Does the morphology of latex affect the electrical properties/morphology of a PEDOT:PSS when a thin film is formed?

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Executive Summary

The worldwide electronics market in the past decade has experienced a manifold increase in the utilization of organic electronics. Research around electronic devices such as solar cells and OLEDs has focused on increasing the cost efficiency of the materials used with little regard for environmental and economic demands. This research explores one area of development: the electrode, which is the interface between the electronic device and power source.

This research investigates latex as a cheaper, organic alternative to PDMS, a common substrate. Latex was used in conjunction with conductive polymer mixture, PEDOT:PSS, which acts as the electrode. The morphological response of the PEDOT:PSS film was observed as it was combined with the latex in a two-layered film.

It was observed that the PEDOT:PSS microstructure was affected by the presence of the latex substrate, regardless of the processing technique. However, rather than the interfacial features of the attached material, it was found that morphological changes were dependent on the molecular properties.

Nevertheless, the changes in the microstructure of the electrode provide opportunities to enhance the conductivity and electrical properties of electronic devices. This research determines that both economical and sustainable materials can be viably incorporated into organic electronics.

Table of Contents

Page

Table of Figures

List of Tables

1. Introduction

Society in the twenty-first century is undeniably more sophisticated and undeniably more electronic than any other century. There is very little work which is not done using an electrical device in some form. With the common-use of electronics, one area recently that has garnered a lot of interest is the organic electronics sector as a more sustainable and inexpensive replacement for their inorganic counterparts.

Organic Electronics

Organic electronics utilizes the electronic properties of molecules or polymers found in natural materials. For example, solar cells can utilise fullerenes, a naturally existing carbon molecule, in place of the typical silicon semiconductor. In addition, televisions with OLEDs (organic LEDs), utilise a thin film of organic material to produce light for electronic displays. Organic electronics has the potential to have a very practical application to everyday life.

The natural abundance, low-cost, and lightweight properties of organic electronics makes them a profitable area of research for development. While historically, research has not focused on the sustainability of using organic material, greater awareness of climate change and scarcity of resource has increased the initiative to produce environmentally friendly products (Girtan, Rusu 2010). This has often created a tension for many commercial manufacturers with maintaining performance while testing andd using new alternative materials.

Electrodes and Current Research

Research and development for improving the efficiency of electronic devices has focused on diverse aspects. This research has chosen to focus on the electrode, investigating organic materials as a safer and natural alternative to inorganic material compositions.

For inorganic materials, research exists for improving efficiency. ITO (indium tin oxide) is a common inorganic material, most notably in Samsung electronic devices, however, the effects upon the user and manufacturers health are unknown and are as yet undocumented (Amata et al. 2015, Andersen, Cropp & Paradise 2017, Chen 2007).

Electrodes are conductors that carry the electrons from the power source to the working active layer of an electronic device. The efficiency of electrodes is calculated by the ability for current to flow freely and quickly (Casiday, Frey 2002) (OSRAM 2017)

The material composition for electrodes needs to be transparent for light to pass through. Transparency is especially important for solar cells and OLEDS as their function is dependent on light being transmitted to and from the device itself. This area of research is important to the development of organic electronics that require some form of light production within the active layer, as they provide the structural integrity, conductive limitations and protection of the active layer itself.

Research studies to improve efficiency and cost have proposed numerous material compositions and electrodes for organic electronic devices. These include silver nanowires embedded within polyimide

(Gupta 2015, Kumar et al. 2013, Liu, Ho & So 2016), graphene-based matrixes (Alahbakhshia et al. 2017, Shina et al. 2013, Zhua et al. 2013), matrixes of polyurethane (Raoa et al. 2012, Chiorcea-Paquima et al. 2014), and ionic liquids (Teo et al. 2017). However, these technologies are uneconomical and research has not yet considered the use of the substrate to support the electrodes.

2. Material Choices

2.1. Latex substrate

Electronic devices commonly use inorganic compounds such as PDMS polymers (Polydimethylsiloxane), commonly known as silicones. Sustained use of PDMS has been found to cause eye irritation in humans, this research seeks to investigate latex as a more sustainable and healthy substitute (Aikawa et al. 2016).

Latex was chosen because it is a commonplace, cheap material which is natural, and therefore, an inherently environmentally friendly product. As a natural material, latex has relatively easy processing steps which has suited it well for many applications, however, rarely in OLED and electroluminescent applications.

Latex has high transparency, making it very suitable for electronics that require light emission (Määttänen et al. 2016). It has used in thin films with graphene, creating a highly elastic material compound (Yu et al. 2017). Latex is a also desirable material for its regenerative properties with very good environmental degradation rates (Aikawa et al. 2016) (Cherian, Jayachandran 2010, Lauzier et al. 1993).

2.2. Isoprene Solution

While research has commonly used PDMS, this research has used isoprene in order to provide a flexible substrate (Andersen 2017). See Figure 1 for molecular structure.

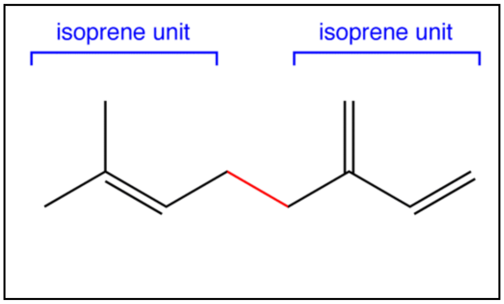

Figure 1: Isoprene monomer unit

Latex consists of an aqueous solution which holds the isoprene molecules.

When the latex is in aqueous solution, the isoprene molecules are dispersed randomly with some interaction between the water molecules and isoprene. It was not determined in this experiment when the crosslinks formed, but it has been logically inferred that the isoprene in solution was already crosslinked. As the water evaporates, the isoprene molecules come closer together, and become entangled.

2.3. Polymer Film

Other research utilise complex and material-specific methods for producing polymer films, requiring unique processes.

This research proposes an alternative solution which simplifies the processes in an electronic device whilst maintaining similar performance. This research proposes the use of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate solution dissolved in water, PEDOT:PSS (see Figure 2 for molecular structure), laminated onto a latex film.

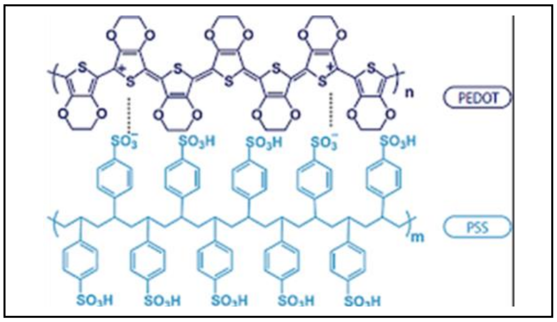

Figure 2: Chemical formula of PEDOT:PSS

2.4. PEDOT:PSS Solution

This research uses PEDOT:PSS over the more common ITO glass as conductor for the transparent layer in solar cells.

PEDOT:PSS has been argued as a better alternative for the conducting electrode for organic electronics (Girtan, Rusu 2010). Girtan and Rusu found that PEDOT:PSS electrodes have an advantage over ITO electrodes with an increase in the open circuit voltage in solar cells tested (2010). The higher open circuit voltage means that when there are no leads connected to the terminals of the solar cell, the electric potential produced in the tested solar cells increased. The higher work function of PEDOT:PSS meant that the electron excitation rate decreased, and this increased the electric field. This is significant for electrode applications in electronic devices such as solar cells, which requires the prevention of electron/hole recombination in order to be effective.

PEDOT:PSS is a polymer mixture which offers great electrical conductivity. The polymer consists of two charged polymers, PEDOT and PSS, which carries positive and negative charge respectively (see Figure 1).

Within a PEDOT:PSS solution, gel-like PEDOT-rich molecule grains are randomly arranged together with a surround by a 'shell' of PSS molecules (see Figure 3). As the solution dries on the latex film, the PEDOT and PSS molecules disperse evenly to form a solid solution.

The effective conductivity of the PEDOT:PSS solution is directly related to the amount of PSS present relative to the PEDOT in the solution before film formation. The conductivity is also related to the PEDOT grain size, with a larger median grain diameter increasing conductivity. Kirchmeyer and Reutera theorized this occurred because there were less PSS boundaries obstructing the flow of electrons (Kirchmeyer, Reutera 2005).

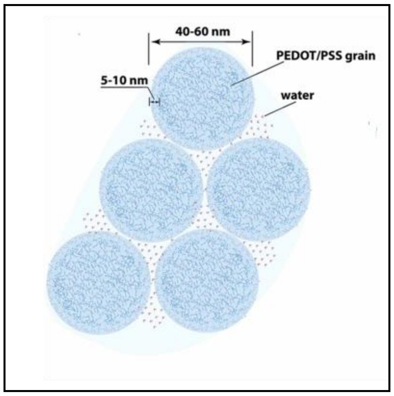

Figure 3:PEDOT:PSS morphology in solution

3. Experimental set-up and methodologies

This section of the report establishes the method of production to create an electrode film for an electronic device. The production process generally is transferring both the isoprene and PEDOT:PSS solutions from storage and layered upon the substrate as a film.

3.1 Assessment of Film Processing Methods

Previously, the simplest processing methods for forming thin films were known as casting techniques (Krebs, 2009). While there is some variance in technique, essentially all follow the basic steps of applying a solution to a substrate, then drying the solution to form the solid film.

The biggest advantage is the simplicity of application and compact workspaces requiring only requiring a horizontal surface to work upon. A large amount of research uses this method because of the quantity of film able to be produced. Though these methods are the simplest and cheapest of the methods given, there is limited ability to control film thickness.

Another technique used in creating films for research was a spin-coater, however, this was not deemed viable due to its large amount of waste.

Finally, roll to roll (R2R) have been implemented in the production of organic devices, such as solar cells. This is another very common technique for creating film because of the control over the thickness and consistency of the film produced. While, R2R methods generally suffer from space restrictions, requiring greater space as the rate of production increases, R2R is very scalable and multiple processing steps can be added on without alterations to the original equipment.

3.2. Wire-Bar Coating

Wire-bar coating is a simple R2R method available in-house for research.

The wire bar coater, this investigation used an Elcometer 4340 motorised film applicator for the processing, consisting of a wire wrapped around a bar which is moved over the solution. Like a rolling pin, the solution is applied to the top layer of the substrate to be processed into a film (see Figure 4). The material is then held by capillary forces and then spread evenly along the substrate.

The method has very little waste compared to spin coating, since all the material is used and controlled relatively easily.

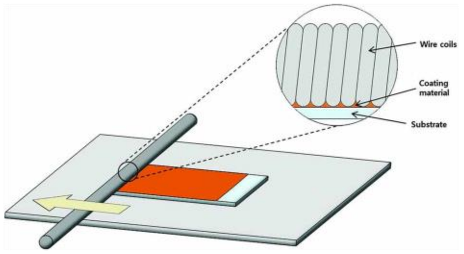

Figure 4: Wirebar coating schematic

3.3. Wire Bar Coating in Research

Research affirms the effectiveness of wire-bar coating over casting techniques for the application of other organic materials to substrates. Wire bar coating allows variable wire heights and speeds which manipulate the thickness and roughness of the film produced. Nketia-Yawson notes the greater control over the macro-characteristics of the film (Nketia-Yawson et al. 2016). Wire-bar coating is the method of choice in research with PEDOT:PSS (Kawahara et al. 2012) and PDFDT (Nketia-Yawson et al. 2016) .

However, research carried out by Del Pozo suggests that wire-bar coating struggles to control the material composition or fine detail (Del Pozo et al. 2015). The changeable parameters of the wire-bar can determine the bulk characteristics of the films produced such as film dimensions, but are unable to manipulate the molecular distribution through magnetic or electrical means. This may be detrimental in this study, as the ability to vary the microstructure is key to determining the effectiveness of PEDOT:PSS as an electrode component. In response to this weakness, different processing methods were used as a means of changing the microstructure.

Other weaknesses include the wire bar’s varying attraction to different components of the solution being processed, leading to travelling fronts and component stratification (Tan et al. 2015). Though in this case, the materials are not complicated, so this is considered negligible.

3.4. Results

With wire-bar coating, the latex monolayer films produced had thickness of 240 ± 30µm and the PEDOT:PSS monolayer films yielded thickness of 1540 ± 200 nm using a profilometer. The films were thin with a satisfactory thickness and consistent application.

4. Materials, Equipment and Processing Overview

This overview detailed below provides the contextual understanding of how the research was carried out including:

- The materials and equipment used. (See 4.1 below.)
- The key steps involved in generation of the latex thin film and PEDOT:PSS film, and annealing process. (See 4.2 to 4.4 below.)
- Different processing methods used. (See 4.5 below.)

4.1 Key Materials and Equipment Used

The key materials and equipment used are as follows:

- Materials used:
    - Silicone glass slide for the film (PEDOT:PSS) to rest upon. The microscope slides used were (26 x 76 x 1.1 mm)
    - Latex (isoprene) to form substrate. The isoprene used was Pebeo Gede latex.
    - PEDOT:PSS for electrode. This was bought from Sigma Aldrich, with a concentration of 3 % wt. PEDOT:PSS
- Equipment used to process the film:
    - Pipette for the PEDOT:PSS
    - A wooden popsicle stick or similar for a disposable means of removing the latex and placing it onto the glass slide
    - Wire bar coater (Elcometer 4340 motorised film applicator)

4.2 Generation of latex thin film

- Scoop ~1 ml latex out of the container and place onto the glass slide. Drawing consistent volumes of latex was difficult due to its viscoelastic properties, so a visual check was used to maintain consistent volumes. Hold the popsicle upright, then push the latex tip onto the glass slide, depositing some of the latex onto the slide.
- The popsicle stick was turned onto an angle (45°). Drag the popsicle stick along the slide to deposit more latex. Afterwards, the stick was discarded.
- Place glass slide under the wire bar coater, the faster the better since the latex will begin to dry once exposed to the air
- Set the speed (5mm/s) and height (when the elcometer was set in its original position, two glass slides, 2mm, were used to prop up the substrate) before switching on the machine (this will determine thickness)
- Turn on power to machine and switch machine to “on” and begin wire bar coating process, hold down the glass slides as the wire bar runs across the latex.

- Once wire bar has run across the whole slide, remove the latex film on the glass slide and place into a vacuum to prevent oxidation, a KNF Neuberger laboport vacuum pump was used and run for 3 minutes to produce an absolute pressure of 400mbar.
- Ensure the film is not exposed to sunlight. Foil was used to shield the samples from sunlight
- Wait 12 hours for the water to completely evaporate

4.3 Generation of PEDOT:PSS film

- Using pipette, deposit ~100-200µL of PEDOT:PSS onto a glass side near the edge (or if forming film on top of the latex, then ensure drop is near one side). Ensure that the drop is in the centre and close enough to the edge so that there is maximum film generation and no loss of material
- Set the relevant speed and height before switching on the machine (this will determine thickness)
- Turn on power to machine and switch machine to “on”
- Begin wire bar coating process, hold down the glass slides as the wire bar runs across the PEDOT:PSS drop.
- Once wire bar has run across the whole slide, remove glass slide with the film and place into a vacuum
- Wait 12 hours for the water to completely evaporate
- For storage, place sample inside a vacuum to ensure that there is no contamination

4.4 Annealing Process

- Place the film inside a furnace at 160°C
- After 30 minutes, remove films from furnace and return to storage

4.5 Different Processing Methods Used

Once the latex monolayer has been formed, the PEDOT:PSS could be applied to form the second layer using three separate methods:

4.5.1 ‘Normal’ Layering Technique

The first method was produced by using the wirebar coater to place the PEDOT:PSS on top of the latex that had dried. The height of the wirebar coater was unchanged when the PEDOT:PSS was applied. Once the PEDOT:PSS was applied to the surface, it was then placed in a vacuum wrapped in Aluminium foil to prevent light degeneration. After 12 hours, the electrode can be analysed. This is referred to as the ‘normal’ layering technique. This is the intuitive and generic production method of generating a bilayer film, and this would serve as the generally accepted method for comparison to the control samples.

4.5.2 ‘Soaked’ Layering Technique

The second method was produced by soaking the latex sample inside a solution of the PEDOT:PSS for 30 minutes. After the time period had elapsed, the sample was removed from the solution, and left to dry in a vacuum. After 12 hours, the electrode can be analysed. This is referred to as the ‘soaked’ layering technique. This method was attempted because it was noted when spincoating was attempted, the PEDOT:PSS left a stain on the latex film. So this method allows the PEDOT:PSS to penetrate deeper into the latex film.

4.5.3. Double Wet’ Layering Technique

The third method used the wirebar whilst the latex film was drying. The latex was applied to the glass substrate using the wirebar coater. Immediately after the latex was applied, the PEDOT:PSS was applied onto the latex using the wirebar coater (< 3 minutes after the latex). The sample was then left to dry under shade and vacuum.

This is referred to as the ‘double wet’ layering technique. This method was attempted as it was theorized that the PEDOT:PSS could penetrate the latex film through aqueous means. The latex itself contains water molecules, and the water attached to the PEDOT:PSS may contribute to the movement of the PEDOT:PSS relative to the latex film.

5. Analysis Process

After layering the latex and carrying out the different processing methods to form the PEDOT:PSS film on top, the samples were analyzed with Optical Microscopy, X-Ray Diffraction, Atomic Force Microscopy. These tests provide an understanding of the microstructure of the film produced.

5.1. Optical Microscopy

Since the PEDOT:PSS is transparent, optical microscopy (OM) provided an surface analysis of opaque, physical abnormalities in the film produced. These features could be characterized and observed across all processing techniques. Trends and relationships can then be established between those features and particular methods.

OM is limited with only geometric dimensions of the microstructure could be presented and analysed.

5.2. Atomic Force Microscopy

Cypher ES Atomic Force Microscopy (AFM) was used to provide information about the depth of topographical features produced on the bilayer film. While microscopy provides a two-dimensional image of the film, AFM maps the three-dimensional topographical features of PEDOT:PSS produced

This provided another level of analysis for the features of the PEDOT:PSS produced. The latex surface could be characterized, and provide an understanding of the effect of the interface upon PEDOT:PSS features (if any), as well as critique the effect of the processing methods on the PEDOT:PSS/latex interface.

AFM uses an oscillating lever which moves across the sample whilst passing over topographical features. The displacement of the lever shifts the reflected laser beam, and this displacement of the beam is measured and recorded. This provides further analysis compared to optical microscopy as it provides depth to the surface features of the samples measured in optical microscopy.

The results from the AFM act as supporting evidence of the conclusions found in OM. The limitation of both AFM and OM is the lack of analysis on the nanoscale, with no information about features and structures that have spacings or dimensions.

5.3. X-Ray Diffraction

X-Ray Diffraction analysis provides a further understanding of the nanoscale spacings that exist within the PEDOT:PSS film produced. Since the molecular geometry as well as crystal structure of each material differs, the intensity of the peak, and at what angle this occurs, changes. This allows for the specific characterization of the PEDOT:PSS film features and these can also be correlated to the processing methods.

For XRD analysis, a Rigaku Ultima IV was used.

XRD operates by generating and passing x-rays onto the sample at different angles. These x-rays diffract through the samples and interfere with each other at different intensities, which is measured and plotted. X-rays are used since their wavelength is similar in size to the distance between molecules and/or atoms within the sample.

If the sample is crystalline, then the x-rays diffract in an orderly fashion, resulting in constructive interference. The waves that pass through the crystalline structure build upon one another, causing a wave of greater amplitude to form. However, with non-crystalline materials, the diffraction of the x rays through the sample are scattered and the resulting amplitude of the waves are weaker. Thus resulting in a weaker wave. The XRD equipment then completes this process at a range of angles, so that a unique spectrum can be produced.

6. Results and discussion

6.1 Optical Microscopy Analysis

In normal operation, the PEDOT:PSS film was heated to 160°C and allowed to cool using a furnace. The heat treatment of films has been found to increase conductivity through the manipulation of surface topography (Kim et al. 2009), and the removal of water from the PEDOT:PSS film (Friedel et al. 2009).

Images of the PEDOT:PSS films from the different processing methods are shown as below (Figure 6):

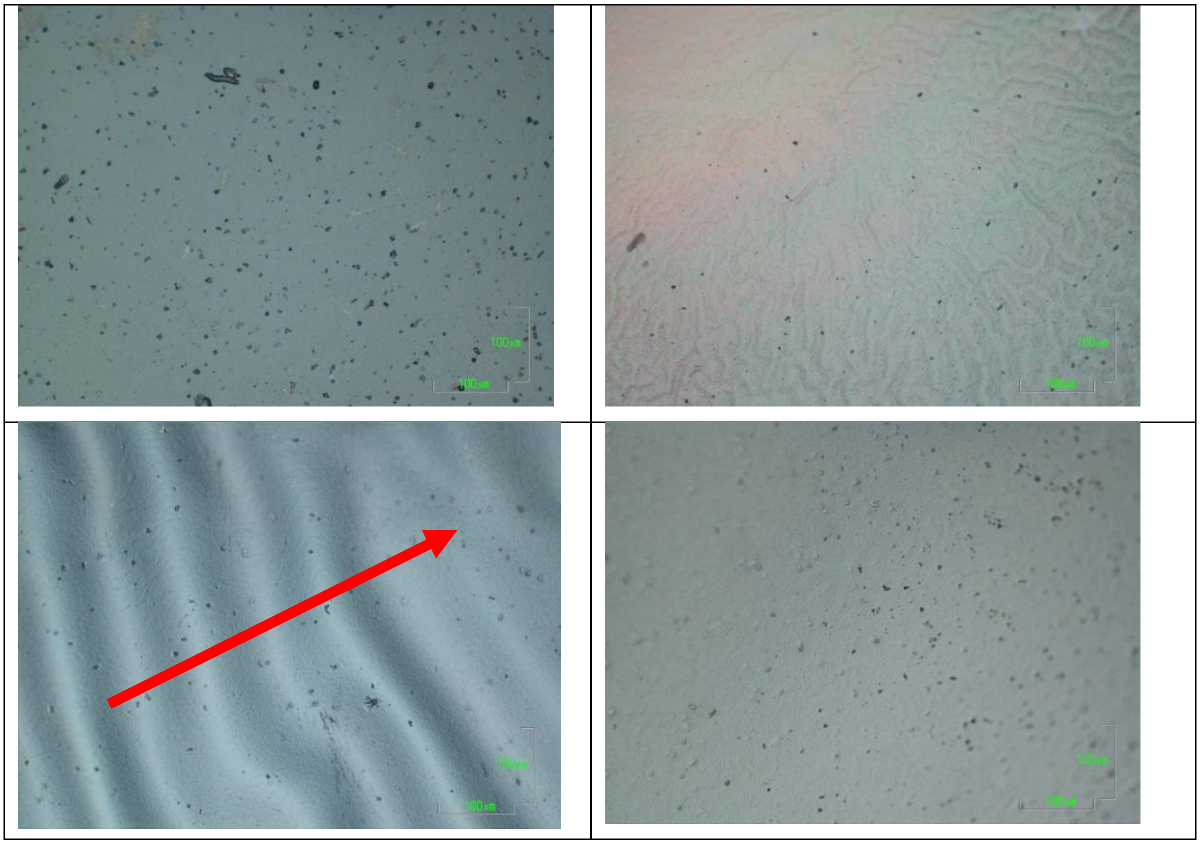

Figure 5: Electrode samples of PEDOT:PSS/latex and PEDOT:PSS
Top left: PEDOT:PSS monolayer, Top right: PEDOT:PSS layered onto latex using 'normal' processing method,
Bottom right: PEDOT:PSS layered with 'Double Wet 'method, Bottom left: PEDOT:PSS layered using 'Soaked' method

6.1.1. Initial Observations

The **PEDOT:PSS** film formed a blue hue as the background (see Figure 5). This phenomenon was presumably caused by the PEDOT:PSS reflecting the blue area of the colour spectrum.

Cracks were discovered in the sample that reveal the clear latex underneath, implying that the PEDOT:PSS chains had stacked randomly on top of one another, covering the whole surface of the glass substrate. As the latex film contracts in different directions, the PEDOT:PSS is also contracted in the same directions. However, it is more brittle compared to the latex, so it tears.

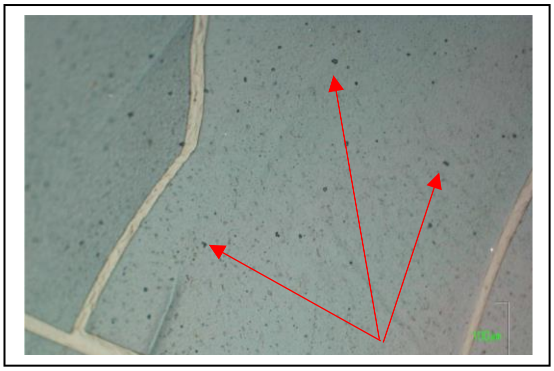

Figure 6: PEDOT:PSS with cracked edges due to lateral forces

6.1.2. Dark Blue Dots

A main feature of the PEDOT:PSS films is the presence of dark blue dots forming within the film (see Figure 6, indicated by the red arrows). Previous studies have attempted to explain the origin of the blue dots in this sample, explaining them as PEDOT cores, with PSS shells. (Takano et al. 2012, Zhou et al. 2014).

HYPOTHESIS: These were hypothesized to be PEDOT grains which are formed within the solution due to hydrophobic/philic attractions.

REASONING: The blue dots are small congregations of the PEDOT:PSS, which have formed like cores within the solution. The PSS chains surround the PEDOT chains and protect the PEDOT:PSS grains from water as they themselves are hydrophilic. As the film dries, these cores remain, and produce small grains of PEDOT within the film. Rivnay, who experienced a similar phenomenon with PEDOT:PSS proposes that the PEDOT chains are darker because of the light properties (Rivnay et al. 2016). The second phase, which is most dominant, is the PEDOT:PSS rich phase provides the lighter blue hue in the pictures.

CONCLUSIONS: Though there was no chemical analysis to determine the composition of these blue particles within the film, there is significant circumstantial evidence to support the conjecture that these blue grains are PEDOT rich grains. This initial conjecture provides a framework to analyze the results obtained from the experiment.

6.1.3. Undulations in Film

Another feature that was apparent in the soaked and normal processing methods, and to a lesser degree in the double wetted techniques was the presence of undulations in the films (see Figure 5. Direction indicated by the red arrow).

HYPOTHESIS: As the latex film contracts, the PEDOT:PSS which has adhesion with the latex film, is also pulled in contraction as well as the latex.

REASONING: PEDOT:PSS has a lower elasticity compared to the latex which prevents the isoprene from fully contracting. In the interface between PEDOT:PSS/latex bi-layer film, potential elastic energy is stored and released. The release is seen as a disturbance that ripples through the whole sample, forming a wave-like feature, bending vertically (both upwards and downwards) since there is no horizontal direction for the film to compress.

CONCLUSIONS: This reasoning is consistent with the results where the rippling effect is more apparent where the solid latex was formed first. In the “double wet” sample, the two films form at the same time, as there is little adhesion between the latex or the PEDOT:PSS. Therefore, when the films dry, any contractions that do occur within the latex sample are absorbed by the PEDOT:PSS solution.

However, with the soaked and normal films the latex film has already dried, and there is more elastic potential energy within the latex that was not dissipated through the liquid PEDOT:PSS. Therefore, any contractions that do occur have a greater effect on the surface topography of the PEDOT:PSS/latex interface. If this effect were to be reproduced, then ensuring the a dry latex/wet PEDOT:PSS surface is important.

6.1.4. Latex – Small Sized Particle Formation

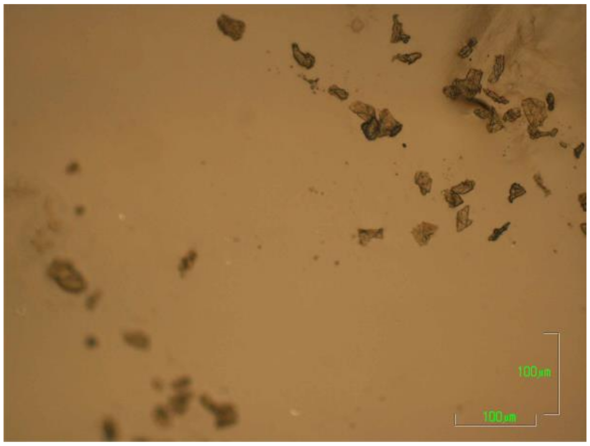

Figure 7: Isoprene with particles.

Another feature of the latex was the small sized particles spread through the sample.

HYPOTHESIS: Possibly, oxides formed in the isoprene during formation and storage of the isoprene film.

REASONING: However, there are many possible reactions that the isoprene could undergo, so further investigation into the composition of these grains would need to be undertaken (see Figure 7). (Fan, Zhang 2004)

CONCLUSION: These particles in the latex were not determined to be effective in changing the microstructure of the PEDOT:PSS structure. However further characterization should be carried to analyze its chemical structure and make-up.

6.2 PEDOT Grains – Frequencies across processing methods

The number of PEDOT grains per average unit area was calculated for every processing method.

Processing method	**Non processed PEDOT:PSS**	**Normal**	**Soaked**	**Double Wet**
PEDOT grains per image	210 ± 90	51 ± 30	70 ± 35	75 ± 40

Table 1: Average PEDOT grains per image taken. The area of an image was 0.4 mm^2

It was found that after PEDOT:PSS was applied onto the latex film, the frequency of PEDOT grains per unit area decreased (see Table 1). With the normal processing method, it had a significantly decreased number of observable PEDOT grains compared to the soaked and double wet methods.

There are two possible theories as to why the frequency of grains found decreased:

HYPOTHESIS 1: the prevention of nucleation by the latex material, or

HYPOTHESIS 2: the micro – nucleation of PEDOT grains on the nanoscale, both reducing the number of observable PEDOT grains in the number of observable PEDOT grains.

REASONING: Previously, the PEDOT:PSS monolayer had a glass substrate base. Though it is not expected to contribute significantly, the micro-surface of the glass compared to the latex may provide some further assistance in preventing the nucleation of PEDOT grain sites. The latex roughness and topographical surface may make it more difficult for the PEDOT grains to form. Alternatively, it is also possible that the latex molecular interactions themselves influence the nucleation rate of the PEDOT:PSS.

CONCLUSION: The increase of PEDOT:PSS grains indicates that the formation of the PEDOT grains is affected primarily by the chemical interactions of the latex with the PEDOT:PSS. The negligible effect of processing method indicates that the microstructural features of the PEDOT:PSS were unaffected by diffusion rates of the PEDOT:PSS into the latex film itself, which is the mechanism that the 'soaked' method' encourages. Nor is the PEDOT grain frequency affected by the removal of elastic forces, which the 'double wet' feature encourages.

6.3 PEDOT Grains - Distributions

When the distributions were standardized and compared to one another, it was found that the distributions of the area were similar, with insignificant deviations (displayed in Figure 8).

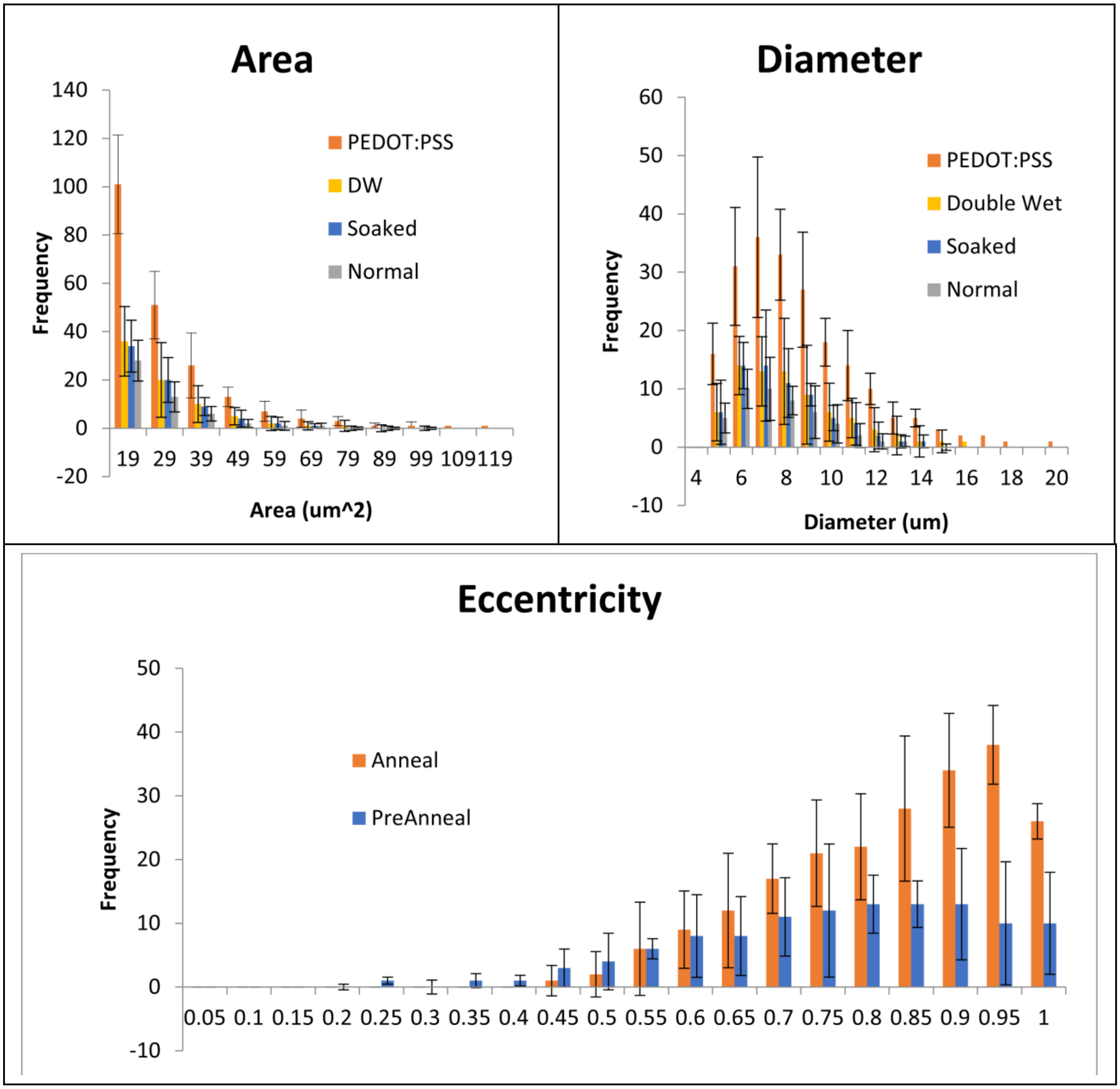

Figure 8: Distributions of PEDOT grains across different processing methods

6.3.1. Area distributions

Across all processing techniques area distributions were largely uniform (see Figure 8). This indicates that the growth of the PEDOT grains were largely unaffected by changes in processing.

The most common PEDOT grain size was ~10-19 µm2, and tailing off at higher areas. It is assumed that once the nucleus of the PEDOT has formed and the PEDOT core is not interacting with the isoprene.

HYPOTHESIS: Therefore, the growth of the nucleus depends not on the isoprene – PEDOT interactions, but the PEDOT - water and PSS – water interactions.

REASONING: Since the substrate only provides the attractive force to bring PEDOT molecules nearer initially, it is reasonable to predict that the removal of this only affects the rate of nucleation. The lack of variation in the other processing methods suggests that the thermodynamic interactions between the PEDOT:PSS and latex had the most significant bearing on the formation of the PEDOT grains. Due to the reduced polarity of the isoprene molecules, there are less attractions between the PEDOT, and the isoprene film. This would reduce the driving force for separation of the two molecules, and the nucleation rate of PSS rich grains would decrease.

Conclusion: The processing methods had small effects on the distribution, though these were overshadowed by the latex interactions and the amount of variation in the frequencies indicates that there are other factors that impact the PEDOT grain formation more strongly. This strongly suggests that the processing method only provides some minor fine tuning of the properties of the final film, whereas the substrate/film thermodynamic properties are more important.

6.3.2. Diameter Distributions

Across all processing techniques the diameter distributions were also uniform (see Figure 8).

The Feret diameter, which is the distance between two parallel planes that are tangential to an object, was used to provide a consistent measurement.

All of the processing techniques yielded very few diameters below 5 µm, and this is most likely because there is not enough repulsion by the water molecules and attractions between the PEDOT to aggregate together. The most common diameters ranged from 6-7 µm, tailing off as the diameter gets bigger.

6.3.3. Eccentricity Distributions

The eccentricity distributions of the process techniques were slightly skewed compared to the PEDOT:PSS monolayer.

In order to accurately measure eccentricity, the PEDOT grains were modelled as ellipses. Eccentricity was measured as the distance between an ellipse's center and either of its two foci was measured with a higher eccentricity value reflecting the increasing sphericity of the particle.

The "double wet" technique provided the most right skewed distribution, followed by the normal and soaked had similar skewed distributions. The most common eccentricities of the PEDOT:PSS monolayer, Normal, Soaked and Double Wet were at 0.95, 0.9, 0.8 and 0.85 respectively.

The differences in eccentricity indicate that the formation of these PEDOT grains were affected by the processing method. However, this does not reconcile with the diameter distribution conclusions, which do not indicate a change in the grain diameter and, by implication, shape. A demonstration of this transformation is in Figure 9 below.

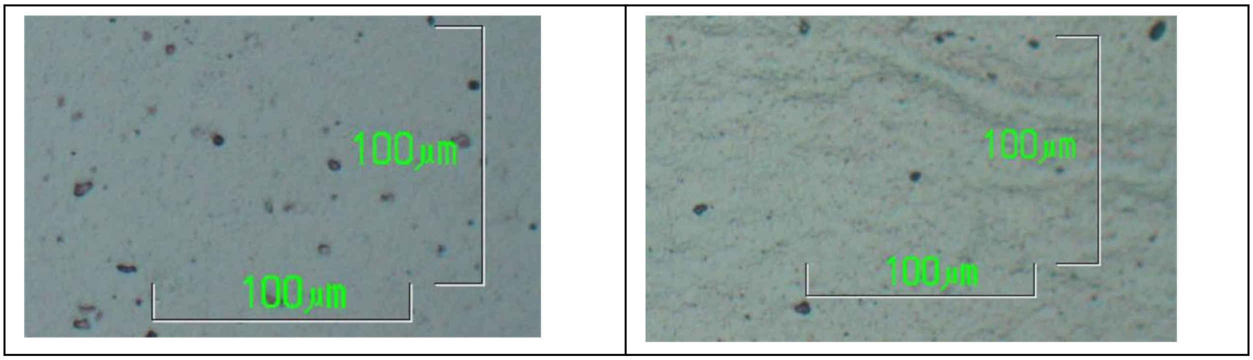

Figure 9: Comparison of PEDOT grains. PEDOT:PSS monolayer (Left) , and Normal layering (Right).

The PEDOT core shape in the "normal' processed distribution is more elliptical compared to the cores of the PEDOT monolayer. Though other articles suggest elliptical models of the PEDOT core (Fan et al. 2016), the size of elliptical structures of PEDOT was suggested to be correlated to the degree of shear force applied to the sample (Ashok, Thomas & Varughese 2015).

HYPOTHESIS: It is theorized that the latex provided some micro shear force to the PEDOT:PSS film as it contracted, causing the PEDOT cores to become slightly elliptical as they were contracted.

REASONING: As the film contracts, the contraction forces are also passed through the PEDOT:PSS film. The PEDOT cores, being an area of increased homogeneity compared to the PEDOT:PSS background, experiences a build-up of the forces as they move towards it. The grains experiencing this directional force, are deformed in from their normally circular shape to become more elliptical.

This also corresponds to the presence of undulations in the films, especially pronounced in the same techniques (refer to section 4.1.3). The technique with more pronounced undulations (Soaked) is also the technique with the greatest shift in eccentricity, indicating a link between the two phenomenons.

CONCLUSION: If the decreased eccentricity of PEDOT grains is a result of the grains absorbing the stresses of the substrate, then films which include more PEDOT grains can be used in applications where constant stressing of the electrode is a risk. The PEDOT grains, able to absorb shear forces, can prevent the electrode and device from shearing for longer periods of time.

6.3.4. Variance of Optical Microscopy Analysis

The optical microscopy analysis seems to have a wide variance in results (see Figure 8). Though there are discrepancies in the Optical Microscopy analysis, the trends remain consistent. Nevertheless, the difference between the methods which used latex as a substrate, and the PEDOT:PSS monolayer demonstrate a definitive trend in spite of the large discrepancy. This could be an issue if careful tuning of the features was required. It also suggests the influence of other factors that were not covered by the variation in processing techniques, which were more impactful upon the structure than the methods tested.

HYPOTHESIS: The occurrence of this large variance was hypothesized to be caused by an external factor that was unaccounted for across all the different processing methods.

REASONING: The reason is possibly a result of the large sample of optical microscopy data taken. The large variance across the sample data taken across even one processing method varied significantly.

CONCLUSION: Therefore, the degree of variation indicates that the PEDOT grain nucleation and growth rates can be achieved by numerous paths, reducing the possibility of unique mechanisms that can controlled by processing techniques.

The seemingly wild variance between different methods illuminates a potential strength of this material composition. If the microstructure produced is not not influenced by processing technique, then optimizations in machinery can be implemented, as the change in processing method does not correlate to a change in microstructure, and therefore properties are unaffected.

6.4 Atomic Force Microscopy

In order to determine the effect of the PEDOT:PSS/latex interface upon PEDOT:PSS microstructure, Atomic Force Microscopy (AFM) was carried out then compared with the PEDOT:PSS microstructure and distribution of the PEDOT grain.

Table 2 present summary statistics of the analysis. The RMS value, is the standard deviation of the sample's height values. The Ra value, is the average of the sample's height values.

	Latex	PEDOT:PSS	Normal
Ra (nm)	20.2	17.3	10.8
RMS (nm)	24.9	21.7	13.3
Height range (nm)	154	124	82

Table 2: Summary statistics of AFM

AFM images were also taken to observe the topographical structure of the different samples.

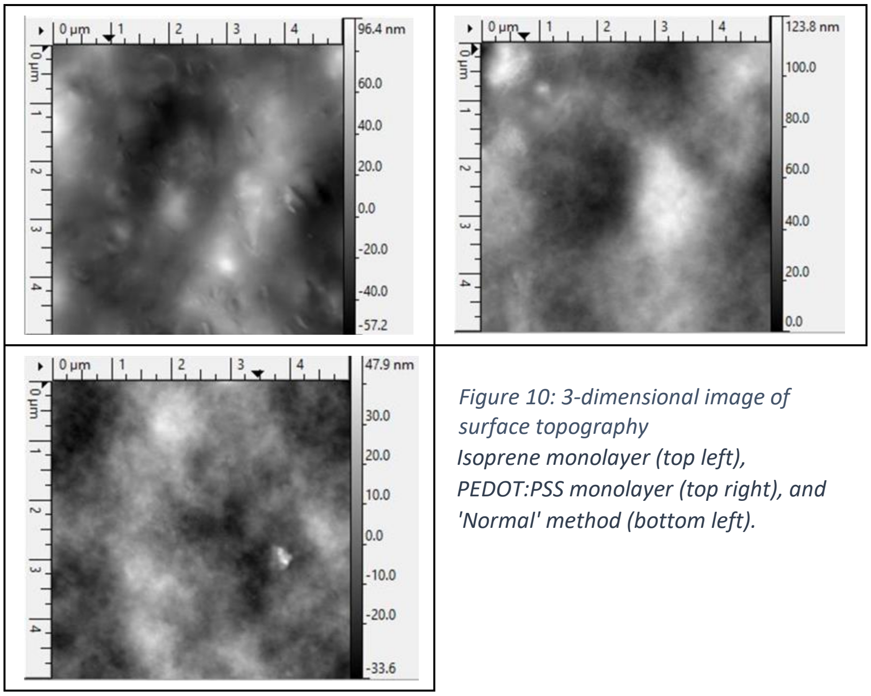

Figure 10: 3-dimensional image of surface topography
Isoprene monolayer (top left), PEDOT:PSS monolayer (top right), and 'Normal' method (bottom left).

6.4.1. Height range of samples

Attention should first be drawn to the latex height range (see Table 2 and Figure 10) compared to the PEDOT:PSS monolayer. The latex film height range almost doubles the PEDOT:PSS, which means that the features present in latex are significantly higher than those of the PEDOT:PSS monolayer.

HYPOTHESIS: This is hypothesized to be caused by the tearing and ductility of the latex film.

REASONING: Given that the isoprene is more flexible and ductile compared to the PEDOT:PSS, any forces applied to the film would cause more deformation compared to the PEDOT:PSS. Whether that be in the form of fronts or tears.

CONCLUSION: The large height range of latex compared to PEDOT:PSS indicates that topographical features of the latex are not translated, or at least smoothed out, as the PEDOT:PSS film is applied. The lack of translatable features of the latex/PEDOT:PSS interface can be an asset in the production of such electrodes, as the PEDOT:PSS film can be reliably produced independently of the underlying substrate.

6.4.2 Variation in sample heights

The latex produced the highest Root Mean Square value (See Table 2), indicating that it had the greatest variation in surface topography. It was hypothesized that the random ordering of the isoprene chains would contribute to different structures within the isoprene film, and produce the large varying structures.

The size of these deformations/impurities in the film were also large compared to the PEDOT grains. The distance between the isoprene features was averaged to 1.5 µm, however, the PSS grain spacing was measured to be 10 µm. If the roughness of the isoprene acted as nucleation sites of the PEDOT:PSS grains, then the grain distribution would match or correspond to this.

The PEDOT:PSS however, has a lower RMS, and this would be determined by the higher organization of the PEDOT and PSS molecules. However, the Normal RMS value is lower than both the latex and PEDOT:PSS. This suggests that the application of the PEDOT:PSS onto the latex film removes the interactions on the PEDOT:PSS topography that cause roughness.

HYPOTHESIS: A theory to explain this trend would be that the reduced interactions of the latex with the PEDOT:PSS, which reduces the frequency of PEDOT rich areas, would generally reduce the amount of topographical features in the sample.

REASONING: It was hypothesized that the PEDOT:PSS chains, being attracted to each other, and possessing no crosslinks, are less likely to be disorganized in microstructure. The reduction in topographical features of the ‘normal’ sample indicates that there. Therefore only features that would stand out would be gradients and impurities in the film. However, as the PEDOT:PSS is layered on, the PEDOT, though affected by the latex, does not find more sites due to the latex roughness.

CONCLUSION: There were no features in the AFM analysis that provided an explanation for the increase of PEDOT rich grains. The AFM analysis indicates that the surface topography of the latex, and therefore, the latex/PEDOT:PSS interface, has negligible effect upon the PEDOT:PSS microstructure. Therefore, if any future electrodes were produced, then any processing methods attempted should not focus on manipulating the interface between PEDOT:PSS and the substrate.

6.5 X-Ray Diffraction analysis to describe Latex structure

For further understanding of the PEDOT:PSS and latex monolayer films, X-Ray Diffraction analysis was carried out. This provides insight into the crystalline structure of PPEDOT and Latex. XRD analysis was carried out over the 0-20° 2Ɵ range as it was not expected for any features to reach any smaller distances. For accuracy, XRD runs were taken twice, and compared against one another to ensure that results were consistent.

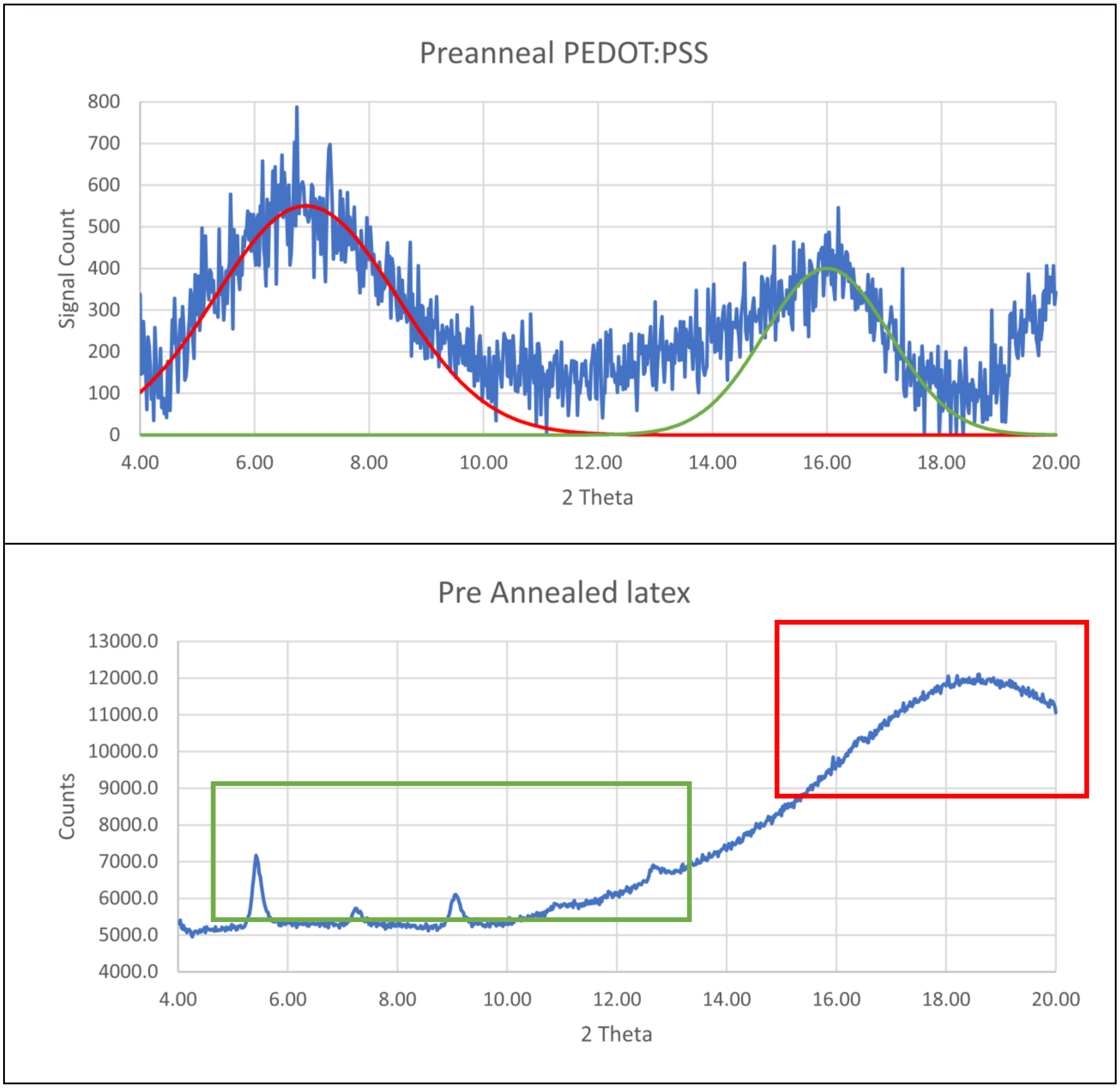

Figure 11: XRD results , pre annealed PEDOT:PSS monolayer (Top), and Pre annealed isoprene (bottom)

To compare the different XRD plots, two transformations were made:

- Each plot's background was removed for more accurate modelling. In the PEDOT:PSS case, a simple quadratic was used to match the baseline, and subtracted. The latex background was simply removed using a flat value. The absence of background effects in the XRD means that the peaks can be modelled with less difficulty.
- The resulting plot features of interest were the peaks, which correspond to a crystal-like feature (e.g. grains), or a regular structure (molecular spacing) within the sample tested. The peaks were fitted using a Gaussian curve ($f(x) = ae^{-\frac{(x-b)^2}{2c^2}}$). The Gaussian plot then allows the half width and position of the peak to be determined.

The latex has two main features, 5 successive small peaks at 5.6, 7.5, 9.2, 11.1 and 12.9, and one large amorphous peak at 18.5° (See Figure 11, indicated by green box). The 5 successive peaks was hypothesized to be caused by small particles in the latex, such as preservatives or oxides. These disappeared when the isoprene was annealed under 160°C for 30 minutes, so they were assumed to be an ingredient included within the isoprene solution.

HYPOTHESIS: It was theorized that the large amorphous peak at 18.5° (indicated by red box in Figure 11 for the latex XRD) is caused by the crosslinking spacing between the isoprene chains.

REASONING: This is supported using the Flory-Rehner relationship to calculate the crosslinking density:

$$-[\ln(1-\upsilon_2)+\upsilon_2+\chi_1\upsilon_2] = V_1 n(\upsilon_2^{\frac{1}{3}} - \frac{\upsilon_2}{2})$$

Where $\boldsymbol{\upsilon_2}$ is the volume fraction of polymer in the swollen mass, $\mathbf{V_1}$ the molar volume of the solvent, n is the number of network chain segments bounded on both ends by crosslinks, and $\boldsymbol{\chi_1}$ is the Flory solvent-polymer interaction term.

The Flory Higgins solvent-polymer interaction term $\boldsymbol{\chi_{12}}$ is calculated using the Hildebrand solubility parameters of water and polypropylene (Hansen 2007):

$$\chi_{12} = \frac{[V(\delta_1 - \delta_2)^2]}{RT} + \beta$$

Where $\boldsymbol{\beta}$ is an empirical constant (0.34 for polymer systems), **V** is the molar volume of the solvent, **R** is the universal gas constant, **T** is the absolute Temperature, $\boldsymbol{\delta_i}$ is the Hildebrand solubility parameter.

This was then used to calculate the number of crosslinks, which in turn determines the length scale that produces the diffraction peak, the mass of latex within with water was measured (17.1 mg). Then the latex mass was heated within the TGA to calculate the mass of water (4.85 mg).

υ_2 was determined to be 0.72 and χ_1 to be 0.3419. The solvent molar volume was 0.28. Solving for the number of average cross links per chain was calculated to be 2.5.

The average length for an isoprene chain with 2.5 cross links is 0.473 nm (assuming normal single carbon bonds forming tetrahedral geometries).

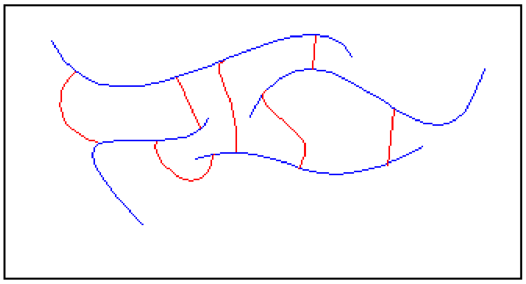

Figure 12: Chains of isoprene (blue) connected by crosslinks (red).

The XRD data for the latex displayed a peak at 18.5°. In order to convert the XRD peak angle into distance q-length:

$d = \frac{1}{4\pi\times\sin\left(18.5\times\frac{\pi}{180}\right)} = 0.476\ nm$, which corresponds to the Flory-Rehner calculations. Therefore, we can assume that the latex peak is caused by the crosslinked segments between the isoprene chains (Figure 12).

CONCLUSION: The length of crosslinking isoprene is useful because it can be used as a basis for comparison. Any changes in the latex crosslinking density can now be quantified if they were to occur.

6.6 X-Ray diffraction analysis to describe PEDOT:PSS structure

The XRD plot for the PEDOT:PSS gives two areas of interest (see Figure 11, indicated by red and green boxes), amorphous peaks at the 7° and 16° peaks.

Previous studies (Takano et al. 2012, Ouyang et al. 2015) have suggested that the first amorphous halo (7°) corresponds to the stacking of the PEDOT in the film (See Figure 12, distance indicated by red bracket). The PEDOT:PSS chains stack and form large columns of the PEDOT, and the spacing between adjacent chains causes the 1st amorphous halo. The relative small height of the peak is likely to be correlated to the distribution of PEDOT throughout the film. Given that the PEDOT stacking would only occur in the grains, the peak generated from this feature would be minimal.

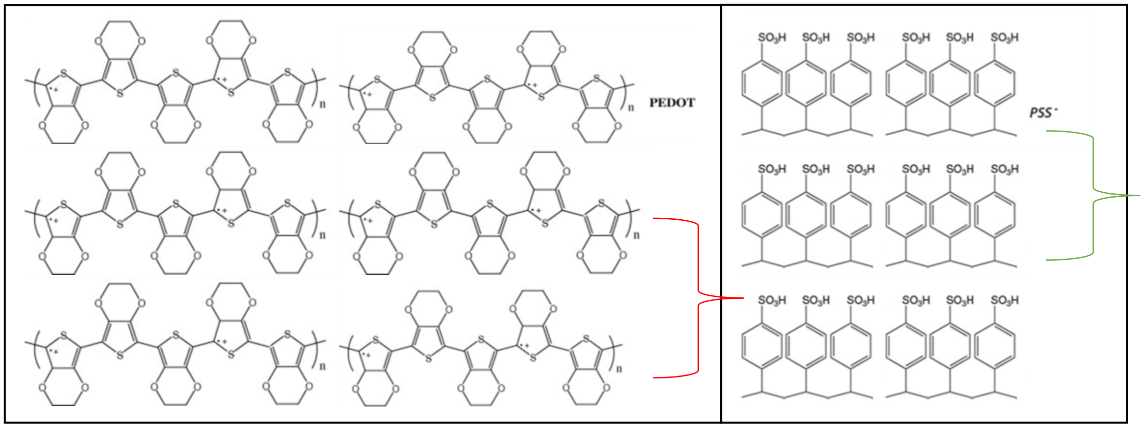

Figure 13: Expected distances that produce XRD peaks in results

The amorphous halo at 16° corresponds to the distribution of PSS through the film, and the spacing in-between those (See Figure 13, indicated by green bracket). This corresponds to the blue hue that was shown in the optical microscopy images. The PSS exists in much lower concentration in the blue cores of PEDOT, with the majority of it randomly distributed throughout the film. Due to molecular attractions, there would some ordering of the PSS chains, however the magnitude of the peak indicates a low degree of organization.

When the PEDOT was applied to the latex peak, it was noted that the latex peak itself was unaffected, indicating that the crosslinking density of the isoprene chains was unaffected. Similarly, the PSS amorphous halo was unaffected, indicating that the PSS spacing was unaffected.

6.6.1 PEDOT peak widening

However, the amorphous halo corresponding to the PEDOT stacking widened considerably:

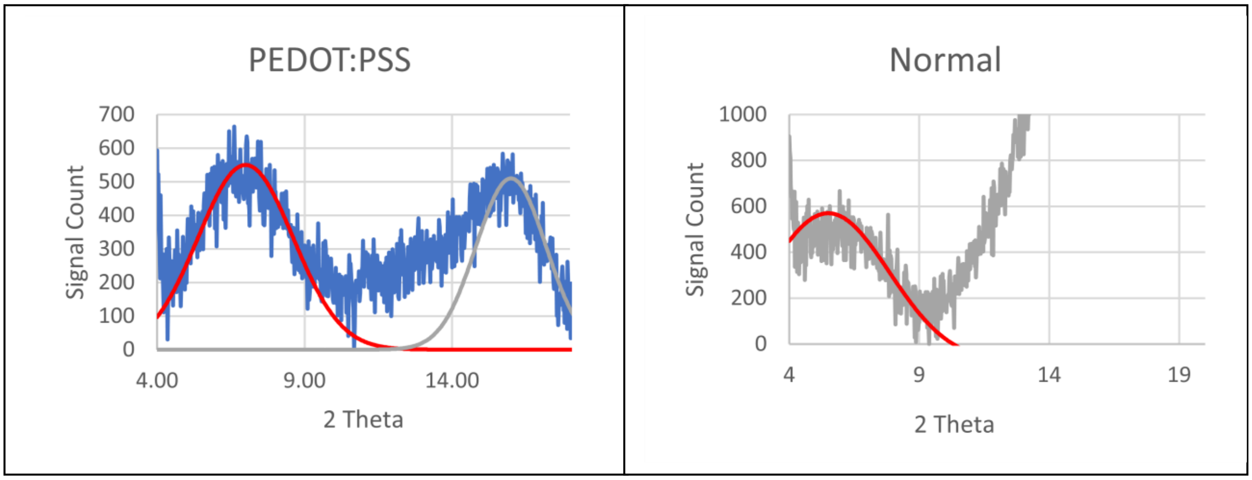

Figure 14: XRD results of PEDOT:PSS layering, PEDOT:PSS monolayer before any processing (left), and PEDOT:PSS film after applied to isoprene film using 'normal' method (right).

The amorphous halo at 6° expands leftwards (indicated in Figure 14 by the red curve). When the PEDOT halo was modelled with a Gaussian curve, it was found that the position of the peak shifted to the left and the half width (width at half the height of the peak) increased considerably (see Table 3).

Sample	Peak width at 4 – 9° (Pre Anneal)	Peak position (Pre Anneal)
Pedot:PSS	3.41 ± 0.01	7°
Normal	5.11 ± 0.03	5.5°

Table 3: Peak properties of XRD results

When the ‘normal’ processing was carried out, the peak width increased from 3.4° to 5.1° (see Table 3), though the right side of the peak base remained at 9°.

The results in table 3 also indicates that the PEDOT stacking distance has varied considerably when latex is used as a substrate. The shift in peak position also indicates that the PEDOT spacing has also increased on average. The XRD results indicate that the distance between adjacent PEDOT molecules range from 4.4 to 1 nm in the normal processing method, compared to the PEDOT:PSS spacing for the monolayer, which ranges from 1 to 1.8 nm.

HYPOTHESIS: Considering the previous results in section 4.1, the increase in peak width is caused by the decrease in the number of PEDOT grains

REASONING: When applied to latex is the PEDOT grains decreased in number. Given less grains per unit area, the spacing between each grain also decreases. Therefore, there is less to also correlate with the average geometric spacing between each PEDOT grain to increase. This increase in grain spacing would further divert the X rays passing through the material, and thus broadening the peak width.

CONCLUSION: The decrease in PEDOT grains has implications for strength properties of the PEDOT and the conductivity. Since PEDOT grains are related to conductivity (Kirchmeyer, Reutera 2005), the decrease in PEDOT grain would also correspond to a decrease in conductivity.

6.6.2 Processing Peak Shift

However, the different processing methods yielded no clear effect on the extent to which method increased the PEDOT spacing (See Table 4), as the error on peak half width is too large for any meaningful changes to be accurately presented. This also correlates to the previous hypothesis which explained that the differing processing methods did not have a large effect upon the PEDOT grains' growth or nucleation.

Sample	**Peak width at 6° (Pre Anneal)**	**Peak width at 6° (Anneal)**
Pedot:PSS	3.41 ± 0.01	3.72 ± 0.76
Normal	5.11 ± 0.03	5.12 ± 0.02
Double Wetted	5.13 ± 0.13	4.83 ± 0.43
Soaked	4.99 ± 0.28	5.96 ± 0.69

Table 4: Peak properties across all processing methods.

The Soaked, Normal, and Double Wet processing methods yielded similar results.

a. The soaked method. This method which increases shear force upon the PEDOT:PSS sample, was found to increase the spacing of the spacing of the PEDOT chains. However, the error for this peak width is large compared to previous methods, so this may not be a reliable value.

b. The **double wetted** method. The film was found to have increased spacing of the PEDOT chains is unaffected by the settling of the PEDOT into the latex molecules. Since the PEDOT:PSS and the latex are in aqueous solution, the PEDOT:PSS may penetrate deeper into the latex film through a diffusion mechanism. Yet the spacing of the PEDOT chain is unaffected compared to the other techniques.

HYPOTHESIS: The increased PEDOT spacing is strongly dependent on the PEDOT:PSS and latex bulk film properties.

REASONING: The results indicate that processing has negligible effect upon the PEDOT spacing. The only factor determined from the results to be affecting the PEDOT spacing is the presence of the latex itself as a substrate.

CONCLUSION: The relationship of the PEDOT chain stacking distance and the latex film opens up possibilities for further optimization of the film. The ability of latex as a bulk film to affect the microstructure supports the hypothesis that the latex chemical properties affect the nucleation of PEDOT. This could also apply to other material combinations and opens up the possibility of including other materials for manipulating the PEDOT:PSS microstructure.

6.7 Effect of annealing upon PEDOT:PSS structure:

One other interesting feature of PEDOT:PSS was the effect of annealing. Using the optical microscopy analysis, it was found that annealing the PEDOT:PSS monolayer causes the number of PEDOT cores to increase (see Figure 15):

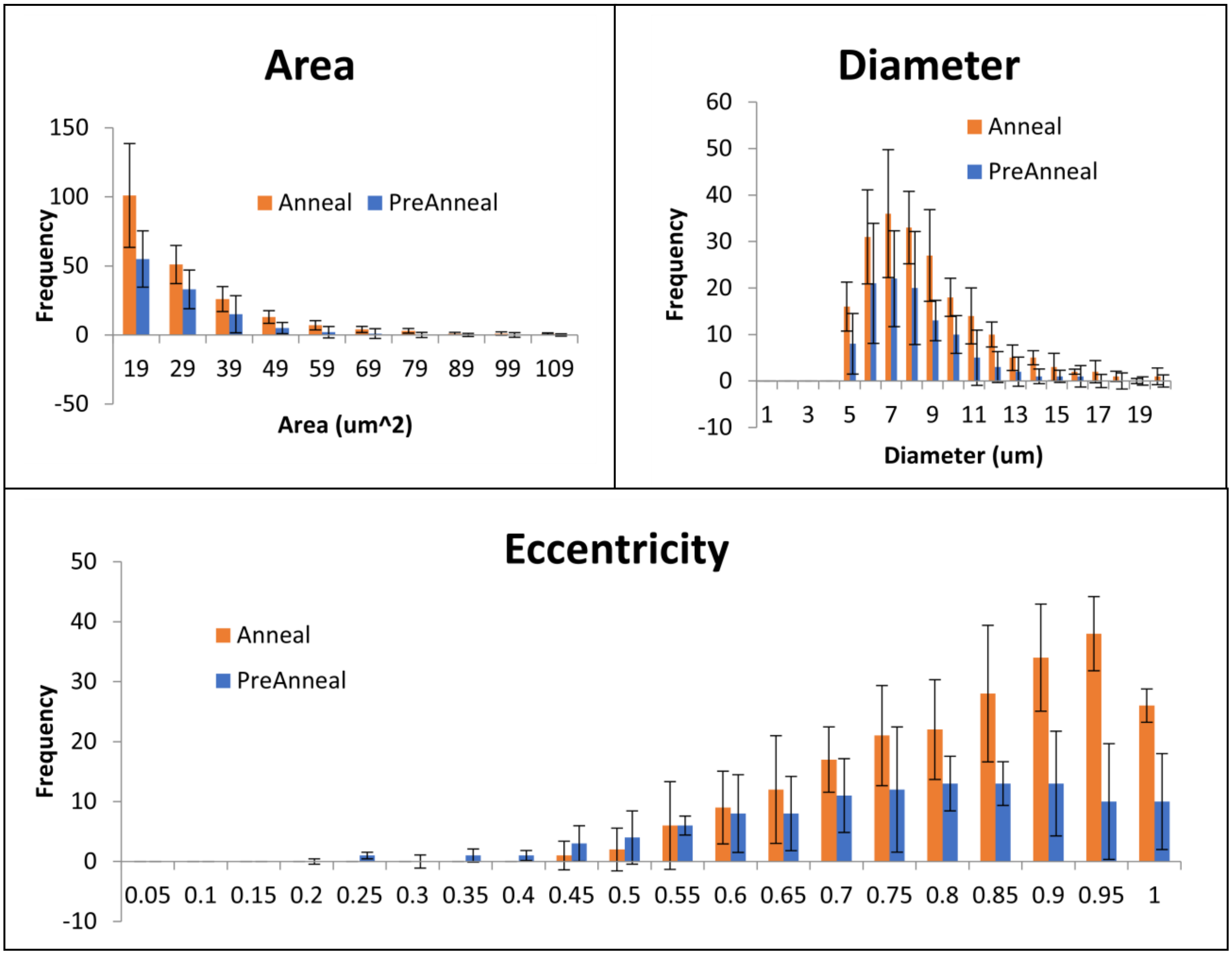

Figure 15: Distributions of PEDOT grains for PEDOT:PSS monolayer when annealed.

HYPOTHESIS: The increase in thermal energy provided more energy for the PEDOT molecules to separate and form individual sites for nucleation of the PEDOT grains.

REASONING: The growth of PEDOT grains are strongly dependent on attractions/repulsions with the PSS and water molecules. Therefore, the addition of temperature would further increase the kinetic energy of the PEDOT chains. This would provide more energy for the PEDOT chains to separate from the PSS and move within the grains as well as form extra sites.

CONCLUSION: Annealing has been demonstrated to increase the frequency of PEDOT grains within the PEDOT:PSS film. Therefore, thermal treatment of the PEDOT:PSS films is demonstrated to be a viable processing method to manipulate the microstructure of the PEDOT:PSS film. Thermal treatment can therefore be used to change the electrical properties of the PEDOT:PSS.

This is supported by the optical microscopy analysis, which demonstrates that the presence of PEDOT grains increases when annealing occurred (see Figure 15, top left). This further supports the hypothesis that the blue dots are in fact grains, as the annealing process would increase the nucleation rate of PEDOT grains as the energy provided increases.

6.7.1. Area distribution

The area distributions of the PEDOT was unaffected (see Figure 15, top right), indicating that the annealing process did not affect the growth rate of the grains.

6.7.2. Diameter distribution

However, the diameter distribution was affected (see Figure 15, top right), indicating that the annealing process did not affect the growth mechanisms of the PEDOT grains. It was found that the standard deviation of the annealed diameter distribution of the PEDOT grains decreased, becoming more akin to a thin normal distribution.

This would support the hypothesis that the PEDOT chains that form the grain disperse out when annealed. However, the error bars calculated from the data are large, which makes any definitive conclusions surrounding the distributions difficult, and conclusions based upon these observations would require further analysis.

However, when annealed, the PEDOT chains that make up the larger grains disperse out, and reduce the size of the grain itself. Therefore resulting in grains that are smaller than the distribution of the preannealed would predict. However, as demonstrated in the area analysis most of that energy is used for nucleation also contribute to larger grains.

6.7.3. Eccentricity distribution

The eccentricity distribution of the PEDOT grains indicates that the growth of the PEDOT grains is affected by the annealing (see Figure 16). The annealing results in more elliptical/rod like structures in the PEDOT.

HYPOTHESIS: Previously, the changes in PEDOT grain eccentricity were explained through the product of shear forces in the latex upon the PEDOT:PSS film. However, the distribution in Figure 15 reflects the PEDOT grains in within the PEDOT:PSS monolayer as it is annealed. Therefore, the latex interactions are not considered in this case, as this was unaffected by the annealing process. It is suggested that though the PEDOT is given energy to disperse out of the grain, if the PEDOT does not leave the grain area, then it orientates itself to a favorable position, which is in this case, a rod like structure.

REASONING: Given that the PEDOT molecule is built as a chain, the final physical structure is likely to reflect this. As the PEDOT grains gain more kinetic energy, the chains can reorganize themselves or dislodge from the main body if they are not tightly held.

CONCLUSION: The ability for annealing to change the geometric shape of the PEDOT grains presents another opportunity for the microstructure to be further optimized.

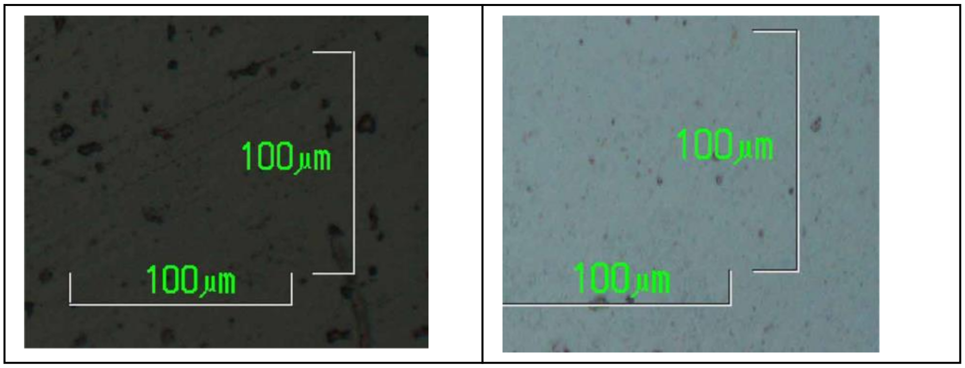

Figure 16: Optical Microscopy images comparing effect of annealing.
Pre Annealed PEDOT:PSS monolayer (Left) and Annealed PEDOT:PSS monolayer (Rght)

As shown in Figure 17, the PEDOT grains have become more rod like and possess more defined and sharp edges compared to the pre annealed. An explanation for this feature would be that the annealing is providing more energy for the PSS rich grains to orientate themselves to more favourable shapes. The annealing reduces the size of the PSS grains, and increases their frequency. The increase in energy is likely to provide more kinetic energy to the PSS molecules to move around and organize themselves, producing the sharp edges of the PSS grain. However, this is not a significant change in the grain shape.

Similarly, the XRD results did not present any developments in the PEDOT:PSS microstructure:

As shown in Figure 17 by the red box, the PEDOT peak does not shift, indicating no further effects on the spacing of the PEDOT grains.

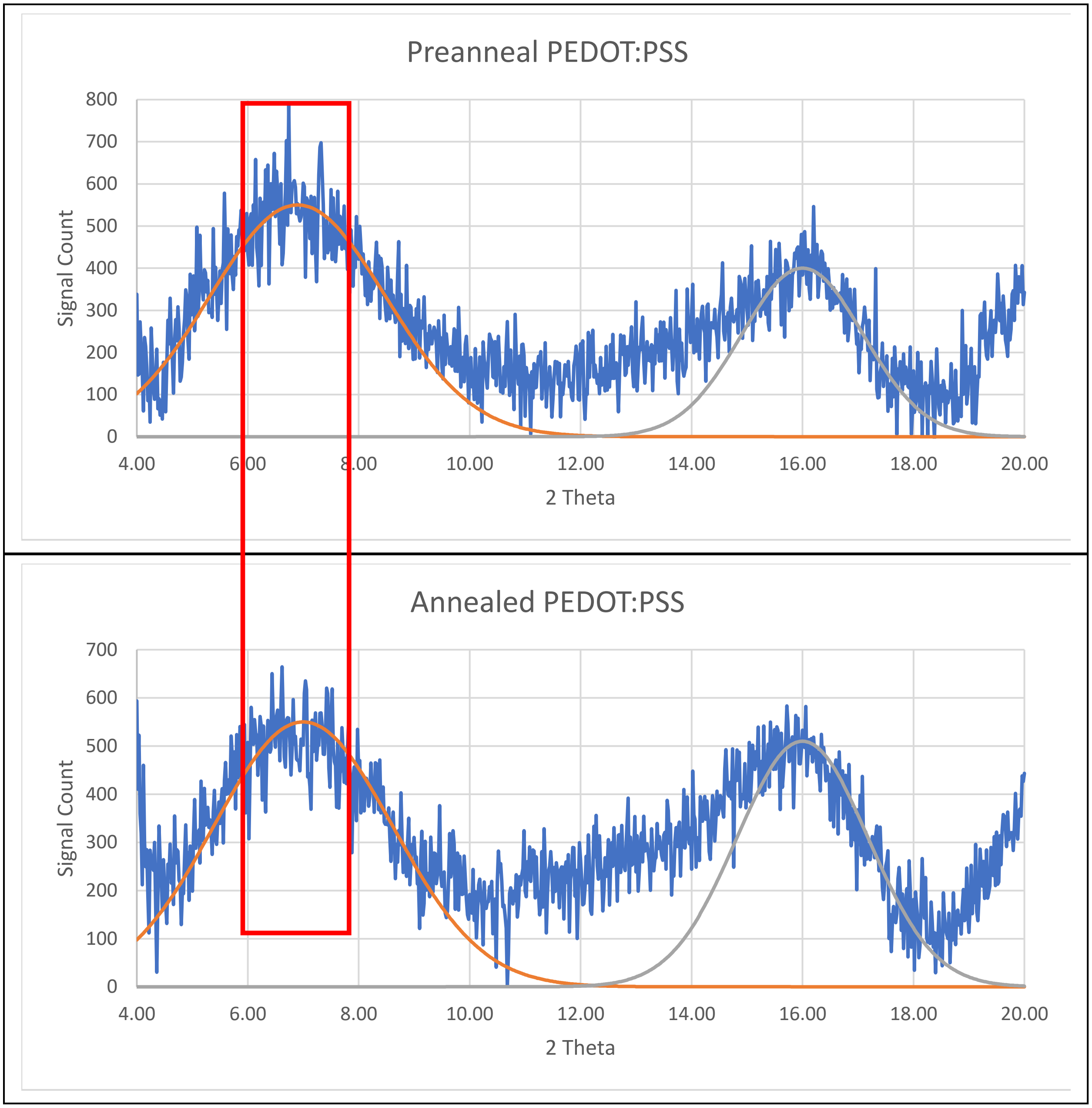

Figure 17: Effect of Annealing upon XRD results for PEDOT:PSS monolayer

7. Conclusions

The formation of a PEDOT:PSS film upon an isoprene substrate produced significant changes to the PEDOT:PSS microstructure.

- The major areas of interest within these samples was the PEDOT grains, which appeared as blue dots with optical microscopy. This seems to consist of PEDOT chains randomly orientated, surrounded by hydrophilic PSS molecules within the film. These grains are correlated to strength and conductivity, so observing the response of these grains to the processing methods and underlying film was important for manipulating the PEDOT:PSS microstructure.

- The chemical properties of the latex was the most important factor as the PEDOT:PSS film was applied. This was manifested through the reduction in PEDOT rich grains if a latex substrate was used, and the increase in distance between adjacent PEDOT chains in the grains themselves.

- Different processing conditions attempted were found to have significant overlap between each other when it came to analyzing microstructure. This could be beneficial in production, as cheaper and/or modifications in the processing technique can be implemented without affecting the microstructure.

- The main effect of annealing affected the PEDOT grain nucleation frequency. Annealing was suggested to provide more energy for the polymer chains within the film, allowing dispersion for more homogenous nucleation sites and grains to form. Annealing was also suggested to affect the internal movement of the PEDOT molecules within the PEDOT grains, producing rod-like features due to the provision of more energy into more favorable shapes.

- The formation of undulations in the PEDOT:PSS layer was an unexpected feature of the latex/PEDOT:PSS system. This was caused by the contraction of the isoprene that was adhered to the PEDOT:PSS. The PEDOT:PSS, being less flexible compared to the isoprene, bunches up and foRMS ‘waves’ in the PEDOT:PSS/latex interface.

The results have demonstrated that the PEDOT:PSS microstructure can be manipulated and controlled by varying the substrate material, regardless of processing method. The latex was found to have a direct impact on the PEDOT grains, which are a key component of microstructure PEDOT:PSS. Therefore, the electrical properties which have been correlated to particular features of the PEDOT:PSS, can also be manipulated and refined.

8. Future Investigations

Though this piece of research is a fundamental investigation for the morphological impacts of latex upon PEDOT:PSS films, the electrodes will be used to improve the electrical properties for real life applications for solar cells and OLEDS. Therefore further investigation is required to correlate the microstructure to electrical properties such as conductivity and efficiency.

The lack of established knowledge and research around the uncommon compounds used was a limitation of this research, and further understanding of the micro-structure of PEDOT:PSS would provide greater certainty for the theories given. Gaining a greater in-depth understanding of the electrical conductivity of the PEDOT:PSS using a 4-point probe would be beneficial in finding any connection between the number of localized PEDOT areas to the conductivity.

Another investigation could include measuring the geometric placement of the PEDOT grains. Optical microscopy only gave a two-dimensional analysis, and while AFM does provided some further in-depth analysis, it did not provide an image of the structure within the film. If the isoprene were to reduce nucleation, it would be expected that the PEDOT grains would decrease in density nearer to the isoprene film. Therefore, in order to validate this theory, determining the three-dimensional distribution of the PEDOT grains would demonstrate if the proximity of the isoprene is a factor.

Only a few processing conditions (soaking and double wetting) were investigated, which produced some changes in the final morphology regardless of substrate. Varying the duration of the methods, such as soaking the latex substrate for shorter/longer times, would affect the growth of the PEDOT grains. Changing the processing conditions of the wirebar coater could also be correlated with the physical characteristics of the film. Other processing methods that could be attempted include mixing the substrate and the PEDOT:PSS to further increase the contact surface area of the PEDOT:PSS/isoprene .

Though the TGA analysis produces support for the crosslinking nature of the isoprene, it was not determined at which point the crosslinking occurs. To investigate the formation of these crosslinks, the latex should be layered on the glass substrate then analyzed in the XRD whilst in liquid form. The results should then be compared to the dry isoprene film XRD results. If the crosslinks form whilst the isoprene is drying, then the amorphous halo peak will be shifted to the right, as the spacing between the isoprene molecules would decrease to the results collected in this investigation.

In order to investigate the undulations in the PEDOT:PSS film, it was theorized that the adhesion between the PEDOT:PSS and the isoprene film contributes to the shape of the PEDOT grain through shear forces. Conducting further tests to investigate the adhesive forces between the latex and PEDOT:PSS film for different processing methods could be carried out to see if there is a correlation between the eccentricity of the particles and the adhesion force.

Stress tests could also be carried out to further investigate the stress characteristics of the PEDOT:PSS films. The PEDOT grains could potentially act as precipitates to prevent further deformation of the PEDOT:PSS film.

In order to carry out further analysis, other equipment may be required. Dynamic light scattering would be a useful technique to further analyze the particle distribution in solution. Microm Ramin would be a useful tool for analyzing the chemical structure of the dark dots present in the optical microscopy.

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- Steve Strover, University of Auckland Lab Technician for Optical Microscopy equipment

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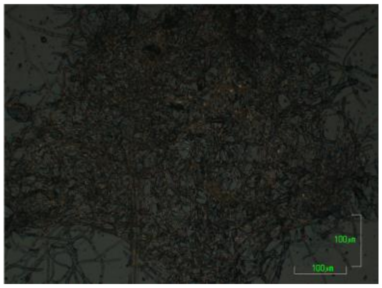
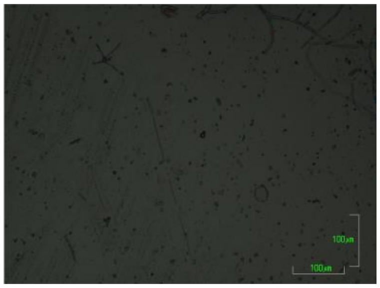
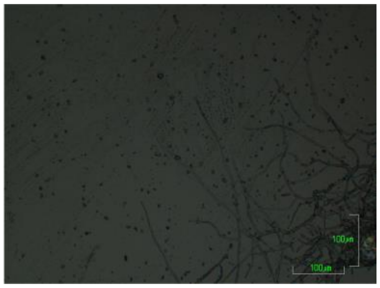
9. Appendixes:

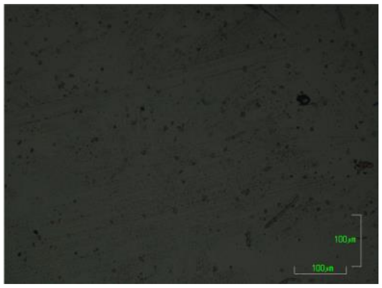
Optical Microscopy:

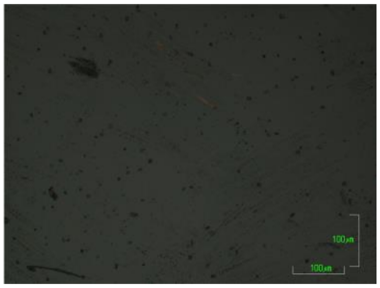
Pre-annealed PEDOT:PSS

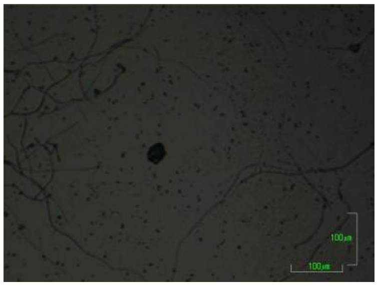


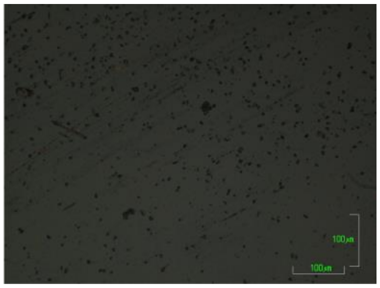


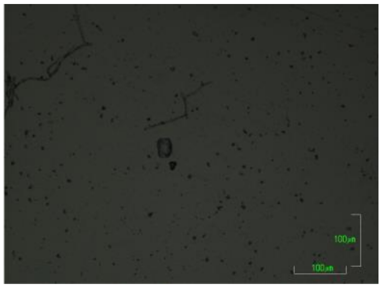




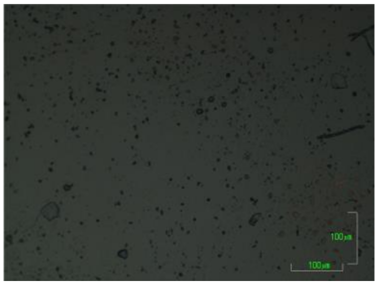


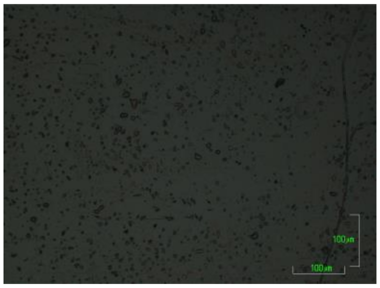


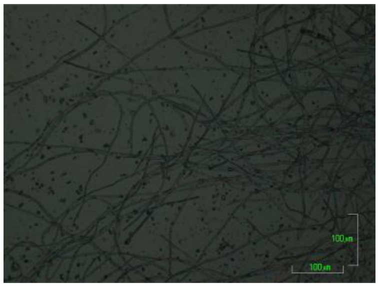


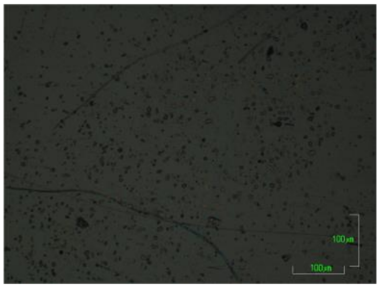


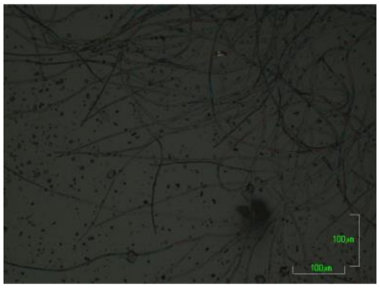
Pre Annealed Normal

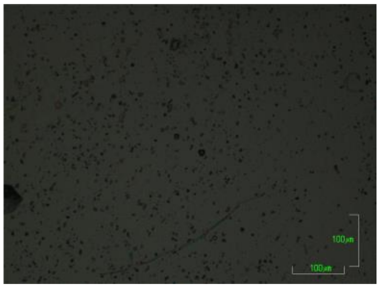


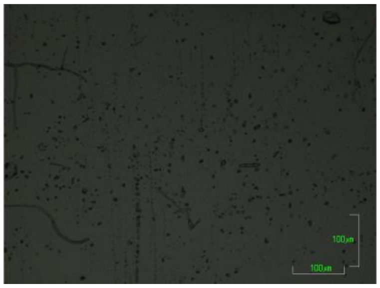


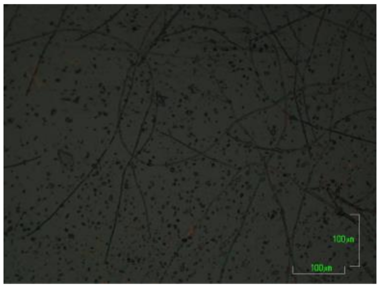


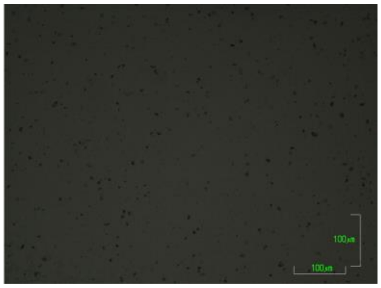


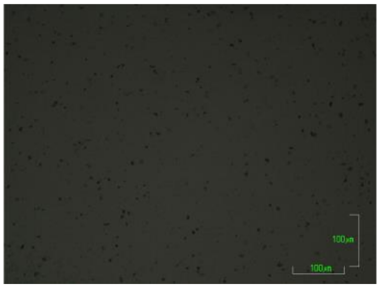


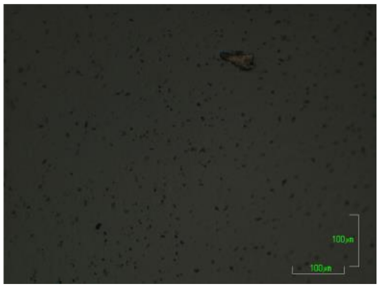


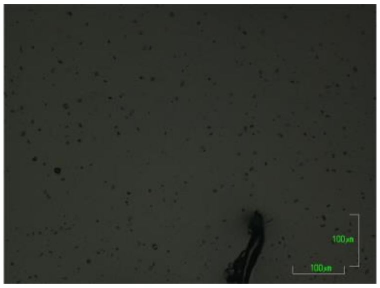


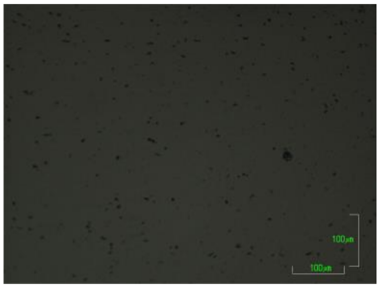


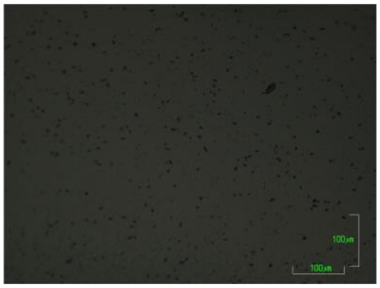
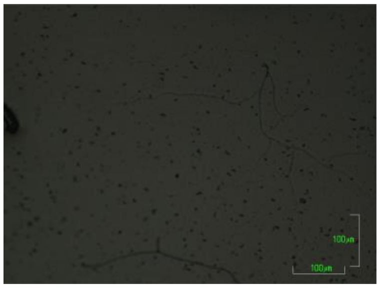
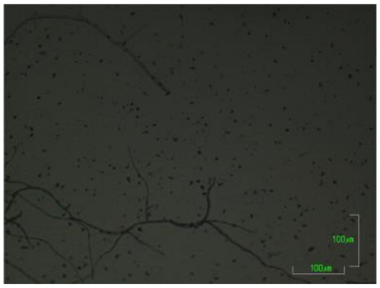
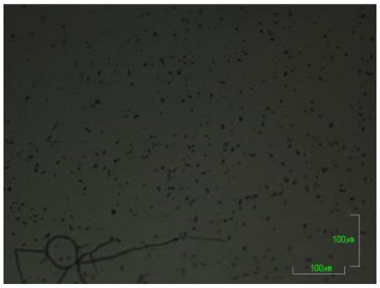
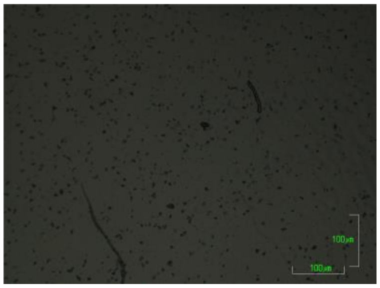










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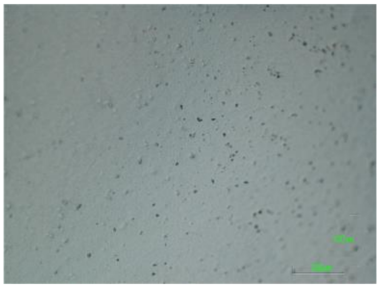	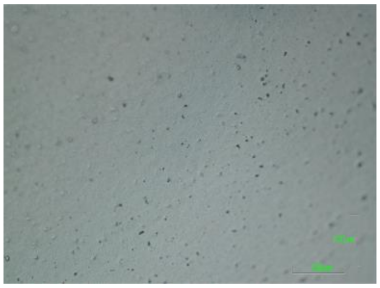	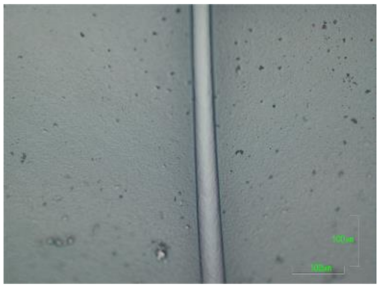
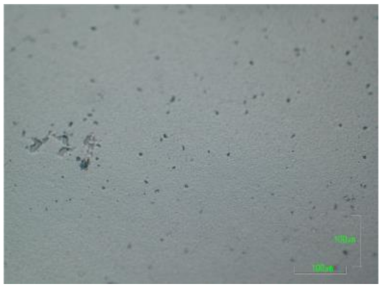	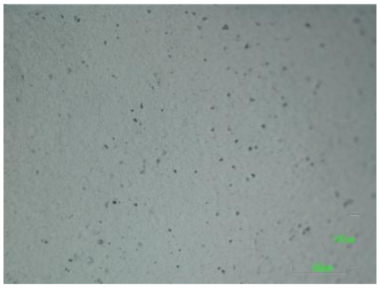	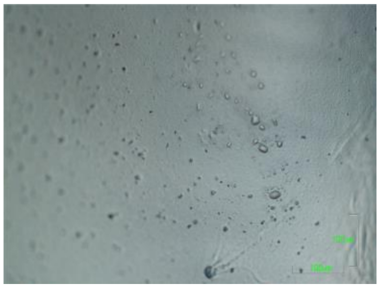

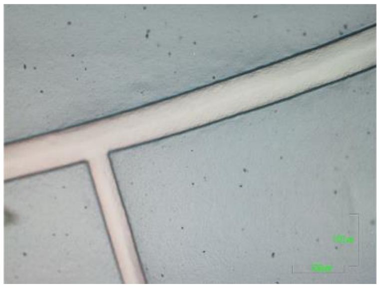	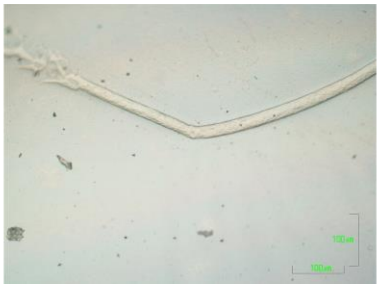	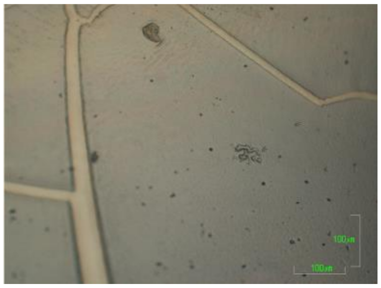

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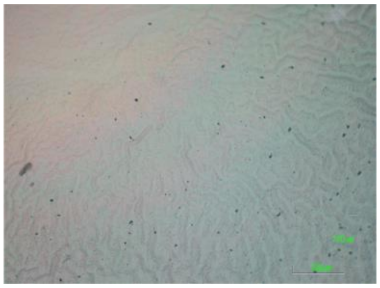
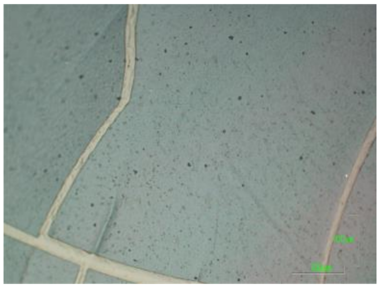
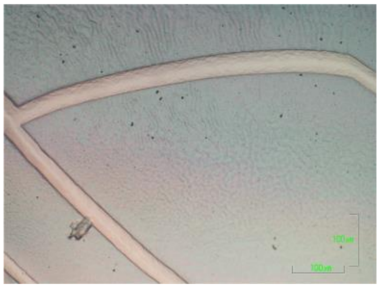
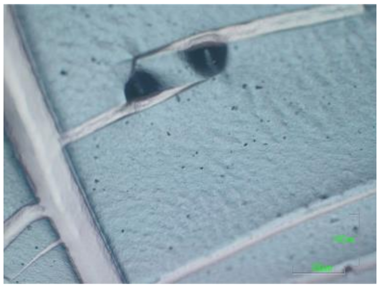
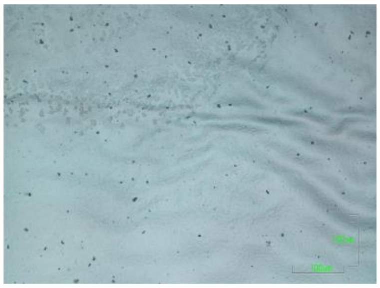
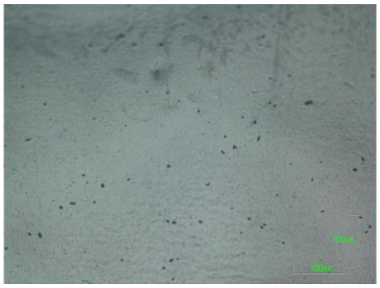
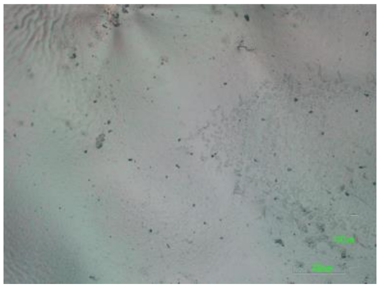
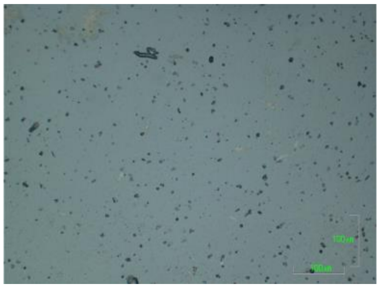
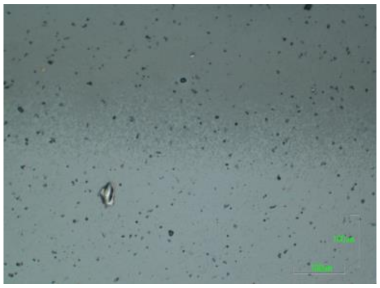
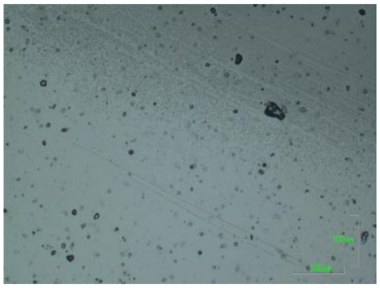
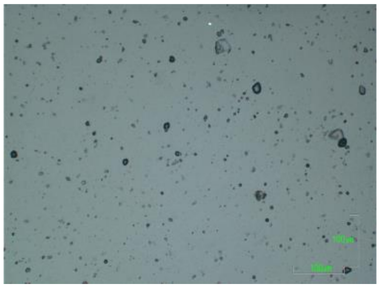
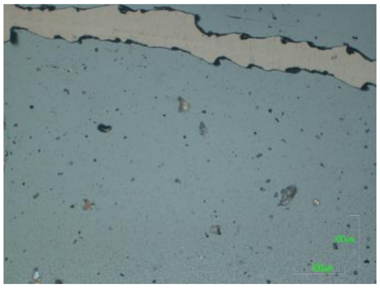
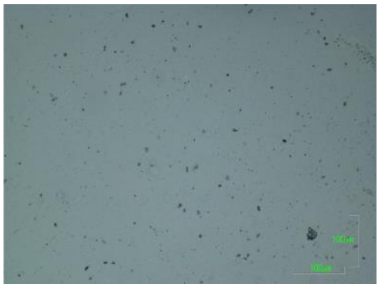
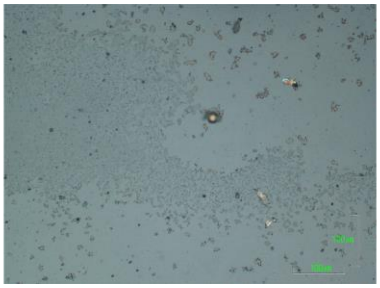
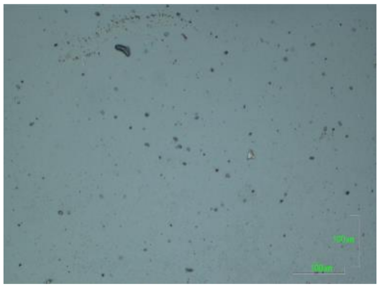
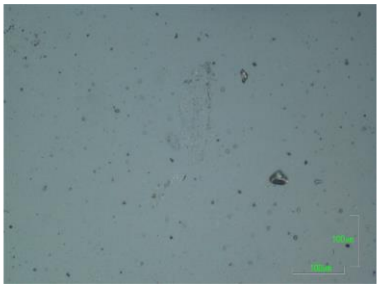
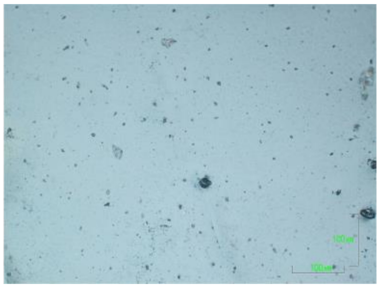
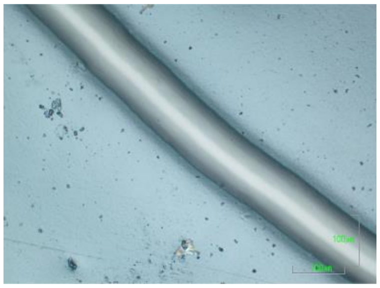
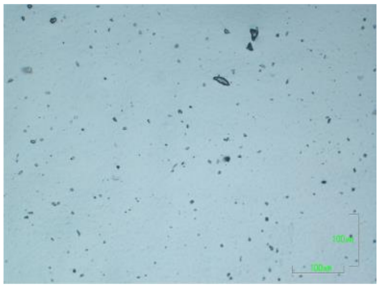
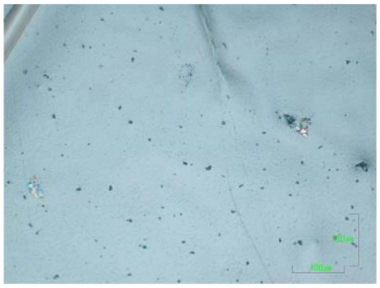
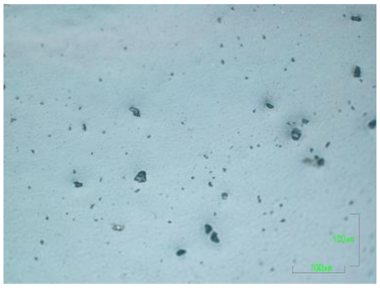
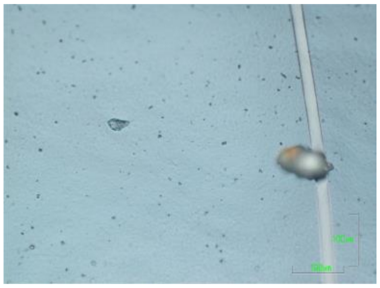
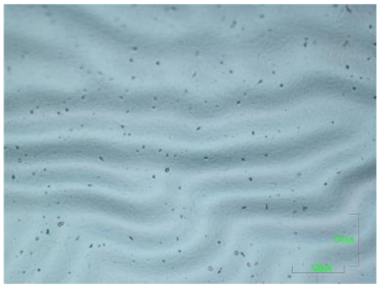
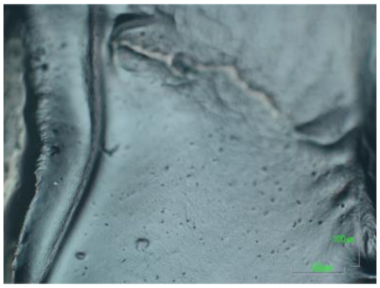
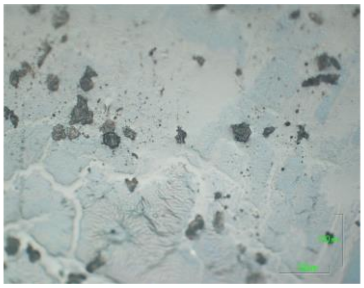
		
		
		

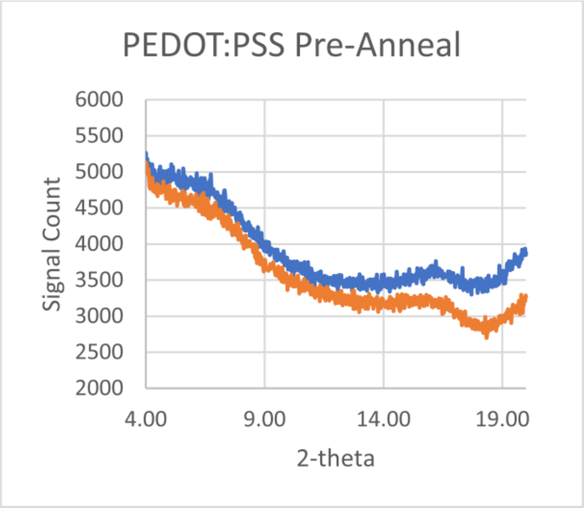
Annealed PEDOT:PSS monolayer

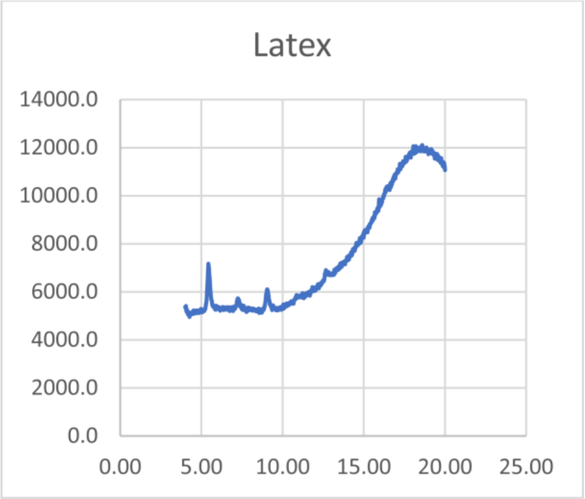
		
		
		

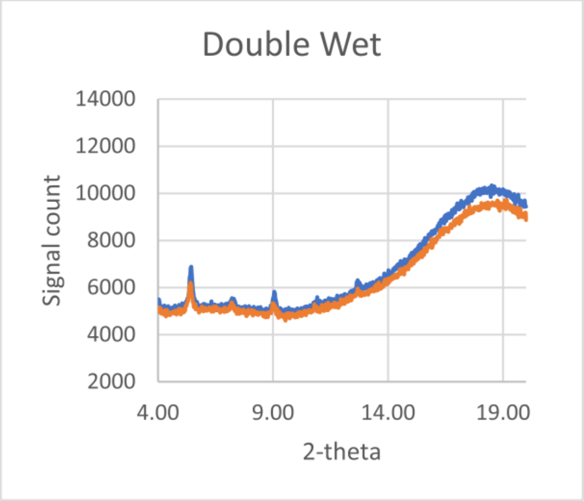
Annealed Soaked

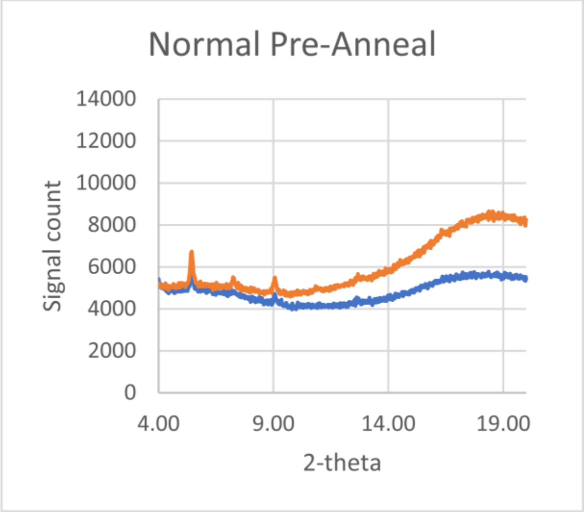
		
		
		

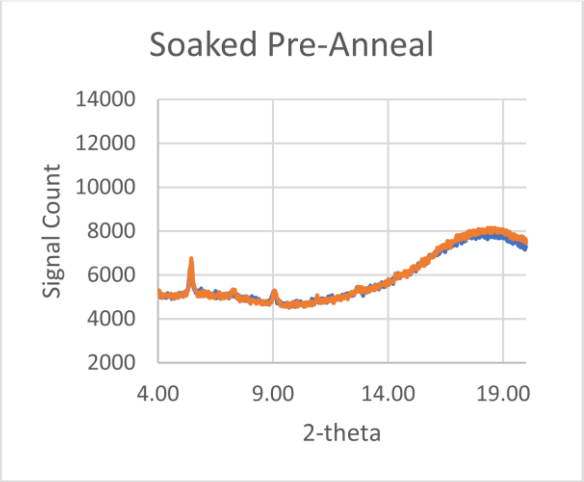
XRD Results – Pre annealed



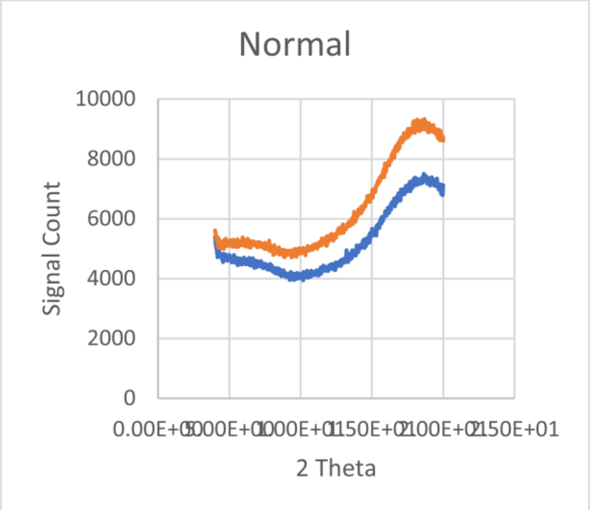


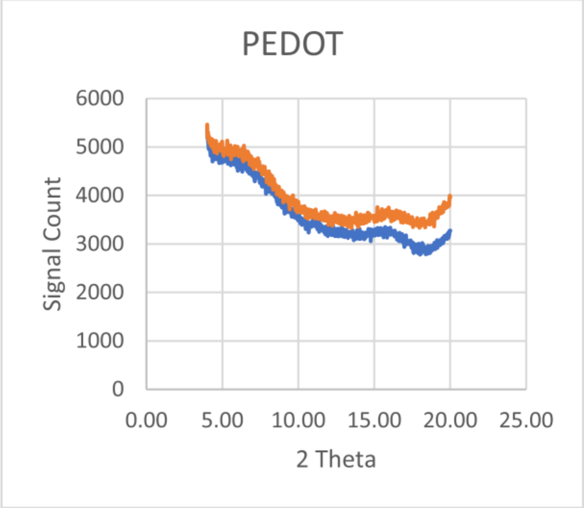


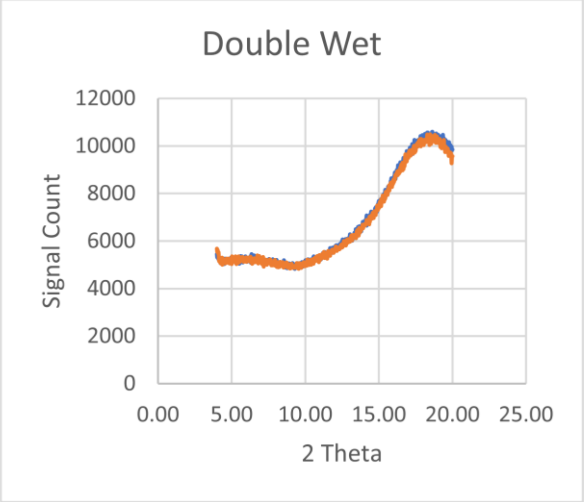


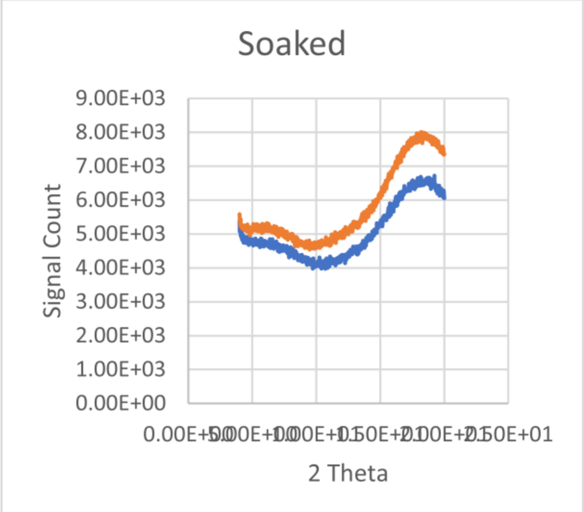


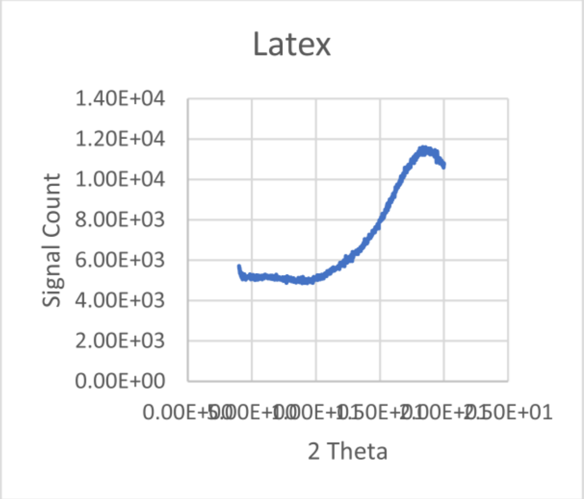
XRD results - Annealed





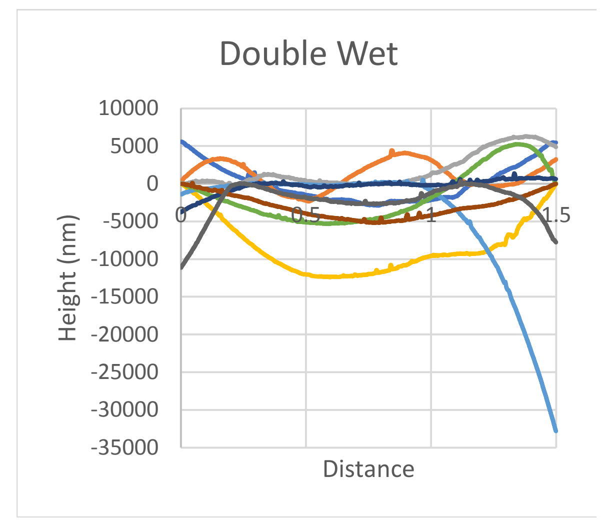


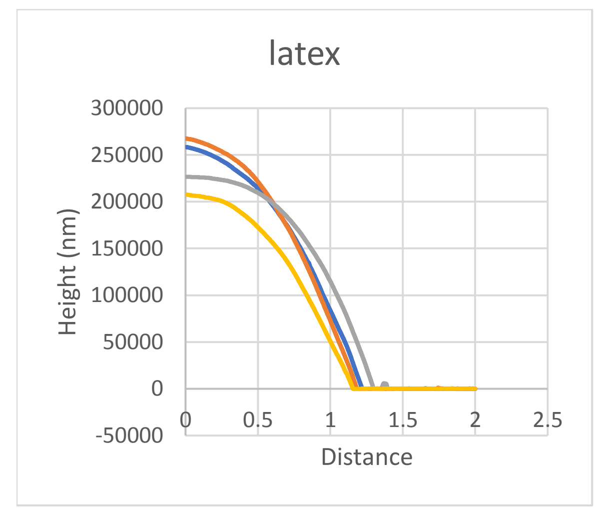


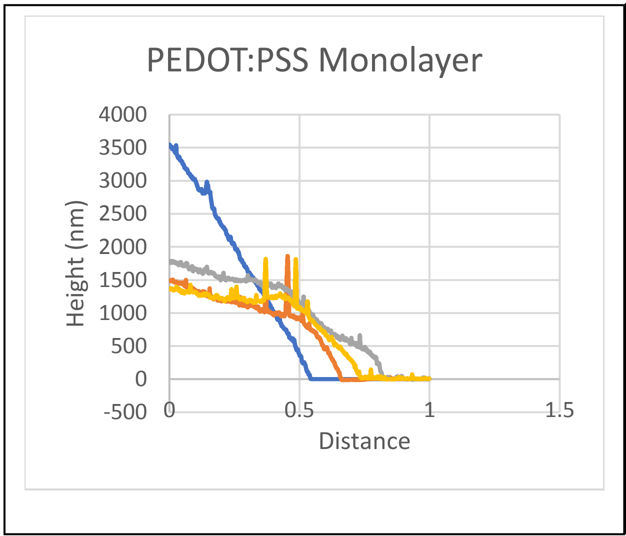


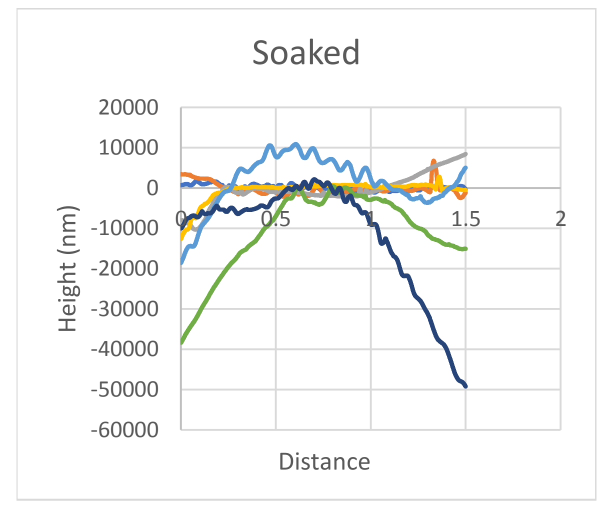
Profilometry data

Double Wet









Safety and Laboratory use

HAZOP report for Electrodes

at the Grafton Campus

Team Members:

Alisyn Nedoma (Supervisor)

Jen Sun Hong (Chemical and Materials student)

Methodology:

- Use of Wirebar coater. Clean glass slides are taken directly from the box
- Spread out the latex onto a glass slide, this solution will take 12 hours to dry out. The maximum area surface area of the latex should be 2 x 1 cm.
- The latex and the PEDOT:PSS are bar-coated onto the glass slide.

Study Nodes:

The key points at which hazards could occur are the:

- Cleaning of the equipment. Other materials could contaminate the sample and produce undesirable products.
- Application of latex and PEDOT:PSS onto substrate. Cross contamination is an issue, as well as if solution is ingested.
- The glass slides required further cutting, so a glass cutter was used.

Intention:

The purpose of this experiment is to produce a film in which the microstructure of an electrode can be modelled.

- The cleaning of the equipment should remove all organic contaminants from the glass and leave a dust-free inner surface with no other stains
- The application of the latex solution should result in an even distribution of latex around the whole surface area of the glass slide
- The application of the PEDOT:PSS solution should result in an even distribution of latex around the whole surface area of the glass slide

Deviations:

- Increased exposure to PEDOT:PSS and isoprene by skin/eye contact, inhalation or ingestion
- Exposure to warm surfaces
- Increased possibility of harm to user or equipment
- Glass shards and knife could harm user

Causes

- Failure to follow safety procedure in handling products and equipment
- Failure to use personal protective equipment
- Faults in the equipment that were not observed, like hairline cracks in a glass pipette that lead to organic solvent squirting out over the work surface
- A vessel containing solvent spills outside of the fume cupboard during solution weighing

- A squirt bottle of solvent ‘mis-fires’ during routine glassware cleaning and solvent contacts the user
- A full bottle of solvent may be dropped or spilled during transfer to smaller vessels
- Slip of knife or cutting edge when slicing glass slides

Consequences:

- Skin or eye contact with solvents may cause irritation; immediate washing/rinsing is required
- Inhalation may cause fatigue, headaches, or nausea
- Small-scale chemical spills may damage equipment, e.g. solvent leaks into the pan of the mass balance
- Injuries in the form of cuts on skin
- Contamination may yield an impure final product; this could lead to the publication of spurious results

Actions arising from the HAZOP:

- Wear covered clothing and safety glasses at all times when using equipment
- Carefully observe methodology at all points
- Use fume hood or similar apparatus when dealing with solvent vapors
- Point knife away from user when cutting.
- Ensure that hand is always kept 1cm away from knife edge
- Use small volumes of solvent to minimize the effects of a spill
- Transfer solvents by pipetting as much as possible to avoid the increased risks associated with pouring
- Perform all film processing, particularly the innovative techniques, in a fume cupboard
- Discuss modifications of the basic procedure with supervisor and update Hazop if required

CHEMMAT 751 A/B - PROJECT COMPLETION SIGN OFF – LABORATORY USE

(The completion of this section is required before your final mark is processed. Scan and attach the completed form to your Appendix section of your final report)

Name of Student: Jen Sin Hong

Research Project Title: Latex effect on PEDOT:PSS microstructure

Supervisor's name: Alisyn Nedoma.

List the labs used for this project: G23, 235A

(If you did not use any of the department labs, simply write 'NA' and obtain your supervisor's signature)

Lab Room(s)	Name of PIC	Area Left Tidy? (Y/N/NA)	Equipment dismantled/returned? (Y/N/NA)	Chemicals handover/disposed safely? (Y/N/NA)	PIC signature
235 A	Peter M	y	y	y In walkin fridge	
G23	Ray	yes	N/A	N/A	

Supervisor's signature: Alisyn Nedoma

(Note to Supervisors: Please ensure the student has correctly included ALL the lab facilities used)