Fabrication and Characterization of an Electrically Conducting Polymer -based Prototype of a Touchscreen Device

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Conducting polymers belong to a class of polymers, which can conduct electricity. This ability rises from the conjugated nature of the polymer backbone, which allows charges to travel across and along them. Conducting polymers have attracted interest for different applications due to their beneficial features, such as high conductivity, sustainability, and high mechanical stability. These make them good replacements for metal oxides used as conducting materials, for example in touchscreens.

A touchscreen is a sensor that can sense a touch input on the surface. There are several different methods for accomplishing this, resistive and capacitive methods being the most used one's accounting roughly 95 % of all touchscreen applications.

In this study, vapor phase polymerization was used to manufacture conducting polymer thin films from 3,4-ethylenedioxythiophene using iron(III)*p*-toluenosulfonate as the oxidant and pyridine as an inhibitor. The films were then used to construct a prototype of a simple surface capacitance touchscreen device.

Keywords: Conducting polymers, vapor phase polymerization, capacitive touchscreen, poly(3,4-ethylenedioxythiophene), PEDOT

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List of Abbreviations

AFM	Atomic force microscopy
CVD	Chemical vapor deposition
oCVD	Oxidative chemical vapor deposition
EDOT	3,4-ethylenedioxythiophene
Fe(Tos)	Iron(III)(*p*-toluenosulfonate), iron(III)(tosylate)
P-cap	Projected capacitance
PEDOT	Poly(3,4-ethylenedioxythiophene)
PET	Poly(ethylene terephthalate)
PSS	Poly(styrene sulfonate)
VPP	Vapor phase polymerization

1 Introduction

1.1 Conducting Polymers

The modern study of conducting polymers began in 1970s, when Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa discovered a new class of electrically conducting polymers. This discovery rewarded the Nobel prize in chemistry in 2000 for the discovery and development of conducting polymers.[1]

However, the first time conducting polymers were prepared was in 1862 by scientist Henry Letheby, when he prepared polyaniline via anodic oxidation of aniline. He noted that polyaniline was conductive and it had electrochromic properties.[1,2] The reaction scheme for electro-oxidation process of aniline on carbon electrode was suggested by Yasui[3] in 1935. The next step in the journey was taken in the in the 1950s by Khomutov and Corbachev when they discovered autocatalysis during electro-oxidation of aniline. In 1962 free radical reaction for polymerization of polyaniline was proposed when David M. Mohilner, Ralph N. Adams and William J. Argensinger, Jr.[4] performed a reinvestigation of anodic oxidation of aniline in aqueous sulfuric acid solution at a platinum electrode.

As the studies continued, different polymers and more attributes of conducting polymers were discovered, such as the discovering that doping the polymer increases the conductivity of the polymer significantly. This discovery launched a new trend in the study of conducting polymers.[5,6]

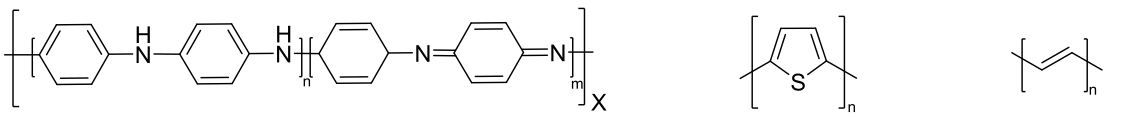

Figure 1: Examples of different conducting polymers.

By the end of the 1980s the method of electron transport was mostly understood and agreed to happen via electron exchange reaction between neighboring redox sites. This happens by the movement of delocalized electrons trough a conjugated system in the conducting polymers. Also in the end of the 80s the first applications of the conducting polymers in devices $FeCl_3$ also appeared as Heeger made diodes by casting polythiophenes from solution onto electrode surface.[1]

1.2 Intrinsic Conductivity

Materials can be divided into three categories according to their ability to conduct electricity: conductors, semiconductors, and insulators. Their properties arise form overlapping of the individual molecular electronic sites. These electronic bands are split in two bands, valence and conduction band. Material can conduct electricity, if sufficient amount of electrons can be excited from the valence band to the conduction band.[7]

For conductors such as metals, the orbitals in the bands are continuous, making the excitation of the electrons to the higher energy states easy with only small amount of energy required. Temperature affects the conductivity, as the thermal energy excites the electrons to the higher energy states. Conductors have some electrons at the conduction band even at temperature of T=0, and above that there is not any distinction between the occupied and unoccupied levels as the thermal energy keeps exciting the electrons to the higher conduction band. The conductivity does decrease at some point as the temperature rises due to the collisions between atoms and electrons disrupt the charge transport.[7,8]

Semiconductors and insulators in contrast have their energy states separated with an energy gap called band gap, and at the temperature T=0, their energetically lower bands, the valence band, is completely filled, while the higher band, the conduction band, is completely empty. As the temperature rises, some of the electrons can make their way into the conduction band and make the material conductive. These materials are called semiconductors. If however the band gap is large enough, the electrons cannot cross the gap to the conduction band and thus the material cannot conduct electricity, making it an insulator. [7,8]

Saturated polymers, such as polyethylene, have all their valence electrons used in covalent σ-bonds. This results in a very large band gap between valence and conduction band and these polymers act as insulators. In conjugated polymers, π-system is formed along the polymer backbone, as the carbon atoms (sometimes others, like nitrogen, are involved) usually responsible for the backbone form three σ-bonds and the remaining p-orbitals form the π-system. This conjugated π-system is the main feature for organic semiconductors, from small molecular systems to large polymeric systems and a band gap of 1.5 – 3 eV. Organic semiconductors also involve ionic molecular states in the movement of charges, as elaborated later.[8–10]

This electrical conductivity is an intrinsic property of the conducting polymers, which means that there is not any conducting filler material in the matrix as the polymer

itself conducts electricity. However, in pristine condition, the conjugated polymers do not conduct. This means that the polymer must be “doped”, which refers oxidising or reducing the polymer backbone either chemically or electrochemically. In doping electrons are either introduced or removed from the backbone, where the former introduces more electrons into the structure and latter forms a hole in the structure, which work as charge transporters. This is called n- and p-type doping respectively. Academic interest lies in the p-doping as the positive charge carriers result in more stable products.[7,8]

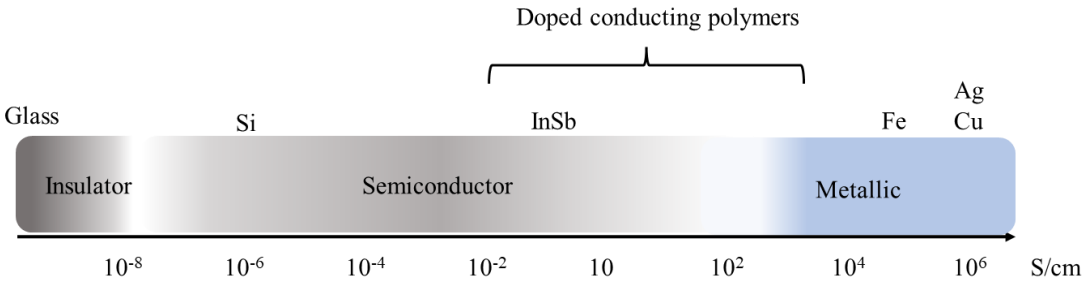

Figure 2: The conductivities of different materials.

The semiconductor band structure allows for excitation or removal or addition of the electrons. When excited thermally or with photons, the electron is moved from the valence band to the conducting band, which results in typical excited state behaviour, such as photoluminescence. Chemically or electrochemically oxidizing the polymer removes electrons from the valence band, which results in presence of charges in the polymer structure. The charges are delocalized over several monomer units. The presence of charges also allows relaxation of the geometric conformation to more energetically favoured conformation. In reduction of the polymer, electrons are added to the conduction band. This introduction of charges is called doping, name taken from condensed materials physics.

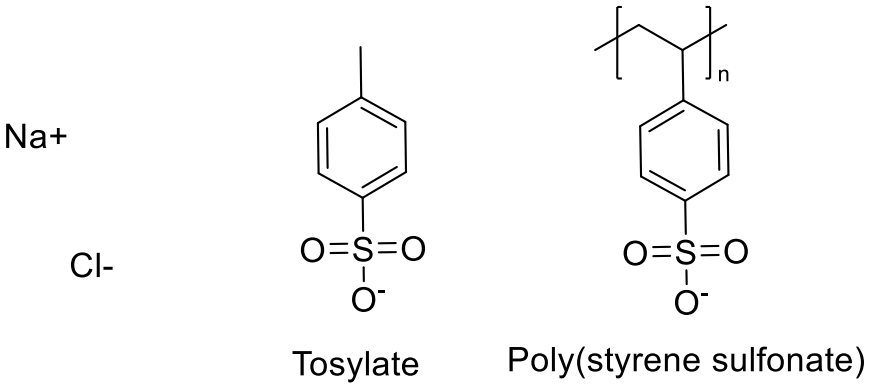

Figure 3: Some common dopants.

The cations or anions that either perform the reduction or oxidation of the polymer backbone or that are injected into the structure to balance the charges introduced are called dopants. Dopants are usually incorporated into the structure during the synthesis of the conducting polymer, but the doping can be performed separately after polymerization process. These dopants also affect the structure of the polymer as they can be just simple anions and cations or even small molecules and polymers (Fig. 3).

The positive or negative charges produced by the dopants are called polarons and bipolarons. The naming of the polarons is remnant from the material physics as was the case with doping and dopants before. These polarons are delocalised over several monomer units in the polymer backbone, giving rise to the conductivity.[7,8]

Polarons are local geometric distortions of the ground states. This requires distortion energy, which gives rise local distortion. This in turn gives rise of localized electronic states in the gap between the conduction and valence band. This distortion results in a small local uplift of the valence band and downshift of conduction band energetically. From this the polaron can be described as radical cation locally associated with a structural distortion in conducting polymers.

Removal of electron creates a local distortion as described above. When another electron is removed from another part of the structure, we have two polarons in the structure, a polaron pair. If however, the second electron is removed from the polaron itself, it creates a bipolaron. For bipolaron to be generated, larger amount of distortion energy is required, which in turn results in a greater sift in the conduction and valence bands. Bipolarons are also more stable in extended structures and are delocalized over several, usually 6-8, monomer units. This makes bipolarons preferred state over two individual polarons. In shorter, oligomeric structures with lower doping levels the polaron pairs are energetically more favoured over bipolarons.[7,11–13]

1.3 Polythiophenes

Polythiophenes are a wide variety of conducting polymers which are based on thiophene, a five-ring of carbon and sulfur. Since the thiophene-monomer is easily modified by attaching sidechains to the carbon atoms in the 3- and 4-positions, the variety of different polythiophenes is rather large. The substitution from these positions force the polymerization taking place from the 2- and 5-positions.

Lately polythiophenes have gained more interest in different applications, such as in photovoltaics, organic light emitting diodes, and touchscreens, due to their properties

suiting these applications. These properties include high stability both in doped and undoped state, ease of modification and ease of processibility in solution.[14]

1.3.1 Poly(3,4-ethylenedioxythiophene), PEDOT

One of the derivates that is getting more and more attention is poly(3,4-ethylenedioxythiophene) (PEDOT), as its properties of high conductivity and high stability that stems from the structure are highly sought after. The high stability of the structure arises from the two oxygen atoms in the structure that act as the balancing for the charges.[15]

PEDOT was created by the researchers at Bayer Ag in the latter half of the 1980s. It boasted lot of good properties including high conductivity, stability and near transparency in oxidized form. Initially the undoped, pristine PEDOT-polymer is insoluble in water, but doping it for example with poly(styrene sulfonate) (PSS) changes the properties of the system creating a water soluble polyelectrolyte system.[14]

The hydrophilic nature of PEDOT:PSS can be both good and bad thing. Hydrophilic nature makes the manufacturing, transporting, storage, and applying easier. On the downside, the finished products, often thin films, are also hydrophilic in nature, making them susceptible to moisture. This makes the use of the films in any applications unviable in humid conditions.[15,16]

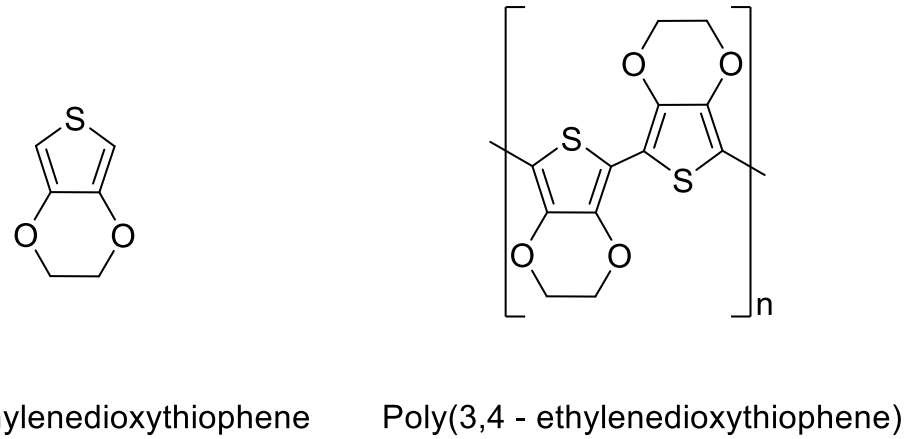

Figure 4: Structure of EDOT and PEDOT

To combat this downside, a new dopant p-toluenosulfonate, also called tosylate, has been used. The smaller size of the tosylate-ion decreases substantially the hydrophilic nature, making the polymer and the finished product more hydrophobic, which in turn

makes the polymer more usable even in humid conditions. The smaller size of the tosylate-ion also increases the conductivity of the polymer compared to the use of PSS. As PSS is longer polymer than PEDOT, it constricts the whole structure, preventing the charges from moving properly. The small tosylate being a single molecule allows PEDOT to relax and adopt better, more linear orientation, allowing the charges to move with ease.[16]

1.3.2 Manufacturing of PEDOT

There are several routes for making PEDOT-polymers, but the two most important are the chemical oxidation method and the electrochemical method. Commercially produced PEDOT is done via the chemical oxidative method, as it allows manufacturing of the polymer in large quantities. Using electrochemical methods only yields small quantities at the time, and thus it is used mostly to study the behavior of the polymer.

Oxidative polymerization is usually done with ionic oxidants, iron(III) preferred but other metal ions with suitable high oxidation states, such as magnesium(IV), can also be used. The solubility requirements for the oxidants are determined by the solubility of the 3,4-ethylenedioxythiophene-monomer (EDOT-monomer) in the solvent used. Usually different alcohols are used, as EDOT has limited solubility in water but is miscible in alcohols. For this reason, alcohol soluble salts, usually sulfonic acids such as *p*-toluenosulfonic acid, are used. Later modifications were made by adding a base, such as imidazole or pyridine, to act as inhibitor and using elevated temperatures. The inhibitor has three major roles in the reaction: it reduces reactivity, thus slowing down the reaction rate of the polymerization, it promotes formation of higher molecular weight chains, and it prevents the polymer from being over-doped. In addition, some form of an adhesion layer on the substrate may be needed for the film to stick to the substrates surface.[8,17,18]

The classic in situ method for polymerization then begins by mixing the chemicals in two steps. In the first step the oxidant and inhibitor are mixed together. In the second step the monomer is added to the mixture and immediately after addition the coating of the substrate must be done, for example by spin coating. The film is then dried, washed with solvent, usually with water, and is then dried again under nitrogen stream.[8,15]

The polymerization process takes place in two steps. In the first step oxidative polymerization of EDOT occurs, forming neutral, undoped PEDOT-polymer. In the second step the pristine undoped PEDOT is doped by the excess of the oxidant still present. The polymerization itself happens via radical cation polymerization, where the

monomer is first oxidized by the oxidant, forming a radical cation. These radical cations then form a charged dimer, which then eliminates a proton to form a neutral dimer. This dimer can be then oxidized again, and then it continues the coupling process with other charged cations or oligomeric structures. Then the polymer is oxidized once more, creating positive charges on roughly every third or fourth monomer sub-unit. The dopants then interact with the polymer, thus balancing the charges within.[8,19,20]

Films made with this method receives conductivities in the area of 400-600 S/cm, though the materials and coating methods will affect the results. Other methods utilizing oxidative polymerization can exceed these values, for example using vapor phase polymerization (VPP), conductivities of 1000-1200 S/cm. [8]

The process of electropolymerisation of conducting polymers is still bit unclear. Currently the most widely accepted, with some modifications, concept was proposed by Diaz et al.[19], and it bears similarities to radical or ionic polymerization. They used pyrrole in their study, and the pyrrole-monomers dimerize at their α-position, creating a double-charged σ-dimer. To form an aromatic neutral dimer, a proton is eliminated from the structure. The dimer is easily oxidized due to its more conjugated structure. After oxidation, the dimer then couples with a monomeric radical cation and after coupling, a proton is eliminated again to form a neutral trimer.[11]

The coupling steps was thought to be the rate determining step, but it seems that it is the elimination of the proton from the σ-dimer that determines the rate of the reaction. At the same time the acidity of the dimer decreases as the chain grows as a function of the length. The stabilization effect of large conjugated oligomeric structure makes elongation of the chain via coupling of the monomeric species unlikely.

The proton elimination was thought to be a fast reaction in while also being the driving force behind the re-aromatizing the system. In reality, the rate of proton elimination from the dimeric coupling intermediates can decrease substantially, where charged σ-dimers with more than four units in a conjugated system are quite stable. This stability means that the proton is eliminated only when the intermediate is oxidized with higher charging levels, thus the reactivity of the whole system is increased.[11]

Medium sized oligomeric chains cannot grow by coupling with monomeric or dimeric species as the intermediates do not eliminate their protons. These oligomeric intermediates and the radical cations tend to couple amongst themselves as a part of the oligomerization process.[21] In studies with donor-substituted thiophenes the oligomerization process begins in the solution. During the reaction dimers are first formed

and then these form tetramers, then octamers and so on. Additional coupling with larger oligomers or radical cations, forming for example trimers, then hexamers and so on, similar to dimeric species.[22,23] During the initial phase of electropolymerization oligomers form in solution and the deposition process depends on the electrodes chemical nature and reactivity.[11,24]

Anodic electro-synthesis of PEDOT was done the first time in the 1980s. Thiophene itself is hard to polymerize using electrochemical methods as its oxidation potential is relatively high. To help with the polymerization process, substitution at the 3- and 4-positions in the monomer structure can be done, since they prevent α-β- and β-β-couplings in the structure. This in turn yields in longer chains with longer conjugation.[8,15,25]

At room temperature, PEDOT has an irreversible oxidation peak at E_{peak}^{ox} =1.2 V, and the reversesweep shows two peaks at negative potentials of -0.2 V and -0.7 V. These peaks correspond to the reduction of the initially deposited polymer. They also act as evidence of nucleation process taking place on the electrode. Redox-system of the polymer is found around -0.7 to -0.4 V as the polymer is deposited on the electrode by repetitively sweeping between positive and negative potentials.

Monomeric, dimeric, and trimeric EDOT all result in PEDOT without any changes to the conjugation length. The anodic polymerization method can be used to form both electrode supported and free-standing films. Different methods exists for the electrochemical polymerization of PEDOT, including potentiostatic, galvanostatic, and repetitive multisweep voltametric methods.[25]

Electro-polymerization and different wet chemical behavior studies are used in paraller to study the properties of the conducting polymers. One of the advantages of using electro-chemical methods is the small amount of material needed for the study, as milligram and submilligram quantities of the chemicals are needed. Other advantages are the fast speed and the high accuracy of the measurements, and the high precision mean that the measurements can be made under the same conditions, helping the comparison between different systems.[25]

Drawbacks for the electro-polymerization methods include small amounts of the product produced and the insolubility of the product. The substrate also needs to be conductive, limiting the available materials for substrate usage. For these reasons, electro-chemical methods are rarely used in the industrial and commercial manufacturing of PEDOT or other conducting polymers. The conductivity values mirror those of chemical oxidative polymerization, reaching values roughly 400-600 S/cm. [8,25,26]

The drawbacks of low yields and lower conductivities of electrochemical methods were the reasons why vapor phase polymerization (VPP) was chosen as the manufacturing method for this study. Also, the requirement for conducting surface for the electrochemical process was an obstacle, since one of the aims of the study was to find a replacement for the conducting materials used today.

1.4 Chemical vapor deposition, CVD

Chemical vapor deposition (CVD) is a deposition method of major use in thin film manufacturing. While pure elements can be used in CVD, most of the time they are used as compounds. The simplest method used in CVD starts by flowing precursor gas/gases into reaction chamber, where they react nearby or on a substrate placed on a heated surface. This leads to thin film formation on the substrate. By-products and unreacted precursor gas(es) are then vented out from the chamber.

There is a large variety of different methods for CVD, such as hot wall and cold wall processing, using pressures over and under the atmospheric pressures, and the temperatures range usually between 200 °C – 1600 °C. These methods can also be enhanced using plasma, ions, photons, and lasers. Hot filaments and combustion reactions can be used to increase the deposition rate and/or decrease in reaction temperature used.[27]

1.4.1 Oxidative Chemical Vapor Deposition, oCVD

OCVD is a single step deposition method, where both the oxidant and the monomer are in gaseous form and are delivered as such on to the substrate´s surface where the polymerization reaction takes places, forming a thin film. Since all the precursors are in gaseous form, the substrate itself can be practically anything in contrast to solution-based deposition methods, where the surface affects the reaction by interacting with the solvents. For example, using PEDOT:PSS dissolved in water for manufacturing films on a hydrophobic surface will be extremely difficult, whereas using them in gaseous forms without solvents circumvents this problem.[28]

Usually, when using conducting polymers, the following process is used: The substrate is placed inverted on a temperature-controlled stage inside a vacuum chamber. The inversion of substrate helps to prevent accumulation of particles on the surface. Oxidant, usually solids at room temperature, for example iron(III)chloride ($Fe^{III}Cl_3$), is heated in a crucible to get it to sublimate. Monomer, usually in liquid form, is also heated

to produce monomer vapor. Both of these are then guided to the substrate to react with each other and form a conducting polymer thin film.[28]

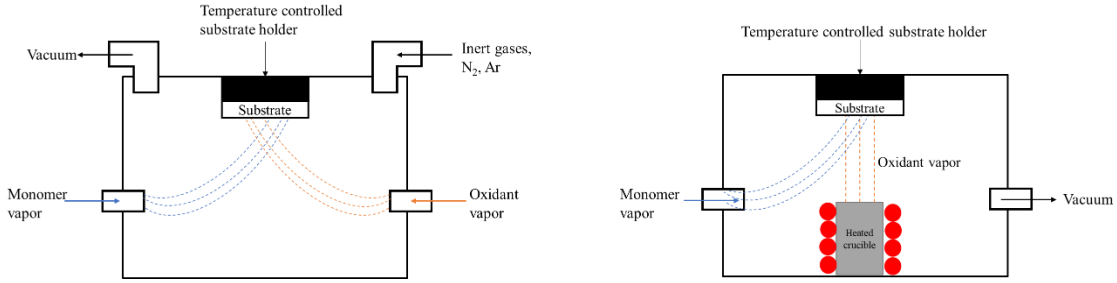

Figure 5: Different oCVD-cells.

1.4.2 Vapor Phase Polymerization, VPP

In contrast to the single step method oCVD, vapor phase polymerization (VPP) is a two-step process. First step is depositing a layer of oxidant, such as $Fe^{III}Cl_3$ or iron(III)p-toluenosulfonic acid ($Fe^{III}(Tos)_3$), on to a substrate. Methods used include for example spin coating, dip coating or sputtering and chlorination of a metallic thin film on the substrate. In the second step the oxidant covered substrate is placed in a chamber, either in ambient conditions or low vacuum pressure, filled with monomer vapor. The monomer vapor then reacts with the oxidant, polymerizing and forming a thin film on the substrate.[28]

After polymerization, the finished product is washed with solvent or solvents, usually with alcohols or acetonitrile. This is done to remove any excess of, unreacted oxidant, monomer and other byproducts. Other post-treatments can also be applied, for example annealing of the film on a hot plate.

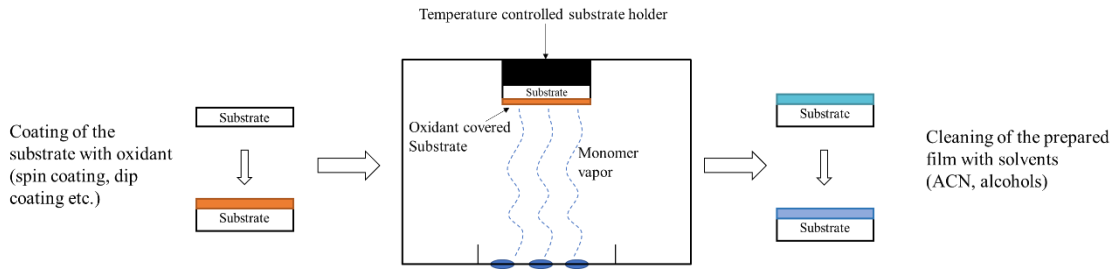

Figure 6: Basic method for VPP.

One report on VPP when used in manufacturing polymer thin films was in 1986 as Ojio et al. used the technique to form poly(vinyl alcohol)-polypyrrole (PVA-PPy)

composite film, where PVA film was coated with $Fe^{III}Cl_3$ to act as the oxidant and it was then exposed to pyrrole vapors. The properties of the resulting film were depended on the polymerization time, temperature and the concentration of the oxidant.[28]

Another tactic to coat the substrate with oxidant is to thermally evaporate or sputter a thin film of metal at the surface of the substrate, the film is then chlorinated to form a metal chloride surface that acts as the oxidant. The first time this method was used was using copper, which was sputtered on a substrate and then chlorinated. After chlorination, the copper chloride film was exposed to pyrrole vapor, forming a polypyrrole thin film. Other metal chlorides have been tried in thin film formation, such as gold, palladium, and iron.

First times, when VPP was used for PEDOT, the results were not ideal, as the conductivities were mostly below 100 S/cm. These films were made by dip coating ormicro-gravure roll coating the substrate with $Fe^{III}Cl_3$ dissolved in methanol. The substrate was then exposed to the EDOT-monomer vapors at ambient conditions.[28]

The results improved drastically when the oxidant was changed to $Fe^{III}(Tos)_3$ with pyridine.[29] The conductivities of the resulting PEDOT:Tos films exceeded 1000 S/cm. Further improvements of the films were made when Levermore et al.[30] introduced low vacuum pressure chamber to use with the VPP.

1.5 Touchscreens

Touchscreens are sensors comprised of a touch sensor and a controlled chip designed to drive and interpret the signals from the sensor and send them to the computer. Several methods for the sensing of the touch input exists and, in this study, we will focus on two of them, resistive and capacitive, since these two methods comprise almost 95% of the market of touchscreens and as the final prototype produced uses capacitive method.[31]

1.5.1 Analog Resistive Touchscreen

Analog resistive touchscreens are the oldest mass-produced touchscreen types, first commercialized by a company called Elograpchics in 1971. The first transparent screen was made in 1977. Analog resistive touchscreen works as a switch, where the layers need to be pushed together to produce a signal. Different variations exist, where the differences are mainly in number of wires, layer construction and optics.

Three different wiring schemes dominate the construction of analog resistive touchscreens, 4-, 5-, and 8-wire systems. The number of wires tells how many connections there are from the sensor to the controller. In 4-wire system, the wires are attached to bus bars at the edges of the conducting layers, two for X- and two for Y-axis. One layer acts as the X-axis and second as Y-axis. When the voltage is applied on the X-axis, the measurements are made from the Y-axis and when voltage is applied on the Y-axis, measurement is taken on the X-axis.[31]

In the 5-wire system, four wires are attached to four corners of the same conducting layer and the one left is attached to the second layer. The second layer acts as a voltage probe while the voltage is switched between two points on the first layer to sweep either the Y- or X-axis. This allows the screen to be always ready for touch input.

The biggest difference between the 4- and 5-wire systems is the lifetime of the sensor. 4-wire systems are usually rated for ~1 million touches, which equals roughly 100 000 characters drawn with a stylus. In contrast, 5-wire systems are usually rated for ~30 million touches, roughly 3 million characters drawn. The difference stems from the wiring and sensing method, since on the 5-wire system one layer is only used as a probe, not as resistive voltage divider. This allows the conducting layer used as the probe to degrade further before it affects the performance of the system.

8-wire system is constructed the same way as the 4-wire system, only difference being that instead of one wire per bus bar, there are two wires connected to the bus bar. This allows the voltage to be measured straight from the sensor. This eliminates the effect of the impedance arising from the wires connected to the controller, which in turn reduces drift during calibration.[31]

Advantages of the analog resistive touchscreen include low cost, wide availability, they work with any non-sharp objects and are easily sealed to meet IP65 or NEMA-4 standards. Disadvantages include poor durability, since the soft outer layer usually made from PET-film scratches easily, poor optical properties, since up to 20% of the light from the screen beneath can be lost to layer reflections, relatively high touch force required and lack of multitouch.

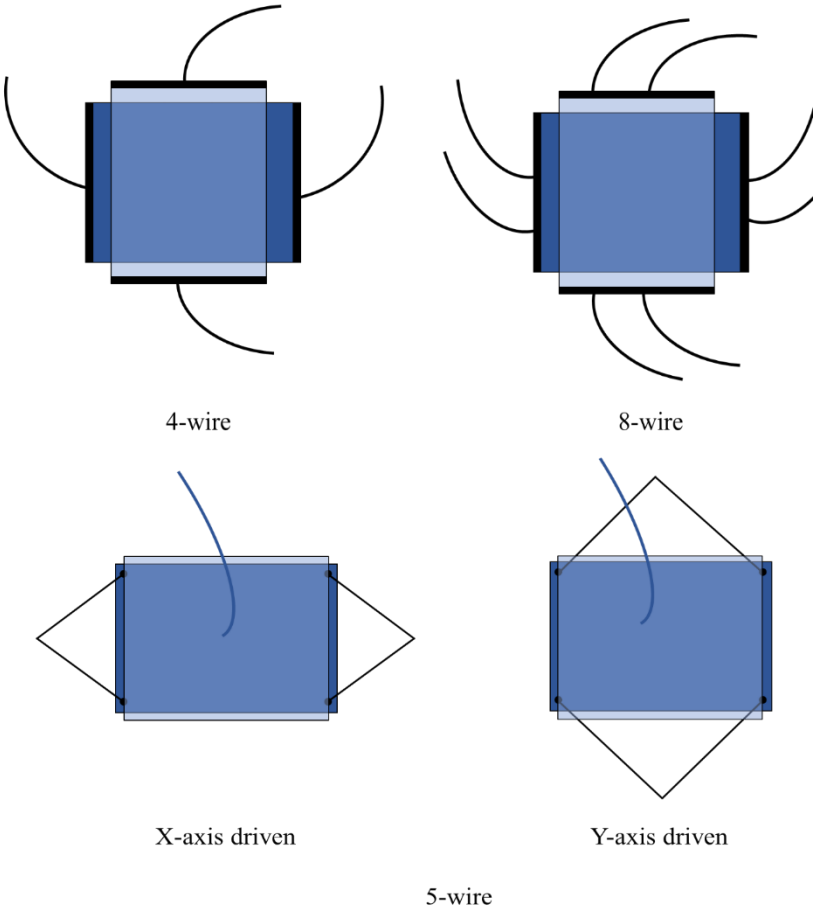

Figure 7: Structures of the dominating wire schemes.

Analog multitouch resistive device, AMR-device, was developed as an answer to the lack of the multitouch on regular devices. In AMR-device, the conductive layers are cut to strips, which are wired separately and positioned on top of each other. Every intersecting square acts as independent 4-wire touch sensor. The squares are quite large, 10-20 mm length on the sides, which prevents the touches to be too close as they will be sensed as one touch (Fig. 8). Making the sensor work properly is difficult, it is not much cheaper to produce compared to projected capacitive sensor and it still has all the rest of the disadvantages of analog resistive touchscreen discussed earlier.

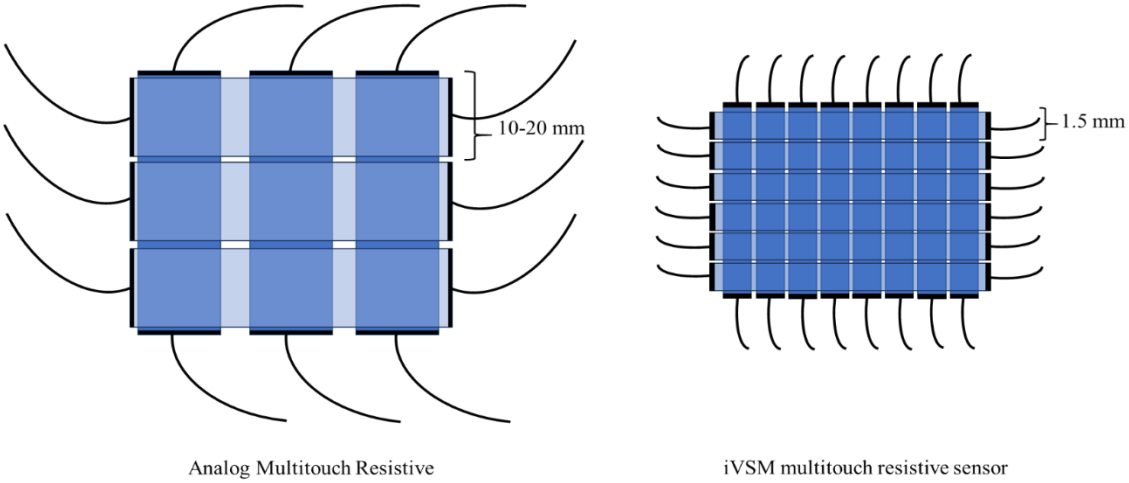

Figure 8: Electrode structure of AMR-sensor and iVSM multitouch sensor.

Stantums iVSM multitouch resistive sensor is slightly better alternative for AMR. The squares used are much smaller, 1.5 mm on the side, and they act as simple ON/OFF-switches instead of individual 4-wire sensors (Fig. 8). Better driver algorithms also improve the performance, but it still possesses the same disadvantages that plague AMR and basic analog resistive touchscreens.[31]

1.5.2 Capacitive Touchscreen

The basic construction of a surface capacitive touchscreen comprises of hard outer coating, usually glass typically 0.55, 0.75 or 1.1 mm thick, and underneath are layers of live patterned electrodes**,** conductive layer, back glass and optionally shielding layer. The outer glass makes the screen flush with rest of the surface and can be decoratively printed to hide the wiring of the sensor, tough nowadays as the bezels are constantly shrinking, the wires are folded beneath the screen. The glass can be chemically treated to increase resistance for chipping and breaking. Making the glass thinner leads to increased performance and if plastic is used, the thickness needs to be ½ of the thickness of the glass to match the performance. Projected capacitive method also allows for curved surfaces to be used as touchscreens. These surfaces require more flexible substrates and conductive materials, such as PET-substrates and PEDOT as a conducting material.[31,32]

In a capacitive touchscreen, AC-current is applied to four corners of the conductive layer with exactly the same voltage, phase, and frequency. This creates uniform electrostatic field across the conductive layer. When the screen is touched, some of the

electrical energy is coupled capacitively from the conductive layer to the finger or stylus, which creates small current flowing through the wires. The controller then compares the new state to the baseline values. The position is calculated from the amounts of current flowing through each wire, which tell the controller how close the touch was to the wires.

Simple surface capacitive touchscreen is not well suited for mobile use since the controller needs stable ground connection to measure the baseline properly. For mobile use, projected capacitance is mostly used.[31]

Projected capacitance, p-cap, touchscreens were commercialized in 1985 by MicroTouch Systems, but the big break in commercial use for p-cap technology came in 2007, when Apple unveiled their new phone, the iPhone, which used p-cap touchscreen, effectively popularizing the technology use in mobile applications. In p-cap touchscreen, the conductive layer consists of individual electrodes patterned on the surface rather than uniform conductive layer. These electrodes are all wired separately.

There are two measurement tactics to measure the change in capacitance: mutual and self-capacitance. In self capacitance approach, the controller measures one electrode in contrast to the ground. In mutual approach, the controller measures capacitance between two adjacent electrodes.[31]

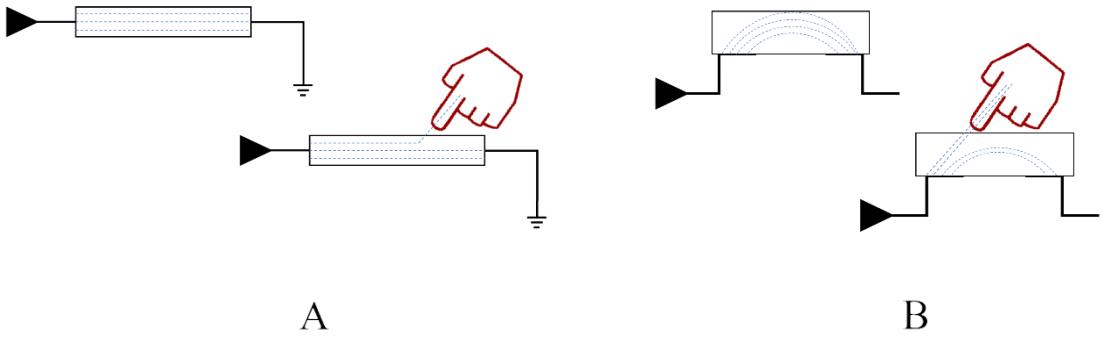

Figure 9: Electrode measurement tactics, A: Self capacitance, B: Mutual capacitance.

In the self capacitance approach the electrodes are measured individually, for example in X-Y-matrix first all the X-axis electrodes and then all the Y-axis electrodes are scanned and measured in sequence. When the screen is touched, nearest X- and Y-electrodes are measured to have maximum capacitance and the coordinates can be calculated. If the screen touched with two fingers positioned diagonally, multiple maxima are recorded, leading to “ghost” images appearing positionally related to the real touches

(Fig. 10). This can be ignored at software level by focusing on the movement of the fingers, as the movement is identical between the real and ghost images.[31]

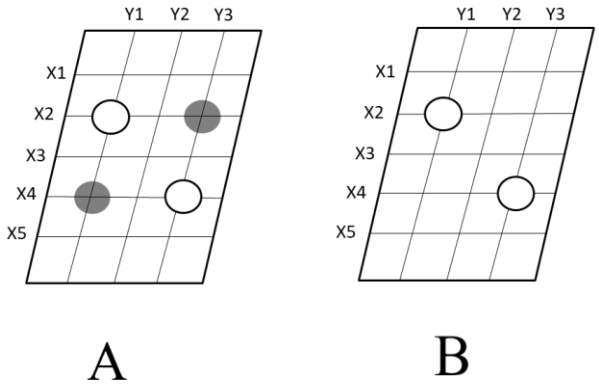

Figure 10: A: Real touches (white circles) and ghost touches (gray circles) on a self-capacitive surface, B: Real touches (white circles) without ghost touches on a mutual capacitive surface[31]

In mutual capacitance every intersection between the electrodes is measured individually. For example, one of the X-axis is driven first and every Y-axis electrode is measured before moving on to the second X-axis electrode, where the whole sequence is repeated. This approach allows identification of every touch point on the surface without any ghost images present. This make sa proper multitouch sensor and is better suited for mobile use.[31]

These electrodes are patterned to make efficient use of the space available on the surface of the sensor. The original iPhone had one of the simplest patterns with 10 columns of 1 mm wide ITO on one side and on the other side 15 rows of 1 mm wide ITO. These rows and columns were 5 mm apart from each other. This 5 mm gap between the electrodes on the surface was filled with unconnected, “floating” ITO to preserve uniform optical properties across the screen.[32]

Since then, the usual pattern used is rows of interlocking diamonds connected to each other. This is made by connecting squares in 45° angle to each other. The size of these diamonds varies with manufacturer, but the usual size is around 4-8 mm. The rows and columns are usually divided by an insulating layer, but some screens use one sided structure, where in the intersections, an insulating coating is applied between the electrodes.[32]

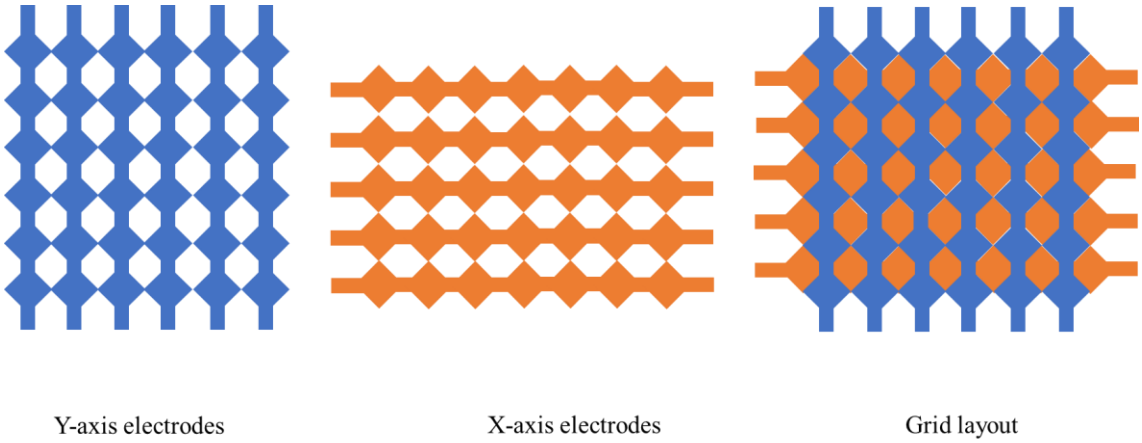

Figure 11: Interlocking diamond electrode pattern.

2 Experimental

2.1 Materials

Iron(III) *p*-toluenosulfonate hexahydrate ($Fe(TOS)_3 \cdot 6\ H_2O$) (technical grade) was purchased from Sigma-Aldrich and 3,4-ethylenedioxythiophene (EDOT) (>98 %) was purchased from TCI. Pyridine (AR-grade) was obtained from Lab-scan analytical, and n-butanol (HPLC-grade) was purchased from Sigma-Aldrich. Acetonitrile (HPLC-grade) was obtained from Sigma-Aldrich. All reagents were used as such without any further purification.

2.2 Synthesis and Optimization

2.2.1 Small PET-substrates

In the original protocol[33] used in the VPP process for the small samples the polymerization was performed in a heated glass cell heated to 75°C using water heater and a pump to circulate water inside the cell walls. Heated metal block made from copper same size as the substrates was heated to 65 °C. The PET-substrates (biaxially stretched, thickness of 125 µm) were cut to shape (2.8 cm x 3.6 cm, half of a microscope slide) using scissors. The substrates were then cleaned first by ultrasonicating them in water, acetone, and ethanol for 5 minutes per solvent. After drying under ambient conditions, they were plasma cleaned for 5 minutes and immediately transported to the spin coater for oxidant coating.

The oxidant solution was prepared using iron(III) p-toluenesulfonate hexahydrate (Fe(Tos)) and pyridine in n-butanol with concentrations of 0.236 M and 0.141 M respectively. 60 µl of the oxidant was used in spin coating of the substrates at a spin speed of 2400 rpm. After spin coating the substrate was dried on a hot plate at 90 °C for 90 s.[33]

When the glass cell had reached the desired temperature, 30-50 µl of EDOT-monomer was pipetted on the cell bottom. It was then let to vaporize and fill the cell with monomer vapor. The dried substrate was then placed into the cell with the oxidant covered side poiting downwards and the cell was covered with a glass lid for 90 s. The lid was then removed and a heated metal block, at 65°C, was placed on the substrate for 90 s. After that, the block was removed. and the glass lid was placed back for 60 s. Following the polymerization, the film was annealed on a hot plate at 90 °C for 90 s and washed with acetonitrile and dried under dry nitrogen gas stream. For multi-layered films, the process was repeated from spin coating onwards.[33]

The first results with the PET-substrates were not great, as the sheet resistances of the films produced were around 2000 Ω/□. At first the reagents were thought to be faulty, and test runs with glass microscope slides suggested some problems were due to the reagents, as when a new bottle of the monomer was opened for use, the results got better. Rest of the reagents used were tested by UV-vis spectrophotometry, and the results showed no other problems and were consistent with tests done with the glass slides.

The physical shape of the substrates was also under study, as the substrates were cut from a larger roll, resulting them to be slightly curved along either side of the rectangle. This made the substrates slightly curved, which in turn could affect the oxidant coverage during spin coating as the solution could either pool in the convex area or fling off before evenly covering the whole substrate in the more concave orientation.

Using pressure from books pressing down on the substrates for 11 days before cutting them into shape and using them in experiments did not work and the film was as curved as before the treatment. This also had high chance of scratching the substrates, even with some protection. Using the hot plate at 90 °C and keeping the small substrates on it for few seconds made them more malleable and this made them to straighten out. The heating did not affect the quality of the films as the results were similar when using the heat-treated substrates compared to the non-heat-treated substrates. This also suggests that the concave nature of the substrates did not affect the finished films.

However, when switching the substrate back to the PET-films, the results were the same as before. This showed that the protocol used does not work properly with PET-

film, as the protocol was originally optimized for glass slides, meaning that it may not function properly with different substrate.

This meant that the protocol needed to be optimized for the new PET-substrates and the first parameter to change the time used in the polymerization. This was done by increasing the time with same ratio as used in the original protocol, which was roughly 3:3:2, and this translates to +45 s, +45 s, and +30 s per stage when using 2 min intervals. 2 min intervals were chosen as they give frequent enough measuring points while still being easily implemented and calculated.

The experiments began with 2 min polymerization time and continued until 16 min, increasing the time in 2 min intervals. The results for these tests show parabolic shape for the sheet resistances of the films. The sheet resistances start from 4000 Ω/□ of the 2 min films and decreases steadily until 14 min films and after which it increased again. Thus polymerization time was chosen to be 14 min for the rest of the experiments (Fig. 12: A).

After the polymerization time was optimized, other aspects of the protocol were tested. From the time tests a window between 12 and 16 min was chosen for these tests, as they produced the best results for the films. First, using only the glass lid for the whole polymerization time without using the heated metal block was tested. This resulted either in the same or slightly worse results than the original. After that, using the heated metal block on top of the substrate for the whole time was tested and the results were better than the results when using the original protocol.

With these results 14 min polymerization time and using the heated metal block for the whole time was selected for preparation of the samples. This does result in a thicker film produced, and this is not always a good thing. This is discussed later in the results and discussion, but still the procedure produced films with low enough sheet resistances for further experiments.

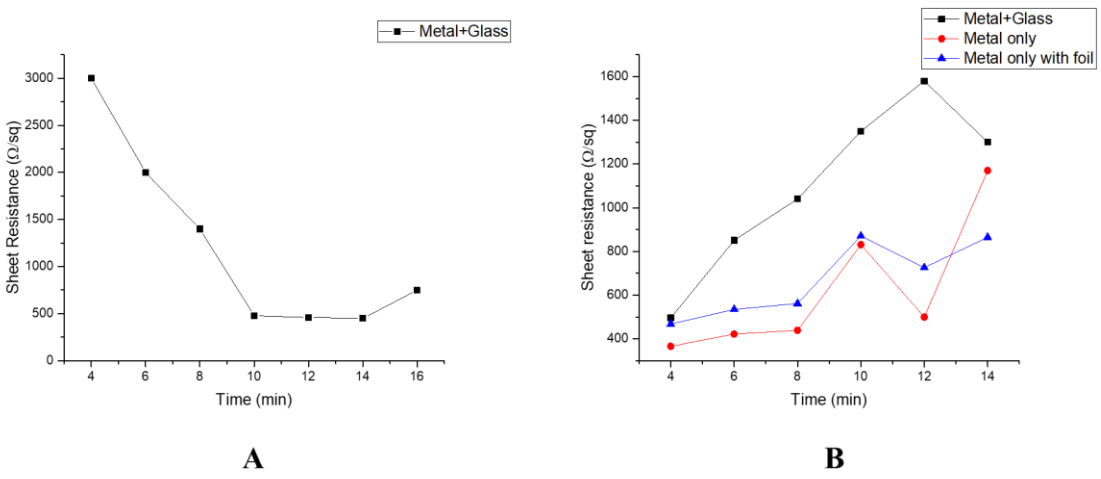

Figure 12: The results of optimization of the polymerization time, A: initial values, B: values after weekend. "Metal + glass" is the same as "Original protocol".

This was the plan to move forward until the next day in the laboratory when new set of substrates were cut from the roll. When these substrates were used in the polymerization for 14 min with only the heated metal block, the resulting films had several kilo-ohms of sheet resistances and the films themselves were tinted green, suggesting over-doping (Fig. 12: B).

Because of this, the polymerization time tests had to be redone, and this time the change in the sheet resistances was almost linear and the best results were at the 2- and 4-min polymerization time and the earlier results for the times were no longer applicable. The usage of the metal block for the whole time resulted in the same results as earlier.

The reason for this shift lays most likely in the substrates themselves as all the other factors were investigated. The reagents were tested again with glass-slide as a substrate, and the results were identical with previous ones. If the reagents were faulty one way or another, there would not be any proper film formation regardless of the substrate, and as seen on Fig. 12: B, a film was formed on the substrate, clearing their involvement in the shift. The temperature in the laboratory and in the fumehood were also stable and the temperatures of the cell and the block were always checked before any attempt, and they were stable too. Air moisture can affect the film formation[34], but it also was checked and found to be stable. All these results point to the substrate being the culprit, as the change occurred when a new batch of them was cut from the larger roll, proving the importance of checking the substrates before experiments.

The final set of samples was done using 2- and 4-min polymerization time with the heated metal block on top for the whole polymerization time. With this protocol, 1-, 2-, and 3-layered films were prepared.

2.2.2 Large PET-substrates for the Prototype

The large PET-substrates were prepared by first cutting them into 18x18 cm squares, which were then ultrasonicated in a solution of 1:1:1 ratio of water, ethanol and acetone for 10 minutes and were left to dry under ambient conditions. After drying, just before spin coating the substrates were cleaned by a plasma cleaner for 5 minutes.

The oxidant was prepared the same way as with the smaller samples. The proper amount of the solution needed was determined by spin coating clean substrates with the oxidant and increasing the amount dispensed. The minimum required volume of the oxidant solution needed for an even coverage was determined to be 1.4 ml and a slight excess was then used to ensure proper coverage. After spin coating, the substrate was dried on a hot plate at 90 °C for 90 s and the moved to the VPP-chamber.

As the dispensing of the oxidant was done manually with either syringe or pipette, there was a high chance of a “hole” appearing in the middle of the film. This was a result from too fast dispensing or too aggressive final push of the syringe or pipette, causing the oxidant to blow away from the centre.

The polymerization process was similar to the final optimized method used with the smaller substrates, as the cleaning and spin coating was done the same way and the larger setup did not allow for switching between the lid and the heated metal block. However, the polymerization time was increased from the 2 and 4 min used with smaller substrates up to 10 min with 2 min intervals starting from 6 min.

After the polymerization, the films were annealed on a hot plate at 90 °C for 90 s and washed with acetonitrile and dried under dry nitrogen gas stream. After drying the sheet resistances were measured.

2.3 Characterization

The optical characterization of the films was done using Cary 60 UV-Vis-spectrophotometer. With this, the absorbance was measured between 320 nm and 1100 nm. Below 320 nm the absorbance of the PET-substrate itself starts to dominate, so it was left out. Transmittances of the films were calculated from the absorbance at 550 nm using equation 1

$$A = 2 - \log_{10} \%T \quad (1)$$

where A is absorbance and %T is transmittance. The wavelength of 550 nm was chosen for the transmittance calculations as it is the wavelength that human eye is the most sensitive for. For a device to be used on top of a screen for viewing, this is crucial area to be as transparent as possible.

The sheet resistances of the films were measured after the washing step with a four-point probe. Same probe was used in the bending tests to monitor the changes in the films to see if they suffer any adverse effects from the bending.

The bending tests were conducted by hand, where the films were secured on a stand and then they were bent manually roughly to 100° angle while the polymer film was facing inwards the bend. The films were bent 500 times each and the sheet resistance was monitored with the four-point probe.

The Veeco diCaliber AFM was used in measuring the thickness of the films and in checking of the bent films to see if they were cracked at the bend-line. Tapping mode and autotune of the cantilever was used as the settings for the measurements.

3 Results and Discussion

3.1 Sheet Resistance

The sheet resistances were measured from 5 different parts of the surface of the finished small sized films after washing to see if the film was uniform. According to the results, the films were quite uniform in nature. From these results, the average was calculated to be used in comparison to each other and to be used later in the calculations.

For 4 min polymerization time, one layer of film had a sheet resistances of 415, 451 and 424 Ω/□, which are good and slightly below desired 500 Ω/□[35], though this value was given for a resistive touchscreen device. Second layer added dropped the sheet resistance roughly in half to 188 and 167 Ω/□, with one outlier of 480 Ω/□. Third layer did see even more decrease down to 109, 107 and 182 Ω/□, but it was not as large drop compared to the drop from one to two layers (Table 1).

Films prepared with 2 min polymerization time follow almost the same pattern, where the one-layer film has the highest values with 319-339 Ω/□ and adding layers drops these values. The big difference compared to the films made with 4 min polymerization

time is that the two layered films have lower sheet resistances than the three-layered films, as they had sheet resistances below 150 Ω/□ whereas the three-layered had resistances of 167-203 Ω/□ (Table 1).

For the large samples, the sheet resistance measurements were taken from 13 different spots on the film, giving an accurate result for the whole film. While the first 6 min film had sheet resistances of 6000-7000 Ω/□, rest of the samples had sheet resistance values between 190-400 Ω/□. These values are in the desired range and are quite uniform across the films (Table 2).

The values of sheet resistance drop slightly from the 250 Ω/□ of the 6 min film to around 218-276 Ω/□ of the 8 min film and then rises again back to the around 250 Ω/□ of the 10 min film (Table 2). This is likely due to the longer polymerization time resulting in a thicker film where the slight defects can accumulate and decrease conductivity and rise the sheet resistance.

Table 1: Measured sheet resistances and transmittances of the small, layered samples, averages taken from the measurements.

		Sheet resistance, Ω/□			Transmittance, %		
Polymerization time, min	Layers	Samples			Samples		
		1	2	3	1	2	3
2	1	322	339	319	85.6	88.7	90.0
	2	135	141	141	79.1	78.3	77.2
	3	167	203	195	67.9	65.6	67.0
4	1	415	451	424	83.9	89.7	89.3
	2	480	188	169	75.4	78.1	77.8
	3	109	107	182	63.4	66.6	69.4

All the sheet resistance values are good for use in the manufacture of the prototype, and the optimal thickness would be two layers done with the protocol, as the third layer does not decrease the sheet resistance as much as the addition of the second layer. The optical measurements need to be considered as well as the final product needs as high optical transmittance as possible.

Table 2: Measured sheet resistances and transmittances of the large samples, averages taken from the measurements.

	Sheet resistance, Ω/□			Transmittance, %		
Sample/polymerization time	6 min	8 min	10 min	6 min	8 min	10 min
1	7060	218	249	91.7	87.9	90.4
2	249	403	254	91.6	91.4	87.7
3		276			91.7	
4		226			90.5	

3.2 Optical Characterization

The UV-Vis absorbance spectra of the films shows that as the layers are added, the absorbance increases constantly with every new layer, which suggests that the layers are almost of identical thickness. This is expected, as the layers are done by the same protocol, which should result in identical layers. Similar thickness is also shown in the transmittance values, as every layer drops the values roughly 10-15% (Fig. 13).

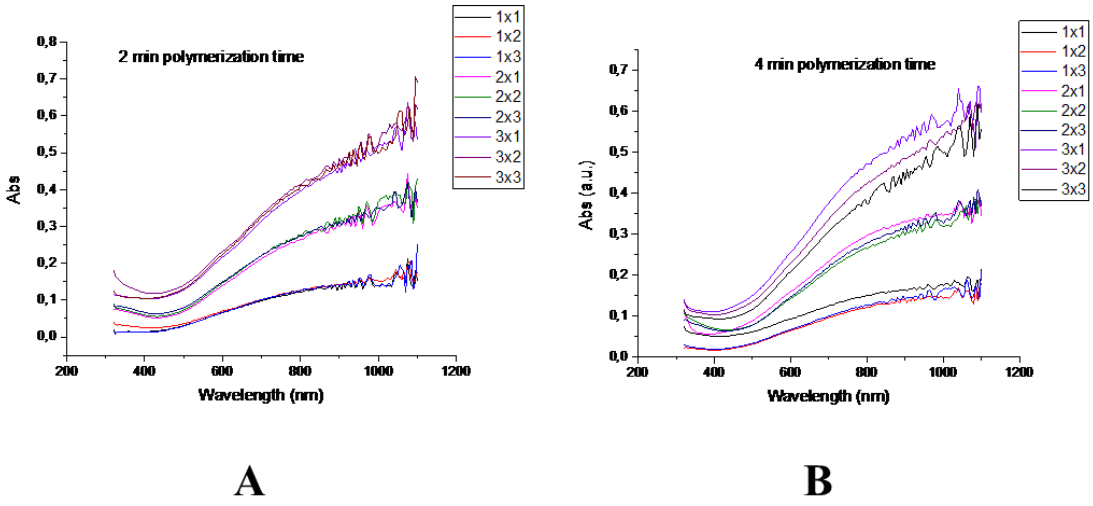

Figure 13: Absorbances of the small sized films manufactured. A: 2 min polymerization time, B: 4 min polymerization time

The absorbance spectra also shows that the films are in a doped state as the peaks are located in the higher wavelengths in the infrared area. If the films were in a pristine, undoped state, the peak would be in the lower wavelengths closer to the ultraviolet area. The 2 min films are similar to each other with every layer added, as the absorbance spectra for them overlap the whole range from 320 nm to 1100 nm. In contrast, the absorbance spectra for the 4 min films are more separate from each other, especially the three-layered

films diverge from each other more. This divergence begins at 320 nm and above 600 nm it gets greater. The spectra for each layer are closer to each other between 320 nm and 500 nm, from where they start to diverge from each other higher the wavelength becomes**.** The lower divergence of the samples of each layer in 2 min films shows that they are more uniform batch to batch compared to the 4 min films. The same separation is seen in the transmittance values, as the three-layered 2 min films are within 2.3 % apart from each other whereas the three-layered 4 min films are within 6 % apart from each other (Fig. 13).

The polymerization time does not show any drastic change in the absorbance spectra as the peaks of films prepared with both 2 and 4 min have roughly same intensities of 5.5, 3.5 and 1.5 for three, two and one layered films, respectively. Transmittance on the other hand shows some slight difference as the films with 4 min polymerization have up to 5% lower transmittances compared to the films with 2 min polymerization time (Fig. 14).

The transmittance values decrease simultaneously with the increase of the thickness of the films with every layer added. This decrease is the same amount with every layer added, 10-15% per layer, which shows that every layer is similar. The trend is similar between the polymerization times, difference being that the initial values of the first samples 4 min polymerization time films are slightly lower due to them already being slightly thicker than films made with 2 min polymerization time (Table 1). Rest of the values are in line with the 2 min films with practically same transmittance values.

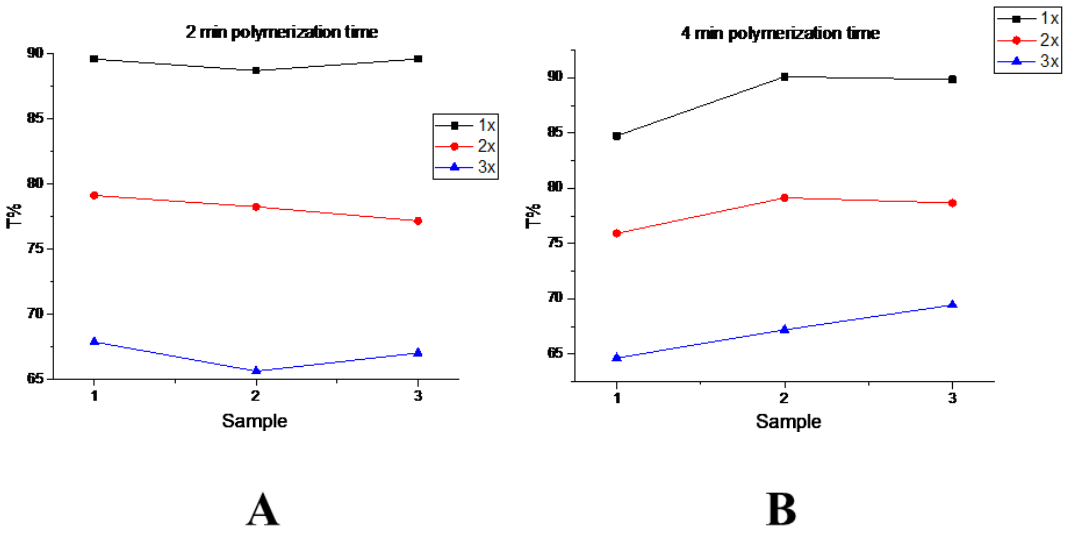

Figure 14: Transmittance of the small films manufactured. A: 2 min polymerization time, B: 4 min polymerization time

The optical measurements show, in paraller with the sheet resistance values and the AFM measurements, that the addition of the third layer is not optimal for later use in touchscreen devices, since the transmittance is needed to be as high as possible, and it decreases below 70% when the third layer is added. The 80% transmittance of the two-layered films would be optimal with the sheet resistance values in use in the prototype.

The UV-Vis measurements taken from the larger samples show similar pattern with the smaller ones as they also have minima around 400-450 nm and from there the absorbance steadily rises reaching maxima at around 1000 nm. This shows that the films are in the oxidized state (Fig. 15).

There are some variations in the measured spectra, as the results do not line up with the polymerization time used as the longest polymerization time, in this case 10 min, should yield thickest film and thus the highest absorbance. However, only one of the 10 min films (olive green, Fig. 15) is on the top with highest while the other one (greyish blue, Fig. 15) is in between of the 8 min films. Also, one of the 8 min films has the lowest absorbance instead of the 6 min films, which were the thinnest ones. This suggests some uniformity issues, as only a small sample was taken from the films to be measured.

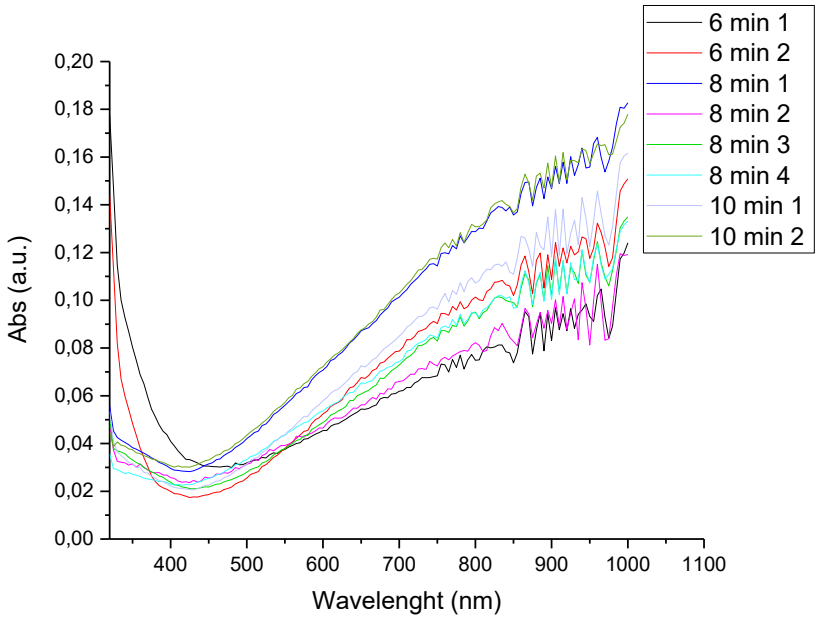

Figure 15: Absorbance of the large films manufactured.

The transmittance values were calculated from the absorbance spectra at 550 nm the same way described earlier with the smaller samples. The results range between 88 % and 92 %. The 6 min film has transmittance of 91.7 % and as the polymerization time was increased to 8 min, the transmittance drops to around 90-91 %, as the thickness

increases. One of the 8 min films has a lower transmittance at 87.9 % and second one has almost 91.7 %, showing the uniformity issues discussed earlier. The increase in polymerization time to 10 min does not show dramatic drop in transmittance, as one of the films has the transmittance of about 90 %. The second one has the lowest value of 87.6 %, only slightly below the 87.9 % of the lowest 8 min film (Table 2 and Fig. 16).

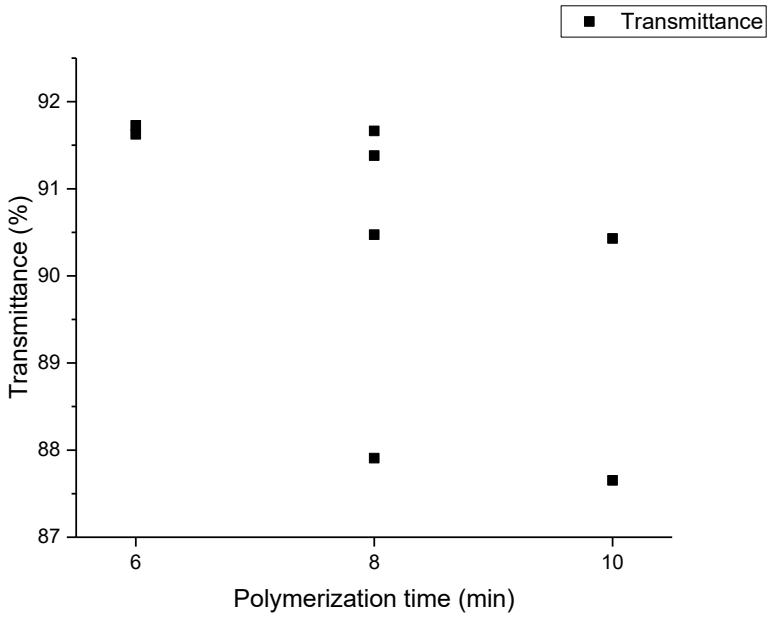

Figure 16: Transmittance of the large films manufactures.

3.3 Bend Tests

The bend tests were conducted using a stand crafted in the laboratory for these tests. The smaller films were attached to the stand with double-sided tape from the backside of the film on the clean PET-surface to prevent any damage done to the PEDOT-film by the tape and stand itself. Bending of the films was done manually by bending the film into 90°-100° angle while the PEDOT-film being inwards. The damage done to the film was monitored by measuring the sheet resistance with the four-point probe and the measurements were taken at 0, 10, 25 and 50 bends and from that onwards every 50 bends until 500 bends.

If there would be any damage done to the film, it would show as an increase in the sheet resistance values. The one and two layered films with 4 min of polymerization time had the highest rise in the sheet resistance values in the end with +6.9% and +11.1% respectively. On the contrary, the three-layered film did not have any change in the sheet

resistance values as the change in the end after 500 bends was -0.5%. For some reason, the three-layered film done with 2 min polymerization time had change of -6.7%, which is probably due some sort of error in the measurements (Fig. 17).

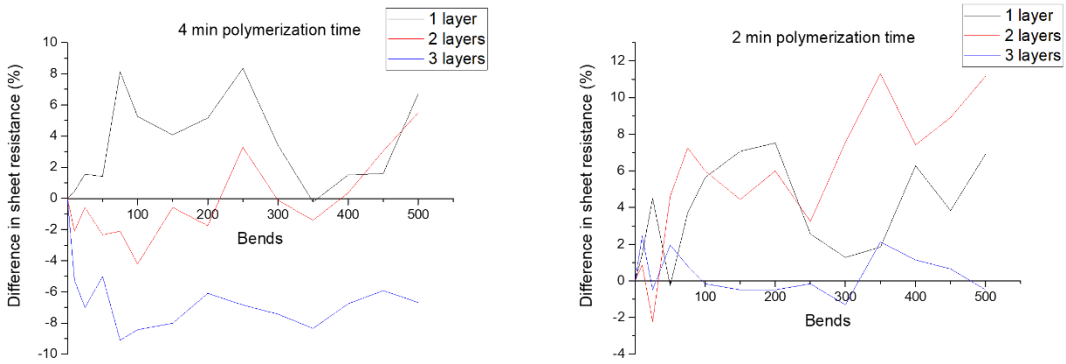

Figure 17: Graphs showing the change in the sheet resistance during bend tests.

The surface was later measured with atomic force microscopy to see if there was any damage done to the polymer film by the bending (Fig. 18). The measurements were taken from the area, where the films were bent. These measurements did not show any damage on the surface, confirming the results of sheet resistance measurements, which showed only a little change in the film. Only some irregularities and dust are visible in the pictures.

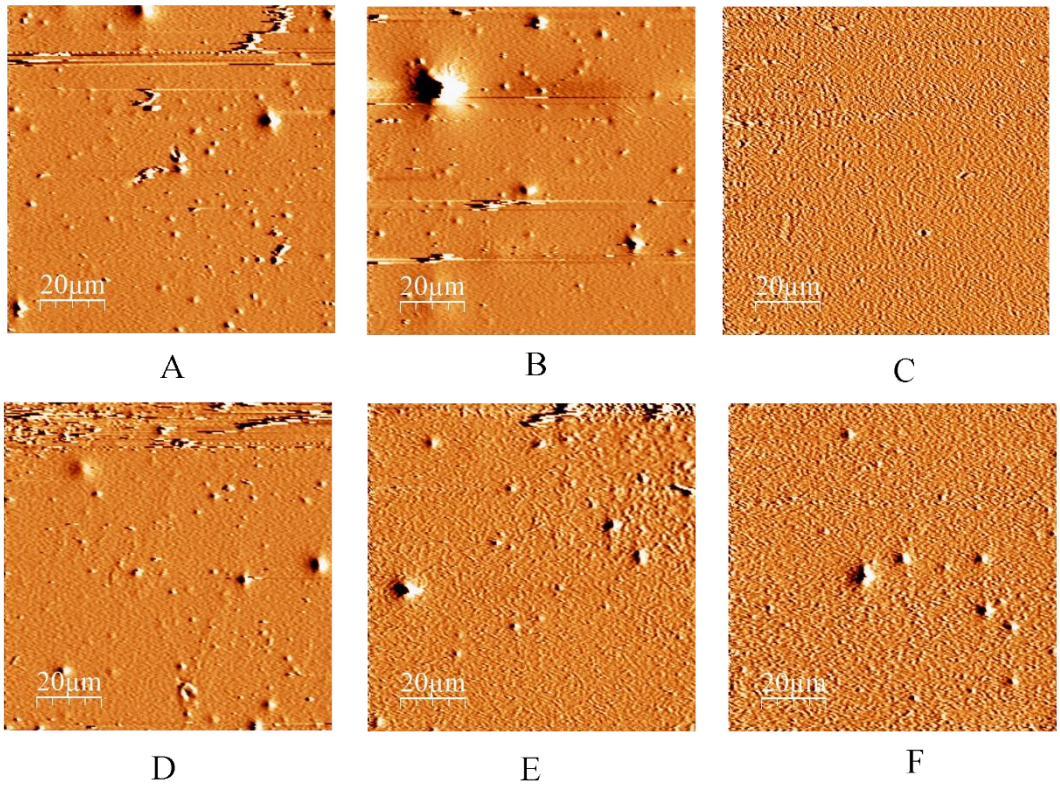

Figure 18: AFM pictures of bended films. 2 min films: A: one layer, B: two layers, C: three layers. 4 min films: D: one layer, E: two layers, F: three layers.

3.4 AFM and Conductivity

Atomic force microscopy was used to measure the thickness of the films and to see if there was any damage done to the films during the bend tests. The thickness values were obtained with Gwyddion-software by first selecting the area in question, then using the software to level the terraces and then measuring from the graph the difference between these terraces. The edges of these terraces can be seen as a dark line in the middle of the pictures in Figure 19.

The images show that the layers made are almost the same in thickness, with slight variations and the third layer of the 2 min polymerization time is thinner than the rest with roughly 30 nm thickness compared to the two preceding ones having roughly 50 nm thickness. 4 min polymerization time results in a slightly thicker and more consistent layers with thickness of roughly 60 nm per layer (Table 3).

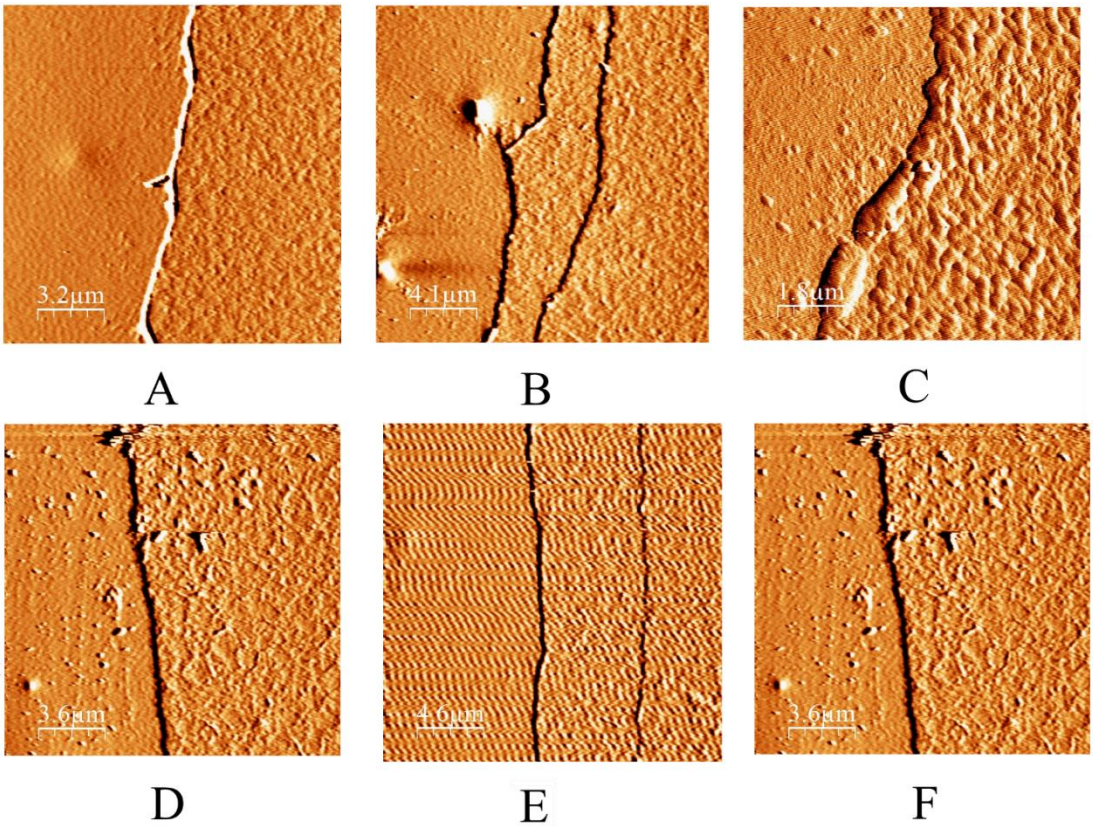

Figure 19: AFM-pictures of films, A-C made with 2 min polymerization time, D-F made with 4 min polymerization time. A: one layer, B: two layers, C: three layers, D: one layer, E: two layers, F: three layers. On the left of the picture is the clear PET-surface and moving right the PEDOT-layers begin.

The conductivities of the films were calculated using the thickness of the layers and sheet resistance of the same films using the equations 2 and 3

$$R_{ho} = R_s * t \quad (2)$$

$$\sigma = \frac{1}{R_{ho}} = \frac{1}{R_s * t} \quad (3)$$

where R_{ho} is resistivity, t is thickness, R_s is the sheet resistance and σ is conductivity.

The conductivities show that making thicker films is not always better (Table 3), as the second layer increased the conductivities significantly by 117 S/cm for 2 min and 137 S/cm for 4 min polymerization time while the third layer either does nothing compared to the second layer added in the 4 min films or even decreases the values in half in the 2 min polymerization time. All the conductivities obtained are in the border between semiconducting and metallic materials (Fig.2), although the line between them more of a gradual change. This is in line with earlier results as the conductivities of doped conducting polymers are in the region starting from semiconducting and moving to metallic conductivities (Fig. 2).

Table 3: Thickness and conductivity of the samples.

Polymerization time, min	**Layers**	**Thickness, nm**	**Conductivity, S/cm**
2	1	52	605
2	2	99	722
2	3	130	461
4	1	63	352
4	2	121	489
4	3	195	484

3.5 Making of the Prototype

The prototype consisted of a film of conducting polymer connected to the controller via four wires form the corners of the film. The larger film was prepared using 8 min of polymerization time in with the process for the larger substrates, and was used as simple, surface capacitive touchscreen. Unfortunately, the process of building of the prototype

was interrupted and delayed because of myriad of technical difficulties, mostly centered on the controller itself. Signal was received from the film and the controller, but it was not significant enough for proper function of a touchscreen device. This problem was not resolved in time for including any results to this study.

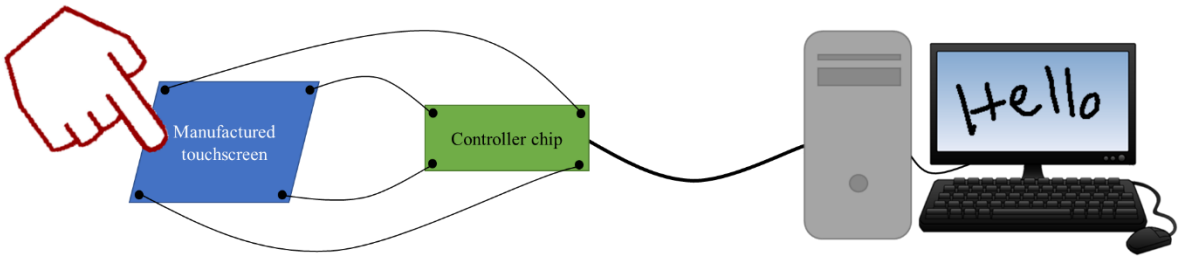

Figure 20: Simplified scheme of the prototype meant to be produced.

4 Conclusions

In conclusion, the preparation of conducting PEDOT-polymer thin films for a prototype of a touchscreen device using vapor phase polymerization was a success as the films produced were thin, 50 nm per layer, with conductivities of up to 720 S/cm. The films were also transparent, with transmittances of 88 % - 92 %, which made them usable in touch screen devices. Largest problems encountered where technical difficulties arising from the computer side of the project, which was out of writer's expertise on the subject. This hindered the project from being completed in the time frame given for the project.

For future continuation of this project, acquiring a better suited controller chip for the finished prototype for it to function and receive signal properly. Some optimizations could be done with the polymerization process in order to have better conductance and uniformity on the films. With the optimizations, patterning the film to form an electrode pattern on the surface similar to commercial touch screens could also be done. Several methods, printing, stamping, masking etc., exists and could be used in patterning the films.

5 References

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