Study of Rheological Behaviour of Coating Paste

Containing Conductive Polymer complex

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Preface

This master thesis is the ongoing research in the field of conducting polymers at the Swedish School of Textile. The main aim of this project was to study the rheological behaviour of the coating paste with rheology modifiers. With this master thesis, I complete my Master degree in Textile Technology. I worked in textile industry for 3 years and after, I served in National Textile University Faisalabad, Pakistan as a lecturer. I am pleased to have the opportunity at the Swedish School of Textiles to study master in textile technology and to research on the new emerging technology area of conducting polymer coating paste rheology.

First of all I am very thankful to the University of Boras where I am given the opportunity to complete my Master degree and provided with the research in master thesis. I would like to thank my supervisor Maria Akerfeldt who is doctoral student at School of Textiles. She really helped me a lot in my project concerning important discussions. I am grateful to my examiner professor Nils Krister Persson who had been very supportive throughout the span and gave me very kind instructions. Finally I would like to thank Maria Bjorklund and Catrin Tammjarv, the technicians in the lab at School of Textiles, who helped me a lot concerning my lab work.

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Abstract

Conducting polymer coating is the new developing area in the field of advanced textiles. In this project the rheological behaviour of paste containing conducting polymer was studied during formulation to coating application. The literature study is done by keeping all the contents of project in mind and a wide area of conductive polymer, coating methods, binder system and rheology modifier is covered. The rheological behaviour of different fluid containing newtanion and non-newtanion behaviour is discussed for better understanding of the project working. Polyester fabric was coated by knife coating method. In paste formulation, the chemicals used were polyurethane binder with two HEUR based rheology modifiers. A lot of experiments were performed to determine the right amount of rheology modifier alone or in combination for paste formulation and coating application and interesting findings were observed during the experimental work which had been justified in results and analysis. After application, the coated fabric was checked for resistivity.

Keywords

Conducting polymer, Surface resistivity, PEDOT/PSS, Coating, Rheology, Binder, Rheology modifier, HEUR.
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1 Introduction

The need of today’s world market is more technical and value added products. Textile sector is focussing on smart textiles to fulfill the requirements of market. Keeping this view in mind, this project is focused on conductive coating application on textiles which belongs to electronic textiles, a sub-group of smart textiles. This project is based on the rheological study of the conductive coating paste. The rheological behaviour was checked by using two rheology modifier, Borchi® Gel L75N and Borchi Gel 0434. The binder used in the paste was polyurethane based along with conductive polymer PEDOT:PSS. The fabric was coated with paste and after drying and curing, the resistivity was checked.

1.1 Background

For every industry to survive in present and future, they have to be a part of the development in new textile products. There are many areas where development is in progress like medical textiles, protective textiles, defence textiles etc. This project is based on ongoing study in conductive polymers area in Swedish School of Textiles. The comparison of different conductive polymers on polyester fabric was done before. This project is based on the study of rheology behaviour of the paste containing conductive polymer.

1.2 Purpose

The aim of the project was to optimize the paste formulation with the right combination of rheology modifier used in the project and then apply the paste on 100% polyester fabric to make it conductive. The number of goals were setup within the project and for this the matrix was formed which is mentioned in the experimental work in detail.

The purpose of the master thesis can be summarized as follows

- Selection of rheology modifier with right amount alone or in combination.
- To optimize the recipe with appropriate viscosity profile suitable for coating method selected.

1.3 Project limits

- Different types of coating methods are discussed, but more focus is on knife coating because this facility is available at the university college of Boras.
From commercially available conductive polymers, all the conductive polymers are discussed in literature review to give the broad idea of this field but only PEDOT/PSS is studied in experimental work.

1.4 Methods

To explore the field of conductive polymers and textile coating, a number of literature reviews, published books, and articles were studied. The company websites gave good information about chemicals and polymers used in the project. As the project aim was based on rheological study, so a deep study was considered in the literature review to clear the concepts for further proceedings. A good coordination between theoretical and practical work was established in the project.

The approach was kept in mind while making the paste matrix concerning with the coating method. The paste was comprising of polyurethane binder system along with conductive polymer PEDOT:PSS. Different amount of rheology modifier were added in alone and in combination to check the viscosity of the paste with Brookfield viscometer. The viscosity was checked at different shear rates to study the rheology profile of the paste and finally conclusion was drawn on the bases of application on fabric with the knife over roll method. The coating methodology was developed in the lab as manual coating as described in detail in coating method section.

The reliability of the paste rheology study was checked by taking different samples of paste, measuring viscosity before further proceedings. After the application, the resistivity of fabric was checked by resistance meter. Here again the reliability was checked by taking readings at different spots and average was taken. Finally the conclusion was drawn on complete study of rheology profile from paste matrix to coating.
2 Coating of Textiles

Coated textiles are those textiles which are surface coated on one or both sides with homogenous or cellular structure coatings (synthetic polymers, natural rubber etc.) [1 P. 110].

Coating is defined as the application of coating compounds on one or both sides of woven, knitted or non-woven fabrics by means of coating machines [1 P.110].

The difference between lamination and coating is, in lamination the polymer materials which cannot be easily formulated in paste can be converted into film first and then applied to textiles by different laminating processes [2 P. 5].

This project uses the knife over roll method of coating. So lamination will not be discussed and literature will be focussed on different coating methods and of course, the knife over roll coating method more in detail.

Coating polymeric materials to textiles imparts different functional and aesthetic properties to substrate such as resistance to soil, water repellency and conductivity etc. There are different methods of coating by which polymer can be applied to textiles and this classification is based on the basis of equipment used, method of metering and the form of coating material. These methods are described below [3].

1) Fluid coating in which the coating material is in the form of paste
   a) Knife coaters
   b) Roll coaters, reverse roll coaters, kiss coaters, dip coaters etc.
   c) Impregnators: in which substrate is dipped into the fluid and excess one is squeezed through squeezing rollers or removed by doctor blades
   d) Spray coaters

2) Coating with dry compound
   a) Melt coating: extrusion coating, powder coating
   b) Calendering
   c) Lamination

There are several factors on which selection of coating method depends [3]

- Nature of substrate
- Form and viscosity of coating paste
• Accuracy of coating desired and end product
• Economical process

2.1 Knife coating

This is the oldest coating method which is also known as spread coating. In this method, the paste is poured on dry fabric over the entire width in front of doctor blade. The fabric movement forward ensures the spreading of even paste on substrate. To prevent the spilling of paste over the edges, the adjustable guard called dams are also provided. Proper tension is necessary for even coating. After that the substrate passes through dryer for drying and curing. The thickness of paste can also be controlled by maintaining the distance between blade and fabric [3].

There are three types of knife coating.

2.1.1 Knife over air

This method is usually used for applying lightweight, impermeable coatings. This method is also known as floating knife because knife does not rest on table. Doctor blade directly rests on fabric due to which more compressive force is applied on paste which helps it entering the interstices of the fabric. However this method is useful for both tight and open woven fabric because strike through does not occur. Add on will be lower due to greater tension in the fabric however it can be increased by increasing the viscosity of the paste because the more will be viscosity, the greater will be its tendency to force substrate away from the knife[3]

![Figure 1 Knife over air](image4)
2.1.2 Knife over roll

This method is the most important, having much higher accuracy with simple in application. Contrary to floating knife method, doctor blade is properly placed on roller. Weight of the coating material is controlled by the gap between the bottom of blade and thickness of fabric passing through roller. The roller may be rubber made or chromium plated steel one. The rubber roller can be advantageously used where small defects like slub or knots need to pass freely through the blade. However steel roll is more precise giving even coating and easy to clean. By this method up to range of 40,000 cps viscous paste can be used.

![Figure 2 Knife over roll](4)

2.1.3 Knife over blanket

In this arrangement, the endless blanket is stretched between two rollers and substrate is placed on this conveyor. Dimensionally unstable fabric can be coated by this technique because fabric is not subjected to stretching and the pressure between blade and fabric is adjusted by the tension applied on blanket. Amount of coating material is controlled by the tension in the blanket which is adjusted by rollers. For even coating, the damage of blanket should be avoided.

![Figure 3 Knife over blanket](3)
2.1.4 **Principle of knife coating**

The knife unit consist of blade holder and blade liner. The coating material is applied to doctor blade and the distance between blade and fabric is set by holder. As the fabric moves, the material also moves under the fixed doctor blade which exerts shear force on paste causing it to flow. This shear force depends on working speed, blade profile and the tilt angle of doctor blade. The angle can be adjusted by doctor blade holder. The coating paste quantity depends upon the distance between doctor blade and fabric and also on tilt angle. By increasing the angle, the amount of paste applied can be reduced. The thickness of paste depends upon [1]

- Doctor blade speed
- Blade tilt angle
- Doctor blade distance
- Substrate tension
- Paste viscosity

2.2 **Roll Coating**

In roller coating the finishes or coatings can be applied by lick roll on one side of the fabric. This method is alternative to dip coating and give advantage by preventing disorientation of pile fabric. This method is used for woven velvet and carpets [2].

There are different types of roll coatings described below [3]

2.2.1 **Mayer Rod Coating**

The mayer rod is a small, round rod made of stainless steel which is wound tightly with wire and used to remove excess coating. The amount of coating depends upon the grooves between wires. The coating thickness is dependent on diameter on wire which varies from 3-4mm to 25 mm maximum. The mayer rod is mounted on rod holder which is rectangular. During coating, the rod is rotated in the opposite direction of the fabric which removes the coating material from the wires and also increases life of the rod due to reduced wear. This method is used for thin coating having viscosity usually in range of 50-500 cps.
2.2.2 Direct Roll Coating
This is also called squeeze roll coating. In this method the amount of paste on fabric is controlled by knife blade passing through the applicator roll. The fabric moves in the direction of rotation of applicator roll. This method is used for low viscosity compounds and the thickness of coating depends on the nip roll pressure.

2.2.3 Kiss Coating
There are two rolls in kiss coating method. One roll which is call the pickup roller, picks the paste from the trough or pan and transfers to the applicator roller on which fabric is passing through by touching its surface. The roll kisses the fabric and transfers the paste to fabric and the amount of coating material depends upon the nip pressure, speed of the operation and the hardness of roll.

2.2.4 Gravure Coating
In this method, engraved roller is used to meter a precise amount of paste which is controlled by etched design on engraving roller. Different amount depends upon different design pattern like pyramid, quadrangular and helical. For lighter amount on fabric, pyramid pattern is used. There are two types of gravure coating method.
a) Direct two-roll coater

b) Indirect gravure coater or offset coater

In first method the paste is picked up by the gravure roller and transferred to the fabric as it passes between the nip of gravure and backup roller.

In second method, an offset roller is introduced between backup and gravure roller. The gravure roll picks the coating material from the pan and transferred to the offset roller which gives impression to the fabric as passes between nip of offset and backup roller. This method is suitable for very light pattern and can handle the viscosity up to 10,000 cps.

This gravure coating is used in the application of laminating adhesives and topcoat on treated fabric.

![Figure 7 Gravure coating](3)

2.2.5 Reverse Roll Coaters

In reverse roll coating method, a uniform coating thickness can be obtained without caring about uniform thickness and tension in fabric. A broad range of coating viscosities and weights can be used with high accuracy. In this method, the roll rotates in the opposite direction of the movement of fabric and hence the paste is applied in opposite direction of fabric moving with respect to applicator roller.

![Figure 8 Reverse rolls coating](3)
2.3 Dip Coating

This method is also known as impregnation or saturation because the fabric is impregnated by chemicals in a trough for a certain time called dwell time and the excess amount of chemical is removed either by nip pressure or by set of flexible doctor blades precalibrated to give fixed pick up. The factor which affects the impregnation is the solid contents in finishing chemical and the absorption capacity of substrate. In this method, the pick is very low and chemical enters into the interstices of fabric due to nip pressure. This process is mainly used for the application of chemical finishes like oil and water repellent, flame retardant and silicone softeners etc.

![Figure 9 Dip coating](#)

2.4 Transfer Coating

In direct coating method, there are certain limitations that fabric processed should be dimensionally stable to withstand higher machine tension. So knitted fabric are not suitable for this method. Moreover, the penetration of chemicals occurs in woven fabric causing decrease in tear strength and elongation resulting stiff fabric.

Transfer coating overcomes these problem and knitted fabric coating is suitable by this method because no tension is applied during processing and this method is usually used for PVC and PU coatings. The mechanism of coating is that, in the first step, the layer of coating material is applied on release paper which is then dried and cured. This layer is called top coat. The release paper is usually embossed and thus an impression made on substrate coating.

In the second step, the adhesive material is coated on the top coat called tie coat which is sticky layer. This release paper containing two layers is laminated to the fabric with subsequent drying and curing. After that the release paper is stripped off leaving the coated textiles.
2.5 Rotary Screen Printing

This method is used both for coating and printing. The seamless perforated nickel cylindrical screen for coating is used which rest on the web. The most important part of rotary is the squeegee system mounted in screen which serves as a supply and distribution of paste. The squeegee blade, mounted to the pipe, pushes the paste through meshes. The amount of paste applied to the fabric depends upon the number and size of meshes, the squeegee pressure and viscosity of paste. After this paste application, the substrate is moved for drying and curing accordingly.
2.6 Variopress by Zimmer

This coating method is used for very light and voluminous webs and can be used for coating by both touching and without touching the fabric. The amount of coating paste and penetration into the fabric is determined by the tooth gear speed. An illustrated diagram is shown in figure [5].

![Diagram](image)

Figure 12 Variopress [5]

2.7 Calendering

A calender consists of set of three or four rollers brought together by high pressure. Some of these rolls can be heated. Calender can be used for direct coating on fabric or to produce a film which is subsequently laminated to the fabric. The flux coating compound can be fed between the nip of rolls and thin coating can be achieved by increasing number of rollers. There are different ways of coating and lamination by calender discussed below

a) Nip coating in which the coating is done at the bottom nip of the calender and the fabric pulls of the sheet of calender

b) Laminating against Calender roll: in this method, the fabric is laminated against last calender roll by means of hydraulically operated squeeze roll.

c) In line lamination: in this method, the sheet produced by calender is laminated to the fabric by laminating roll. This method is suitable for heat sensitive substrate

d) Coating of elastomers: in this method, the rolls rotate in opposite direction and the penetration depends upon the different speed of rotation of rolls at nip. If the speed of all rolls is even then penetration is low.
2.7.1 Hot Melt Lamination
This is a method in which two fabrics are joined together by melt adhesive film or powder in between. The tactile and mechanical properties like strength depend upon the choice and type of adhesive. Both non-reactive and reactive adhesives are used [6].

2.7.2 Hot melt extrusion coating
The mechanism of this method is very simple. Thermoplastic polymer is found in chips or granules which are fed into extruder giving melt. The melt is extruded downward through a die into the nip of preheated calender rolls where it meets the fabric and both are pressed together in the nip giving coated fabric.

This method is used for polyolefins, polyvinylchloride and polyurethane coatings. For thin film coating, the uniform across the width of fabric is very difficult to obtain by this method.
3 Paste

The paste formulation is the most important part of this project. This is the one of the aim of the project to formulate the paste recipe which best suits the rheology profile and coating concerning conductivity. The ingredients used in paste were

a) Conducting polymer: This is explained in next portion in detail
b) Binder: polyurethane binder was used in this project
c) Rheology modifier: HEUR (hydrophobically modified ethylene oxide urethane based) thickener was used

3.1 Binder

There are a lot of polymers which are used for textile coating like natural and synthetic rubber, PVC, polysiloxane, polyacrylate and polyurethane etc. But the emphasis is given on polyurethane binder here.

3.1.1 Polyurethane

![Polyurethane structure](image)

Polyurethane is formed by the polyaddition of diisocyanate with polyol. Branched or crosslinked polymers can be obtained if the functionality of the reactant is three or more. So a wide range of product with crosslinking, flexibility, rigidity can be obtained. There are mainly two segments in polyurethane called hard segment which is constituted by urethane or urea group, and the soft segment obtained by polyol. In hard segments of course polar groups are found which are responsible for H-bonding or other interactions. The hard and soft segments are basically responsible for the elastomeric properties e.g. if hard segment is increased the polymer will be more elastomer giving low temperature properties while by increasing hard segment, the tensile modulus and rigidity increases [3].

The figure below shows the illustration of soft and hard segment in polyurethane.
For polyurethanes, there are two methods of preparation [3]

a) One-shot process: the formation of polyurethane in this process occurs in one step by simultaneous mixing of polyols, diisocyanate, chain extenders and catalyst. This reaction is very exothermic.

b) Prepolymer process: this is a two stage process, in which the first step involves the reaction of polyol and diisocyanate to form the intermediate prepolymer of molecular weight of about 20,000. The prepolymer can be NCO or OH terminated. NCO is of great technical importance because it can react further to give high molecular weight polymer with chain extender by a polyfunctional alcohol or amine.

Polyurethane can be obtained not only as coatings but also films for lamination and as adhesives. Polyurethanes are very good adhesives and they are used in hot melt lamination as an adhesives and form very good interaction with the substrate. Polyurethanes have very good abrasion, elongation and flexible properties which can be obtained even at very low add on as compared to other polymers. Polyurethane is micro porous due to which they are used in waterproof breathable clothing and shoes for both protection and comfortability. They are relatively expensive polymers [3].

Both types of polyurethane based on polyether and polyester are used in textile applications and polyurethane coating based on polyester gives more skin like handle while the polyether gives more rubber like handle but the polyester based polyurethane is more susceptible to hydrolytic attack. In textile coating, it is more advantageous to have low Tg because of that a softer handle of coated fabric is achieved. As mentioned that polyurethane is more susceptible to hydrolysis, this can be controlled as a remedy by adding glycol of usually C-
chain length of 4 and increasing the ratio of urea or urethane segments in macromolecules [40].

3.2 Rheology modifier

These are also called associative thickeners. They are hydrophobically modified water soluble polymers. They act in thickening mechanism by both in water phase and associating with other species. There are mainly two types of rheology modifier [41]

a) HASE: hydrophobically modified alkali swellable emulsion
b) HEUR: hydrophobically modified ethylene urethane oxide rheology modifier

In this project, the rheology modifier used was HEUR. So more emphasis will be given in explaining the chemistry and properties of HEUR. However a little introduction of HASE will be necessary to differentiate both.

3.2.1 HASE

They are ASE type thickeners with hydrophobic groups attached with polymer backbone. They are anionic in nature and thicken above 7 pH by the repulsion of carboxylate ions present in polymer backbone and also by the interaction of hydrophobes with the emulsion particles which prevent flocculation [41].

3.2.2 HEUR

This rheology modifier has achieved a particular attention in different applications such as in paints and coatings formulation. This polymer consist of polyethylene glycol (PEG) extended by diisocyanate and comprising of long chain capped hydrophobic alcohol or amine [43].

![Chemical structure of HEUR](image-url)

Figure 16 Chemical structure of HEUR [44]
The molecular weight of HEUR is usually of the order of 40,000 to 50,000. They can be considered as “double ended surfactant”. The two ends of the polymer are very hydrophobic while the centre portion is quite hydrophilic as shown in figure 16. The mechanism of thickening is that, these hydrophobic groups interact with each other forming micelles and also interact with the emulsion particles increasing the viscosity of the solution. There are number of factors on which the degree of association of hydrophobes depends [41]

- Emulsion composition (hydrophobic or hydrophilic)
- Particle size because degree of association depends on total surface area
- Emulsion stabilization

Viscosity is dependent on the hydrophobic chain length. As the length of hydrophobic group increases, the viscosity increases and the longer hydrophobic groups give increased residence time for hydrophobic groups within the micelle which increases the life time of aggregate [42].

At very low concentration this HEUR consist of unimers or oligomers with low aggregation number and by increasing the concentration, the micelles formation starts giving the flower like structure as shown in figure 17. And this micelle formation is favoured by the increasing length of hydrophobic group. With increasing concentration, the distance between the flower micelles reduces and the larger aggregates are formed into cluster and again upon increasing concentration giving possibility to micelles get closer and formed finally into three dimensional network. So this average cluster size is increasing due to increase in hydrophobically modified PEG concentration [42].

![Figure 17 Schematic diagram of aggregation of HEUR](image-url)
E.Orgiles-Capena et al determined in their findings with addition of HEUR in polyurethane adhesives by confocal laser microscopy in which micrographs showed that the cross linking between polyurethane with the addition of thickener was due to the interaction between thickener and polyurethane which was also contribute in thickening mechanism[44].

With increasing amount of thickener, there is improvement in rheological properties with polyurethane adhesives and the behaviour is more pronounced as compared to previous when amount of thickener is increased as this improvement in rheological properties in polyurethane system is due to the cross linking specially when content of thickener is increased [44].

3.3 Rheology

When the paste is applied on substrate in coating, the paste has to flow in a proper way. The viscosity decides the appropriate way of spreading. If the paste has less viscosity, it behaves more fluid and penetration in the fabric is more. If paste has higher viscosity then it’s hard to flow. The viscosity is the resistance to the flow of any fluid. Viscosity in paste formulation depends on many factors like, amount of thickener, particle size, emulsifier, dispersing agent which changes the flow behaviour under shear force [3].

When paste is applied on fabric during coating, the shear force is applied on the paste. This shear rate differs with the various coating methods. In knife coating, the paste is applied under the shear action in front of blade while in rotary the paste is forced through profiled hexagonal holes. In both cases, the viscosity of the fluid decreases under the action of shear rate [3].

There are five basic types of rheological behaviour described below

3.3.1 Newtonian

In this behaviour, the shear rate of the substance varies with shear rate in direct proportion and the graph between shear stress and shear rate passes through origin. More conveniently, the viscosity of the fluid in totally independent of the shear rate. The viscosity of a substance can be therefore measured at any shear rate giving the same value [41].
3.3.2 Pseudo plasticity
This property describes the situation where viscosity decreases with increasing shear rate. So to know the true picture of rheology profile, several viscosity measurements are necessary at different shear rates [41].

3.2.3 Dilatancy
This is also called shear thickening. This is opposite to pseudoplastic behaviour as increase in viscosity by increasing shear rate [41].
3.2.4 Plasticity and Viscoplasticity

Some of the materials do not flow until certain shear stress is applied. This material need some shear stress before react. When the graph between shear stress and shear rate is straight line once the yield value exceeding, then the material flow is called plastic and if graph is curve, then type of flow is called viscoplastic. The examples are toothpaste, grease etc. [41]

![Plasticity Graph](image)

Figure 21 Plasticity [46]

3.2.5 Thixotropy

This property is time dependent. If the viscosity decreases with time at constant shear rate then the material flow is called thixotropy. On removal of the shear force, the material tends to regain its original viscosity. This is due to weak interactions between substance particles which are broken by shear force [41].

![Thixotropy Graph](image)

Figure 22 Thixotropy [46]

In knife coating, to understand the flow properties of the paste, there is need to understand the movement of paste and velocity of paste. In knife coating, the bank of paste is placed in front of knife which is forced to move. When the paste to be applied is forced to move, the top layer is hindered by the shear force exerted by blade profile and angle while the lower layer attached to the fabric will move faster. When molecules of paste want to move from one layer
to another, the resistance to the flow occur due to the internal friction between the layers which is viscosity and the energy is released. To keep the paste to flow, energy must be given into the system. So energy needed depends upon the viscosity of the paste. With higher viscosity of paste, more energy is needed. This energy or force which is needed for the paste to flow is called shear force [3].

\[ h = \text{gap between blade and substrate} \]
\[ x' \text{ is blade width} \]

*Figure 23 Coating Rheology [3]*
4 Conductive Polymers

Electronic textiles have its own importance and application in different areas like military, sports, medical and industrial textiles. But electronic textiles are not suitable for daily use and uncomfortable to wear. So to make user friendly wearable electronic textiles, there is need of development in new textiles having electrical properties and research is going on in metallic and optical fibres, conductive coatings on different textiles. Conductivity is the main requirements in electronic textiles and this can be achieved in different ways [10].

a) Using metallic filament in textiles but this has a drawback of being brittle, heavier and difficult to process
b) By using metallic salts coating on textiles. These also have limitation of durability to laundry
c) By using conductive polymers like polypyrrole, polyaniline and polythiophene to induce conductive character in textiles.

4.1 Applications of Conducting Polymers

A novel and interesting technical textiles are obtained by coating substrates with conductive polymers [10]. The conductive textiles contain properties which make their use in intelligent materials systems. They are sensitive to numerous stimuli and they can respond to them and also can store energy and information performing intelligent functions [11].

4.1.1 Used as Capacitor

A conductive polymer has its own different characteristics. It can lead current and behave as an electroactive material and it is possible to either charge or discharge it so it can be used in rechargeable batteries. They can also be used in super capacitors as they can store energy and discharge it. For the conductive polymers, thin coating is done on textiles with large surface area to make it act as a super capacitor. Polypyrrole and polythiophene are reported to store charge up to 18 F/g. The conductive polymers are also used together with photosensitive polymers to make the part of photovoltaic devices. This is claimed that conductive polymers have not so good efficiency as compared to other photovoltaic materials like silicon semiconductors but it is still believed that if it is used in roofs and buildings, it can give good supply of electricity at lower cost [12].
4.1.2 Electromagnetic Shielding Application
The utilization of lightweight conductive polymers has replaced the use of metals in many applications to some extent. But there is need in development in this field to get good mechanical properties and stability; however the materials with low conductivity value (100-200 S/cm) have proved their use in electromagnetic shielding application [11]

4.1.3 Antistatic Applications
Another area where conductive polymers have found its application is utilization of semiconducting nature in antistatic applications. All electronic components are transported in antistatic packaging. The use of conductive polymers in antistatic packaging is to provide both surface conductivity and transparency along with scratch resistance which are the main requirements of packaging materials [11].

4.1.4 Applications in Microelectronics
Combination of certain properties of conducting polymers makes them attractive to used in replace for certain materials in microelectronics. The conductive properties of conductive polymers are controlled by different aspects like [13]

a) The manipulation of polymer backbone.
b) The nature of dopant
c) The degree of doping
d) Blending with other polymers

In spite of all these, they are easy to process, lightweight and flexible. Conducting polymers have another important application in microelectronics. Polyaniline can eliminate distortion by preventing the build up of charge in resist layer giving improvement in resolution of electron beam pattern. This is reported that polyaniline producing conductivity of $10^{-4}$ S/cm is effective to eliminate resist layer. IBM has also introduced water soluble polyanilines eliminating resist layer when used as 200 nm thick layer [11].

Conductive polymers are also found to be effective in reducing charge of nonconducting specimens during SEM (Scanning Electron Microscopy). Polyaniline is also used for coating electroless deposition of copper connectors [11].
4.1.5 Application in Ion-Selective Sensors
Conductive polymers are also used for *ion-selective sensors* by using polymer as a conductive component or by using as a matrix in conductive system. Some ionic exchange occurs when these analytes under investigation comes in contact with this conductive system and transmits the electronic signals for display [14].

4.1.6 Application in pH Sensors
Polyaniline is also used in *sensing pH* in aqueous medium. Conductivity decreases with the change in pH at constant potential or at constant pH, the change in conductivity with respect to potential can be measured [14].

4.1.7 Application in Humidity Sensors
The conductive polymers are popular for their use in sensors for alcohol vapours like methanol, ethanol etc. They are also used to find the Relative Humidity in *Humidity Sensors*. These sensors containing electroactive polymers senses relative humidity by change in conductivity with water vapours [14].

4.1.8 Application in Gas Sensors
Conductive polymers have its great application in *industrial/ chemical sensors*. Nylander *et al* found polypyrrole as a gas sensing material by exposing filter paper impregnated with polypyrrole to ammonia vapour and same was investigated by Dhawan *et al* with polyaniline [14].

Conductive polymers such as polypyrrole, polyaniline and polythiophene have been found their use in *Gas Sensors* since 1980s. The gas sensors made of conducting polymers have improved characteristics as compared to the commercially available sensors which based on metal oxides and work at higher temperatures. These sensors have high sensitivity, short response time and the most attractive property that they can work at room temperature [15].

4.1.9 Application in Biosensors
One of the most important applications of conducting polymers is its use in *Biosensors*. To improve the quality of lives, the control of disease is necessary and this can be done by diagnoses different biochemical compounds in body fluids. Thus the rapid, continuous and sensitive monitoring is required to measure the body fluids concentrations to control the diseases. So electrochemical biosensors are used in this regard. The conducting polymers are used in biosensors due to their unique properties along with possibility to entrap enzymes
during electrochemical polymerization. Conducting polymers are electrochemically produced on small electrode probe and used in monitoring of biomolecules such as enzymes, DNA etc. [16].

By modification of the chemical structure and physical properties, the conducting polymers can be widely used in different categories of biosensors and the polymer itself can be made such as to bind protein molecules. The other useful property of conducting polymers is, with electrochemical synthesis, the polymer can be deposited on the electrode probe which can capture protein [17].

4.2 Electrically Conducting Textiles

With the rise in electronic industry, the need of flexible conducting and semiconducting materials also arose. The highly conducting materials were firstly woven with metal wires like brass and aluminium. Flexible semiconducting textiles were made by incorporating conductive carbon and metal powder on woven, non-woven and knitted textiles. These materials are incorporated in fabrics with the help of binders. This substrate finds many applications in the field of electromagnetic interference shielding and static dissipation [18].

One way to produce less expensive material is to incorporate conductive filler in plastics. However the significant amount of filler in polymer/filler blend causes loss of mechanical properties and hence difficult to produce textile fibres. Commercially available products are nylon and polyester yarns made with conductive filler as core or sheath [18].

Another route to produce conductive textiles is to coat textile with metals like copper, silver, nickel etc. Copper sulphide can be coated on synthetic fibres to produce moderately conductive textiles which have its application in static dissipating carpets.

Conductive polymer coating is a good and interesting alternative for filled or metal coated textiles. Although this method has its own limitation but it gives good flexible thin coating on textiles which can be used in different areas of application [18].

Textiles coated with conducting polymers instantly dissipate static electricity and they have different applications like coated fabric, abrasive belts, carpets, high speed composite roller, uniforms, gloves etc. [19].

Conductive polymers playing a great role in the development of smart/interactive textiles. Electrotextiles have a great impact on the market for medical textiles, protective clothing, and
military and sports textiles. Smart textiles get signals for electric sensors and act to environment accordingly [20]. The conductive polymers are lack in textile fibres’ properties like dyeability, resistance to wear and comfortness. Resistance to wear has been solved by coating conventional textiles by conductive polymers. Coating the textile substrates with conducting polymer is also called “organic synthetic metals” [21].

4.3 Types of Conducting Polymers

There are four types of semi-conducting polymers [22]

a) The polymers which are filled with conductive materials like carbon black, graphite, metals particles etc.

b) Ionically conducting polymers which have a wide range of applications in the field of electronics including rechargeable batteries, fuel cells and polymer light emitting devices.

c) Charge transfer polymers is the most established one because of its wide use in xerographic photocopiers.

d) The last one is conjugated conducting polymers. In conjugated polymer class, to get the conducting filled polymers, polyaniline and modified polyaniline are used as fillers.

4.3.1 Chemical Structure of different Conducting Polymers

![Chemical structure of conductive polymers](image)

Figure 24 Chemical structure of conductive polymers [21]
As shown in Fig. 14 that there are many conducting polymers like polyaniline, polypyrrole, polythiophene etc. But the working of this project is related to poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) or simply PEDOT/PSS. So PEDOT/PSS will be explained in a detail as compared to other conducting polymers. A brief description of other conducting polymers is given below

4.3.2 Polyacetylene

This is the first conducting polymer synthesised. Polyacetylene is the simplest conjugated polymer. It precipitates as black, infusible interactable powder out of solution in its linear form and cannot be processed. Ant et al were the first who polymerize acetylene in hexane with alkyl aluminium and titanium tetraalkoxide using as a mixed catalyst. The first example of conducting polyacetylene by doping with halogens was adopted by Shirakawa’s route (Noble Prize for Chemistry 2000) to yield polymer film up to 0.5 cm thickness [23].

Polyacetylene was the first polymer showing high conductivity comparable with metals when exposed to oxidizing agents. Due to oxidation, the formation of charge carriers occur on conjugated polyene structure. Polyacetylene is found in two isomeric forms as shown in the figure below in which the trans form is more thermodynamically stable at room temperature [21].

![Figure 25 Isomeric forms of polyacetylene [21]](image)

Shrikawa worked with both the cis and trans form of the polyacetylene and his work included to control the cis, trans bond ratio in polymer. Originally, polymer fibrils are oriented randomly having contact with each other causing decrease in conductivity. The orientation along the stretch results in the increase in conductivity 100 times more than the fibrils oriented perpendicularly. So the trans form of polymer which is oriented and more stable give higher conductivity than cis form of polymer [24].

Polyacetylene is not accepted for commercial application and there is other conjugated conducting polymers for which gain their commercial importance.
4.3.3 Polyaniline

Polyaniline is conductive polymer which is soluble in selected solvent and usually is solution and melt processable. They give good conductivity over a wide range and phase compatibility. They are easily blendable with bulk polymers causing easy processability and giving conductivity at low cost with transparent and coloured thin films and coatings. For neat polyaniline polymer the conductivity can be achieved up to $100 \, \text{S/cm}$ and in composition a wide range of conductivity can be achieved from $10^{-10}$ to $10^{-1} \, \text{S/cm}$ for melt processed and $10 \, \text{S/cm}$ for solution processed [25].

Among the all conducting polymers, polyaniline is the most air and moisture stable polymer in its both doped i.e. conducting and dedoped i.e. insulating form having very simple acid/base doping-dedoping chemistry. It has a lot of potential applications including anticorrosion, industrial sensors, and antistatic coatings. Conventional synthesis of polyaniline give irregular structure shape so special “structural directing agents” are added to make nano structured polyaniline during chemical polymerization and these structural directing agents can by surfactants, liquid crystals or polyelectrolytes and relatively complex bulky organic dopants [26].

Polyaniline has the unique conduction mechanism among all the conducting polymers because it is doped both by protonation as well as p-type doping. This results in the formation of nitrogen cation which is different from other polymers in which p-doped carbonium ion is formed. The different properties of polyaniline are due to its A-B type configuration as compared to other conducting polymers which have A-A type configuration. Furthermore this B type is the N heteroatom which is found in conjugation of polyaniline more than the heteroatom involved in polypyrrole and other similar conducting polymers. Thus the conductivity of polyaniline depends on both the oxidation state and degree of protonation of the polymer [12].

Polyaniline exists in a range of oxidation state and one which is doped to high conducting state is called emeraldine. In base form they exist in both amine (-NH-) and imine (=N-) states in equal proportions. The imine site can be protonated to dication called bipolaron...
emeraldine salt. However these undergo further rearrangements to form delocalized polaron lattice as shown in figure below [12].

![Diagram showing the doping of emeraldine base with proton to form the conducting emeraldine salt of polyaniline](image)

Figure 27 The doping of emeraldine base with proton to form the conducting emeraldine salt of polyaniline [12]

Theoretical calculations describes that bipolaron state is energetically more favoured than polaron and this is also agreed that in polyaniline, the polarons are the charge carriers responsible for conductivity. This is also shown that the bipolarons are few in number and are not associated with the conducting portion of polymer [12].
### 4.3.3.1 Chemical Polymerization of aniline

Chemical polymerization is the simple and widely used commercial method in the production of polyaniline producing powder, dispersions and coated products.

For this polymerization process, the chemical oxidant in solution is used which is usually aqueous ammonium persulphate \((\text{NH}_4)_2 \text{S}_2\text{O}_8\). The dopant in this case is usually \(\text{HSO}_4^-\) and \(\text{SO}_4^{2-}\) under acidic pH \((\leq 3)\) to make aniline water soluble and to avoid by products formation. Two electrons are removed from each aniline monomer in this polymerization. The mechanism of chemical polymerization is considered to be similar with electrochemical polymerization. At first the aniline cation radical is formed with the subsequent formation of \(N\) and para-radical cation. Then further rearomatization and oxidation occurs forming “head to tail “(N-para-position) polymer but also N-ortho is formed as a result of defect in conjugation. The difference of this type of polymerization with electrochemical is when the chain propagation and final product is formed. Here the final product is formed by oxidation while in electrochemical, it is formed by reduction [12].

There are certain parameters which affect the properties of resulting conducting polymers and are discussed briefly below [12]

- Temperature has the great impact on molecular weight of polymer. The polymer initially formed at room temperature resulting in the formation of low molecular weight product. Then the temperature is decreased to 1-5 C° to get the molecular weight upto 30,000 to 60,000 g/mol and even more if temperature is decreased to zero or below.
- The nature and concentration of protonic acid in polymerization with \(\text{S}_2\text{O}_8^{2-}\) affect the molecular weight, the time of reaction, morphology and physiochemical properties of polymer.
- More often aqueous solution is used as solvent in the chemical polymerization of aniline yielding 65% emeraldine salt products with conductivity range in 10 S/cm.

### 4.3.3.2 Electrochemical Polymerization of aniline

Electrochemical polymerization method for aniline is the same like that of pyrrole except the difference of acidic pH in system for aniline. Due to this acidic environment, the cell and electrode must withstand the acidic environment. To avoid the risk of over oxidation, a constant potential is provided [12].
In the polymerization start, the cation radical is formed in oxidation step. In second step, the radical coupling and rearomatization occurs simultaneously with the elimination of two protons. In chain propagation step, the reaction further goes on with oxidation under doping of HA (acid) simultaneously and the reaction is reported to be as self catalysing. The mechanism is explained in figure below as [12]

*Step 1. Oxidation of Monomer*

\[
\text{Ar-NH}_2 + \text{HA} \xrightarrow{-e^-} \text{Ar}^+\text{N}^+\text{H}^- + \text{HA}^-\text{N}^+\text{H}^- \xrightarrow{e^-} \text{Ar-NH}^-\text{H}_2^- + \text{Ar}^-\text{N}^+\text{H}^-\text{N}^+\text{H}_2^-.
\]

*Step 2. Radical Coupling and Rearomatization*

\[
\text{Ar-NH}^-\text{H}_2^- + \text{Ar-NH}^+\text{H}^- \xrightarrow{\text{HA}} \text{Ar-NH}^-\text{N}^+\text{H}_2^- \xrightarrow{e^-} \text{Ar-NH}^-\text{H}_2^- + \text{Ar}^-\text{N}^+\text{H}^-\text{N}^+\text{H}_2^-.
\]

*Step 3. Chain Propagation*

\[
\text{Ar-NH}^-\text{H}_2^- \xrightarrow{\text{HA}} \text{Ar-NH}^-\text{H}_2^- + \text{Ar}^-\text{N}^+\text{H}^-\text{N}^+\text{H}_2^-.
\]

*Step 4. Oxidation and Doping of the Polymer*

\[
\text{Ar-NH}^-\text{H}_2^- \xrightarrow{\text{HA}} \text{Ar-NH}^-\text{H}_2^- + \text{Ar}^-\text{N}^+\text{H}^-\text{N}^+\text{H}_2^-.
\]

Figure 28 Electrochemical polymerization of aniline [12]
The type of electrode plays an important role. To obtain good conductivity, the surface chemistry of electrode must be compatible with polyaniline. In electropolymerization, the polyaniline is directly deposited on aluminium or steel active substrate to avoid corrosion protection. To obtain the conductivity of polyaniline, the strong acid has to be used. The anion employed by the acid has a great influence on the structure of polymer e.g. oxyacids give structure like sponge and HCl gives structure like spaghetti [12].

The acid electrode provides the right pH in the aqueous solution and also provides dopant anion A\(^-\) which is conjugate base of an acid. Dopant having larger molecules can be incorporated with the addition of polyelectrolytes. Optically active cations can also be incorporated to get optically active water soluble sulfonated polyaniline. In electrochemical polymerization, to obtain the colloidal dispersion of optically active polyaniline, a hydrodynamic flow through electrochemical cell is used [12].

4.3.4 Polypyrrole

Polypyrrole was first prepared in powder form very long ago in 1916. But after 1979 the electrochemist took interest in this conducting polymer when they come to know that by the anodic oxidation of pyrrole, a continuous film can be made [29]

They are space fillers rather than fibrillar polymers and show moderate conductivity in reduced form but they are good conductors when oxidized and doped with anions. The polymer material and properties differs depending upon the following [29]

- The extent of oxidation
- Doping anion
- The length of polymer chain
- The bonding within the chain
- The organization of chains within the polymer system
Polypyrrole is the most frequently used conductive polymers in all the intrinsically conducting polymers because of its good conducting stability and its possibility to form homopolymers and composites with good mechanical properties. This polymer is a serious candidate in technological applications such as antistatic coatings, electromagnetic shield coatings, sensors, batteries, molecular devices and electrodes due to its soluble and processable preparation and good atmospheric stability [30]

4.3.4.1 Electrochemical polymerization of Pyrrole
The electrochemical polymerization occurs in an electrochemical cell which is moving or rotating. The electrochemical polymerization takes place under specific conditions in a solution in which monomer, solvent and a counter ion interacted with electrode plays their specific role. The polymer deposited on electrode and there are some parameters which are responsible for the disposition of the resultant polymers [12].

- The applied potential influences the rate of oxidation and polymerization
- The nature and material of electrode determines how easy the oxidation is taking place while the size of electrode determines the conductivity.
- Solvent has a great impact of conformational structure of polymer as should be used as pure as possible. A broader range of counter ion can be used in aqueous solvent rather than organic solvent.
- The structure of monomer and substituted groups has great impact on electrochemical process.
- The electrolyte has influence on the interaction between polymer and solvent, influencing conductivity and the properties of polymer.
- The size, type, concentration and charge on counter ions have great influence on the conducting polymer properties.

![Figure 30 the three electrode electrochemical polymerization cell](image-url)
The chemical steps involved in electrochemical polymerization contains oxidation step in which monomer oxidation occurs followed by radical-radical coupling. The next step is rearomatization followed by chain propagation as shown in figure below [12].

**Step 1. Monomer Oxidation**

\[
\text{X}_\text{Y} + \text{A}^- \xrightarrow{\text{OXID}} \text{X}\text{Y}^+ \text{A}^- 
\]

*Resonance forms:*

\[
\text{X}_\text{Y} + \text{A}^- \xrightarrow{\text{OXID}} \text{X}\text{Y}^+ \text{A}^- 
\]

(i) \[ \xrightarrow{\text{Resonance}} \]

(ii) \[ \xrightarrow{\text{Resonance}} \]

(iii) \[ \xrightarrow{\text{Resonance}} \]

**Step 2. Radical-Radical Coupling**

\[
\text{X}_\text{Y}^+ \text{A}^- \cdot \text{X}_\text{Y} + \text{A}^- \xrightarrow{\text{Radical-Radical Coupling}} \text{X}_\text{Y}^+ \text{A}^+ + \text{X}_\text{Y} + \text{A}^- 
\]

**Step 3. Deprotonation/Re-Aromatization**

\[
\text{X}_\text{Y}^+ \text{H} \text{Y}^+ \text{H} \xrightarrow{-2\text{H}^+} \text{X}_\text{Y} + \text{Y}_\text{X} 
\]

(dinner)

**Step 4. Chain Propagation**

\[
\text{X}_\text{Y}^+ \text{X}_\text{Y}^+ \text{X}_\text{Y}^+ \text{X}_\text{Y}^+ \xrightarrow{\text{OXID}} \text{X}_\text{Y}^+ \text{X}_\text{Y}^+ \text{X}_\text{Y}^+ \text{X}_\text{Y}^+ + 2\text{H}^+ 
\]

*Figure 31 polymerization steps in the formation of polypyrrole [12]*
4.3.4.2 Chemical Polymerization of Pyrrole

Chemical polymerization offers advantages from processing point of view as it is easy to process in large quantities and it is in the form of powder or colloid and can be coated to substrate to make it conductive. Polypyrrole has been deposited on glass and plastics but it is also widely used on textile fibres and fabrics. Nylon fabric is also used in which hydrogen bonding takes place between the carboxylic group of nylon and pyrrole to give more ordered polypyrrole product. Due to molecular orientation, it increases the molecular anisotropy which infect increases the conductive property [12].

Chemical polymerization of pyrrole can be done in neutral medium which is advantage over aniline in which the medium is acidic. A range of organic solvent can be used in polymerization, but the limitation involves both the dissolution of monomer and oxidant. It is assumed that the chemical polymerization is very similar to the electrochemical polymerization but the studies showed that the product duplicate is difficult in electrochemical polymerization using a chemical oxidant. Synthesis of 3-methyl-4-carboxy-pyrrole by both polymerization methods showed that the product is similar in chemical composition but differ a lot in polymer morphology [12].

Chemical polymerization process is influenced by the following parameters

- The chemical oxidant is the initially used source of counter ions, where FeCl₃ and (NH₄)₂ S₂O₈ are most widely used. H₂O₂ is an interesting alternative due to environmental aspect. Two electrons are required to oxidize one unit of pyrrole.
- The solvent influences the conductivity. Both the aqueous and organic solvents like alcohol and benzene are used.
- The polymerization temperature has influence on conductivity and experiments shows that maximum conductivity is obtained at 0 C° between the temperature range of -20 to 60 C°.
- The nature of the dopant counter ion affects both the polymerization process as well as the properties of conducting polymer similar in way to electrochemical polymerization.

Polypyrrole is not soluble in both water and organic solvents. There exist both intermolecular and interamolecular forces between polymer chains which make it difficult to process and infusible product [12].
4.3.5 Polythiophene

Polythiophene can be synthesized by both chemical and electrochemical polymerization as polypyrrole and firstly it was synthesized electrochemically. The polymerization mechanism is the same as for polypyrrole in which counter ion is incorporated into the polymeric structure in polymerization mechanism and radical cation reacts with the starting monomer or with each other [12].

The polymer way to produce in non aqueous solvent is more common as it is more soluble in non aqueous medium. It is reported that the solvent used in electrochemical polymerization has great impact on solubility of polythiophene and a small amount of monomer is needed for polymerization. If the polymerization process is taking place in aqueous medium then surfactant is needed to solubilise the monomer. The optimum properties are obtained at the temperature range of 15 C° to 20 C°. The first chemical polymerization route for polythiophene was reported in 1980. Because this is insoluble in aqueous media, so a non aqueous medium had to be used. Polycondensation process was used to dehalogenate the halogentiophene and this remained the most common method for chemical polymerization [12].
4.3.5.1 PEDOT

PEDOT is poly(3,4-ethylenedioxythiophene) and also abbreviated as PEDT. This is also known under the trade name of Baytron®. Early chemistry of polythiophene was achieved by the synthesis of mono and dialkoxy substitution developed by Laclerc and scientist at Hoechst AG. But these polymers show low conductivity in oxidized, doped state. So the synthesis of bicyclic EDOT (3,4-ethylenedioxythiophene) electrochemically polymerized by Heinze et al and chemically polymerized by Jonas et al of the Bayer Corporate Research Laboratories overcame this problem and showed that this PEDOT has good stability and high conductive cationic doped state. PEDOT plays an important role in the application of antistatic coatings, conductive coatings, and electronic devices and displays [32].

4.3.5.2 PEDOT:PSS

PEDOT:PSS is poly(3,4-ethylenedioxythiophene)-poly(styrene sulphonate). A wide spread applications has been developed by PEDOT having complex with polystyrene sulfonic acid also known under the trade name of Baytron® P. PEDOT cannot be easily processable and coatable because this is insoluble in most commonly used solvents. Polystyrene sulphonic acid is a water soluble polymer and hence when its complex is formed with PEDOT, it acts as a good dispersant. Polymerization with an oxidant sodium peroxodisulfate yields a conductive and cationic form of PEDOT:PSS complex as shown in figures below [32].

There are three structures as primary, secondary and tertiary shown below in the figure 26, 27 and 28 respectively. The figure shows the oxidative polymerization of EDOT monomer in the presence of PSS.
Figure 36 Primary structure of PEDOT:PSS [32]

Figure 37 Secondary structure (purposed) of PEDOT oligomers on PSS chain [32]

Figure 38 Tertiary structure: water-swollen gel particles of PEDOT:PSS
In the above structural model, it is shown that PEDOT is tightly, electrostatically attached to the high molecular weight PSS segment. The high conductivity of PEDOT:PSS is due to the stacked arrangement of PEDOT in the tangled, loosely cross linked water-swollen PSS gel particles in film. These particles are usually 90 to 95% of water. The amount of solid content and stable dispersion depends upon the ratio of PEDOT and PSS, which increases with increase in the amount of PSS. The PEDOT:PSS gel particles have excellent film forming properties and can be easily coated to thin film on a variety of substrate [32].

There are two main roles of PSS in the complex. The first role is to provide charge balancing counter ion to the PEDOT without which 3,4-ethylenedioxy-2(5H)-thiophene is formed instead of desired PEDOT:PSS. And the second function is to provide dispersible PEDOT. Although PEDOT is not truly water soluble, the reaction forms stable, easy to process deep blue dispersion [32].

Some of the properties are summarized in the table below which depends upon the different ratio of PEDOT:PSS [32]

<table>
<thead>
<tr>
<th>PEDOT:PSS ratio</th>
<th>Solid Content %</th>
<th>Conductivity (S/cm)</th>
<th>Typical Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2.5</td>
<td>1.3</td>
<td>10</td>
<td>Conductive Coatings</td>
</tr>
<tr>
<td>1:2.5</td>
<td>1.3</td>
<td>1</td>
<td>Antistatic</td>
</tr>
<tr>
<td>1:6</td>
<td>1.5</td>
<td>$10^{-1}$</td>
<td>OLEDs</td>
</tr>
<tr>
<td>1:20</td>
<td>3</td>
<td>$10^{-3}$</td>
<td>Passive matrix displays</td>
</tr>
</tbody>
</table>

Table 1 PEDOT:PSS ratio and their characteristics [32]

The conductivity also depends upon the particle size of the polymer. Particle size can be varied by applying different shear rates during synthesis. Small particle size does not only decrease the conductivity but also viscosity [32].

PEDOT:PSS has replaced the well-known expensive inorganic Indium tin oxide (ITO) in optoelectronic devices as anode, like organic photovoltaic cells and OLEDs (organic light emitting diodes) and is a good competitive for electrodes in field-effect transistors due to its high conductivity [35].

One of the major problems for conducting polymers is their processability. So a lot of working is done to make blends of conducting polymers with conventional polymers also to give good synergic effect. Among these the PEDOT:PSS is the best one due to its low gap
energy and good solubility in polar solvents and can be blend with polyethylene oxide (PEO). PEDOT materials show high transparency, stability in oxidized state and high mobility of carriers and when PEDOT:PSS is blended with PEO, it increases the ionic mobility in the final product. When PEDOT:PSS is mixed with PEO, it shows the similar conductivity as presenting by carbon-graphite [36].

In all the conducting polymers PEDOT:PSS has appeared the most successful materials. It contains some advantageous properties which the other conducting polymers like polypyrrole and polyaniline don’t have. It has low oxidation potential, moderate bandgap and good stability in oxidized form. A more regiochemically defined material can be prepared by blocking the β-position of the ring and α-β linkages can be avoided [37].

Thermal treatment also has a great impact on PEDOT:PSS coated film. The roughness of film increases as the temperature is increased and reaches a maximum at 200 °C. By increasing the temperature more, the roughness decreases. The reason is not clear but hypothesis is given that when the temperature is increased initially, the colloidal particle size increases giving the surface roughness and when it is further increased to 250 °C, the decreasing roughness can be due to film degradation [38].
5 Experimental working

The experimental working was done in the laboratory of the “Swedish School of Textiles” at the University of Boras.

5.1 Purpose of Experimental Study

The purpose of experimental study was to formulate the paste recipe along with conducting polymer. In this study, two rheology modifiers were used and it was to be found that what amount should be used of both rheology modifiers in alone or in combination to get the optimum paste viscosity and smooth coating.

5.2 Materials

The materials used in this project were binder, thickener, the conducting polymer and the polyester fabric which are described below.

5.2.1 Fabric

The fabric used for coating was 100% polyester fabric with GSM 112

5.2.2 Coating Paste

The ingredients used in the paste were

a) Alberdingk® U 2101: This is solvent free polyester polyurethane BINDER which has pH 8.5 and elongation at break 800%.

b) Borchi® Gel L 75 N: This is HEUR THICKENER for water borne system coatings.

c) Borchi® Gel 0434: This is high Shear THICKENER which is also HEUR based.

d) Clevios™ PH 1000: This is aqueous dispersion of PEDOT/PSS of H.C. Starck Germany having solid content 1-1.3%.

5.2.3 Instrument for resistivity measurements

The instrument used for resistivity measurement was Metriso 2000 resistance meter.

5.2.4 Instrument for viscosity

The instrument used for measuring viscosity was Brookfield viscometer DV I+. Complete manual was studied before using this Brookfield viscometer. Different viscosity readings were taken for paste at different shear rates keeping the spindle # constant and in this case the
spindle chosen was 3 (which has corresponding code for spindle S63 from the appendix given in manual).

![Viscometer](image)

**Figure 39 Viscometer**

5.3 Paste Matrix

The paste matrix was made using PEDOT/PSS %age constant and varying amount of rheology modifier either alone or in combination. The amount of binder was used according to recipe to make the composition 100%. Different recipe formulations were made and interesting findings were determined in case of paste viscosity. Some of important results are discussed here and complete matrix can be seen in the appendix.

5.3.1 Pseudoplastic behaviour

Pseudoplastic is the property of fluid which decreases its viscosity with increase in shear rate while thixotropic is the property of fluid which decreases its viscosity over time at constant shear rate. The first experiment was done to check the behaviour of paste and it was determined that it is pseudoplastic in nature as shown in the graph below.
5.3.2 Reliability of Results

Different trials were done to check the reliability of viscosity measurements. The graph shown below shows the reliability of results.

5.3.3 Gel L75N

Gel L75N is a rheology modifier which is hydrophobically modified ethoxylated urethane based. Different %ages of L75N were used to get the optimum viscosity. It is shown in the graph below that using Gel L75N alone, minimum amount required to get good viscosity is 4.5%. As the amount is increased, the rise in viscosity then previous one, also increases.
The reason in the above results is due to, when amount of thickener is increased, the rheological properties of polyurethane adhesive increases and improvement in viscosity from the previous one is due to the crosslinking within the polyurethane system when amount of thickener is added more and more due to the interaction between thickener and polyurethane adhesive which also take part in thickening mechanism.

5.3.4 Gel 0434

This rheology modifier is not so effective as compared to L75N, as 27% amount in the paste just give the viscosity up to 13000cps which is not sufficient for coating application. So Gel 0434 cannot be used alone as a rheology modifier thickener.
The reason for the above results is may be due to the solid content of the polymer. The solid content in Gel L75N is more than Gel 0434 and Gel 0434 is newtonian associative thickener which is suitable for high shear rates (brush, paint) while L75N is pseudoplastic material giving good rheological properties.

5.3.5 Combination of L75N and Gel 0434

The rheology modifier Gel 0434 if used in combination gives very good rise in viscosity even with the addition of small amount. Below graph shows that with 2% of Gel 0434 in combination with Gel L75N gives 10000 cps rise in viscosity which is impossible to gain such viscosity even with very large amount of Gel 0434 alone as previously shown. This is may be due to the reason that hydrophobic chains are mainly responsible for the thickening mechanism and when they are used in combination, it is obvious that the more synergic effect is obtained which gives high interactions with polyurethane binder system and hence increases in viscosity.

![Figure 44 Viscosity vs shear rate in combination](image)

An interesting finding is seen in combination trials. When Gel 0434 is added before L75N, the rise in viscosity is remarkable while the later one is added first with the subsequent addition of Gel 0434 does not give any remarkable increase in viscosity. This means while making paste in combination with both rheology modifier, the order of addition of chemicals should be taken into account. This is may be due to the homogeneous mixing, because when L75N is added earlier giving high viscous paste making the mixing of 0434 difficult homogenously but when 0434 is added before the mixing is quite easy and does not give so viscous solution and hence by adding L75N subsequently, the required viscosity can be
attained. Below in graph, the green line shows the addition of 0434 after L75N while the red line shows the addition of 0434 first, giving remarkable difference.

![Graph showing viscosity comparison](image)

**Figure 45 The order of addition of Gel 0434 comparison**

One another interesting finding was that the rise in viscosity with the addition of Gel 0434 in combination increases with the increasing %age of Gel L75N. In the graph below, it can be seen clearly that by the addition of 2% of 0434 in 4%, 4.5% and 5% Gel L 75 N increases the viscosity by 1200 cps, 4800 cps and 10,000 cps at 0.6 rpm shear rate respectively. The reason is quite simple as explained in the section 3.2.2 that by increasing amount of associative thickener, the improvement in viscosity before previous one is considered to be due to the cross linking with the polyurethane system which is due to more interaction between thickener and polyurethane binder as amount is increased, hence giving more viscosity than previous one rise.

![Graph comparing viscosity with different %ages of L 75 N](image)

**Figure 46 Comparison of addition of 0434 with different %ages of L 75 N**
5.3.6 Acrylate binder with rheology modifier

The action of rheology modifier on acrylate binder is very different as compared to polyurethane binder system. The increase in viscosity with Gel L75N in acrylate binder is very much high as compared to polyurethane binder. The graph is shown below which illustrates the comparison.

Figure 47 Comparison of PU and Acrylate binder with 5% L75N

The same viscosity obtained by 5% L75N in PU binder can be achieved with Acrylate binder by the addition of only 3% L75N as shown by the graph below.

Figure 48 Comparison of PU and Acrylate binder for same viscosity
5.4 Coating method

We know that in many industries, coating is done manually on experiences bases. This coating was done manually in the Swedish school of textile laboratory keeping the “knife over roll method” in mind. For this purpose, the fabric was placed on smooth leather and was fixed with tape. The steel ruler was used to spread paste on fabric. The main parameters in knife over roll coating are, the distance between ruler and fabric, and the angle of ruler with fabric. The distance was kept 0.5mm by wrapping the tape on both edges of the ruler. The paste was poured on fabric and spread throughout the width of fabric by ruler keeping the angle of application as 90°. The size of fabric was a little bit more from A4 size.

Then the fabric was placed on wooden frame carefully to avoid sagging and kept in the dryer for 15 min at 80°C just to know it is properly dried. Then the fabric was mounted on stenter frame and frame was inserted in the stenter machine. The fabric was cured for 3 min at 120°C. Then the resistivity of fabric was measured.

![Figure 49 curing of coated fabric](image)
5.5 Electrical Resistance

The electrical resistance of the material is its opposition to the passage of steady electric current. The SI unit for resistance is ohm (Ω) and is reciprocal quantity is electrical conductance whose unit are Siemens.

In this project, more emphasis was on rheology study and the paste formulation. But of course, the measurement of electrical resistance was necessary to check the effect of viscosity and amount of rheology modifier on conductivity or resistivity. The amount of conducting polymer was 30% which was kept constant in all the trials. The resistance checked was at 100V. The resistance was checked from four different areas to check the reliability of results.

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<td>5% L75N</td>
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Table 2 Electrical resistance of coated fabric

In the above table we can see that as the amount of rheology modifier increases, the resistivity decreases means conductivity increases. This is probably due to the increase in viscosity of paste by increasing amount of rheology modifier. And the thicker layer is formed on the surface of the fabric giving more surface conductivity as shown by the graph below. The results conversion into conductivity can be checked in the appendix 2.

![Rheology modifier Vs Resistance](image_url)

Figure 50 Decreasing electrical resistance with increasing rheology modifier
6 Conclusion

The project was focused on the study of rheological properties of coating paste concerning with the coating method. The rheology of paste was studied and conclusively it is drawn that to obtain the good viscosity of paste in polyurethane binder system, Gel L75N should be used minimum at 4.5% if used alone. This is because when L75N is used is less than mentioned amount, the sagging occurs in the sample and also there is no sufficient conductivity seen at used %age of conducting polymer. And the best properties are obtained when these two rheology modifier are used in combination such as increases in smoothness and viscosity as synergic effect. The same rheology in polyacrylate binder can be obtained by using less amount of thickener as compared to polyurethane binder.
7 Future Research

As this field of conducting polymer coating is very complicated and there is a lot of research needed in this area. The rheology study in this project was focused mainly on polyurethane binder system and just a few trials were done on acrylate binder just for comparison. There is a need to study the rheology modifier behaviour for acrylate binder system and must be compared with polyurethane binder for better result interpretation. A comparison of lab coating vs bulk machine should be done with coating application for better understanding and analysis.
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## Appendix 1

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<td>Gel L 75 N %</td>
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## Appendix 2

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### Resistance $R$ (Ω) | Length $l$ (m) | Area $A$ ($m^2$) | Resistivity $\rho$ (Ωm) | Conductivity $\sigma$ (S/m) |
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