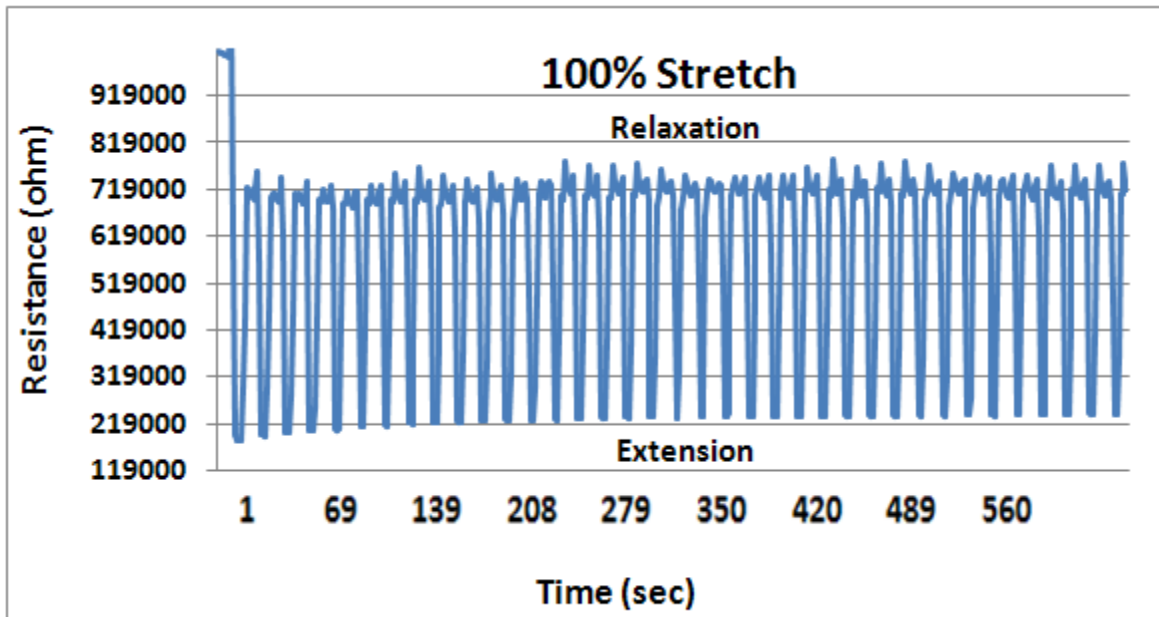


Figure 31: After washing resistance measurement at stretch and relax position of knitted structure of PEDOT coated viscose fiber max. 100% of samples for 600 sec (20 cycles)

8.5.2 PEDOT coated viscose fibers

Electrical Properties:

It was observed that after hand washing of PEDOT coated viscose fibers with tap water, fibers color was still darkish blue which means coating was not removed totally from the fibers. Fig. 32 shows the resistance values of the PEDOT coated fibers before and after washing (with intense and normal stirring). Graphs shows that after every washing either with normal or intense

stirring, resistance of the PEDOT coated viscose fibers increased but fibers are still conductive. As described above that PEDOT is insoluble in water but mechanical forces in washing remove PEDOT coating from fibers. It can be observe from the graph that increase in resistance is more in the case of intense stirring because it put more force on the PEDOT coating due to which more coating might be removed from the fibers and resistance values increased. Fig.32A illustrated the hand washing with normal stirring and it shows that resistance values increase after every wash which means PEDOT coating removed after every wash. Fiber resistance after hand washing with intense stirring of PEDOT coated viscose fiber can be seen in fig 32B. It shows that increases in resistance is more after 1st and 2nd wash as compared to samples which are washed with normal stirring.

It means after every washing (normal or intense stirring) coating of PEDOT polymer was removed from the fiber but intense stirring removed more coating because more mechanical force was applied in form of stirring.

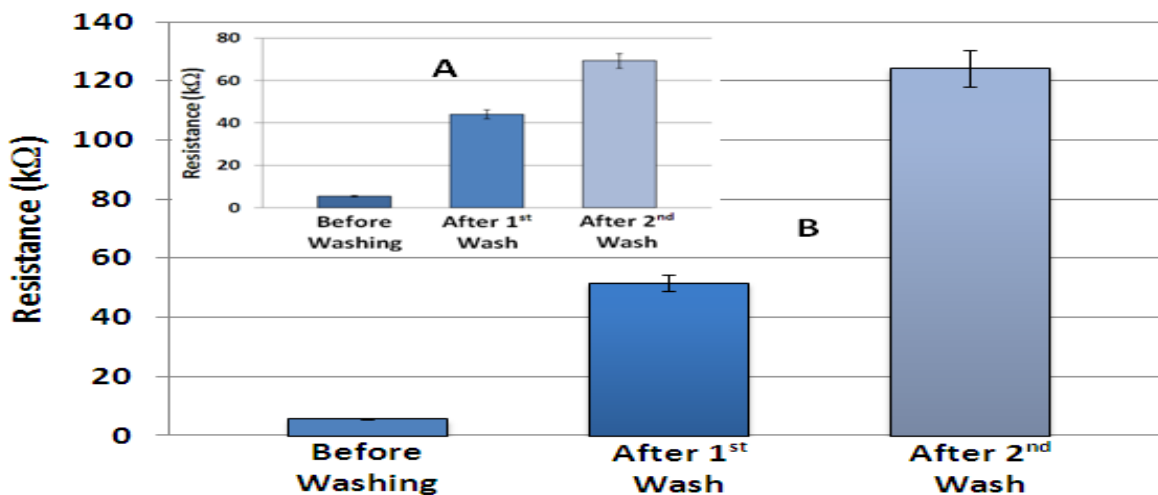


Figure 32: Effect of washing cycles on resistance values of PEDOT coated viscose fibers, (A) with normal stirring, (B) intense stirring

Mechanical Properties:

Strength of the PEDOT coated fibers decreased a lot after washing. Table 8 shows that pure viscose have maximum strength 61.3 and without washing fibers have strength 29.7. But in case of normal stirring, strength reduced to 24.1 N and reduced even further to 10.6 N when intense stirring applied. There are several points which can be considered when discussing the decrease of fibers strength with washing. First it might be happens because of the tendency of the viscose fiber that it absorbs water readily and swells. This swelling opens the twist of the fibers and causes reduction in physical strength of the viscose fiber. Secondly, when stirring is applied it put more mechanical force on the fibers which are already swelled and untwisted to some extent. So, it can be evaluated from the table that stirring plays important role with respect to fibers strength, that is, higher the stirring rate lesser the strength of the fibers. It can be seen from the results that after washing with intense stirring, fibers strength decrease almost 3 times as compared to without washing and washing with normal stirring.

Table 8: Mechanical properties after 2 time washing with normal and intense stirring

Sample Type	Strength (N)	
	Avg.	SD
Pure viscose	61.3	±5.3
Without Washing	29.7	±5.0
Washing Normal Stirring	24.1	±1.4
Washing intense stirring	10.6	±5.2

Thermogravimetric analysis:

After washing, in order to check the wt. % of PEDOT coating present on the surface of viscose fibers, TGA analysis was performed on PEDOT coated viscose fibers washed with intense and normal stirring. TGA of pure viscose fibers, pure PEDOT were already taken and put them in the graph to compare the thermal behavior of the washed samples with them. Thermogram of pure viscose fig 33(a) shows the stability of wt % of the viscose fibers upto 350°C but after that it decrease drastically. Thermogram of pure PEDOT fig 33(e) shows that the weight loss of PEDOT is quite high in 150-300°C temperature region but after that it becomes stable. The thermal behavior of PEDOT coated viscose fibers without washing fig. 33(d) shows the presence of PEDOT due to which weight lost is not as high as in case of pure viscose between 200-350°C and also in between 400-550°C. Thermal degradation of PEDOT coated viscose fibers with normal stirring fig 33(c) shows that, the weight loss is very similar to that in case of pure viscose between the temperature 200-350°C. Also, thermal behavior of PEDOT coated viscose fibers washed with intense stirring fig. 33(c) is similar to pure viscose and PEDOT coated viscose fibers with normal stirring. The weight loss for both PEDOT coated viscose fibers with normal and intense stirring is same with pure viscose at 400-600°C and remaining weight % at 600°C for washed samples is also same with that of pure viscose. Therefore, it can be illustrated from the results that, after washing either with normal of intense stirring PEDOT coating is mostly removed from the fibers due to which thermal behavior of the washed samples become more like to that of pure viscose.

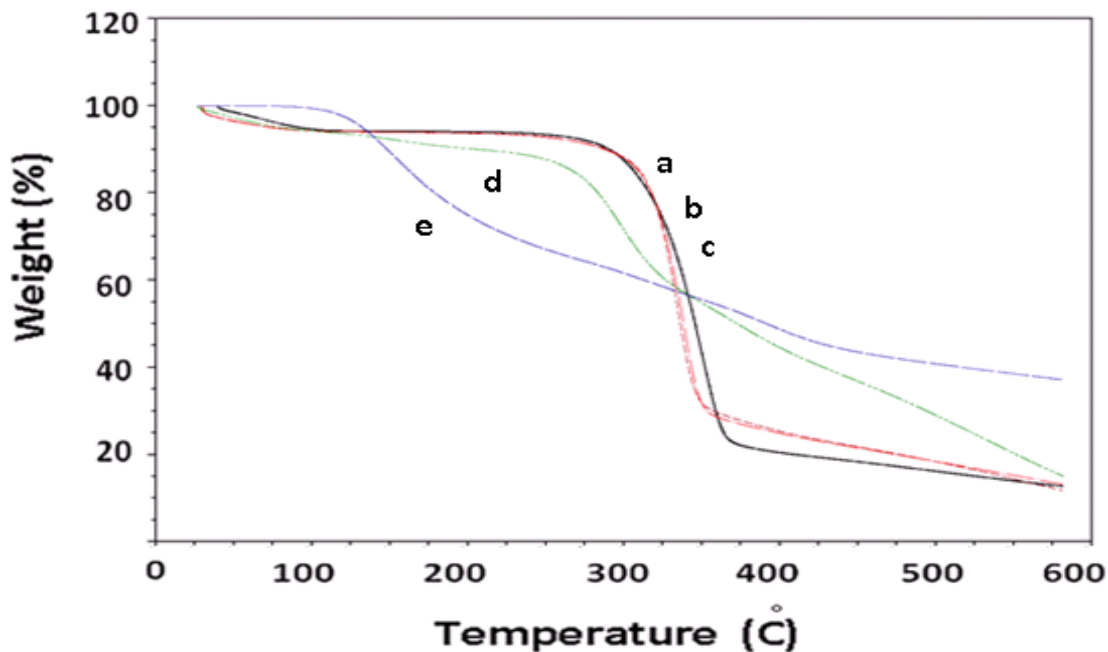


Figure 33: TGA analysis of (a) pure viscose, (b) PEDOT viscose fiber washed with normal stirring (c) PEDOT coated viscose fiber washed with intense stirring, (d) PEDOT coated viscose fiber without washed (e) pure PEDOT

9 Conclusions

This thesis demonstrates the preparation of PEDOT coated viscose fibers with oCVD process using different solvent for surface cleaning, comparison of oxidant ferric (III) tosylate and ferric (III) chloride, effect of drying time and temperature of oxidant treated fibers, knitted structures of PEDOT coated viscose fibers and washing of knitting structures as well as PEDOT coated viscose fiber. TGA and FTIR analysis show that more quantity of PEDOT is deposited on viscose fibers in case of oxidant ferric (III) tosylate but it gives high resistance values even after more deposition of PEDOT polymer. It can be conclude from the results that using ferric (III) chloride, good electrical properties can be achieved but mechanical properties are not as good as with using ferric (III) tosylate. Although mechanical properties are good with ferric (III) tosylate but electrical properties decrease. Therefore, oxidant can be selected according to the properties required in the conductive fibers with respect to their final usage. Electromechanical testing of solvent treated PEDOT coated viscose fibers shows the decrease in fiber strength as well as decrease in electrical properties of the PEDOT coated fibers. Drying of oxidant treated viscose fibers prior to polymerization step at high temperature for longer period of time decreases the surface resistance of the fibers and increases the fiber strength but at high temperature such as 60°C, fiber strength decreases again. TGA analysis of hand washed PEDOT coated viscose fibers shows that PEDOT coating removed after washing, but fibers conductivity still persist to some extent which enhances the hypothesis of PEDOT penetration inside the viscose fibers. Tensile testing of hand washed sample shows the decrease in fiber strength which is obvious because of the tendency of viscose fibers to absorb water and swell. . Cyclic testing of knitted structures shows that decrease in resistance at extension point and increase in resistance at relaxation point. This property of change in resistance with change in dimension favors the possible use of knitted structures as stretch sensors. Although, resistance of knitted structures increases after washing but still they show the same piezoresistive behavior. Washing also decreases the stretch recovery of the knitted structures, therefore different knitted structures of PEDOT coated viscose fibers can be prepared and evaluated before and after washing.

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Appendix A

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Table 1 — Washing procedures for horizontal rotating drum machine — Type A^a

Procedure No.	Agitation during heating washing and rinsing	Total load (dry mass) a kg	Washing			Rinse 1			Rinse 2			Rinse 3			Rinse 4			
			Temp. b °C	Liquor level c, d cm	Wash time e min	Cool down f	Liquor level c cm	Rinse time e, g min	Liquor level d cm	Spin time e min	Liquor level c cm	Rinse time e, g min	Liquor level d cm	Spin time e min	Liquor level d cm	Rinse time e, g min	Spin time e min	
1A ^h	Normal	2 ± 0,1	82 ± 3	10	15	Yes ⁱ	13	3	3	13	3	13	2	13	2	13	2	5
2A ^h	Normal	2 ± 0,1	60 ± 3	10	15	No	13	3	3	13	3	13	2	13	2	13	2	5
3A ^h	Normal	2 ± 0,1	60 ± 3	10	15	No	13	3	3	13	2	13	2	13	2	13	2	—
4A ^h	Normal	2 ± 0,1	50 ± 3	10	15	No	13	3	3	13	2	13	2	13	2	13	2	—
5A	Normal	2 ± 0,1	40 ± 3	10	15	No	13	3	3	13	3	13	2	13	2	13	2	5
6A	Normal	2 ± 0,1	40 ± 3	10	15	No	13	3	3	13	2	13	2	13	2	13	2	—
7A	Gentle ^k	2 ± 0,1	40 ± 3	13	3	No	13	3	3	13	3	13	1	13	2	13	2	—
8A ^l	Gentle ^k	2 ± 0,1	30 ± 3	13	3	No	13	3	3	13	3	13	—	13	2	13	2	—
9A ^l	Gentle	2	82 ± 3	10	12	Yes ⁱ	13	3	3	13	3	13	—	13	2	13	2	—
Simulated Hand wash	Gentle ^k	2	40 ± 3	13	1	No	13	2	2	13	2	13	2	—	—	—	—	—

^a For procedures 1A, 2A and 6A an alternative load of 5 kg and for procedure 7A an alternative load of 1 kg is recommended where articles are being tested for washing efficiency. possible abrasion sensitivity or similar effects.

^b All filling temperatures for wash and rinse are (20 ± 5) °C.

^c Liquor level is measured from the bottom of the cage after the machine has been run for 1 min and allowed to stand for 30 s.

^d The volumes of liquor corresponding to the quoted levels are determined by a separate test using a graduated measuring vessel.

^e The stated times may have a tolerance of ± 20 s.

^f Cool down: top up with cold water to 13 cm level and agitate for a further 2 min.

^g Rinse time is measured when liquor level is reached.

^h Heat to 40 °C, hold for 15 min before heating to wash temperature.

ⁱ For safe laboratory practice only.

^j Short spin or drip dry.

^k No agitation during heating.

^l This programme is retained because it is part of ISO 3758.