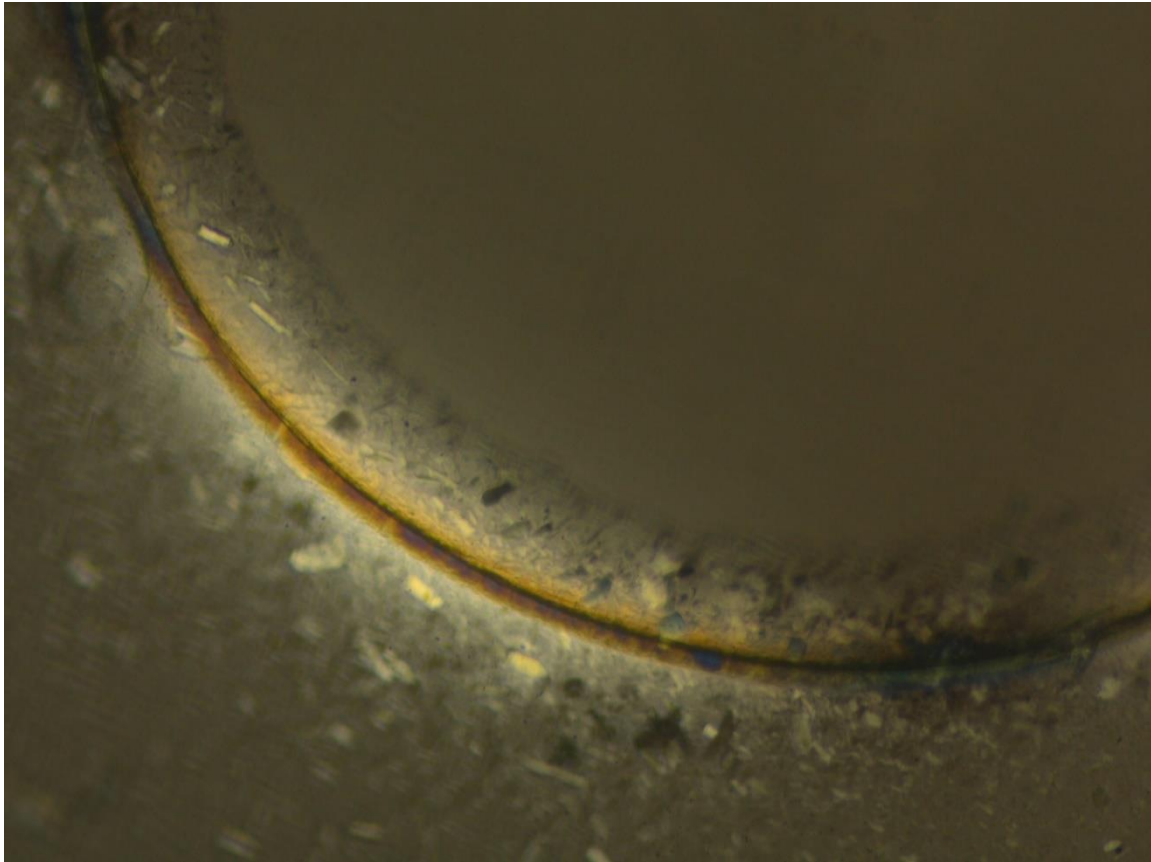




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Improving Conductive Properties in Films of Cellulose Nanocrystals

Bachelor's degree project report in Chemical Engineering

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CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2024

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Abstract

Films made from cellulose nanocrystals show promise as a platform for creating transparent, water-stable, flexible, and conductive films using conductive polymers. This study covers the work done to improve the conductivity of cellulose nanocrystal (CNC) films, moving from a proven method for producing transparent and water-stable films. Ten different experimental batches were created, each based on a unique theory for achieving and enhancing conductivity. It was discovered that drenching polymer-containing films in *p*-Toluenesulfonic acid (*p*-TSA) significantly enhances their conducting properties without affecting water stability or flexibility. However, the high polymer concentrations needed for conductivity result in a moderate decrease in transparency when using poly(3,4-ethylenedioxythiophene) (PEDOT) and a significant decrease when using polypyrrole (PPy).

Keywords: cellulose nanocrystal, conductive polymer, *p*-Toluenesulfonic acid, poly(3,4-ethylenedioxythiophene), polypyrrole.

List of Abbreviations

BC	Bacterial cellulose
BTCA	Butane-1,2,3,4-tetracarboxylic acid
CNC	Cellulose nanocrystal
CNF	Cellulose nanofibers
EDOT	3,4-ethylenedioxythiophene
EGDE	Ethyleneglycol-diglycidyl
MeOH	Methanol
PANI	Polyaniline
PEDOT	Poly(3,4-ethylenedioxythiophene)
POM	Polarized optical microscopy
PPS	Potassium persulfate
PPy	Polypyrrole
PSS	Poly(styrenesulfonic acid)
<i>p</i> -TSA	<i>p</i> -Toluenesulfonic acid
PVA-S	Polyvinylalcohol sulfonate
SEM	Scanning electron microscopy
SHP	Sodium hypophosphite
TBAHS	Tetrabutylammonium hydrogen sulfate
TEAB	Tetraethylammonium bromide
TEOA	Triethanolamine

Acknowledgements

We would like to thank our examiner, Gunnar Westman, for sharing deep insights and encouraging us greatly in our work. Thank you to our supervisor, Jelka Feldhusen, for helping us with SEM analysis and thanks to her along with Elin Horn and Gabriel Sigfridsson for their assistance in the laboratory!

Thanks to Yuge Yao for introducing us to the project with assistance and knowledge about the method for producing the films. You gave us a great head start and a lot of inspiration!

Lastly, we want to thank Youngseok Kim for teaching us about and advising us on the four-point probe analysis and calculating the conductivity of our films.

Nils Fredriksson, Hugo Rosvall, Gothenburg, June 2024

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Introduction

The demand for environmentally friendly and sustainable materials is a rapidly growing market with increasing interest [1]. Extensive research has been conducted on utilizing renewable biomass as a sustainable carbon source to prepare materials with sufficient electrochemical properties due to its environmentally friendly and cost-effective nature [2]. Cellulose is a component that can be extracted from trees, plants, algae, bacteria, or tunicates [1]. Cellulose fibers can be processed into cellulose nanofibers (CNF), cellulose nanocrystals (CNC), and bacterial cellulose (BC), each with unique properties and uses [2]. Since the focus of this project is flexible, water-stable, transparent, and conducting nanocellulose films, this text will primarily discuss CNC, rather than CNF or BC.

Cellulose is the most abundant polymeric raw material in the world and is widely used in various industrial fields, including textiles, paper, and chemicals [3]. At the simplest level, cellulose consists of β (1,4)-bound D-glucopyranosyl monomer units twisted at 180° to their neighbors [3]. These polymer chains link together to form crystalline structures known as elementary fibrils, which then bundle together to form microfibrils, macrofibrils, and cellulose fibers (see Figure 1) [3].

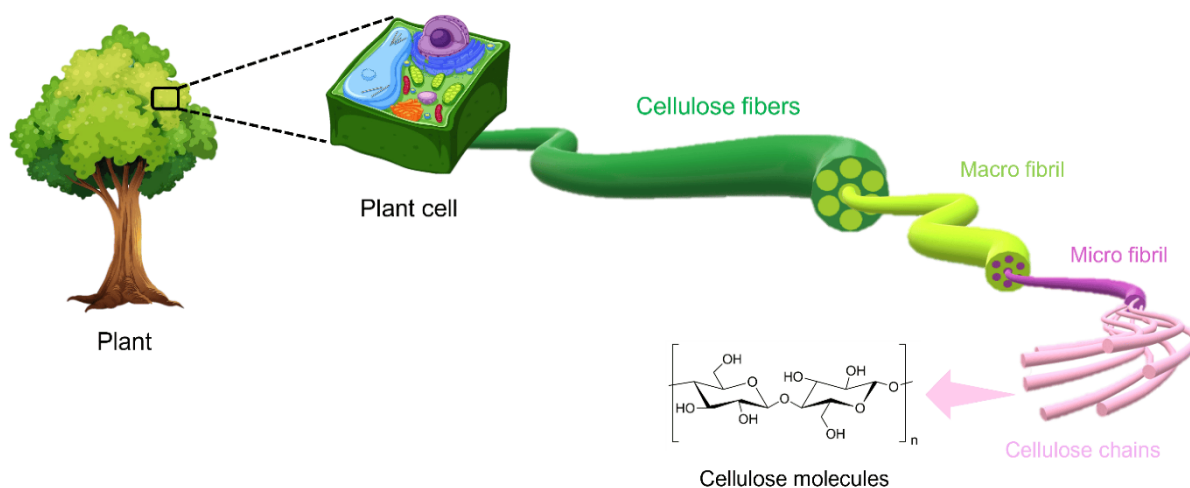


Figure 1: The components of cellulose, from cellulose fibers to nanocellulose [4].

This report will cover the work done to examine the effects of the choices of methodology and chemicals used in production on flexible, transparent, water-stable, and conductive

nanocellulose films. Specifically, nanocellulose films refer to films made from cellulose nanocrystals. To properly understand the rest of this text, it is crucial to understand the key components necessary for producing these films.

The reaction mixture includes cellulose nanocrystals, a softener, a combination of cross-linking compounds, a monomer that will polymerize into the film, and an initiator that will start the polymerization process. It is essential to acknowledge the role of cross-linkers in making the films water-stable, softeners in ensuring flexibility, and the necessity of a conducting polymer for conductivity. From previous research, it is evident that the choice of cross-linkers and softeners significantly impacts the film's properties. Conductivity is achieved through the addition of a conducting polymer.

Aim

This project aims to determine how production methods and the chemicals used can be altered to improve the flexibility, transparency, and polymer quality of films, specifically focusing on how these changes impact conductivity.

Specification of Aim

To ensure the thoroughness of this study, the aim must be as specific as possible. This means that the number of factors the project seeks to improve must be reduced. Therefore, this project will primarily investigate ways to enhance the conductivity of films made from cellulose nanocrystals, while still considering transparency. Initially, the factors believed to affect conductivity were the monomers used and the film structure, specifically the orientation of polymer chains and film porosity. As a result, the methods and chemicals investigated will focus on enhancing film porosity, how the polymer coordinates with the CNC, and the ability of different monomers to form polymers that yield highly conductive films.

Limitations on the Aim

The project will not explore any consequences related to economic, environmental, or social sustainability. However, sustainability will be considered when determining what will be examined, and the project will only use chemicals that are scalable and safe. The project will not investigate how the films produced could replace or compete in the economic market. Additionally, potential modifications to the monomers themselves outside of what is done in the film production process will not be examined.

Theory

CNC Production

In the production of CNC, the purification and pre-treatment of cellulosic materials are necessary to isolate cellulose nanocrystals and nanofibers from the cellulosic sources, involving the removal of hemicellulose and lignin. After purification, nanocellulose can be extracted from the pre-treated cellulosic materials through mechanical treatment, acid hydrolysis, enzymatic hydrolysis, or a combination of these processes [2]. The cellulose used for this project was created using acid hydrolysis with sulfuric acid (H_2SO_4), as shown in Figure 2 below. Acid hydrolysis is a common method for treating CNC, which adds sulfate groups to the surface of the CNC [5]. The resulting CNC features negatively charged sulfate groups on the surface, giving it unique properties such as forming intermolecular bonds with other molecular structures.

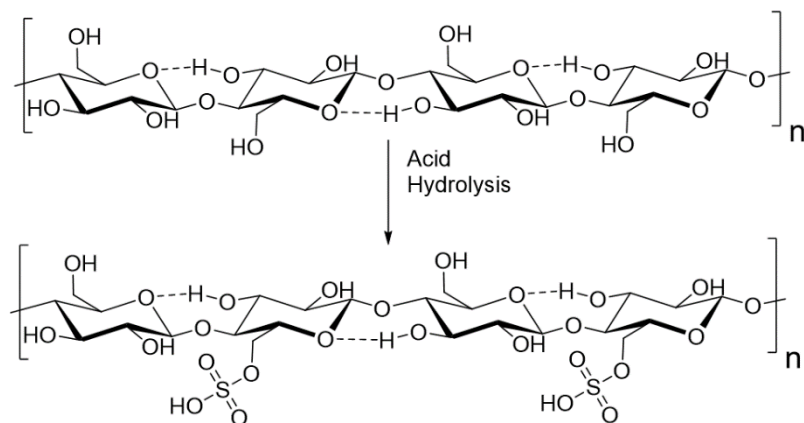


Figure 2: Acid hydrolysis of CNC with sulfuric acid.

Conductivity

As explained in the *Introduction* section, CNC films can be made conductive by bonding with a conductive polymer. Some of the most researched polymers used for this application are poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI) and polypyrrole (PPy) [2]. Conductive polymers are flexible and exhibit excellent electrical, optoelectrical, and photovoltaic properties [2]. Additionally, conductive polymers offer the advantage of easy property tuning through doping or post-treatment, enabling customization to meet specific performance requirements for various applications [2].

Conductive CNC films have been successfully produced and can be split into four main categories: CNC with conductive polymer, carbonized CNC, carbon-based materials such as CNC-CNT and CNC with metal coating [2]. Figure 3 below shows the categories with possible use cases.



Figure 3: Different applications for conductive CNC [2].

In this project the films require four fundamental properties as mentioned earlier: conductivity, flexibility, transparency and water stability. Transparency is typically a trade off with conductivity and the objective of this report is to delve deep into this challenge. Films with higher concentrations of conductive polymers have less electrical resistance and perform better in conductive tests, however, they become increasingly dark in color with increasing polymer concentration. PPy has better conductive properties than most other conducting polymers, but films made with it are completely black at high concentrations [6]. PEDOT makes the films dark blue, and films with PANI are generally dark green or yellow, depending on which oxidation state of PANI is used, with the most conductive one being dark green [7].

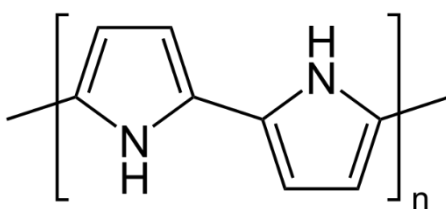


Figure 4: PPy [8].

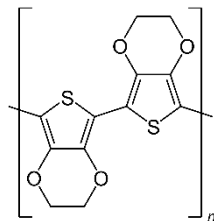


Figure 5: PEDOT [9].

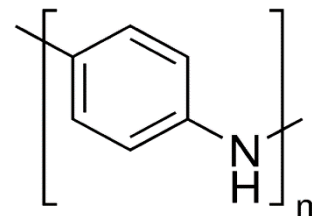


Figure 6: PANI [10].

The polymers are made of subunits called monomers, which are polymerized with the help of an *initiator* that starts the polymerization process. Initiators are oxidizing agents that catalyze

the polymerization reaction to form the conductive polymer chain. In this project we used iron(III) chloride (FeCl_3) and potassium persulfate (PPS) as initiators.

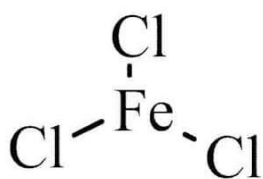


Figure 7: Iron (III) chloride [11].

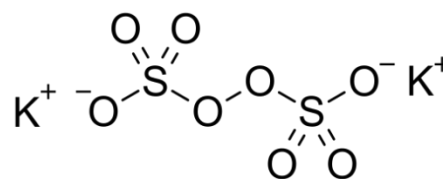


Figure 8: Potassium Persulfate [12].

In order to plan experiments and make hypotheses about different changes to the film production method or the chemicals used it is necessary to first understand the structure of the CNC in the formed films, how the structure can potentially be changed with different additives, how this affects how polymers are able to coordinate to the CNC and how the nanocellulose is modified to enable coordination. As stated previously, CNC prepared with sulfuric acid yields CNC coated with sulfate groups. Figure 9 below shows how the sulfate groups allow different additives, such as the PEDOT polymer, to bond with the nanocellulose [2].

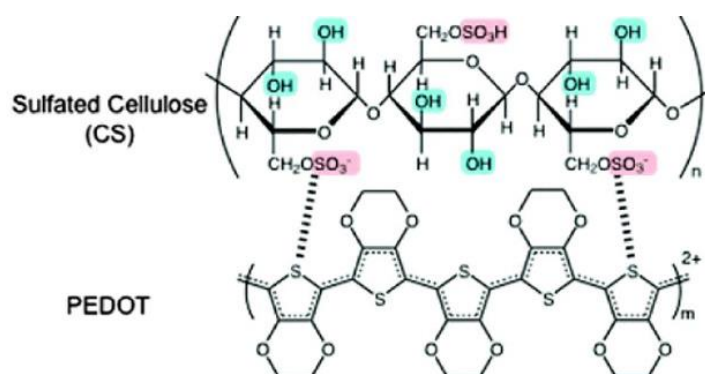


Figure 9: Sulfated nanocellulose interacting with PEDOT polymer [2].

Figure 9 demonstrates how the intermolecular forces interact between the negatively charged sulfate groups on the CNC and the positively charged sulfate on the PEDOT polymer. This hybrid polymer is referred to as CNC:PEDOT. However, Figure 9 is misleading on several levels. As mentioned earlier in this section, it is only the surface of the CNC that can have these sulfate groups. The middle sulfate group should not be there as it is only the surface of the CNC that can be subjected to sulfuric acid during acid hydrolysis. The sulfate groups are randomly distributed on the CNC surface as illustrated in Figure 10 below.

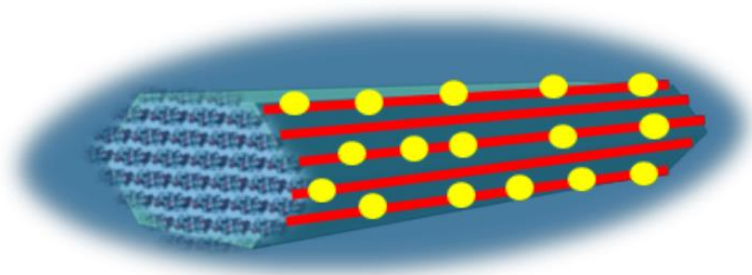


Figure 10: CNC crystals with sulfate groups illustrated as yellow dots.

For Figure 9 to accurately represent how PEDOT interacts with CNC, it must also be interpreted as showing the CNC laying down flat horizontally as if it were on a surface and the PEDOT standing up vertically, coordinating perpendicularly to the CNC. Figure 11 below shows a more accurate illustration of how the chains interact in reality. The CNC is light grey to illustrate that it is behind the PEDOT chain.

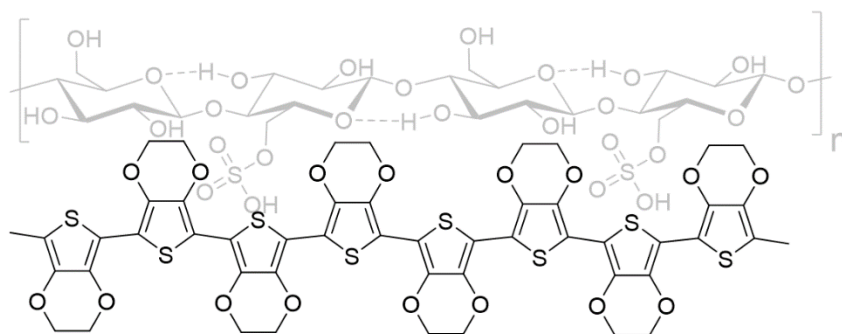


Figure 11: Accurate illustration of intermolecular interactions between CNC and PEDOT.

As explained above, it is the intermolecular forces between the polymer chains that hold them together. The interaction between them and the flow of electrons in the polymer chain are the reason for the conductive properties of conductive CNC films. This means that the concentration of sulfate groups on the CNC is of high importance in their conductive properties. The more sulfate groups on the CNC allow for more conductive polymer to interact with it, allowing for a higher degree of conductivity. Figure 12 below shows more sulfate groups present on the surface, compared to the amount in Figure 10.

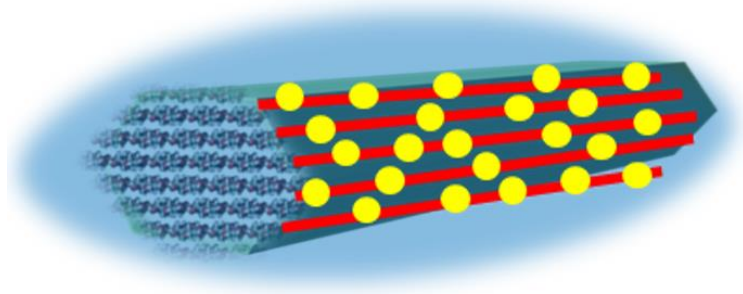


Figure 12: CNC crystals with a higher degree of sulfate groups on the surface.

The CNC:PEDOT hybrid combination is one of many that utilize the anionic and cationic properties of two different polymers. Another well-known example of such a hybrid combination is that between PEDOT and poly(styrene sulfonic acid) (PSS). This hybrid is commonly referred to as PEDOT:PSS and it possesses excellent conductive properties [13]. PSS is commonly used to increase the water solubility of PEDOT and to improve the ability of PEDOT to coordinate to the CNC. The structure of PEDOT:PSS is visualized in Figure 13 below with the PSS chain above and the PEDOT chain below it.

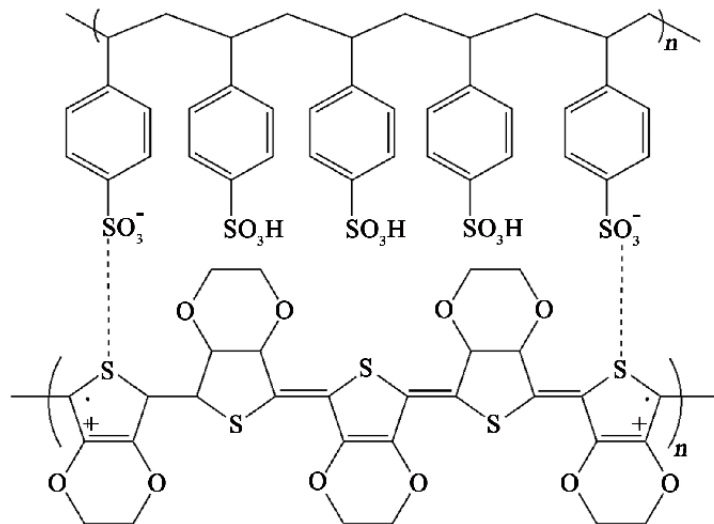


Figure 13: The hybrid polymer PEDOT:PSS [14].

Water Stability and Flexibility in CNC Films

The conductive properties of CNC are not inherent, nor are the flexible or water-stable properties. This means that the films break when subjected to physical strain and dissolve in

water. To combat the challenge of water stability, molecules referred to as *crosslinkers* are utilized. Crosslinkers form covalent bonds between adjacent CNC crystals to hold them together. There are several different types of crosslinkers and in this project we used the following two: 1,2,3,4-Butanetetracarboxylic acid (BTCA) and Ethyleneglycol-diglycidyl (EGDE). Sodium hypophosphite (SHP) was another component acting as a catalyst in the formation of these covalent bonds. Figure 14 below shows schematically how BTCA links two different CNC crystals with SHP as a catalyst, making the system stable, and water can no longer dissolve the chains.

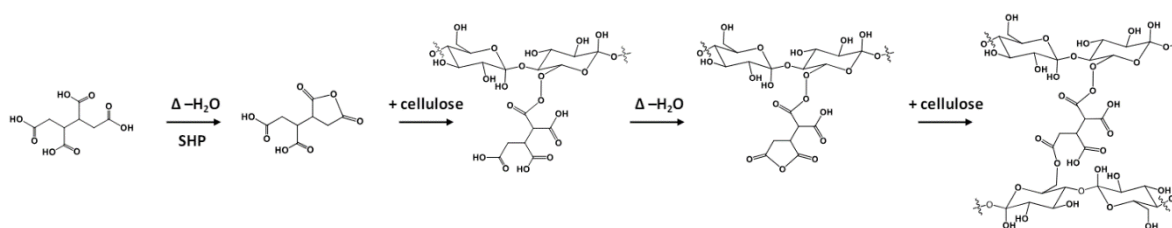


Figure 14: Crosslinking reaction of BTCA and nanocellulose crystals [15].

To make the films flexible a substance called a *softener* is added. In this project three different softeners were used, all serving the same purpose. They were all amines with varying side-chain lengths and side groups. The three softeners were triethanolamine (TEOA), Tetraethylammonium bromide (TEAB) and Tetrabutylammonium hydrogen sulfate (TBAHS). These amines coordinate and form intermolecular bonds with the sulfate groups on the CNC, increasing the distance between CNC crystallites.

To properly investigate how the bonding between CNC and different additives can be affected, the macrostructure of the films, meaning how the cellulose nanocrystals arrange themselves in relation to each other, must be considered. Steric hindrances must be discussed: if the macrostructure in the CNC film is too tight, meaning that the distance between the crystals is small, the steric hindrances may be too great for polymers to coordinate with the sulfate groups between two crystals. Therefore, softeners with longer and more side chains are of interest as they could increase the distance between the crystals in the films. Take TEOA, for example. It has three ethanol chains, attached to a nitrogen atom. Compare this to tetrabutylammonium, which has four butane chains, attached to a nitrogen ion and the impact of switching from one to the other becomes clearer. Firstly, tetrabutylammonium has four chains, instead of the three

chains that TEOA has. Secondly, tetrabutylammonium has longer hydrocarbon chains than TEOA. Combined, these two factors lead to tetrabutylammonium creating larger spaces between the nanocellulose crystals which could reduce the steric hindrances that would otherwise inhibit larger molecules from coordinating with the CNC sulfate groups located between two crystals.

Characterization

In this section, the methods used to analyze the films and primarily assess their conductivity will be described. Here, you will also find which calculations are needed to convert the measurements to sought-after figures. The main objective of this study was to investigate how the conductivity of the films could be improved, and the primary characterization method used was a four-point probe to measure the resistance of different films.

Four-point Probe

The four-point probe method is a widely used technique to measure the resistance of thin films [16]. This resistance can be used to calculate the conductivity. This method is based on passing a small electric current between the outer two probes while measuring the drop in voltage between the two inner probes [16]. By using four probes instead of two, the four-point probe method eliminates errors associated with contact resistance and sample inhomogeneity, providing more accurate results [16].

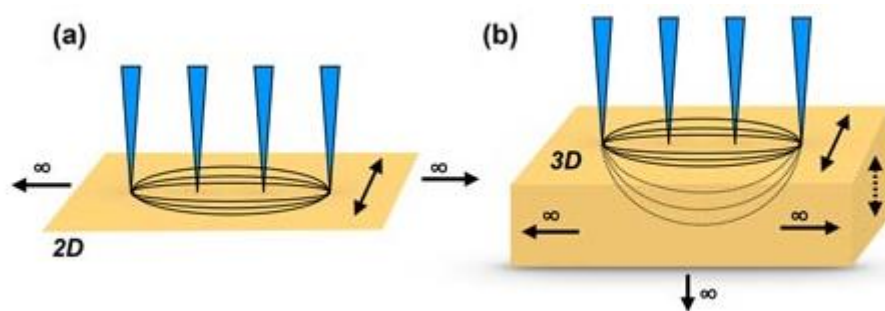


Figure 15: Schematic image of a four-point probe [16].

Studies have utilized the four-point probe method to characterize various thin films, including semiconductors and conducting polymers [17]. The four-point probe method offers a robust

and accurate means of measuring the resistance and determining the conductivity of thin films enabling precise electrical measurements of various materials [16]. When conducting the four-point probe measurements, a set number of electric currents at varying intensities are applied within a set interval and the potential between the probes is measured. The measuring software then plots these points with a straight line through the points, the resistance is given as the slope of this line. Additionally, an error value, representing the average deviation of each point of measured potential from a straight line, was obtained. If the points fall on a perfectly straight line the deviation is zero, indicating that the calculated resistance is correct, without error. The deviation value represents how much each individual measurement deviates from where it would fall in a theoretical series of perfectly accurate measurements, not how accurate or inaccurate each individual measurement actually is. This corresponds roughly to the inverse of an R^2 value given by an Excel plot in a manner where the decimal fraction of the deviation over the average resistance is equal to $1-R^2$. In this report, a margin of error of 5% is used, meaning that the R^2 value cannot be lower than 0.95 for a measurement to be accepted and conductivity to be calculated.

When a resistance (R) value is obtained, the conductivity (S) must be calculated [18]. To do this, the resistivity (ρ) must be calculated according to Equation 1 below, where t is the thickness of the film [18].

$$(1) \rho = \frac{\pi}{\ln(2)} tR$$

After this, the conductivity can be calculated as the inverse of the resistivity according to Equation 2 [16].

$$(2) S = \frac{1}{\rho}$$

The expression in Equation 3 is equal to 4.5325 and a correction factor that must be included to obtain the resistivity accurately [18]. The correction factor depends on the relation between the probe spacing (s) and the lateral dimensions (d) and thickness (t) of the substrate [18]. Because these factors have the relations $d \gg s$ and $s \gg t$, the width of the substrate can be treated as infinite, which allows for the usage of the correction factor in Equation 3 [18].

$$(3) \frac{\pi}{\ln(2)}$$

Polarized Light Microscopy

Polarized light microscopy (POM) was also used to examine the films. POM uses polarized light to enhance contrast and produce clearer images of crystalline structures [19]. POM also

allows for the usage of polarization filters to select which directions of light rays are shone through the substrate, enabling the user to see in which direction a given crystal structure is oriented [19]. In this project, POM was used primarily to examine how changes in method and what chemicals are included in production of the films change their crystal structure, particularly how this affected the shape and distribution of the polymer.

Scanning Electron Microscopy

A scanning electron microscope (SEM) is an analytical method used for studying the surface of solid substrates, in this case CNC films [20]. SEM scans the substrate with a focused electron beam that hits the substrate and facilitates emission of high energy and low energy electrons from the substrate [20]. These electron emissions are detected by the SEM to produce high resolution images with very high magnification [20]. For non-conductive substrates to be analyzed, they must first be plated with a thin layer of metal [20]. In this project, 5.13 nm of gold plating was used.

Method

In this section, the standard methods, materials and chemicals used for the synthesis of the nanocellulose films will be introduced and explained. The methods used for film production were provided by the master's dissertation *Transparent conducting water-stable films of cellulose nanocrystals*, by Yuge Yao, which succeeded in producing transparent, flexible and water-stable films. The methods described in Yao's dissertation can be divided into different stages. The first stage is the synthesis of the films themselves, which involves adding the additives described in the *Theory* section to a solution of cellulose nanocrystals and letting it dry on a flat surface to form a film. The second stage is polymerization, which involves polymerizing a monomer into a conductive polymer and having it coordinate to the negatively charged sulfate groups on the CNC surface.

Chemicals

The CNC was prepared through acid hydrolysis using sulfuric acid (H_2SO_4). The CNC had a concentration of 1 wt.% and was stored as an aqueous solution in a refrigerator. To create the films, 15 ml of the 1 wt.% CNC solution was used and depending on the specific film, a selection of the solutions from Table 1-4 below was also added.

Table 1: The chemicals used in the crosslinker combination.

Chemical	BTCA	EGDE	SHP
Type	Crosslinker	Crosslinker	Catalyst
Concentration	100 $\mu\text{mol/ml}$	50 $\mu\text{mol/ml}$	100 $\mu\text{mol/ml}$

Table 2: The different softeners used.

Chemical	TEOA	TBAHS	TEAB
Type	Softener	Softener	Softener
Concentration	100 $\mu\text{mol/ml}$	100 $\mu\text{mol/ml}$	100 $\mu\text{mol/ml}$

Table 3: The different monomers used.

Chemical	Pyrrole	Aniline	EDOT
Type	Monomer	Monomer	Monomer
Concentration	1000 $\mu\text{mol/ml}$	1000 $\mu\text{mol/ml}$	1000 $\mu\text{mol/ml}$

Table 4: The anionic polymers.

Chemical	PSS	PVA-S
Type	Polymer	Polymer
Concentration	30 wt. %	260 $\mu\text{mol/ml}$

Materials

The following materials were used in the production of the nanocellulose films: automatic pipettes with volumes ranging from 30 μl to 10 ml, plastic petri-dishes, plastic bottles with lids, sonicator, tweezer, spatula, refrigerator and an oven.

Solvents

The main solvents used for the two methods described below are DI-water and a 1:9 methanol/water mixture. These solvents were, however, switched for pure methanol when working with chemicals with low solubility in water, such as EDOT. Also of note is that in later experiments (see *PSS and PVA-Sulfonate* in the *Experiments* section) the anionic

polymers PSS and PVA-S are used. When using these, DI-water should be used as solvent because methanol can cause the PSS and PVA-S to precipitate out of solution.

Methods for Water-stable and Flexible Films

Two main methods for film production were used. The difference between them is when polymerization happens. In the in-situ method, the polymerization takes place in the film solution, before the film is dried. In the ex-situ method, polymerization occurs after the film is dried by drenching the film in a solution of monomer and initiator. Below, the two methods will be described.

In-situ Method:

15 ml of 1 wt.% CNC solution is added to a plastic bottle. 300 μ l of 100 μ mol/ml TEOA solution is added to the bottle and the contents of the bottle are sonicated to homogenize the solution. After this, 300 μ l of 100 μ mol/ml BTCA solution, 600 μ l of 100 μ mol/ml SHP solution, 300 μ l of 50 μ mol/ml EGDE solution and 50 μ l of 100 μ mol/ml FeCl₃ solution are added, and the contents are sonicated again for 30 s. The bottle is placed in the refrigerator to cool for 1 hour. Then, 150 μ l of cold 1000 μ mol/ml pyrrole solution is then slowly added to the chilled bottle contents while it is simultaneously swirled. When all of the pyrrole solution is added, the cap is put on the bottle and then it is shaken. The contents are poured out onto a petri-dish and then put in a well-ventilated area to dry for 2 – 3 days. After drying, the film is peeled off the petri-dish and heated in an oven at 140°C for 30 minutes to activate the cross linkers, making the film water-stable.

Ex-situ Method:

15 ml of 1 wt.% CNC solution is added to a plastic bottle. 300 μ l of 100 μ mol/ml TEOA solution is added to the bottle and the contents of the bottle are sonicated to homogenize the solution. After this, 300 μ l of 100 μ mol/ml BTCA solution, 600 μ l of 100 μ mol/ml SHP solution and 300 μ l of 50 μ mol/ml EGDE solution are added, and the contents are again sonicated for 30 s. The contents are poured out onto a petri dish and placed in a well-ventilated area to dry the film for 2 – 3 days. After drying, the film is peeled off the petri-dish and heated in an oven at 140°C for 30 minutes to make the film water-stable. The film is left to cool for a few minutes (just until it is handleable by hand) and then submerged in a mixture of Solution A and Solution B, in a petri-dish. It is then put into the refrigerator to cool for 1 hour. After cooling, 2 ml 1000 μ mol/ml pyrrole solution is slowly added to the petri dish by dripping it in a circular or spiral pattern. After all of the pyrrole is added, the film is turned over in the solution

to ensure complete submersion. It is then put back into the refrigerator to polymerize for 24 h. After 24 h, the film is washed with MeOH and DI-water and left to dry on a clean petri-dish. The formulation of Solution A and Solution B are as follows: Solution A is 5.995×10^{-3} mol FeCl_3 , 4.485×10^{-3} mol PPS and 100 ml of Solution B. Solution B is a methanol/water solution in a 1:9 ratio.

Of the two methods described above, the ex-situ method was primarily used in experimentation. The ex-situ method was preferred because it offers the possibility to produce a set of films, which can then be cut into smaller pieces to test many different monomers and initiators on the same batch of films. Note that the methods described above are the base methods for producing water-stable and flexible films and they are the methods on which the experiments were based.

Experiments

In this section, we will describe the experiments conducted, the rationale behind their design, and the objectives they aimed to achieve. It is important to note that the batch numbers used in the subsequent sub-sections may not be sequential, as some batches were used for practice or may have been completed out of order. Film labeling will also be utilized, with the format being BX-Y-Option, where B represents batch, X denotes batch number, Y indicates film number within the batch, and "Option" may specify additional ingredients or methods used in film production.

Batch 3: PANI and PEDOT

Initially, we sought to determine if the low conductivity and transparency were attributed to PPy as the conducting polymer. PPy, being inherently dark in color, was suspected to contribute to the low transparency. Hence, we investigated two alternative polymers: PANI and PEDOT. This investigation was divided into two batches using the ex-situ method, where aniline replaced the pyrrole monomer in one sub-batch, and EDOT monomer replaced pyrrole in the other, in equal proportions. Upon completion, the films were assessed for conductivity using a four-point probe. The results indicated high sheet resistance, exceeding the instrument's range, consistent with films containing pyrrole. However, films with EDOT exhibited significantly improved transparency, prompting a shift to EDOT as the primary monomer for the project.

Batch 4 & 6: Replacing Softener with Pyrrole or EDOT

We hypothesized that the softeners in the film formula might diminish conductivity by binding to sulfate groups on the CNC, hindering polymer-CNC binding. To test this theory, films were produced with the ex-situ method, substituting the softener with an equivalent amount of pyrrole in one experiment and EDOT in another. Batch 6 encountered challenges in dissolving the EDOT monomer, resulting in monomer bubbles in finished films. Both Batch 4 and 6 were dried in darkness to prevent light from initiating polymerization. Neither Batch 4 nor 6 yielded linear resistance measurements, precluding conductivity calculations. Nevertheless, the films maintained good flexibility and water stability, with PPy films exhibiting lower transparency compared to EDOT films.

Batch 7: Examining Different Softeners

Another potential cause of low conductivity was a tight crystalline film structure impeding polymer integration. This issue was attributed to the softener TEOA, leading us to investigate alternative softeners with longer, branched chains. The effects of TBAHS and TEAB were evaluated by creating films through the ex-situ method. Films were produced using TEAB (film label: B7-1) and TBAHS (film label: B7-2) as softeners, with both pyrrole and EDOT monomers to create four film variants. Unfortunately, linear resistance measurements were not obtained with the four-point probe, rendering conductivity calculations unfeasible. Despite this, the films maintained good flexibility and water stability, with PPy films exhibiting reduced transparency compared to EDOT films, which were nearly transparent.

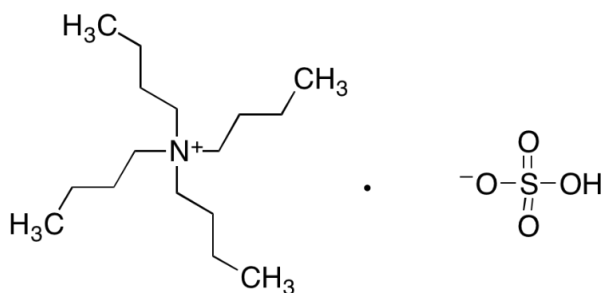


Figure 16: Tetrabutylammonium hydrogen sulfate [21].

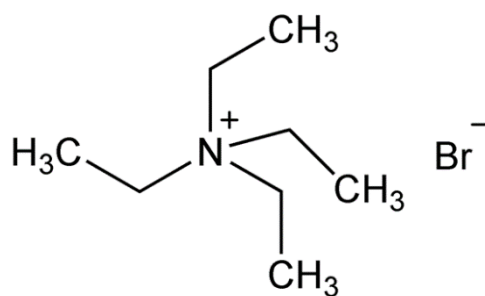


Figure 17: Tetraethylammonium bromide [22].

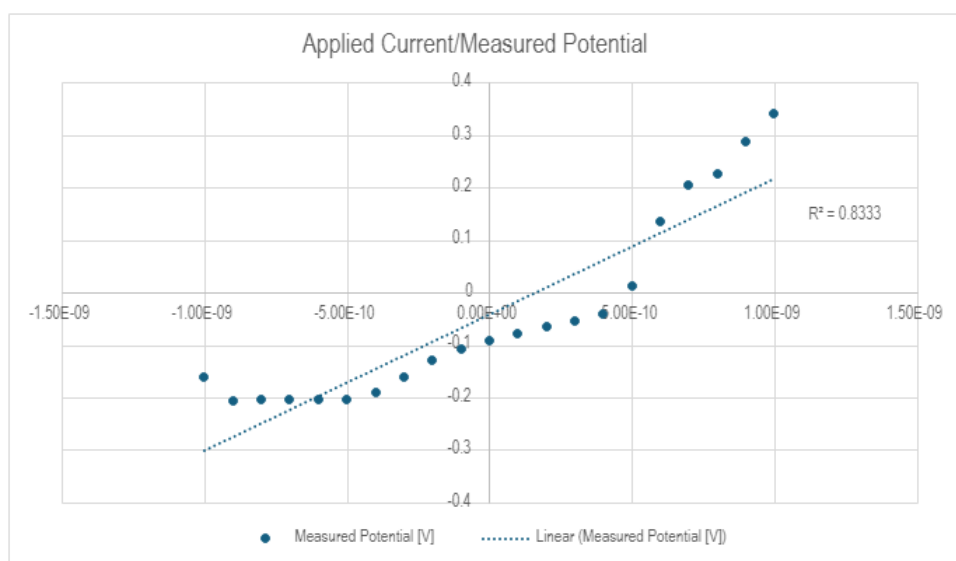


Figure 18: Graph of the film B7-1 with PPy.

Film B5-1: Examining the Usage of Both EDOT and Pyrrole

Alongside Batch 7, the effect of mixing different monomers during the polymerization step was examined. The decision to explore this was to investigate the hypothesis that some monomers may be less likely to bind with the sulfate groups on the CNC, and that a monomer more prone to binding could assist the other monomer in binding with the CNC. In this case, EDOT was suspected to be less likely to bind than pyrrole, leading to an experiment using the ex-situ method and a 9:1 mixture of EDOT and pyrrole. The combination of pyrrole and EDOT in the polymerization stage did not yield linear resistance measurements, and consequently, the conductivity could not be calculated. The films exhibited good flexibility and water stability, and due to 90% of the polymer being PEDOT, the film maintained good transparency.

Batch 8: Pre-polymerized PEDOT

Further examination was conducted to determine if the polymer could be more easily integrated into the film if it was already formed, rather than using a monomer in the film and creating the film around the polymer. This method involved polymerizing the monomer, specifically EDOT, in methanol using Solution A as described in the *Method* section. The resulting PEDOT polymer was then added to a film solution formulated according to the ex-situ method, poured onto a petri dish, and allowed to dry. This approach eliminated the need for the final polymerization step of the ex-situ method by utilizing a pre-made polymer and aimed to create sufficient space for the polymer within the film. Although this batch yielded non-linear results, it showed the most linear results in the project thus far (see Figure 19).

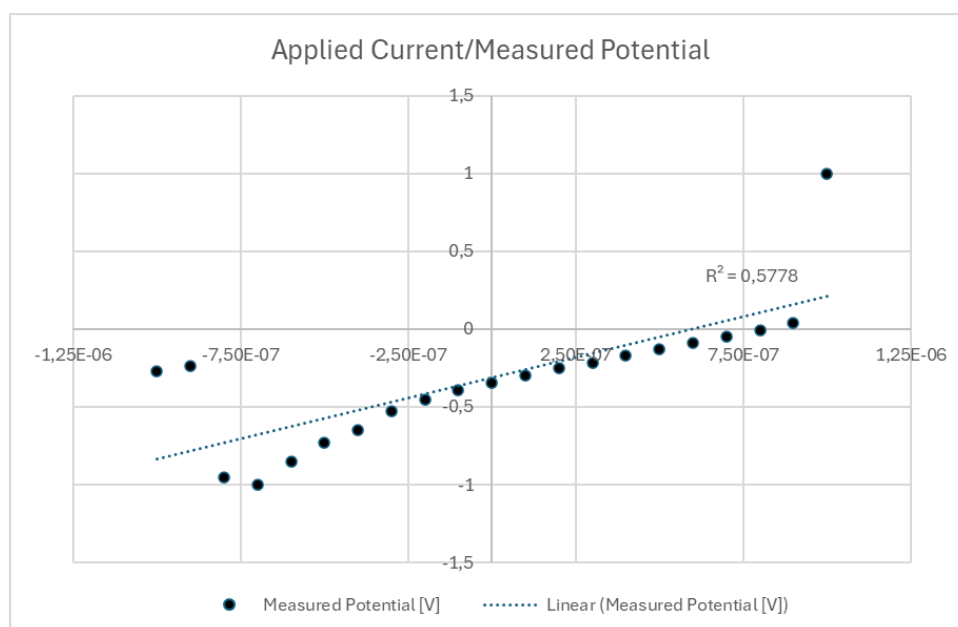


Figure 19: Graph of film B8-1, demonstrating the most linear results obtained at this point in the project.

These films displayed good flexibility and water stability, but the transparency was slightly lower than films without polymer or previous PEDOT-containing films. The reduced transparency was likely due to more EDOT being polymerized in this method, and the addition of pre-polymerized PEDOT to the film solution ensured that all the added PEDOT remained in the film after drying.

Batch 9: In-situ with Longer Polymerization

In the in-situ method, a significant issue arose that hindered proper analysis of the films: they adhered easily to the petri dishes during drying. This was attributed to the monomer not being

fully polymerized before pouring out the film solution onto a petri dish. To address this, a longer polymerization time of approximately 48 hours was implemented using EDOT as the monomer. As shown in Figure 20 below, the film solution exhibited a dark color after polymerization, indicating substantial polymerization of the monomer.



Figure 20: Film solution for Batch 9 after polymerization.

However, upon drying, the film was completely stuck to the petri dish, impeding analysis. The film also displayed significantly reduced transparency compared to other PEDOT-containing films, and its flexibility and water stability could not be accurately assessed due to the film's adherence to the petri dish.

Batch 10: Increasing the Amount of Pre-polymerized PEDOT

It was hypothesized that the film in Batch 8 might require more polymer to reduce resistance to measurable levels. To test this, approximately 10 times more PEDOT was added to Batch 10 than in Batch 8. However, when Batch 10 dried, it adhered completely to the petri dish, preventing proper analysis. Attempts to loosen the film by placing it in a water bath at 55°C for 2 hours proved unsuccessful. Similar to Batch 9, the film in Batch 10 could not be assessed accurately for water stability, flexibility, or transparency due to its adhesion to the petri dish.

The issue of films sticking to their petri dishes, as observed in Batches 9 and 10 may have potential solutions that were not explored in this project. One possible solution is to dry the

films on glass dishes that have been washed with acetone and isopropanol and then treated with oxygen plasma etching [23]. While the method has been successful with films made solely of PEDOT:PSS, its effectiveness with CNC/PEDOT:PSS films remain uncertain [23]. Further research is necessary to determine if this approach could be a viable solution.

p-Toluenesulfonic acid Drenching

p-Toluenesulfonic (*p*-TSA) acid, having a molecular structure similar to a single PSS subunit (see Figures 21 and 22), was explored as a potential counter ion to aid in the coordination of conductive polymers to the CNC. Films from Batch 7 with TBAHS and PPy, and Batch 8, were drenched in separate 1000 $\mu\text{mol/ml}$ solutions of *p*-TSA for 15 minutes. Following drying, the resistance was analyzed using the four-point probe method.

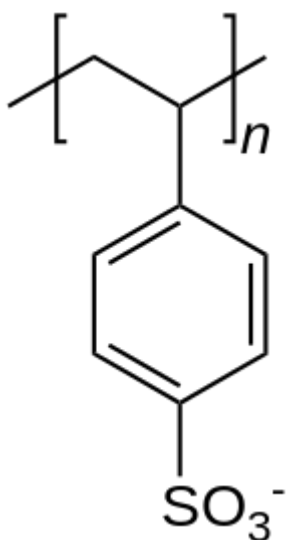


Figure 21: PSS molecular structure [24].

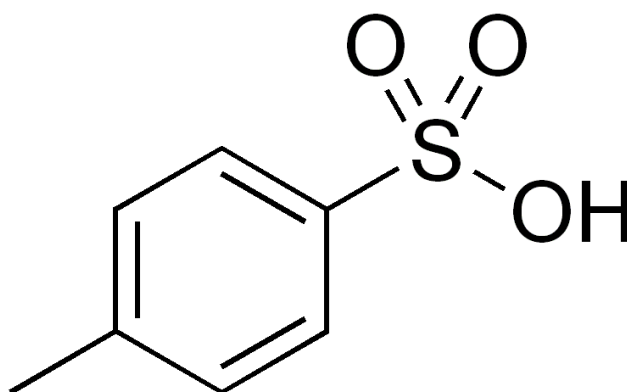


Figure 22: *p*-TSA molecular structure [25].

These experiments resulted in the first films to exhibit linear measurement plots in the project. Subsequent drenching in water for 30 minutes revealed lower resistance for Batch 7 with TBAHS and PPy, while Batch 8 showed higher resistance. A second film from Batch 7, containing TEAB and PPy, was also subjected to *p*-TSA drenching.

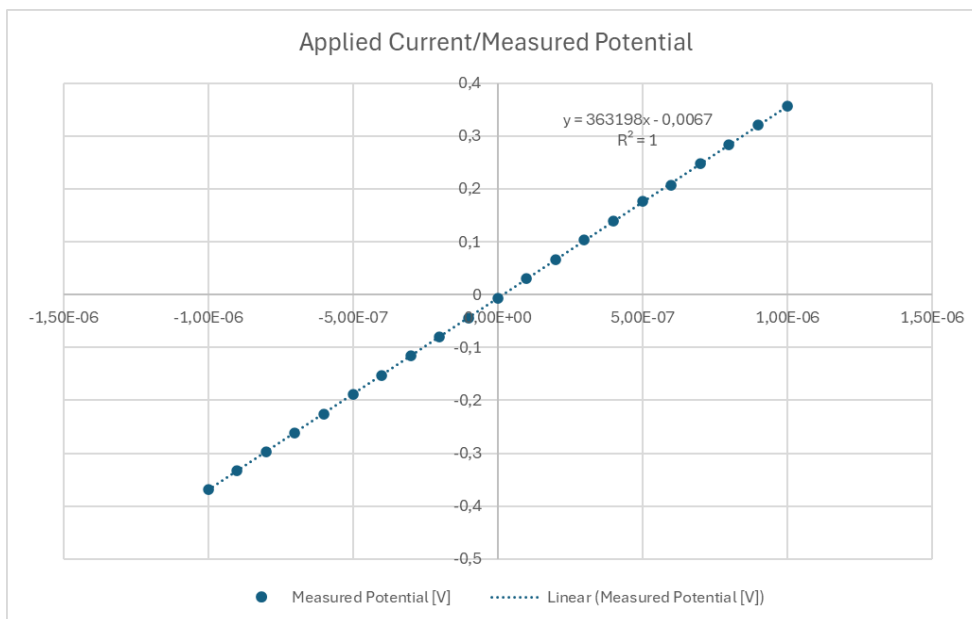


Figure 23: Graph illustrating resistance measurement for B7-2-PPy after *p*-TSA drenching.

The successful experiments with *p*-TSA are detailed in the *Results & Discussion* section. These experiments produced the most conductive film in the project, Batch 7 with TEAB and PPy, boasting an average conductivity of 258.337 $\mu\text{S}/\text{mm}$. Figure 24 displays the ten conductivity measurements conducted on this film, showcasing high linearity and low variance between the sets.

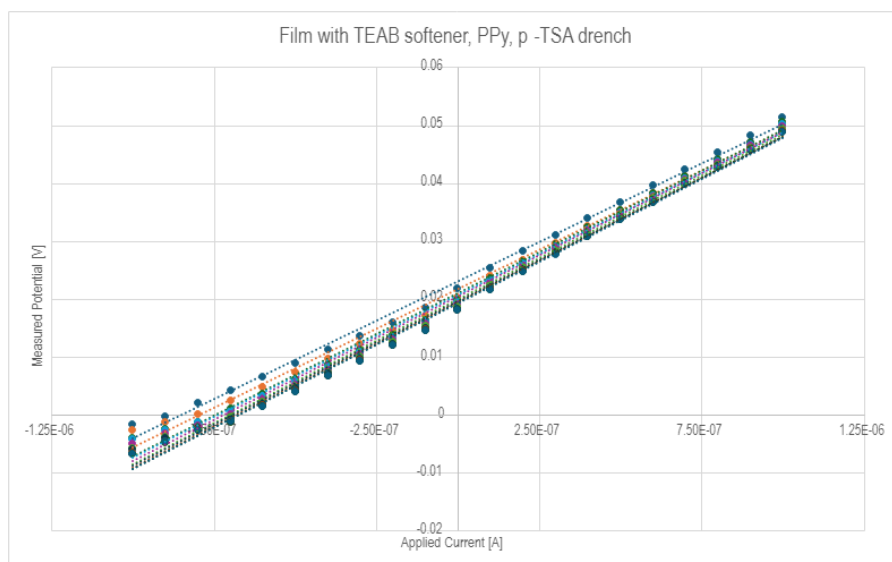


Figure 24: Graphed conductivity measurements for highest conductivity film.

Despite good flexibility and water stability, the films with PPy exhibited significantly reduced transparency compared to films with EDOT, which maintained almost complete transparency.

PSS and PVA-Sulfonate

As mentioned in the *Theory*, polystyrene sulfonate (PSS) is a sulfonated polymer, where the sulfate groups are negatively charged. PSS is commonly used as one half of the hybrid polymer PEDOT:PSS to increase the water solubility of PEDOT and, specifically in conductive CNC films, to improve the ability of PEDOT to coordinate to the CNC. Another sulfonated polymer is polyvinyl alcohol sulfonate (PVA-S). Seen in Figure 25 is the structure of polyvinyl sulfate which is a more general description of polyvinyl sulfates. The only difference between it and PVA-S is that PVA-S always has hydrogen as the cation. Notice, in Figure 25, how PVA-S is less bulky than PSS, which suggests that it would have an even greater effect on improving the ability of PEDOT to coordinate to the CNC in the films.

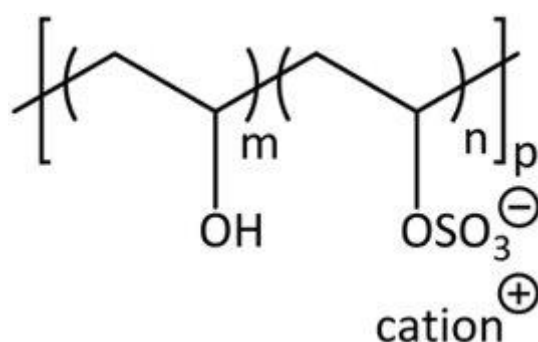


Figure 25: Structural formula of polyvinyl sulfate [26]

PSS and PVA-S were compared to assess their efficacy as counter ions aiding conductive polymers to coordinate with the CNC, PSS and PVA-S were compared in two series of experiments. The first of which followed a regular ex-situ polymerization of ready films, as described in the *Method* with PSS or PVA-S added in a 1.5:1 molar ratio of monomer to counter ion. This was done in four different variations to produce four different films, each with one of the following hybrid polymers: PEDOT:PSS, PEDOT:PVA-S, PPy:PSS and PPy:PVA-S. All four films had low coloration after polymerization and, in accordance with this, exhibited conductivity measurements without linearity. Despite this, the films still exhibited good flexibility and water stability.

Batch 11: Continued Experiments with PSS and PVA-S

A second series of experiments involved creating two films using the pre-polymerization method described in Batch 8, with added PSS or PVA-S in a 1.5:1 molar ratio of monomer to counter ion. The films, one with PEDOT:PSS (film label: B11-1) and one with PEDOT:PVA-

S (film label: B11-2), exhibited a clear very light blue color when dry. Only the film with PEDOT:PSS showed linear conductivity measurements, albeit with some deviations affecting the calculation of conductivity.

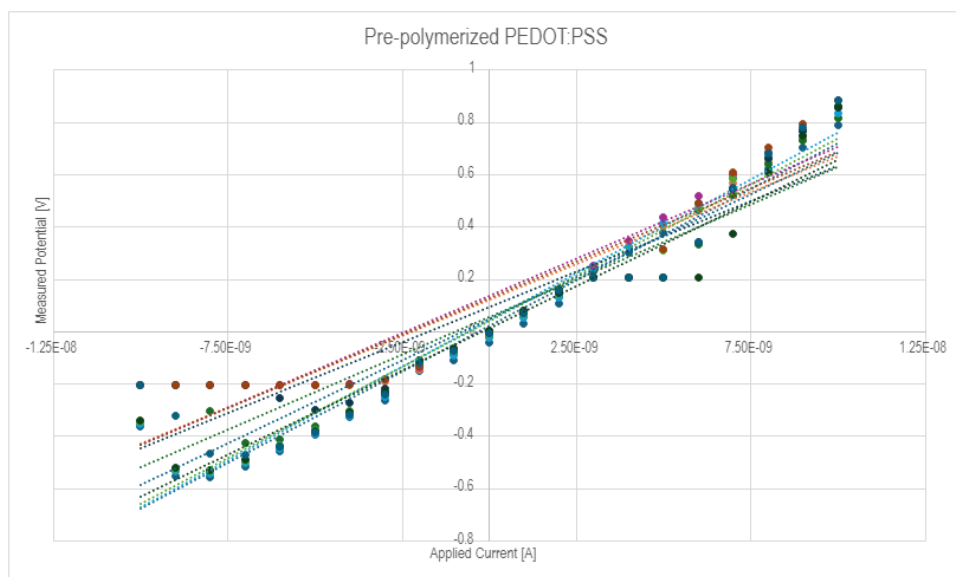


Figure 26: Ten conductivity measurements with potential on the y-axis and current on the x-axis.

In Figure 26, observe the ten measurements done on the film with pre-polymerized PEDOT:PSS and notice the deviating data points. As explained previously, each measurement series must have low deviations from linearity to enable calculation of the conductivity. Thus, the deviating data points mean that the entire affected series of measurements is invalidated in terms of calculating the conductivity of the substrate. Out of the ten measurements conducted on the film with pre-polymerized PEDOT:PSS, only three yielded sufficiently linear results for conductivity calculation, averaging $0.095 \mu\text{S}/\text{mm}$. Both films in this batch displayed good flexibility and water stability.

Results & Discussion

In this section, the results are presented and discussed. As previously stated, in the *Experiments* section, the results for most early experiments were inconclusive since the resistance of the films was out of range and unable to be measured by the four-point probe.

Below in Table 5 the results of the successful experiments are shown, meaning all experiments where a film that gave linear conductivity measurements was produced. Column 1 shows a

reference film, which is free from any conductive polymer but drenched in *p*-TSA. Column 2 shows a film with PEDOT where *p*-TSA was included in the polymerization step. Column 3 shows a film created in accordance with the ex-situ method with TEAB as the softener and PPy as the polymer that was drenched in *p*-TSA. Column 4 shows a film created in accordance with the ex-situ method with TBAHS as the softener and PPy as the polymer that was drenched in *p*-TSA. Column 5 shows the same film as column 4 but after it was drenched in water for 30 minutes. Column 6 shows a film created in accordance with the pre-polymerization method with TBAHS as the softener and PPEDOT as the polymer that was drenched in *p*-TSA. Column 7 shows the same film as column 6 but after it had been drenched in water for 30 minutes. Finally, column 8 shows the film created according to the pre-polymerization method with TBAHS as the softener and PEDOT:PSS as the hybrid polymer.

Table 5: Numeric results of all experiments where measurable conductivity was obtained.

Film	No polymer- <i>p</i> -TSA	<i>p</i> -TSA- polymerized PEDOT	TEAB, PPy, <i>p</i> -TSA	TBAHS, PPy, <i>p</i> -TSA	TBAHS, PPy, <i>p</i> -TSA, Water	TBAHS, PEDOT, <i>p</i> -TSA	TBAHS, PEDOT, <i>p</i> -TSA, Water	TBAHS, PEDOT:PSS
Thickness [mm]	0.034	0.026	0.033	0.033	0.019	0.020	0.020	0.025
Resistance [ohm]	2822524	11470742	28202	363198	220589	370116	1175961	70380306
Possible error	80097	194384	421	428	2408	13130	22679	3358653
Error [%]	2.840	1.690	1.493	0.118	1.144	3.548	1.929	4.773
Resistivity [ohm*mm]	434955	1351740	4218	54323	18996	33550	106599	10526726
Conductivity [μ S/mm]	2.299	0.741	258.337	18.408	53.273	29.806	9.381	0.095

There are a few noteworthy points shown in Table 5. The first is that including *p*-TSA in the polymerization of PEDOT produced lower conductivity than drenching a polymer free film in *p*-TSA. This is likely due to *p*-TSA having high electron mobility, which is lost when included in the polymerization reaction.

Second, the film with pre-polymerized PEDOT:PSS also produced lower conductivity than the polymer free, *p*-TSA drenched film. This may be due to either the polymerization reaction yielding very low concentrations of the PEDOT:PSS hybrid polymer, or the hybrid polymer organizing unfavorably for conductivity on a macrostructure scale.

Third, conductivity was increased for films with PPy by drenching in water after *p*-TSA drenching but reduced by water drenching after *p*-TSA drench for films with pre-polymerized PEDOT. However, in both cases, the conductivity remained higher than before the *p*-TSA drenching, as indicated by the conductivity measurements being non-linear before *p*-TSA drenching.

Finally, the film with the greatest conductivity was obtained with PPy as the polymer and only drenching in *p*-TSA. It is surprising, however, that this film contained the less bulky softener which would, theoretically, produce a less porous film that would allow less polymer to coordinate in between cellulose nanocrystals. This suggests that the relationship between the bulkiness of the softener and the film porosity or between the porosity and how much polymer can coordinate to the CNC in the film may not be as straightforward as initially theorized and should be investigated further.

SEM Analysis

To analyze the films further, SEM analysis was performed on a total of five films, four of them were plated with gold. These films were: two samples of B7-1 with PPy drenched in *p*-TSA (one with gold plating and one without), B7-2 without polymer, B11-1 and B11-2. The B7-1 films with PPy had the best conductivity according to our tests which led us to want to investigate its surface more thoroughly. As explained in the Categorization section, the samples in SEM usually require a thin layer of gold coating to be visible in the SEM. However, since this film (B7-1 with PPy) displayed great conductivity, we hypothesized that it could work without the gold coating. As can be seen below in Figures 27 and 28, the B7-1 PPy film was visible both with and without the gold coating.

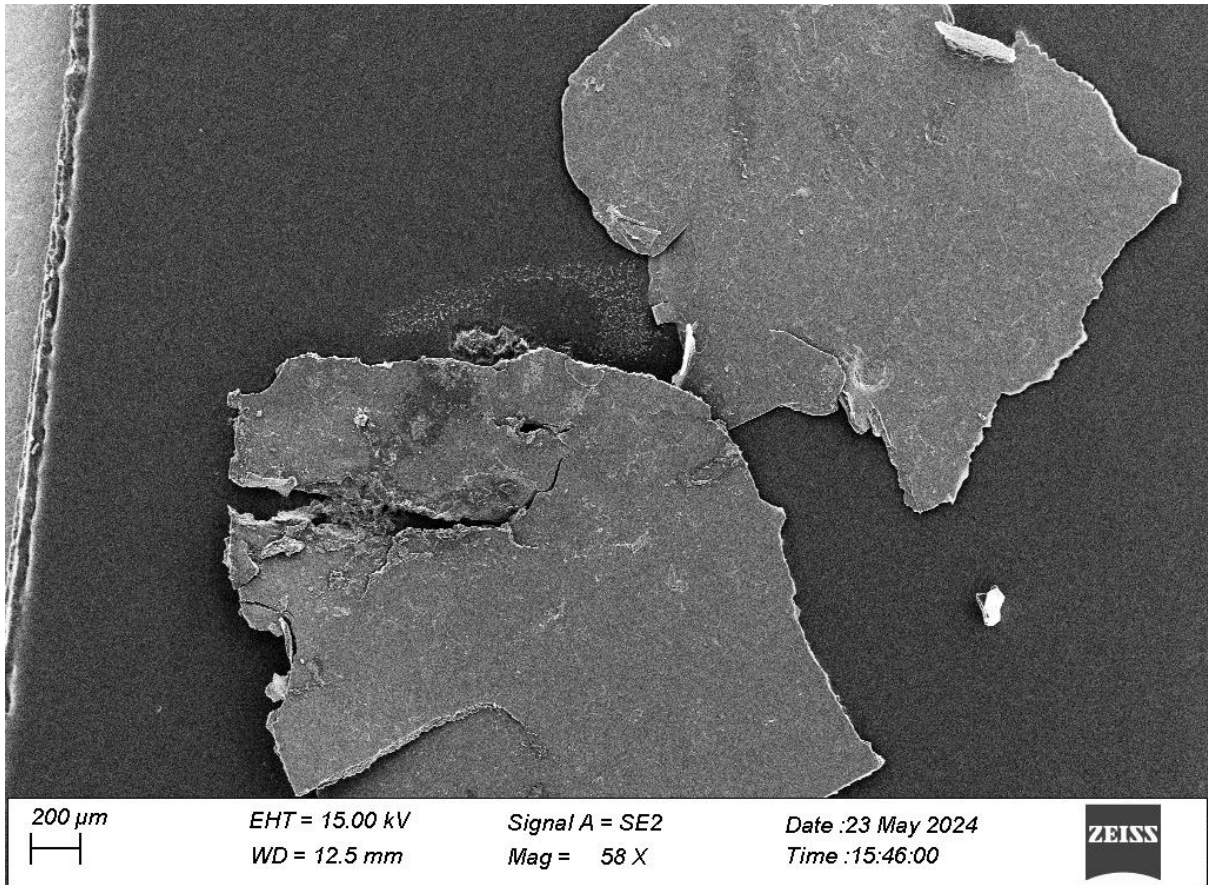


Figure 27: The B7-1 PPy film with gold coating at 58x zoom.

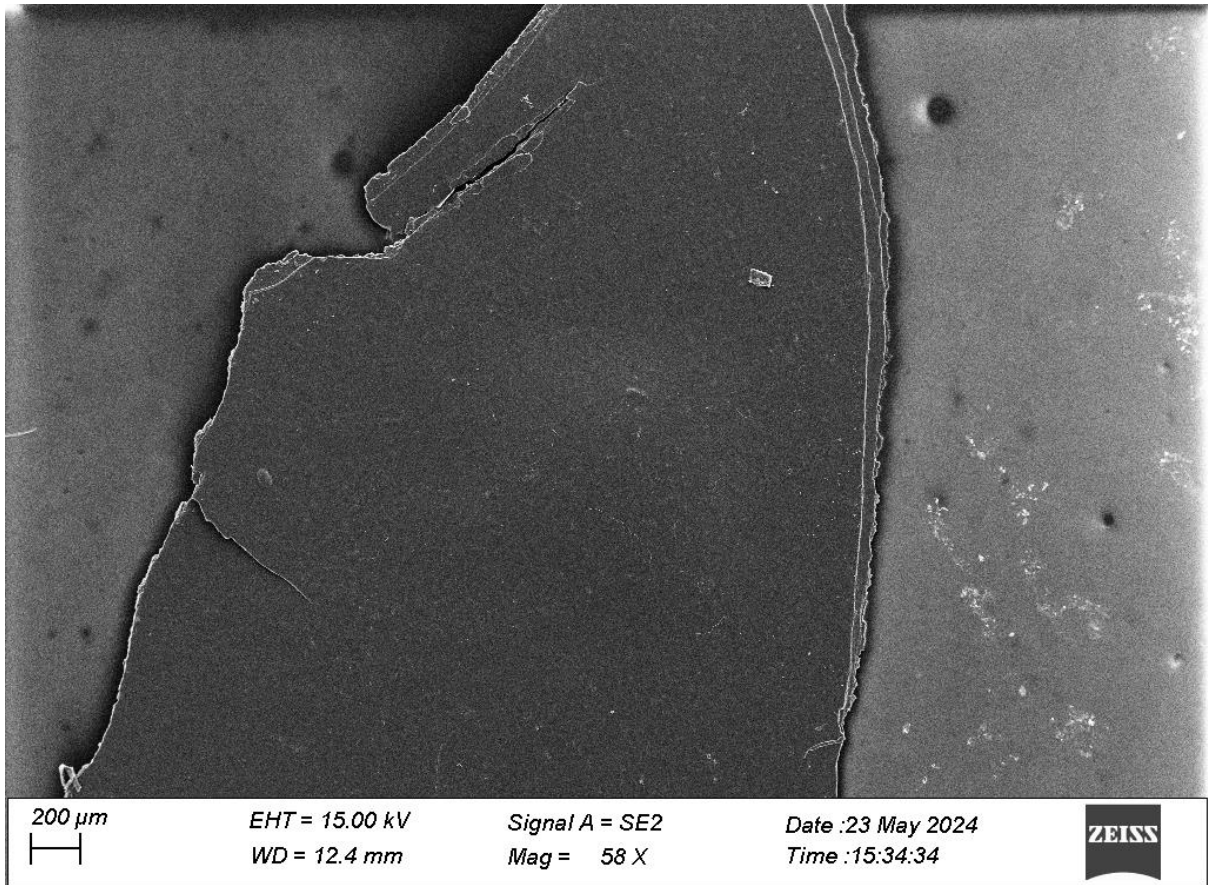


Figure 28: The B7-1 PPy film without gold coating at 58x zoom.

The pieces were of different sizes and the images were taken at slightly different settings (brightness and contrast); however, the structure is clearly visible. Both films had a few cracks, yet both had a smooth surface. Two more figures below with greater zoom show the more detailed structure of the surface.

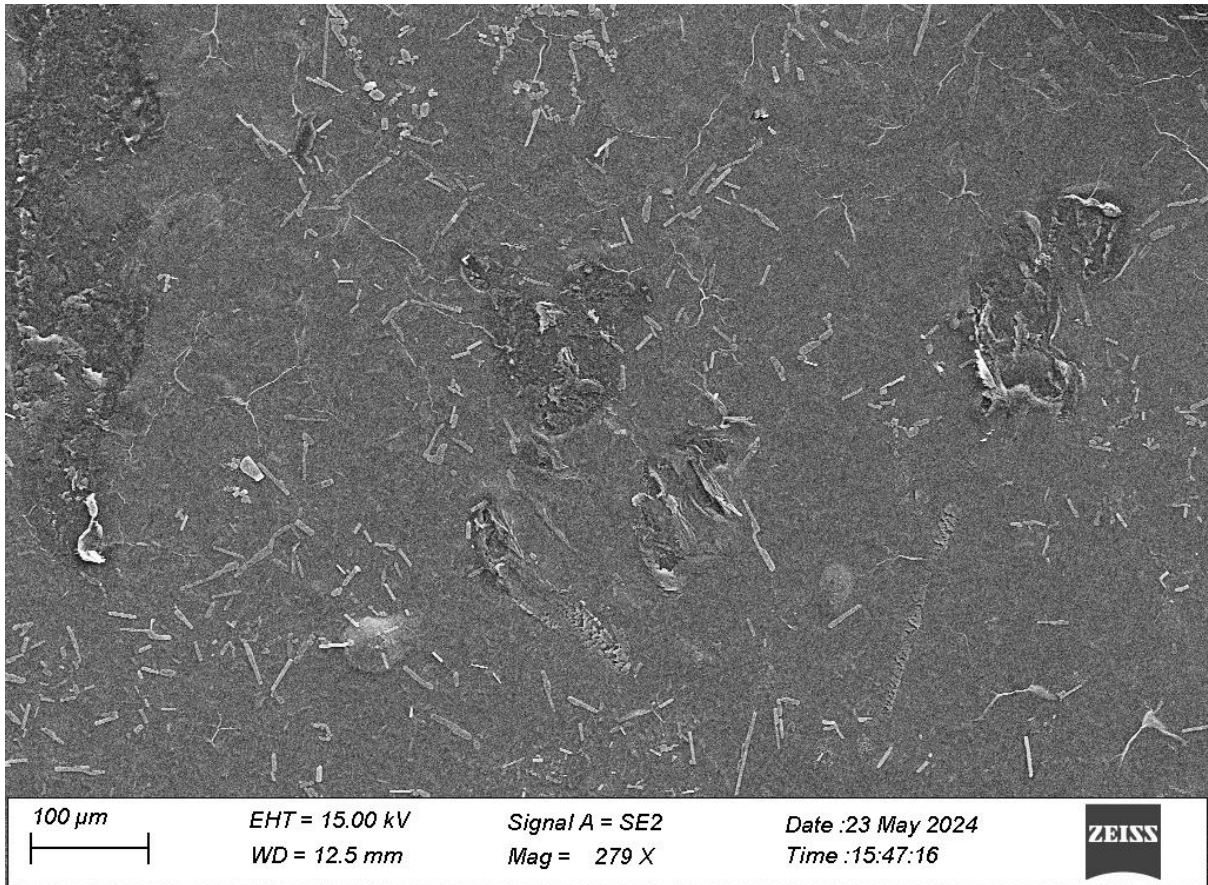


Figure 29: The surface of the B7-1 PPy film with gold coating at 279x zoom.

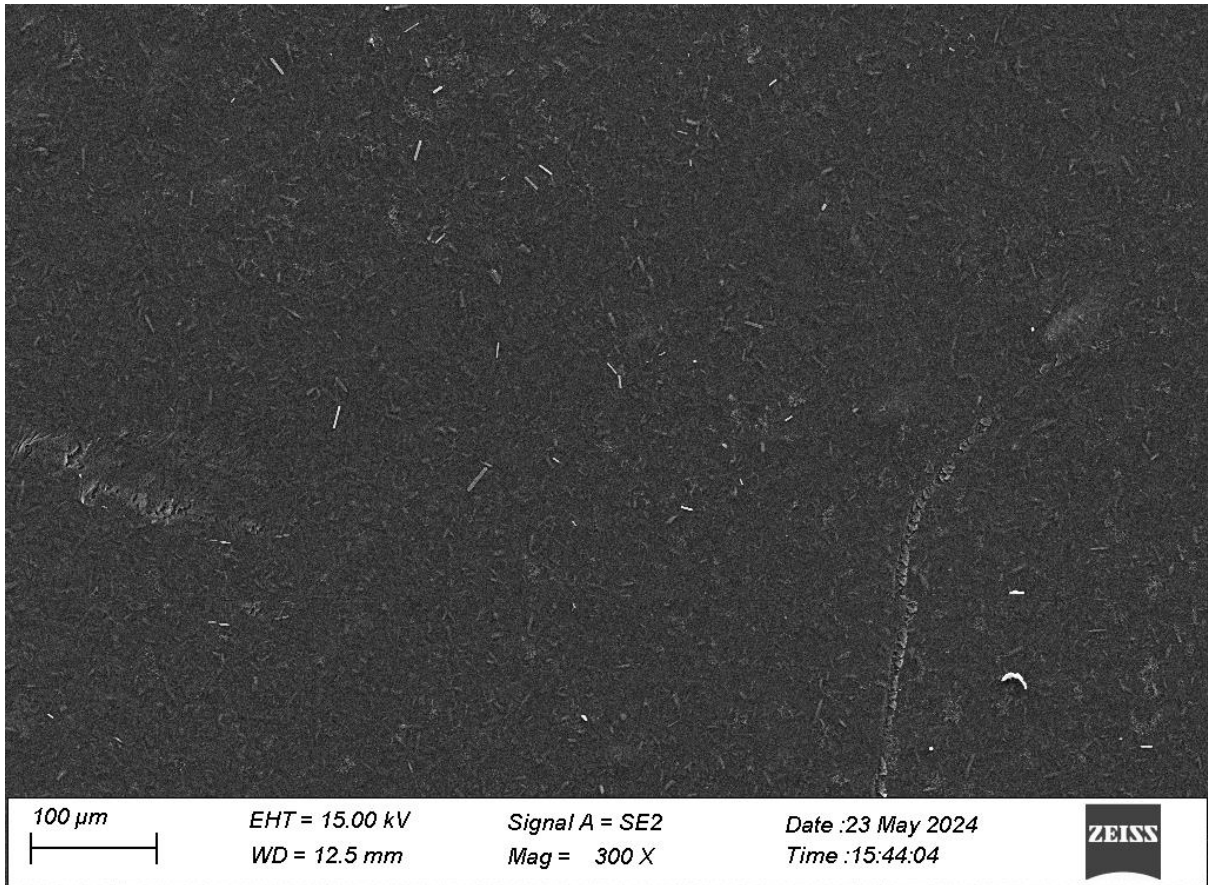


Figure 30: The surface of the B7-1 PPy film without gold coating at 300x zoom.

The B7-1 film with PPy in Figures 27-30 exhibit expected appearances, considering its composition. As it's mostly composed of CNC, the surface appears relatively smooth and grey with strands of what is probably PPy or some impurity such as dust or dirt.

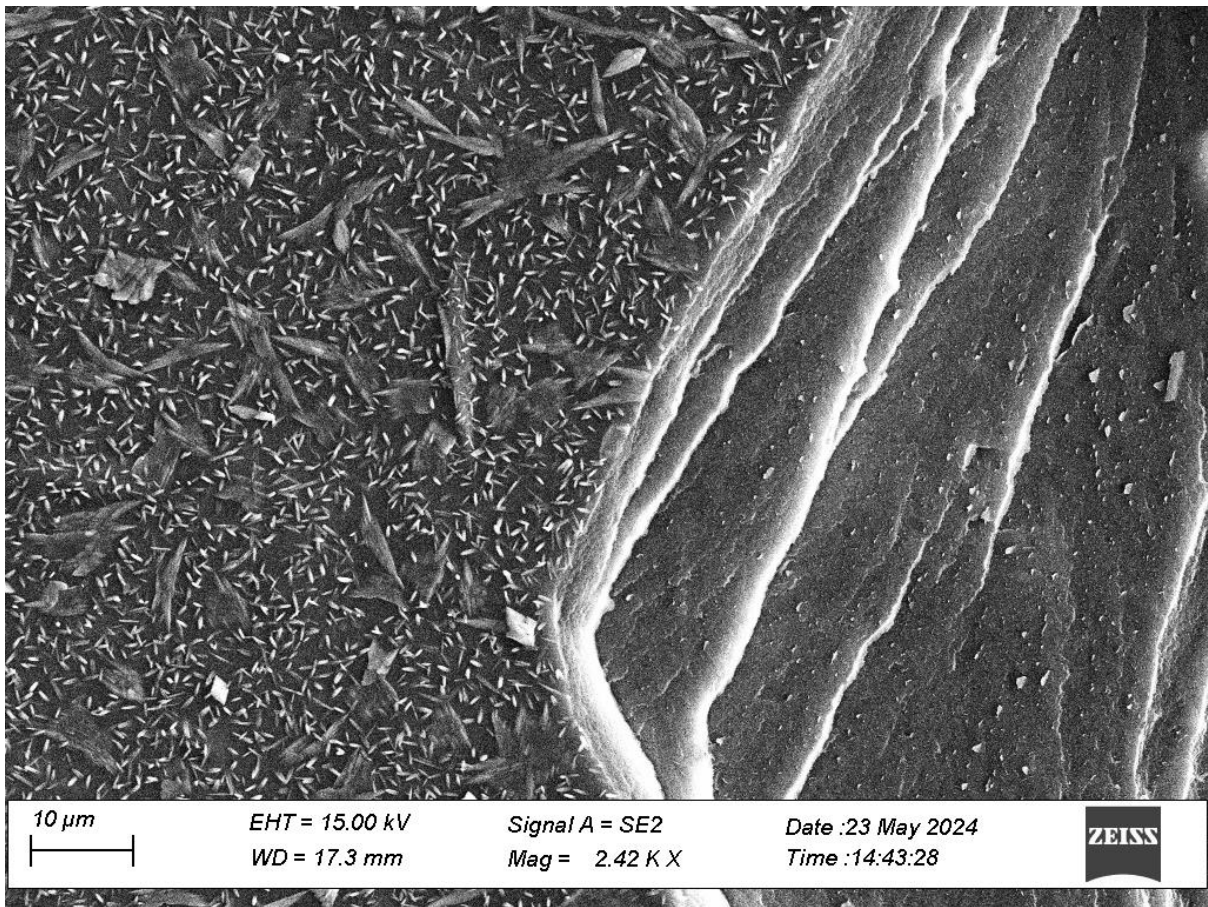


Figure 31: The surface and edge of B7-2 film without conductive polymer at 2420x zoom.

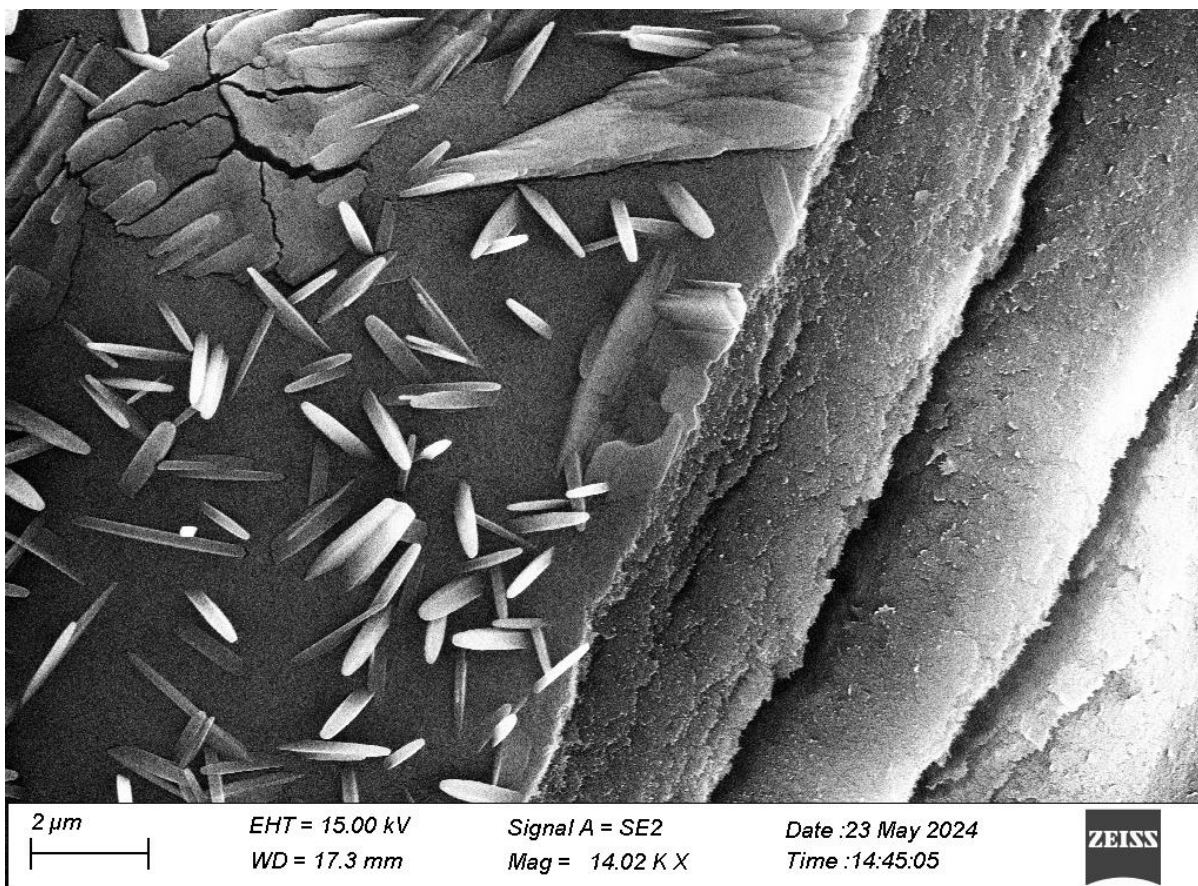


Figure 32: The surface and edge of B7-2 film without conductive polymer at 14020x zoom.

In Figures 31 and 32, the surface of B7-2 without any conductive polymer added is shown. Theoretically, the surface should look smooth and grey, however, this is not the case. Notice the pointy structures that are jutting out of the surface. These structures are likely one of the film components, other than the CNC, that has remained unreacted and crystallized out. Specifically, the crystals are probably SHP, the catalyst used in the crosslinking reaction. Due to SHP being a catalyst, it is not consumed during the cross linking of the CNC and could therefore crystallize on the film surface during drying. Furthermore, the absence of these crystals on films which have undergone the ex-situ polymerization step, or a *p*-TSA drenching is then explained by SHP being an ionic compound and thus easily dissolving in polar solvents, such as the water or methanol that is used in the polymerization and *p*-TSA solutions. A similar phenomenon can be observed on the surfaces of films B11-1 and B11-2, as shown in Figure 33 and 34. In the cases of B11-1 and B11-2, however, there are two distinct size categories of crystals on each film, indicating that more than one compound has remained unreacted and crystallized out.

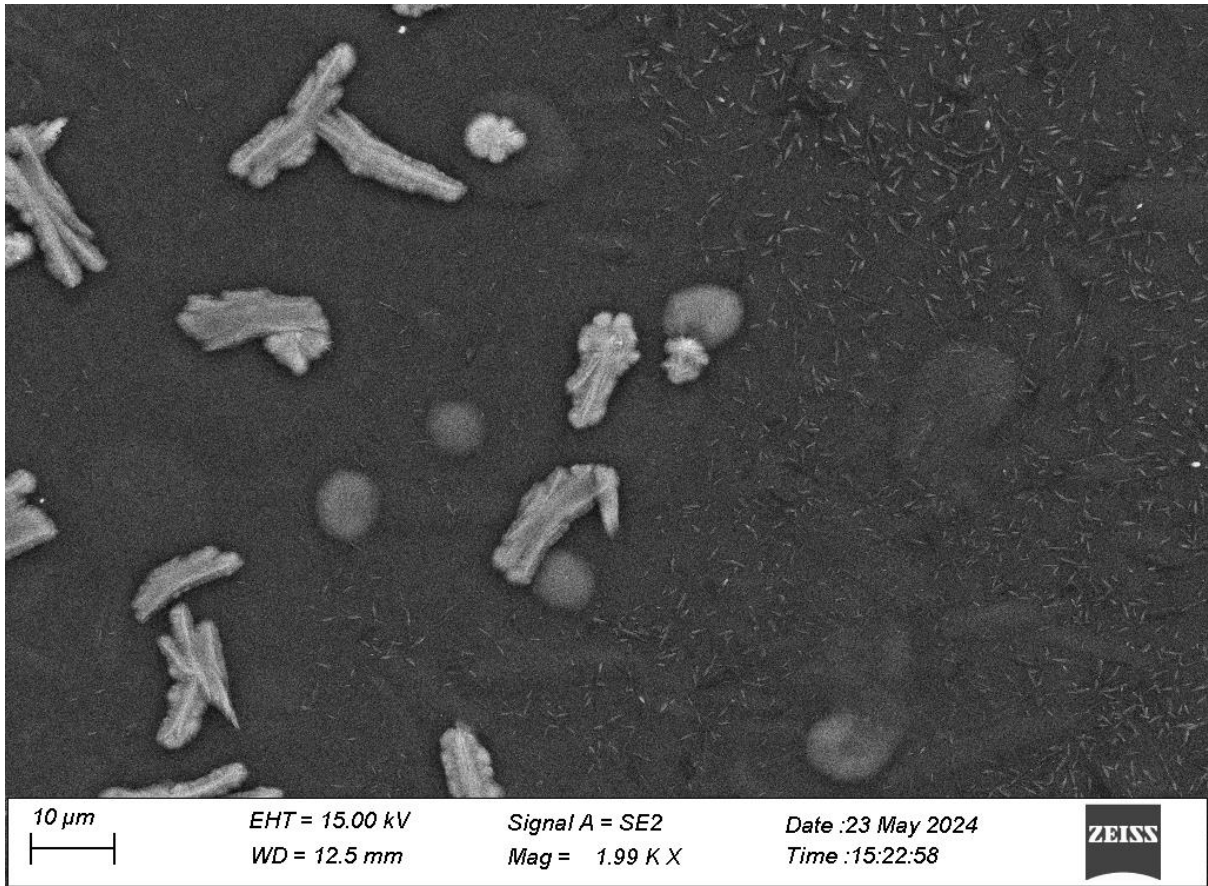


Figure 33: The surface of film B11-1 at 1990x zoom.

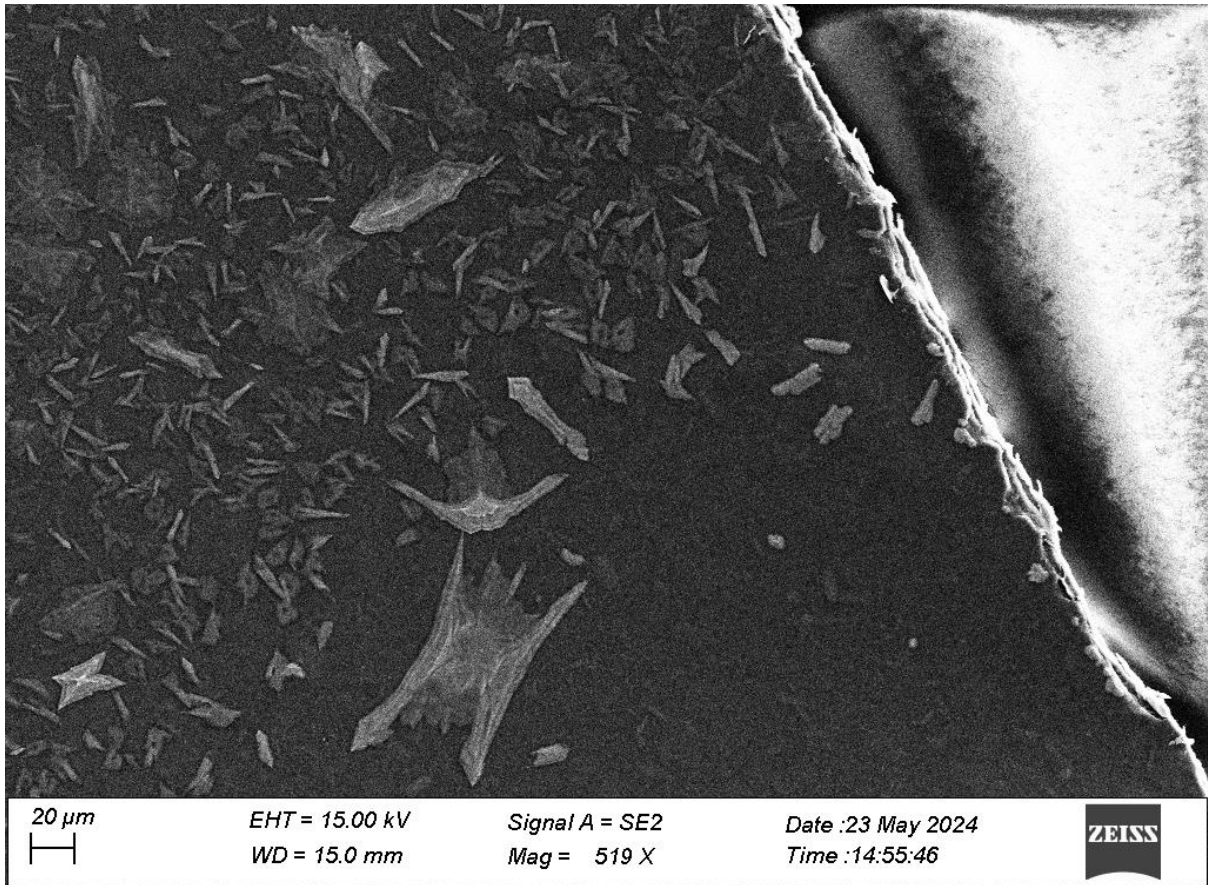


Figure 34: The surface and edge of film B11-2 at 519x zoom.

Issues with Resistance Measurements

As mentioned in previous sections, the resistance measurements often turned out inconclusive. This limitation in the four-point probe measuring method has hindered the progress of this project. For future research, it is suggested to try other methods for measuring film resistance, such as dielectric measuring methods.

Transparency and Use Cases

Transparency is an inherent property of CNC films that is important for certain product applications requiring transparency. The proposed applications for transparent conductive CNC films include as an ITO replacement and transparent scannable films. Transparency is essential for these applications, and currently, there are no CNC films with sufficient conductivity and transparency to make such products. Therefore, more research is needed in this area.

The most direct solution to increase conductivity is to raise the polymer concentration in the films. However, increasing the conductive polymer content results in a loss of transparency. Therefore, other aspects within film production should be explored. This could involve altering production techniques to improve the way polymers orient themselves in the film's macrostructure. This could significantly enhance conductivity and should be investigated in future research. Additionally, it would be advantageous to use a polymer other than PPy, as it demonstrated the greatest decrease in transparency compared to other polymers.

Conclusions

In this project, we have investigated several variations in methods, two different polymers, and three different softeners. The polymer PPy appears to have the most potential for conductive applications based on our evaluations. However, it is not a viable option for making transparent films due to its dark color. While the results may not definitively show that one method produces more conductive films than another, it is clear that soaking the films in *p*-Toluenesulfonic acid significantly enhances their conductive properties. Unfortunately, the high concentrations of polymer needed to achieve conductivity result in a moderate reduction in transparency with PEDOT and complete loss of transparency with PPy.

Future Research

During this project, several questions arose that present opportunities for future research. Here, three major points that should be subject to further research are presented. Firstly, one area of research that could be explored further is the alignment of the CNC crystals. In theory, a higher degree of structure and crystal alignment within the CNC matrix would result in more conductive films. If the crystals are arranged in a random manner, as they do in our films, electrons may have to travel further and encounter more resistance, leading to lower conductive properties. Conversely, if the crystals are arranged in a more constructive manner, films with lower resistance and higher conductivity would be expected. Further exploration of the alignment of CNC crystals and the possibility to manipulate this structure should be conducted.

Secondly, the issue of films sticking to their petri dishes, as described in the subsections on Batches 9 and 10 under the *Experiments* section should be further investigated. An example of

an existing method for preventing this issue is outlined in those sections, but it is uncertain whether it would be effective in the case of CNC films with conducting polymer.

Lastly, another area of future research is comparing the effect of PSS and PVA-S on the ability of PEDOT or other conducting polymers to coordinate with the CNC sulfate groups. This was briefly explored in this project but the failure to produce conductivity is suspected to have been caused by errors in the execution of the production method. Therefore, it is recommended to thoroughly investigate how the ability of PSS and PVA-S to increase conductivity compares in conductive CNC films.

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