Novel Crease and Wash-Resistant Electrically Conductive Inks for SMART Textile Applications

Sam Jordan Hill

Supervised by Prof. Long Lin

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Abstract

Due to the worldwide aging population, methods have been sought to improve the efficiency of health care services. It is envisaged that remote monitoring of patients would form part of the solution. Monitoring of patients would be *via* the use of functionalised undergarments with the required technology embedded within. There have been significant advances in flexible electronics but metal wires are still required for electrical interconnects which compromise the comfort that the garment offers when in contact with skin. Electrically conductive polymers are considered as viable replacements for these metal wires. Electrically conductive polymers can have high electrical conductivities but they can be brittle due to their inherent stiffness.

From studies reported in this thesis, various routes to the synthesis of PEDOT, which would lend itself to function in crease and wash resistant conductive inks, were investigated. The task was highly challenging due to the confliction between high conductivity and structural rigidity of typical conductive molecules. A series of monomers, described within, were designed, synthesised and characterised. These monomers provide a foundation for further syntheses to the subsequent novel electrically conductive polymers. In order to assess potential challenges in the formulation of crease and wash resistant conductive inks based on conductive polymers, systems containing PEDOT:PSS were designed, prepared and characterised. It was found that the use of just PEDOT:PSS as the coating for cotton fabric provided an electrically conductive coating which was susceptible to degradation during creasing and washing. To overcome this challenge, a composite of a synthesised latex and PEDOT:PSS was devised which provided an electrically conductive coated cotton fabric with an electrically insulating surface. The electrical resistance could still be measured by incorporating electrodes prior to the application of the final latex layer. Encouragingly, this composite provided a formulation having very low electrical resistances pre- and post-wash.

Table of Contents

Intellectual Property and Publication Statement ii

Acknowledgements iii

Abstract iv

Table of Contents v

List of Figures ix

List of Tables xviii

List of Schemes xix

Abbreviations xx

1 Chapter One 1

- 1.1 Preamble 2
- 1.2 Overview 3
- 1.3 Electrically conductive polymers 4
- 1.4 Mechanism of conduction 5
  - 1.4.1 Factors affecting conductivity 6
- 1.5 Processibility and stability 7
- 1.6 Doping 9
  - 1.6.1 Introduction 9
  - 1.6.2 Solitons, polarons and bipolarons 9
  - 1.6.3 Methods of doping 15
  - 1.6.4 Doping-induced processibility 17
- 1.7 Conductive textiles 18
  - 1.7.1 SMART textiles 19
  - 1.7.2 Existing methods of achieving textile conductivity 20
  - 1.7.3 The use of conductive polymers for textile conductivity 21
  - 1.7.4 Required properties of conductive polymers 22
  - 1.7.5 Properties provided by existing technologies 22
  - 1.7.6 *In-situ* polymerisation on textiles 23

1.7.7 Post-polymerisation application on textiles 24
1.7.8 Limitations of conductive polymers for textiles 25
1.8 Poly(3,4-ethylenedioxythiophene) – PEDOT........ 26
1.8.1 History of PEDOT use 26
1.8.2 Derivatives of the monomer, EDOT 27
1.9 Research Aims........ 28
1.10 References 30
2 Chapter Two 35
2.1 Aim of experiments........ 36
2.2 Materials 36
2.3 Methods of characterisation........ 36
2.3.1 NMR spectroscopy 36
2.3.2 Microanalysis 36
2.4 Synthetic procedures. Results and discussion 36
2.4.1 Procedure 1........ 36
2.4.2 Procedure 2........ 38
2.4.3 Procedure 3........ 41
2.4.4 Procedure 4........ 43
2.4.5 Procedure 5........ 46
2.5 Discussion........ 48
2.6 Conclusions 51
2.7 Experimental........ 52
2.7.1 Dimethyl thiodiglycolate (2) [1] 52
2.7.2 Synthesis of disodium dimethyl-3,4-dioxythiophene-2,5-dicarboxylate (3) [2] 53
2.7.3 Synthesis of dimethyl-3,4-dihydroxythiophene-2,5-dicarboxylate [2] 53
2.7.4 Synthesis of dimethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (9) [4] 53

2.7.5 Synthesis of diethylthiodiglycolate (12) [7] 54

2.7.6 Synthesis of diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (13) [5] 54

2.7.7 Synthesis of diethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (14) [7] 55

2.7.8 Attempted synthesis of diethyl 2,4-dimetyl-3-oxo-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine-6,8-dicarboxylate 55

2.7.9 Synthesis of diethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylic acid (10) [4] 55

2.7.10 Synthesis of 3,4-ethylenedioxythiophene (7) [4] 56

2.7.11 Synthesis of diethyl-3,4-dimethoxythiophene-2,5-dicarboxylate (15) [2] 56

2.7.12 Synthesis of diethyl-3,4-dimethoxythiophene-2,5-dicarboxylic acid (5) [2] .. 56

2.7.13 Synthesis of 3,4-dimethoxythiophene (6) [3] 57

2.7.14 Synthesis of 2,3-dimethyl-1,4-butandiol [9] 57

2.7.15 Attempted synthesis of 3-methyl-2,3,4,5-tetrahydrothieno[3,4-*b*][1,4]dioxocine 57

2.8 References 58

3 Chapter Three 59

3.1 Experimental design 60

3.2 Sample preparation 60

3.2.1 Application of PEDOT:PSS to a cotton fabric substrate 60

3.2.2 Creasing samples 65

3.2.3 Wash testing 66

3.3 Results and discussion 66

3.3.1 Thermogravimetric analysis (TGA) 66

3.3.2 Differential Scanning Calorimetry (DSC) 67

3.3.3 Electrical resistance of coated cotton fabric 68

3.3.4 Topology of non-creased PEDOT:PSS coated cotton 72

3.3.5 Electrical resistance of creased coated cotton fabrics 83

3.3.6 Electrical resistance of the washed, coated cotton fabrics 87

- 3.3.7 Topology of washed coated cotton fabric 92
- 3.4 Summary 99
- 3.5 Conclusion 100
- 3.6 References 101
- 4 Chapter Four 102
  - 4.1 Experimental design 103
  - 4.2 Sample preparation 103
    - 4.2.1 Synthesis and application of the aqueous latex dispersion to the carton board substrate 103
    - 4.2.2 Application of PEDOT:PSS layers to the latex coated carton board 103
    - 4.2.3 Application of copper wire electrodes to the PEDOT:PSS and latex coated carton board 104
    - 4.2.4 Application of the latex top layer to the PEDOT:PSS-latex-carton board composite 104
  - 4.3 Results and discussion 104
    - 4.3.1 Topology of the initial latex layer on the carton board 104
    - 4.3.2 Electrical resistance of PEDOT:PSS layers 105
    - 4.3.3 Topology of PEDOT:PSS layers applied to the latex coated carton board 112
    - 4.3.4 Electrical resistance measurements of the composite with copper wire electrodes 118
    - 4.3.5 Electrical resistance measurements of the composite with electrodes and the latex top layer 123
    - 4.3.6 Discussion 128
  - 4.4 Conclusions 133
- 5 Chapter Five 135
  - 5.1 Experimental design 136
  - 5.2 Sample preparation 136
    - 5.2.1 Synthesis and application of latex to a woven cotton fabric substrate 136
    - 5.2.2 Application of PEDOT:PSS layers 136

5.2.3 Application of electrically conductive epoxy electrodes 136
5.2.4 Application of latex top layer 137
5.3 Results and discussion 137
5.3.1 Application of latex to the woven cotton fabric substrate 137
5.3.2 Application of PEDOT:PSS Layer 138
5.3.3 Application of electrically conductive epoxy electrodes 149
5.3.4 Application of the latex top layer to the treated cotton fabric 152
5.3.5 Wash Testing 159
5.4 Discussion 173
5.5 Conclusion 176
5.6 References 179
6 Chapter Six 180
6.1 Summary 181
6.2 Future work 183

List of Figures

Chapter One

Figure 1.1 Molecular structures of poly(acetylene) (1), poly(aniline) (2) and poly(thiophene) (3) 5
Figure 1.2 Molecular structures of cis-poly(acetylene) (4) and trans-poly(acetylene) (5) 5
Figure 1.3 Three forms of poly(aniline); Leucoemeraldine (L), Emeraldine Base (EB) and Pernigraniline (P) 6
Figure 1.4 Acetone soluble polymer precursor routes for the production of poly(phenylene vinylene) [19] 8
Figure 1.5 poly(3-methoxy-6-(2-ethylhexyloxy)-*p*-phenylenevinylene) 8
Figure 1.6 Oxidative p-type doping of poly(acetylene), A is the dopant 10
Figure 1.7 Reductive n-type doping of poly(acetylene) 11
Figure 1.8 Oxidative p-type doping of poly(thiophene) [9] 11
Figure 1.9 Band structures of polymers at differing oxidation levels. Neutral polymer lowest oxidation level, Bipolaron bands highest oxidation level 12

Figure 1.10 Soliton formations in poly(acetylene) 13
Figure 1.11 Redox and acid-base doping of poly(aniline) 14
Figure 1.12 Poly(3-decanylpyrrole) 24
Figure 1.13 Non-homogenous coverage of poly(3-decanylpyrrole) on wool applied by spray deposition [69] 25
Figure 1.14 Poly(3,4-ethylenedioxythiophene) (PEDOT) 26
Figure 1.15 Examples of EDOT derivatives 27
Figure 1.16 “Ethylenedioxy bridge” of EDOT 28

Chapter Two

Figure 2.1 NMR spectrum of synthesised EDOT (7) 44
Figure 2.2 Derivatives of diethyl-3,4-ethylenedioxythiophene dicarboxylate attempted *via* use of dibromo compounds 45

Chapter Three

Figure 3.1 Single layer of PEDOT:PSS on cotton 61
Figure 3.2 Residue remaining after single layer application 61
Figure 3.3 Layer 1 before drying. Top row left to right, samples 1-5. Middle row left to right, samples 6-10 and bottom row left to right, samples 11-15 62
Figure 3.4 Dried second layer applied to samples 2-5, 7-10 and 12-15 63
Figure 3.5 Slight residue remaining after the application of second layer 63
Figure 3.6 Third layer applied to samples 3-5, 8-10 and 13-15 64
Figure 3.7 Fourth layer applied to samples 4, 5, 9, 10, 14 and 15 64
Figure 3.8 Layer five applied to samples 5, 10 and 15 65
Figure 3.9 Image of all 15 samples with the creases set 66
Figure 3.10 TGA of PEDOT:PSS showing degradation over increasing temperature 67
Figure 3.11 DSC of PEDOT:PSS showing heat flow with respect to temperature 68
Figure 3.12 The top plot shows that as the trend that as the total mass of polymer applied to the cotton fabric the resistance decreases while the bottom plot shows the average masses of each layer of PEDOT:PSS applied and their corresponding average resistance, layers 1 to 5 are the points left to right 71
Figure 3.13 The relationship that after the application of the first layer, the electrical resistance of the fabrics decreases at a constant rate with increasing applications of PEDOT:PSS 72
Figure 3.14 3D microscope image of the untreated cotton substrate at 500x magnification 72

Figure 3.15 3D microscope image following the single application of PEDOT:PSS to the cotton substrate at 500x magnification ... 73

Figure 3.16 3D microscope image of a cross section following single application of PEDOT:PSS to the cotton substrate at 300x magnification ... 74

Figure 3.17 3D microscope image of a fabric sample following the second application of PEDOT:PSS to the cotton substrate at 500x magnification ... 75

Figure 3.18 3D microscope image of a cross section of a fabric sample following the second application of PEDOT:PSS at 500x magnification ... 75

Figure 3.19 3D microscope images of a precipitated region of PEDOT:PSS on the surface of the cotton fabric substrate. Upper image at 250x and the lower image at 1000x magnification ... 76

Figure 3.20 3D microscope image following the third application of PEDOT:PSS to the cotton fabric substrate and the build-up of polymer at the warp and weft junctions ... 77

Figure 3.21 3D microscope image of a cross section following the third application of PEDOT:PSS to a cotton fabric sample ... 78

Figure 3.22 3D microscope image of a speck of polymer present on the surface of the cotton fabric following the application of the third layer of PEDOT:PSS at 250x magnification ... 78

Figure 3.23 3D microscope image of the interface between three applications of PEDOT:PSS coated cotton fabric, left, and untreated cotton fabric, right, at 250x magnification ... 79

Figure 3.24 3D microscope image of a cotton fabric following four applications of PEDOT:PSS at 500x magnification ... 80

Figure 3.25 3D microscope image of the cross section of a cotton fabric following four applications of PEDOT:PSS at 300x magnification ... 80

Figure 3.26 3D microscope image of a cotton fabric following five applications of PEDOT:PSS at 500x magnification ... 81

Figure 3.27 3D microscope image of a cotton fabric following five applications of PEDOT:PSS at 500x magnification. A speck on the surface looks glassy, sitting above the cotton weave ... 82

Figure 3.28 3D microscope image of a cross section of a cotton fabric following five applications of PEDOT:PSS at 500x magnification ... 82

Figure 3.29 Directions electrical resistance was measured of the creased coated cotton fabric samples ... 83

Figure 3.30 Resistance measurements of the creased coated cotton fabrics. The top plot compares all values while the bottom plot omits values from samples 1, 6 and 11 to visualise the differences at the lower resistance values 85

Figure 3.31 Average resistance measurements with respect to applied layers of PEDOT:PSS after creasing the sample. The top plot compares all values while the bottom plot omits layer 1 to compare the lower resistance values 86

Figure 3.32 A comparison of the resistances of the coated cotton fabrics initially and post creasing, the top plot shows average values for each layer while the bottom plot omits layer 1 to display the differences at lower resistance values 88

Figure 3.33 Resistance measurements of washed coated cotton samples. The top plot displays all data while the bottom plot omits samples 1, 6 and 11 to compare the lower resistance values 90

Figure 3.34 Average resistance measurements of washed coated cotton fabrics with regard to the number of layers of PEDOT:PSS applied, the top plot displays all values while the bottom plot omits layer 1 to observe the lower resistance values 91

Figure 3.35 Comparison of electrical resistance of coated cotton initially, post crease and post wash, the top plot displays all data while the bottom plot omits layer 1 to compare the lower resistance values 93

Figure 3.36 3D microscope image of a washed control cotton fabric sample, at 250x magnification 94

Figure 3.37 3D microscope image of a washed fabric sample with a single layer of PEDOT:PSS applied at 250x magnification 94

Figure 3.38 3D microscope image of a washed cotton sample with two layers of PEDOT:PSS applied at 250x magnification.. 95

Figure 3.39 3D microscope image of a washed cotton sample treated with three layers of PEDOT:PSS applied, at 250x magnification 96

Figure 3.40 3D microscope image of a washed cotton sample treated with three layers of PEDOT:PSS but with precipitate on the surface, at 250x magnification............................... 96

Figure 3.41 3D microscope image of a washed sample treated with four layers of PEDOT:PSS, at 250x magnification 97

Figure 3.42 3D microscope image of precipitation formation on a thread at 1000x magnification 97

Figure 3.43 3D microscope image of a washed cotton fabric sample treated with five layers of PEDOT:PSS, at 250x magnification........98

Chapter Four

Figure 4.1 A 3D microscope image of the latex base layer on the carton board substrate at 1000x magnification........105

Figure 4.2 Resistance measurements recorded with a two point probe of the PEDOT:PSS coated and latex treated carton board substrate. The top plot shows all data while the bottom plot omits samples with one layer of PEDOT:PSS for clarity........107

Figure 4.3 Average resistance measurements with respect to number of layers of PEDOT:PSS applied to the latex treated card substrate. The top plot shows all data while the bottom plot omits layer 1 for clarity........109

Figure 4.4 Resistance measurements recorded of the samples after they had been dried in the oven. The top plot shows only dried resistance while the bottom plot displays the comparison to the ambient resistance........110

Figure 4.5 Average resistance measurements recorded of the samples after they had been dried in the oven. The top plot shows only post dried resistance while the bottom plot displays the comparison to the ambient resistances. Layer 1 of the ambient measurements was omitted for better comparison of the later samples........111

Figure 4.6 The increased mass of the sample attributed to moisture with respect to the number of layers of PEDOT:PSS applied........112

Figure 4.7 3D microscope image after one layer of PEDOT:PSS has been applied to the latex coated carton board substrate at 250x magnification........113

Figure 4.8 3D microscope image of a sample with two layers of PEDOT:PSS applied to the latex treated carton board substrate displaying the lines from application with a K-bar at 250x magnification........114

Figure 4.9 3D microscope image of a sample with three layers of PEDOT:PSS applied to the latex treated carton board substrate at 250x magnification. Lines due to the K-bar are present once more........115

Figure 4.10 3D microscope image of a sample with four applications of PEDOT:PSS on a latex treated carton board substrate........115

Figure 4.11 3D microscope images of a sample with five layers of PEDOT:PSS applied to a latex treated carton board substrate, at 250x, which show the damage caused to the surface due to the use of the two point probe. The top image shows the sample normally while the bottom image has colours to show the relative height of the areas, blue is low while red is high 116

Figure 4.12 3D microscope image of a sample with five applications of PEDOT:PSS to a latex treated carton board substrate, at 250x magnification, displaying the brittleness of the surface coating 117

Figure 4.13 Photograph of the PEDOT:PSS coated samples. Samples are numbered 1-15 from top left to bottom right. Increasing number of applications of PEDOT:PSS from one to five layers from left to right in triplicate 117

Figure 4.14 Ambient resistance measurements of the samples after nickel coated copper electrodes were attached to the conductive polymer surface. The top plot shows resistances of individual samples while the bottom plot shows average readings with respect to the number of layers of PEDOT:PSS applied 120

Figure 4.15 Resistance measurements taken of the samples with copper electrodes after they had been dried in the oven. The top plot shows only dried resistance while the bottom plot displays the comparison to the ambient resistances 121

Figure 4.16 Average resistance measurements taken of the samples with copper electrodes after they had been dried in the oven. The top plot shows only dried resistance while the bottom plot displays the comparison to the ambient resistances 122

Figure 4.17 Photograph of the copper electrodes that have been attached to the conductive polymer surface 123

Figure 4.18 Ambient resistance of samples with a final application of latex after application of the copper electrode and PEDOT:PSS coating. The top plot shows values for each sample, the bottom plot shows average resistance values with respect to the number of applications of PEDOT:PSS applied to the sample 125

Figure 4.19 Electrical resistances of the samples with a latex top layer and copper electrodes after they had been dried. The top plot shows only the data post drying while the bottom plot compares ambient and post drying resistances 126

Figure 4.20 Average resistance measurements with respect to the number of layers of PEDOT:PSS applied, of the samples with the latex top layer and copper electrodes after they were dried. The top plot shows only the data post drying while the bottom plot compares ambient and post drying resistances 127

Figure 4.21 A comparison of all the resistance measurements taken when the samples were left to reach ambient conditions. The top plot shows resistance measurements of all samples while the bottom plot displays average resistance measurements with respect to the number of applications of PEDOT:PSS to the card substrate 130

Figure 4.22 A comparison of all the resistance measurements of the samples post drying. The top plot shows resistance measurements of all samples while the bottom plot displays average resistance measurements with respect to the number of applications of PEDOT:PSS to the card substrate 132

Chapter Five

Figure 5.1 Electrically conductive epoxy on the surface of the PEDOT:PSS and latex coated cotton fabric substrate 137

Figure 5.2 The amount of PEDOT:PSS that is applied to the latex coated cotton fabric substrate after each application. The top plot is individual samples and the bottom plot is averages with respect to the number of layers applied. 140

Figure 5.3 The relationship between the amount of PEDOT:PSS applied to the substrate and the resistance over 10 mm. The top plot is of individual samples, the bottom plot is averages with respect to the number of layers applied. 142

Figure 5.4 Sheet resistance of layer averages of PEDOT:PSS on the latex treated cotton substrate 143

Figure 5.5 3D microscope image of a latex treated cotton fabric sample with one application of PEDOT:PSS at 250x magnification 144

Figure 5.6 3D microscope images of a latex treated cotton fabric with two applications of PEDOT:PSS, the top image at 250x magnification and the bottom image at 500x magnification 145

Figure 5.7 3D microscope images of a latex treated cotton fabric with three applications of PEDOT:PSS, the top image at 250x magnification and the bottom image at 500x magnification 146

Figure 5.8 3D microscope image of a latex treated cotton fabric with four applications of PEDOT:PSS at 250x magnification 147

Figure 5.9 3D microscope images of a latex treated cotton fabric with five applications of PEDOT:PSS, the top image at 250x magnification and the bottom image at 500x magnification 148

Figure 5.10 A comparison of the amount of PEDOT:PSS applied to the latex treated substrate and the untreated cotton substrate described in Chapter Three 149

Figure 5.11 A comparison of the measured resistances after the application of the electrically conductive epoxy. The top plot displays all data while the bottom plot has omitted the resistance values of the initial PEDOT:PSS of samples 1, 6 and 11. 150

Figure 5.12 A comparison of the measured resistances after the application of the electrically conductive epoxy. The top plot displays average resistances of the number of layers applied and the bottom plot omits the initial value for layer one for greater clarity of difference between the layers 151

Figure 5.13 3D microscope image of the electrically conductive epoxy on the surface of a PEDOT:PSS and latex treated cotton fabric at 250x magnification 152

Figure 5.14 Comparison of the resistance initially after application of PEDOT:PSS, application of conductive epoxy and after the application of the latex top layer to the cotton fabrics. The top plot shows all data for comparison and the bottom plot has removed the resistance value for the initial resistance after application of PEDOT:PSS for samples 1, 6 and 11. 153

Figure 5.15 Comparison of the average layer resistance initially after application of PEDOT:PSS, application of conductive epoxy and after the application of the latex top layer to the cotton fabrics. The top plot shows all data for comparison and the bottom plot has removed the resistance value for the initial resistance after application of PEDOT:PSS for layer 1 154

Figure 5.16 Mass of latex applied as a top layer 156

Figure 5.17 3D microscope image of a sample with a latex top layer above one application of PEDOT:PSS at 100x magnification 157

Figure 5.18 3D microscope image of a sample with a latex top layer above two applications of PEDOT:PSS at 100x magnification 158

Figure 5.19 3D microscope image of a sample with a latex top layer above three applications of PEDOT:PSS at 100x magnification 158

Figure 5.20 3D microscope image of a sample with a latex top layer above five applications of PEDOT:PSS at 100x magnification 159

Figure 5.21 Resistance measurements of the samples after a wash cycle. The top plot shows all data while the bottom plot has removed samples 1, 6, 7 and 11 and removed the error bars on samples 2, 7 and 12 for greater clarity. 161

Figure 5.22 Average resistance measurements with respect to the number of layers of PEDOT applied to the surface after a wash cycle. The top plot shows all data while the bottom plot has removed layer 1 and the error bars of layer 2 for clarity. 162

Figure 5.23 A comparison of the resistance values of the samples post wash, after the latex top coat and after the application of the conductive epoxy alone. The top plot shows all data while the bottom plot omits data similar to Figure 5.22. 163

Figure 5.24 A comparison of the average resistance values with respect to the number of layers post wash, after the latex top coat and after the application of the conductive epoxy alone. The top plot shows all data while the bottom plot omits data similar to Figure 5.22 165

Figure 5.25 An image of the samples after washing and drying. Damage can be seen on a number of samples in the form of creases and even holes. 166

Figure 5.26 Closer inspection of the more damaged samples show the extent of the damage. Electrodes have been removed and the conductive polymer looks to have been removed from the surface by friction. 167

Figure 5.27 3D microscope images for a comparison of the parts of a sample, with one layer of PEDOT:PSS, which had a latex top layer (top image) and which did not (bottom image) at 250x magnification. 169

Figure 5.28 3D microscope images for a comparison of the parts of a sample, with two layers of PEDOT:PSS, which had a latex top layer (top image) and which did not (bottom image) at 250x magnification. 170

Figure 5.29 3D microscope images for a comparison of the parts of a sample, with four layers of PEDOT:PSS, which had a latex top layer (top image) and which did not (bottom image) at 250x magnification. The woven fabric appears to be becoming less unwoven during the wash and drying processes. 171

Figure 5.30 3D microscope images for a comparison of the parts of a sample, with five layers of PEDOT:PSS, which had a latex top layer (top image) and which did not (bottom image) at 250x magnification. The woven fabric appears to be becoming less unwoven during the wash and drying processes. 172

Figure 5.31 A comparison of the average electrical resistance with respect to the number of layers of PEDOT:PSS applied after the latex top layer and the PEDOT:PSS treated cotton from Chapter Three. The top plot shows all data while the bottom plot omits layer 1 of Chapter Three data for clarity 174

Figure 5.32 A comparison of the average electrical resistance measured with respect to the number of layers of PEDOT:PSS applied, post wash of the latex treated samples and the PEDOT:PSS treated cotton from Chapter Three. The top plot shows all data while the bottom plot omits layer 1 data for clarity 178

List of Tables

Chapter Three

Table 3.1 Amount of polymer (PEDOT:PSS) applied to cotton substrates. Single layered samples are # 1, 6 and 11. Double layered samples are # 2, 7 and 12. Triple layered samples are # 3, 8 and 13. 4 layered samples are # 4, 9 and 14. 5 layered samples are # 5, 10 and 15. As noted previously, Sample 1 had 0.5 mL aqueous dispersion of PEDOT:PSS applied in one application......70

Table 3.2 Resistance measurements of samples 1-15; A and B are taken over the x-axis crease on each side of the y-axis crease; C and D are taken over the y-axis crease on each side of the x-axis crease, all over 10 mm......84

Table 3.3 Resistance readings of the coated cotton fabric samples post washing and drying 89

Chapter Four

Table 4.1 Mass of conductive polymer applied and resistances measured at ambient conditions and after drying measured with the two point probe and average values with respect to the number of applications of PEDOT:PSS applied......108

Table 4.2 Resistances measured of samples with copper electrodes both at ambient conditions and after drying and average values with respect to the number of applications of PEDOT:PSS applied. $^{+}$ Outlier, * average taken disregarding outliers. 119

Table 4.3 Resistances measured of samples with copper electrodes and a latex top layer both at ambient conditions and after drying and average values with respect to the number of applications of PEDOT:PSS applied. $^{+}$ Outlier, * average taken disregarding outliers.......124

Table 4.4 Resistance measurements of the samples after PEDOT:PSS has been applied, after application of the nickel coated copper electrodes and after the final layer of latex had been applied. Bottom shows the average resistance measurements with respect to the number of PEDOT:PSS applications made to the latex treated substrate. These measurements were taken at ambient conditions. $^{+}$ Outlier, * average taken disregarding outliers. 129

Table 4.5 Resistance measurements of the samples after PEDOT:PSS has been applied, after application of the nickel coated copper electrodes and after the final layer of latex had been applied. Bottom shows the average resistance measurements with respect to the number of PEDOT:PSS applications made to the latex treated substrate. These measurements were taken directly after treatment in the oven. $^{+}$ Outlier, * average taken disregarding outliers $^{+}$ Outlier, * average taken disregarding outliers. 131

Chapter Five

Table 5.1 Masses of the woven cotton fabrics before and after application of latex 139
Table 5.2 Mass of PEDOT:PSS applied to the latex treated cotton fabric substrate and the percentage mass increase, to which this equates, and the measured electrical resistances of the samples and layer averages 141
Table 5.3 Mass of latex applied as a top layer and the measured electrical resistance and layer averages 155
Table 5.4 Mass losses of the samples during washing, their respective measured electrical resistance and layer averages 164

List of Schemes

Chapter One

Scheme 1.1 Chemical doping of poly(acetylene) with halogens [6] 15
Scheme 1.2 Chemical doping of poly(acetylene) with arsenic pentafluoride [6] 15
Scheme 1.3 Oxidation *via* doping with nitronium salts 16

Chapter Two

Scheme 2.1 Procedure 1 - Synthesis of EDOT (7) [1-3] 37
Scheme 2.2 Reaction mechanism of dimethyl thiodiglycolate (2) to 3,4-dimethoxythiophene-2,5-dicarboxylate (4) and further pathway to 3,4-dimethyoxythiophene-2,5-dicarboxylic acid (5) 38
Scheme 2.3 Procedure 2 - Synthesis of EDOT (7) [4] 39
Scheme 2.4 Reaction mechanism for the conversion of thiodiglycolic acid (8) to dimethyl thiodiglycolate (2) 39
Scheme 2.5 Reaction mechanism of disodium dimethyl-3,4-dioxythiophene-2,5-dicarboxylate (3) to dimethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (9) [4] 40
Scheme 2.6 Procedure 3 - Synthesis of EDOT (7) [5-8] 41
Scheme 2.7 Reaction mechanism of dimethyl-3,4-dihydroxythiophene-2,5-dicarboxylate and 1,2-dibromoethane to dimethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (9) 42
Scheme 2.8 Procedure 4 - Synthesis of EDOT (7) 43

Scheme 2.9 Procedure 5 - Synthesis of EDOT (7) 47
Scheme 2.10 Derivatives of 3,4-ethylenedioxythiophene attempted via the use of 2-methyl-1,4-butanediol (to give c) and 2,3-dimethyl-1,4-butanediol (to give d) ………..48

Abbreviations

DBSA	Dodecylbenzene sulphonic acid
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulphoxide
DSC	Differential scanning calorimetry
EB	Emeraldine base
EDOT	3,4-Ethylenedioxythiophene
FET	Field effect transistor
HDPE	High density poly(ethylene)
HPLC	High performance liquid chromatography
L	Leucoemeraldine
LC-MS	Liquid chromatography-mass spectrometry
LED	Light emitting diode
NMR	Nuclear magnetic resonance spectroscopy
OECT	Organic electrochemical transistor
P	Pernigraniline
PAN	Poly(acrylonitrile)
PANI	Poly(aniline)
PCB	Printed circuit board
PEDOT	Poly(3,4-ethylenedioxythiophene)
PET	Poly(ethylene terephthalate)
PPV	Poly(*p*-phenylene vinylene)
PSS	Poly(styrene sulphonate)
ROMP	Ring opening metathesis polymerisation
TGA	Thermogravimetric analysis
UHMWPE	Ultra-high molecular weight poly(ethylene)

Chapter One

Electrically conductive polymers and their uses in SMART textiles

1.1 Preamble

The key aim of the research study reported in this thesis was to attempt to develop a conductive ink that would have the following features:

- be based on a conductive polymer (importantly, rather than on the inclusion of conductive dopant);
- could be applied onto textile fabrics to form a conductive film; and
- be crease and wash resistant.

Hence, the study consisted of several parts including:

- design of flexible conductive polymer molecules;
- design of routes to the synthesis of conductive monomers;
- synthesis, characterisation and improvement of conductive monomers; and
- design, preparation, characterisation and improvement of conductive inks for printing on textile fabrics.

The thesis is structured in such a way to provide a logical flow through the topics mentioned above. Chapter One provides an introduction to understand the nature of intrinsically electrically conductive polymers and the background of SMART textiles.

Chapter Two describes the exploratory synthetic work undertaken. There are many published routes towards the synthesis of EDOT and PEDOT so initial synthesis focused on repeating the routes provided in the literature. The intention was to understand different synthetic routes in order to find potential points of derivatisation of the EDOT monomer for novel monomer synthesis.

Chapter Three is an examination of the performance of PEDOT:PSS on a woven cotton fabric. The electrical resistance of the conductive polymer was monitored to understand the effects of creasing and washing. The results of washing conductive polymer coated textiles are not widely reported, instead individual threads are treated in solutions which do not necessarily translate to the effects of a full scale washing machine.

Chapter Four describes the creation of a multi-layered composite of PEDOT:PSS with a synthesised latex on a carton board substrate. This work was designed to examine any negative effects of using the latex layers and also to investigate the use of electrodes made with an electrically conductive epoxy as a means of measuring the electrical resistance of the conductive polymer which, when coated with latex, has an electrically insulating surface.

Chapter Five examines the use of the composite described in Chapter Four on a woven cotton fabric. Electrical resistance measurements were recorded pre and post wash for comparison with the measurements recorded from Chapter Three. The improvements described in this work could be applied to other electrically conductive polymers, specifically those which would come from further experimentation of Chapter Two.

1.2 Overview

SMART textiles have been identified as an area for technological development by the UK Technology Strategy Board [1] . As the UK develops an aging population, there is a need for more innovative health care systems. Recently, there have been developments in the area of healthcare devices that incorporate SMART textiles. These include t-shirts and bed sheets that have embedded sensors for the monitoring of electrocardiographs, respiration, pulse rates, body temperatures, blood oxygen levels and information concerning the body movement of a patient [2]. The data acquired by these devices are then transmitted over a wireless network, for example “Wi-Fi” or *via* a mobile connection to a server for processing [2].

Some of the methods used to render textiles conductive include the use of melt spun conductive polymer fibres [3]; the use of electrically conductive polymer coatings [4] and printing electrically conductive inks [5]. The use of melt spun conductive polymer fibres is reliant on good homogeneity of the produced fibre, the fibres are created, in this example, with poly(aniline) and poly(propylene) which is determined by the quality of the blend (mixing) and the draw ratio of the fibre. This method achieves good mechanical properties and the electrical resistance of a bundle of 16 fibres is 1.9 x 10^6 Ω over 100 mm [3]. The coating with an electrically conductive polymer was achieved with a binder system and multiple layers were applied to a woven textile substrate but the electrical resistances measured were high, surface resistivity of *ca.* 10^8 Ω per sq. [4]. It was noted that exposure to heat increases the resistance while exposure to ageing in the atmosphere, the resistance decreased to 10^4 Ω per sq. [4]. Electrically conductive inks (silver metal containing) have proven to be highly conducting but are susceptible to fracture during washing cycles therefore becoming no longer electrically conductive, Karaguzel *et. al* [5] attempted to solve this issue by laminating a protective layer to the surface to achieve a more wash resistant coating though this reduced the electrical conductivity. They observed that the viscosity of the conductive ink had a large impact on the adhesion to the surface of the textile substrate, the higher the viscosity the greater the amount of ink that remained on the textile surface.

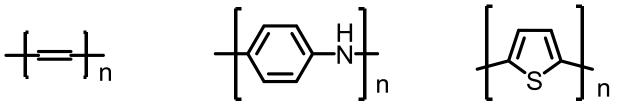
The exploitation of SMART textiles requires the availability of a low cost, crease and wash-resistant and highly electrically conductive fabric. This project is based on attempts to tackle such issues through the use of conductive polymers as coatings for textile fabrics.

This Introduction gives an overview of the current status of conductive polymers, the mechanism of conduction and some conductive polymer structures. Also addressed are the issues concerning what is required for high conductivity and what factors can affect intrinsic conductivity. Some discussion will centre on the processibility and also the stabilities of the intrinsically conductive polymers. The concept of the benefits of doping polymers will be discussed and an overview of the methods of doping is provided. The current situation regarding the use of conductive polymers in SMART textiles is covered as are the limitations that have been found and ways in which the polymers can be improved.

The Introduction is concluded by the provision of an outline of the aims of the research that is discussed in subsequent chapters.

1.3 Electrically conductive polymers

Carbon based polymeric materials have traditionally been thought of as electrical insulators. PVC (poly(vinyl chloride)) is used on this basis as an insulating coating around electrical transmission wires. Polymers are generally insulators because of the high band gap they possess between the valence band and its electrons and the conduction band. In order to become conductive, the electrons must receive energy to be promoted above this gap to then conduct charge. Recently, some carbon based polymers have been found to be electrically conductive [6-8]. These conductive polymers have conjugated backbones. Examples of such conductive polymers include poly(acetylene) **(1)**, poly(aniline) **(2)** and poly(thiophene) **(3)**, see Figure 1.1 for respective molecular structures. These particular conductive polymers are noteworthy as, poly(acetylene) was the first conductive polymer to exhibit metallic conductivity [6], poly(aniline) is one of the older conductive polymers, first synthesised in 1862 [8], discussed later and poly(thiophene) has led to further developments of commercially available conductive polymers, including poly(3,4-ethylenedioxythiophene), which is discussed later in the Introduction.

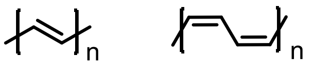


1 2 3

Figure 1.1 Molecular structures of poly(acetylene) (1), poly(aniline) (2) and poly(thiophene) (3)

1.4 Mechanism of conduction

Poly(acetylene) is considered to be the simplest of the conjugated polymers having two isomers, cis-poly(acetylene) **(4)** and trans-poly(acetylene) **(5)**. Figure 1.2 gives respective molecular structures. Poly(acetylene) predominantly exists in the trans-form **(4)** as this is the more thermodynamically favoured form.



4 5

Figure 1.2 Molecular structures of cis-poly(acetylene) (4) and trans-poly(acetylene) (5)

As the carbon atoms of poly(acetylene) are all sp^2 hybridised, the structure can be described as a one dimensional analogue of graphite. There is a fundamental difference between graphite and poly(acetylene) however. The C-C bonds are not equal in length in the latter, considered to be 1.35 and 1.44 Å [9]. They are alternately shorter and longer due to a Peierls distortion [9, 10]. This difference in the bond lengths of the polymer thus opens up a gap between the HOMO (highest occupied molecular orbital), π-band (valence band), and the LUMO (lowest unoccupied molecular orbital), π^*-band (conduction band). Poly(acetylene) can be classified as an intrinsic semi-conductor since the band gap is 1.5 eV [11, 12].

The π-conjugation band is a result of the overlap of the p_z orbitals in the conjugated polymer units. There is another family though, represented by poly(aniline). Here, the p_z orbitals of the nitrogen atom also contribute to the conjugation. The poly(anilines) have different chemistry to other conjugated polymers because of the basic centres due to the amine and imine nitrogen atoms in the backbone of the polymer [6].

Poly(aniline) is one of the older conductive polymers. First made in 1862 by Letheby, it is known to exist in three different forms; leucoemeraldine, emeraldine base and pernigraniline [8], Figure 1.3.

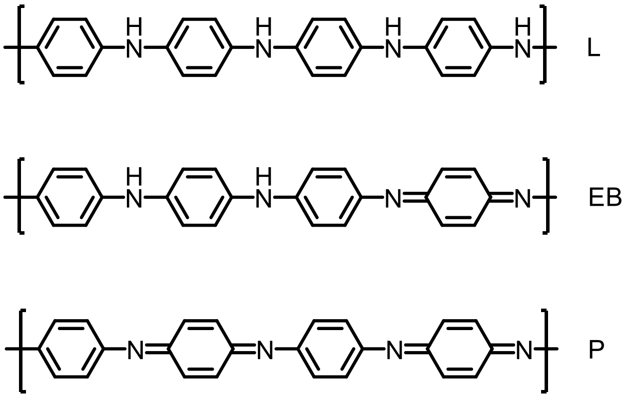


Figure 1.3 Three forms of poly(aniline); Leucoemeraldine (L), Emeraldine Base (EB) and Pernigraniline (P)

These different forms of poly(aniline) exist at different oxidation levels, leucoemeraldine being the most reduced form and pernigraniline being the most oxidised form [13].

1.4.1 Factors affecting conductivity

The band gap between the valence band and the conduction band is a major factor governing conductivity; the larger the band gap, the lower the chance of conductivity. These band gaps can be decreased by introducing the correct amount of electron withdrawing groups and electron donating groups into the conjugated backbone. The introduction of these groups lowers the bond alternation so the band gap decreases [6]. Details of the first “narrow band gap polymer”, poly(isothianaphthene), with a band gap of 1 eV, was published in 1984 by Wudl *et al.* [7]. Poly(isothianaphthene) was polymerised and doped by both electrochemical methods and chemical methods and shown to have a band gap much lower than the parent polymer, poly(thiophene). Bromine doped poly(isothianaphthene) achieved an electrical conductivity of 4.0 x 10^{-1} S cm^{-1} [7]. Though work has been carried out to reduce the band gap by as much as possible, a polymer with no band gap is still to be discovered [6].

As the method of conduction through the intrinsically conductive polymers is *via* the conjugation of the backbone, the polymer must be as linear as possible. Defects in this linearity can arise because of the attached groups along the conjugated backbone. These cause the polymer chain to twist or otherwise deform and thus reducing the “quality” of the conjugated π-band system.

1.5 Processibility and stability

Poly(acetylene) is neither melt nor solution processible [6]. Thus, the selection of the synthesis method is crucial achieving the desired morphology of the polymer. Edwards *et al.* demonstrated a method that provides a soluble polymer precursor, 1,2-bis(trifluoromethyl)benzene [14]. Thin films of the polymer precursor were then cast from acetone while further thermal treatment results in the formation of poly(acetylene). However, the *cis*/*trans* ratio differs according to the temperature used [14]. Poly(acetylene) is environmentally unstable, undergoing irreversible oxidation in air. This creates carbonyl groups on the backbone of the polymer, which break the conjugation and, hence, the electrical conductivity of the polymer [15].

Heterocyclic conjugated polymers can be prepared by the chemical or the electrochemical oxidation of their monomer counterparts, e.g. pyrrole to poly(pyrrole) and furan to poly(furan) etc [6]. When these polymers are produced using electrochemical methods, they form thin films over the working electrode that can be easily removed [6]. In order to obtain the conjugated polymers in their neutral form, the polymer must be reduced electrochemically or chemically.

Polyconjugated heterocyclic polymers have, sometimes, very different properties from one another. For example, in its neutral state poly(pyrrole) is extremely reactive with oxygen in the atmosphere whereas neutral poly(thiophene) is stable under ambient conditions [6]. Poly(3,4-ethylenedioxythiophene) (PEDOT) and other poly(alkyloxythiophene)s have a low oxidation potential [6]. Thus, in their neutral (undoped) forms, they are very unstable when in contact with oxygen and oxidise quickly, so they must be handled in an inert atmosphere. PEDOT is insoluble however, some alkyl derivatives of PEDOT are soluble but this increased solubility can negatively impact the electrical conductivity of the polymer [16-18].

In the 1990s a family of conjugated polymers, poly(*p*-phenylene vinylene)s (PPV) attracted interest because of their properties of electroluminescence. PPV can be made by several synthetic routes only leading to low molecular weight conjugated oligomers [19]. This is because PPV is insoluble in the matrix, unlike the monomer. Thus, the PPV precipitates out of solution, in a powdery form, as it is formed.

As a consequence of the precipitation of PPV from solution, different methods of synthesis are required, as an insoluble powder has only limited technological uses. This problem can be overcome by forming PPV from precursor routes. The precursor needs to be a soluble polymer which can be formed into PPV, preferably by thermal methods.

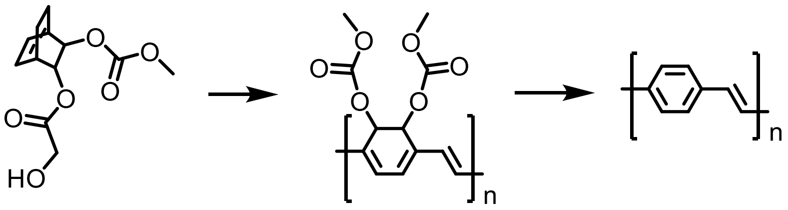


Figure 1.4 An acetone soluble ROMP route for the production of poly(phenylene vinylene) [19]

One route to the synthesis of a soluble precursor to PPV is shown in Figure 1.4. This route is the ring opening metathesis polymerisation (ROMP) of a derivative of bicyclooctadiene [19]. The product can be solution processed in organic solvents and subsequently heated to produce the PPV film.

The solubility of PPV can be tuned by the addition of alkyl chains to the phenyl ring. The addition of alkyl chains not only induces solubility but also allows the tuning of the band gap it possesses of great importance for the uses of this material [6]. Soluble PPV precursors and precursor derivatives have been produced [19, 20, 21]. An example of a soluble PPV derivative is poly(3-methoxy-6-(2-ethylhexyloxy)-p-phenylenevinylene), soluble in cyclopentanone see Figure 1.5 [20]. These examples demonstrate the ability to derivatise electrically conductive polymers to tune the mechanical, chemical and electrical properties.

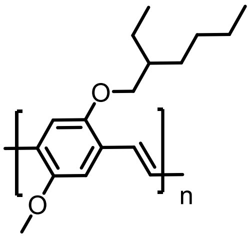


Figure 1.5 poly(3-methoxy-6-(2-ethylhexyloxy)-*p*-phenylenevinylene)

1.6 Doping

1.6.1 Introduction

Conjugated polymers can exist either in their natural, neutral states or as a doped version. Undoped conjugated polymers are intrinsically semi-conducting with a band gap that is not only dependent on chemical composition of the conjugated backbone but also on the substituents that are attached to the backbone [6].

Two classifications of doping are redox doping and acid-base doping. For conjugated polymers without strong basic sites, such as poly(acetylene), poly(thiophene), poly(furan) and their derivatives, the redox method of doping is more suitable [6]. Poly(aniline) and other conjugated polymers that contain strong basic centres on the backbone can undergo the acid-base type of doping [6].

p-Type, oxidative doping can be accomplished *via* electrochemical methods or chemical methods using the anodic or chemical oxidation, respectively, of the polymer to polycarbonium cations while introducing the required number of anions to balance the charge in between the polymer chains. The positive charges of the polycarbonium cations are mobile. It has been shown from the Hall effect and thermoelectric power, that oxidised poly(acetylene) is a positive hole conductor. The Hall effect is the development of a difference of voltage across a conducting medium transverse to the direction of current flow through the medium and perpendicular to an applied magnetic field. Thermoelectric power, or thermopower, is the measure of a difference in voltage across a conducting medium with respect to a difference in temperatures across the medium [22-24].

1.6.2 Solitons, polarons and bipolarons

The doping of conjugated polymers introduces a charge to the conjugated backbone of the polymer. The doping of a polymer can occur in both reductive processes and oxidative processes. In an oxidative process, the charge is localised on the chain, causing a local distortion of the chain. This distortion decreases the ionisation energy of the chain, which allows for easier accommodation of the new charge that has formed. The localisation of charge and distortion of the chain increases the energy of the polymer less than if the charge was delocalised over the chain [11]. A similar process occurs during the reductive, n-Type process.

Figure 1.6 shows the p-Type doping process. Firstly, an electron is removed from the conjugated π-system of the polymer backbone, resulting in the formation of a radical-cation. The removal of a second electron results in a second-radical cation that then combines with the first and, after further oxidation, produces a species called a soliton, which is described later.

Figure 1.7 shows the reductive, n-Type doping of poly(acetylene). In this case, the neutral chains are either electrochemically or chemically reduced to polycarbonium anions while being charge compensated by introducing cations between the polymer chains. The final species is a negatively charged soliton which, in this case, is the charge carrier [6].

The oxidation of poly(thiophene) proceeds *via* an electron being removed from the π-system of the conjugated backbone of the polymer, producing a radical cation, depicted in Figure 1.8. The radical and the positive charge are coupled *via* localised resonance. The distortion produced is of higher energy than the ground state sections of the chain and limits the distance the two entities can separate. The product of the formation of a free radical and a positive charge is termed a polaron [11].

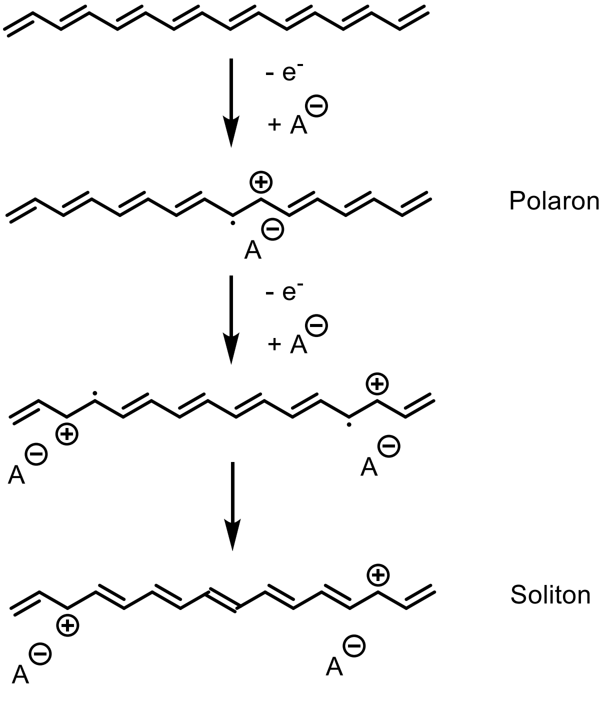


Figure 1.6 Oxidative p-type doping of poly(acetylene), A is the dopant

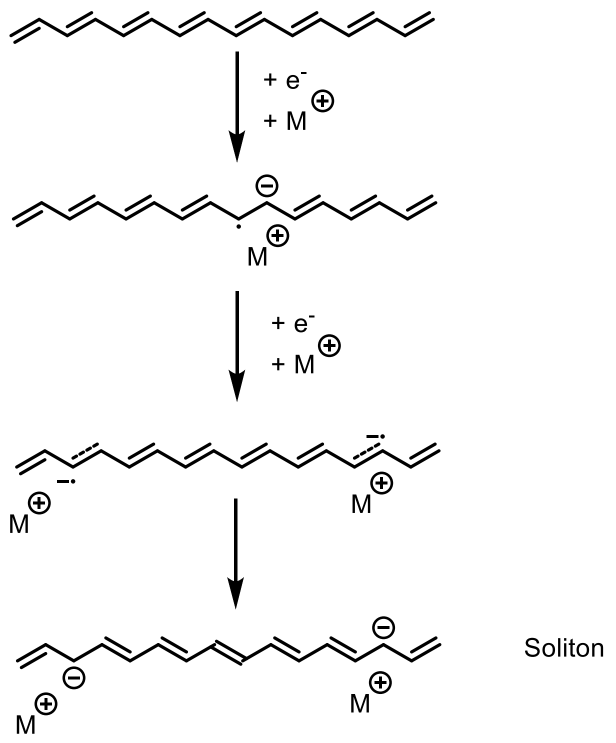


Figure 1.7 Reductive n-type doping of poly(acetylene)

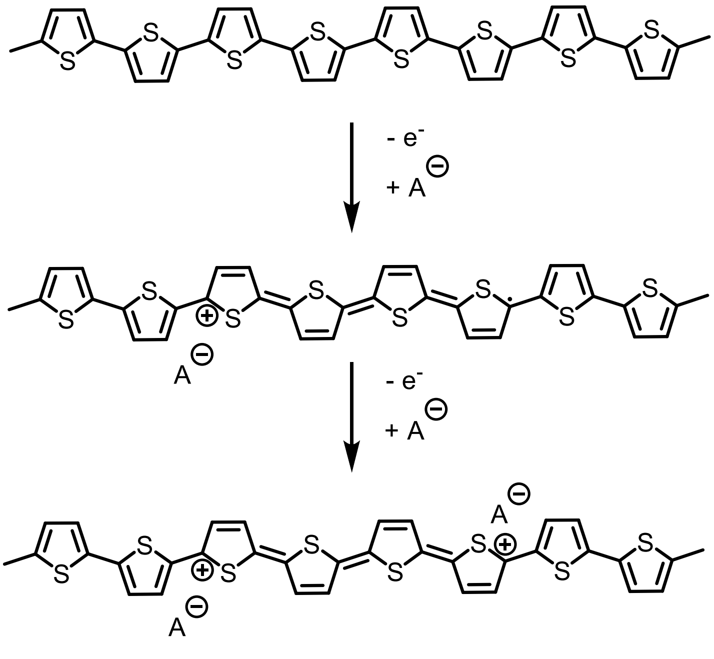


Figure 1.8 Oxidative p-type doping of poly(thiophene) [9]

When polarons are formed in poly(thiophene), a different domain is introduced into the chain of quinoid-like rings. With increasing oxidation, the free radical of the polaron is removed and this then forms a bipolaron. Bipolarons are of lower energy than two distinct polarons. Also, at higher doping levels, it becomes possible for two polarons to combine into a bipolaron. As doping increases, the bipolarons give a continuous bipolaron band across the backbone of the polymer. It is thought that at these levels of oxidation the upper and lower bipolaron bands combine with the conduction and valence bands respectively [11].

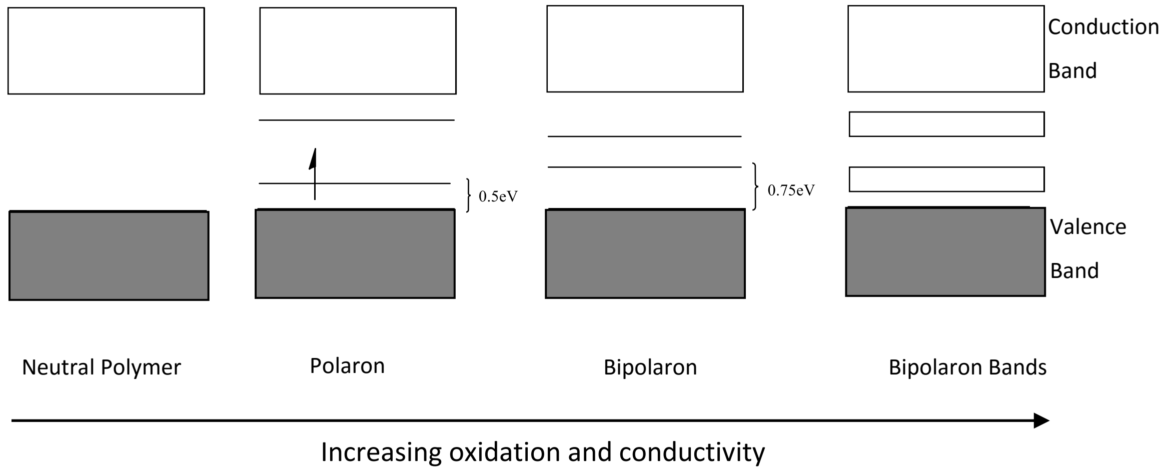


Figure 1.9 Band structures of polymers at differing oxidation levels. Neutral polymer lowest oxidation level, Bipolaron bands highest oxidation level

In conjugated polymers, such as poly(acetylene), the ground state is degenerate and the polymers are capable of producing polarons and bipolarons. The cations, however, are not bound to each other and can travel freely along the chain of the polymer. Because these charged species are independent of one another, they can form two distinct, separate charged regions. These are known as solitons. The solitons that occur in poly(acetylene) are thought to be separated by 12 CH units of the chain, the highest charge density can be found near the dopant ion [11]. Soliton formation brings about new localised electronic states in between the conduction band and the valence band. Similar to bipolarons, these solitons can interact with each other at high dopant levels to form continuous soliton bands that can merge with the edges of each of the bands to produce true “metallic” conductivity, as described by Akagi *et al.* [26]. Akagi *et al.* achieved this “metallic” conductivity by forming the poly(acetylene) film within an applied magnetic field. This produced fibrils of polymer oriented with respect to the applied magnetic field which produced large poly(acetylene) fibrils, 800-1000 Å and gave a high volume density of

550 mg cm^{-3}, usually the poly(acetylene) fibrils are around 200 Å and a density of 300 mg cm^{-3} [26].

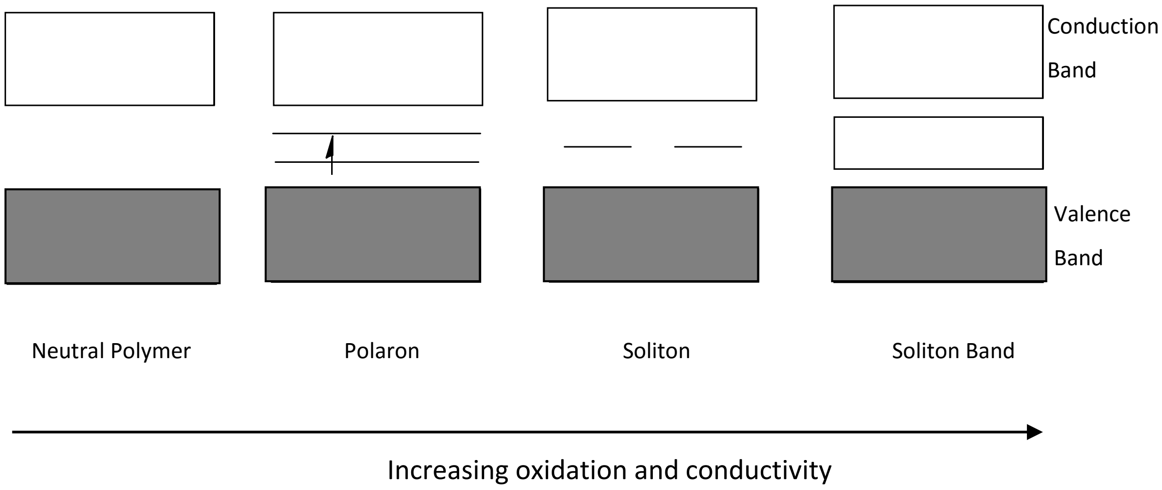
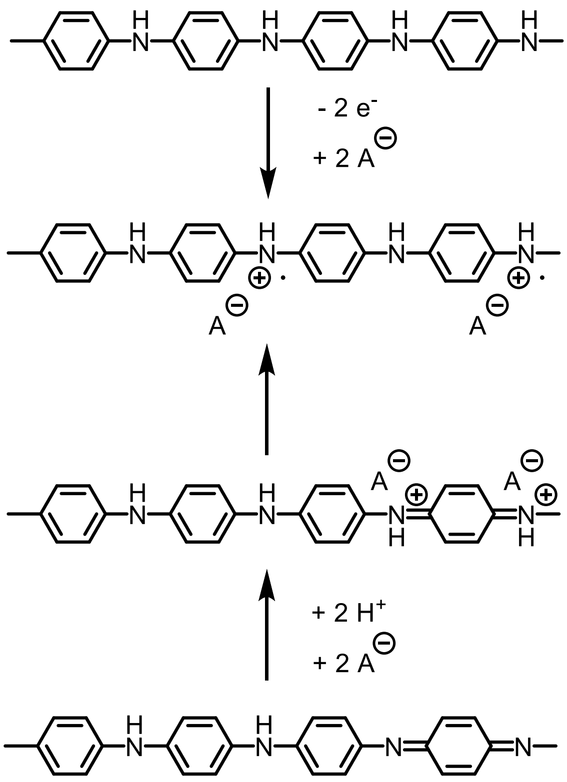


Figure 1.10 Soliton formations in poly(acetylene)

Leucoemeraldine, the most reduced form of poly(aniline) can also undergo oxidative doping, losing electrons to form radical-cations, polarons (see Figure 1.11, which depicts that L species are converted to species **6**). The emeraldine base form of poly(aniline) can be used to demonstrate the acid-base types of doping. The use of strong protonic acids can cause the protonation of the emeraldine base into its corresponding salt (see Figure 1.11, depicting that the EB species are converted to species **7**). From spectroscopic studies, including X-ray photoelectron spectroscopy [27], it has been concluded that the imine nitrogen atoms are preferentially protonated. Protonation of emeraldine base gives structures that store their charge in the form of bipolarons. An internal redox process redistributes these charges, transforming the bipolarons into polarons, forming what is known as a polaron lattice (see Figure 1.11, depicting species **7** being converted to species **6**) [6].



L

(6)

(7)

EB

Figure 1.11 Redox and acid-base doping of poly(aniline)

Overall, regardless of the method of doping used, charge is added or removed to or from the π-band of the conjugated backbone of the polymers. The σ-bonds of the polymer are unaffected and so the structure of the polymer remains. Other properties, such as the vibrational energy and the electronic properties, are affected drastically when doping is applied. The most notable change after doping is the change in the electrical conductivity of the polymer; the conductivities of the polymers can increase by several orders of magnitude. There have been cases recorded in which the polymers can reach conductivities that are comparable to those of metals with negative temperature coefficients, a characteristic of metallic conduction [27-31]. Naarmann *et al.* produced poly(acetylene) films in a silicone oil with aged catalysts and polymerising at room temperature. These films were stretched and doped with I_2 and produced films with conductivities higher than 120,000 S cm^{-1}, greater than any elemental metal. They found their method produced a higher proportion of the *cis*-form which was more stable over time when exposed to air, when compared with other synthetic routes to poly(acetylene) [28]. Hagiwara *et al.* noted that the polymerisation conditions have an effect on the maximum conductivity of a film of poly(pyrrole). The difference between a two electrode system and three electrode system of polymerisation produced films which achieved their peak conductivity at -30 and -40 °C respectively [29].

1.6.3 Methods of doping

1.6.3.1 Chemical doping

The first dopants to be used to convert conjugated polymers into conductive polymers were iodine, bromine and arsenic pentafluoride [6, 31]; these dopants were used in the 1970's in order to dope poly(acetylene). One simple doping method was to expose films of poly(acetylene) to vapours of the dopants [6]. The reaction that occurs when doping with halogens is summarised in Scheme 1.

$$(-\mathrm{C_2H_2}-)_x \; + \; \frac{3}{2}\mathrm{y}x\mathrm{X_2} \; \rightarrow \; \left[(-\mathrm{C_2H_2}-)^{\mathrm{y}+} \; (\mathrm{X_3^-})_{\mathrm{y}}\right]_x$$

X_2 = halogen molecule (Cl_2 etc.)

Scheme 1.1 Chemical doping of poly(acetylene) with halogens [6]

Scheme 1.1 shows that when using halogens to dope poly(acetylene)s, halogens effectively become linear polyhalogen anions, such as I_3^- and Br_3^- entering the poly(acetylene) matrix. Care must be taken when doping with bromine because the further oxidation can occur. The addition of bromine can form over a double bond. This addition over the double bond converts sections of the poly(acetylene) chain to poly(dibromovinylidene), which is an insulating polymer. This removes the conjugation of a section of the backbone of the polymer. To avoid this unwanted side reaction, very mild conditions should be used [6].

The reaction with arsenic pentafluoride can be described as being both redox and acid-base doping, see Scheme 1.2 [6].

$$(-\mathrm{C_2H_2}-)_x \; - \; \mathrm{y}x\mathrm{e^-} \; \rightarrow \; [(-\mathrm{C_2H_2}-)^{\mathrm{y}+}]_x$$

$$\frac{3}{2}\mathrm{y}x\,\mathrm{AsF_6} \; + \; \mathrm{y}x\mathrm{e^-} \; \rightarrow \; \frac{1}{2}\mathrm{y}x\,\mathrm{AsF_3} + \; \mathrm{y}x\,\mathrm{AsF_6}$$

$$[(-\mathrm{C_2H_2}-)^{\mathrm{y}+}]_x \; + \; \mathrm{y}x\,\mathrm{AsF_6^-} \; \rightarrow \; \left[(-\mathrm{C_2H_2}-)^{\mathrm{y}+}\,(\mathrm{AsF_6^-})_{\mathrm{y}}\right]_x$$

Scheme 1.2 Chemical doping of poly(acetylene) with arsenic pentafluoride [6]

In this reaction, one third of the dopant molecules are oxidants while the remaining two thirds act as a Lewis Acid.

Purely redox type oxidations are achieved by using dopants, such as nitronium salts of hexafluorophosphates, arsenates or antimonates ($NO_2^+XF_6^-$, where X = P, As or Sb), or nitrosonium salts ($NO^+XF_6^-$, where X = P, As or Sb), because the cations act as the oxidants [34], see Scheme 1.3.

$$\mathrm{y}x\,\mathrm{NO_2^+\,XF_6^-} \rightarrow \left[(-\mathrm{C_2H_2}-)^{y+}\,(\mathrm{XF_6^-})_\mathrm{y}\right]_x + \mathrm{y}x\,\mathrm{NO_2}$$

Scheme 1.3 Oxidation *via* doping with nitronium salts

In the doping depicted in Scheme 1.3, the reaction preferably would be carried out in solution of nitromethane [6].

Oxidising transition metal halides can be used as dopants for poly(acetylene). In their respect, a popular compound is iron(III) chloride ($FeCl_3$) [32]. This dopant has been shown by Mössbauer spectroscopy to be incorporated into the matrix as $FeCl_4^{2-}$ [33]. Sulphuric acid and perchloric acid are other more commonly used oxidising dopants which gave highly conducting films of poly(acetylene) that were stable in air for two days [34].

1.6.3.2 Electrochemical doping

Electrochemical doping is a method that is used with respect to conjugated polymers. These conjugated polymers can be soluble or insoluble in their medium. The soluble conjugated polymers can be deposited onto electrodes made from platinum or other metals, by spin-coating or dip-coating from solution. The insoluble, conjugated polymers can be electropolymerised on the electrode or can be deposited in a manner that is similar to that used with soluble conjugated polymers, from colloidal dispersions [6].

The majority of conjugated polymers are electropolymerised in their doped states and do not require further doping [35]. If a different dopant is required, an exchange must occur by electrochemically reducing the conjugated polymer to the neutral state and then chemically or electrochemically doping with the desired dopant. A major disadvantage of electrochemical doping, compared to chemical doping is that due to the limited surface area of an electrode, a relatively smaller amount of conjugated polymer can be doped. The advantage that electrochemical doping has over chemical doping is the ability to control precisely the doping level, *via* coulometric measurements, provided that the current yield of the doping is known [6].

Doping electrochemically is usually carried out from non-aqueous solutions of, for example, acetonitrile and propylene carbonate that contain quaternary amine salts of anions such as PF_6^- and BF_4^- as the electrolyte [6]. During electrochemical doping, the conjugated polymer is being oxidised at the anode while the dopant anions in the solution are being inserted into the polymer matrix. Electrochemical doping can be carried out under a constant current or at a constant potential.

Monitoring electrochemical doping using cyclic voltammetry (CV) can be used to prevent any irreversible over oxidation of the conjugated polymer, that would result in the formation of an insulating, electrochemically inactive polymer [36]. When p-type doping of a neutral conjugated polymer occurs, an anodic peak appears in the cyclic voltammogram. This is followed by a plateau, associated with the high capacitance of doped conjugated polymers [37, 38]. On the reversed potential CV scan there is a cathodic peak arising from the dedoping process, occurring due to the transition of the doped polymer to the neutral one. p-Type doping produces a semi-oxidised conjugated polymer. Further increasing of the potential can lead to a second peak that corresponds with the over oxidation of the polymer. This event is irreversible as shown by the fact that there is no corresponding cathodic peak [6].

1.6.4 Doping-induced processibility

In order to induce solubility to the rigid back-boned polymers, flexible side chains are attached. This enables the production of soluble derivatives of poly(thiophene) for example. Poly(thiophene)s are only soluble in their undoped neutral form, even when these flexible side chains have been provided. As these poly(thiophene)s are doped in solution they rapidly precipitate from solution [6].

Industrial, post-doping processing would be required. Therefore the need for the availability of soluble polymers, in their doped forms has been recognised. The method being approached is that of introducing these flexible side chains as part of the dopant species. This is a fundamentally different approach since these flexible side groups will now be attached to the polymer back-bone by ionic bonding, rather than the previously outlined covalent bonding. One approach to this end concerns the doping of poly(pyrrole) with anionic surfactants of the alkysulfate and alkylsulfonate types. However these resulted in a conductive polymer that was still insoluble in the doped form [39].

Poly(aniline) has been studied extensively in this respect. A soluble, doped form of poly(aniline) was developed in 1992, by Cao *et al.* [40]. They used *n*-dodecylbenzene sulphonic acid (DBSA) as the acid-base dopant to protonate the poly(aniline), which was in the emeraldine base form. This resulted in doped poly(aniline)s that were soluble in non-polar solvents or weakly polar solvents, which meant that compositions could be solution processed.

A more recent attempt to produce a soluble, doped conjugated polymer concerned the use of a derivative of poly(thiophene). Poly(3,4-ethylenedioxythiophene) was produced in the search for more stable, conducting polymers in 1992 [41]. The ethylenedioxy group improved the stability of the polymer by having the ability to stabilise the positive charge, while having a minimal effect on the structure of the polymer backbone.

One dopant that can be used in the case of poly(3,4-ethylenedioxythiophene) is poly(styrene sulphonic acid). This polyelectrolyte allows the formation of a water-dispersible, conductive polymer that has good film forming properties, gives high conductivities, has visible light transmissivity (transparency) and offers extensive stability [42].

1.7 Conductive textiles

Since the progress in the miniaturisation of silicone chips, it has been envisioned that textiles could be used to harbour personal electronics [43]. In the earliest forms, this idea was taken literally by implanting small electronic pieces of equipment into the textile substrate. This concept has now been advanced towards forming the textile itself into a piece of electronic equipment [44]. De Rossi writes of a method of coating textile fibres with a conductive medium and utilising the junctions of the woven substrate, with a solid electrolyte reservoir, as an organic electrochemical transistor (OECT) [44].

Once textiles have been functionalised to become conductive, they can have many applications. One of these applications is in the use of resistive yarns, as electrodes, for the electrocardiography of a patient [45]. To monitor the electrocardiography, two methods were employed, steel threads wound around acrylic yarns and a multi-layered system of an acrylic/cotton fabric and a second layer containing stainless steel threads [45]. Since the development of textile based field effect transistors (FETs), in 2003, there is now the possibility that more complex circuits, on/in textile substrates, can be designed [46].

Since the textile is the substrate for the electronic device, the development of flexible electronic devices has arisen in comparison to the rigid devices, for example, those used in printed circuit boards (PCBs) and in light emitting diodes (LEDs).

1.7.1 SMART textiles

A SMART textile is a textile which has functionality, in addition to its primary use. The other uses are based on integrated circuitry based within the textile itself. As well as the example given previously, this circuitry can be used to power mounted gas sensors [47, 48], heating devices [49-53] and biomedical sensors [54-56].

Kincal *et al.* prepared a poly(pyrrole) coated textile fabric and monitored its electrical conductivity on exposure to gases, such as, CO_2 and NH_3. They noticed that the conductivity of the fabric decreased on exposure to these gases and that the change was reversible [47].

Bhat *et al.* produced a poly(pyrrole) coated textile fabric, which remained flexible and breathable, which when a voltage was applied, generated heat could be as much as 1000 W m^{-2} [49]. The cotton fabric was coated by being placed in a bath of a solution with the monomer in varying concentrations before the oxidant, $FeCl_3$, was added to carry out the polymerisation [49]. It was noted that at mass loadings of conductive polymer over 35 % began to reduce the flexibility and smoothness of the cotton fabric [49]. Knittel *et al.* coated poly(ethylene terephthalate) (PET) fabrics with poly(3,4-ethylenedioxythiophene) and investigated the effect on tensile strength of the fabric and the abrasion resistance of the coated fabric. Due to the method of which the fabric was coated, immersion in a bath of monomer solution, the resistance was not severely affected by abrasion. The tensile strength was not affected on PET but a cotton fabric lost 20 % of its tensile strength [50].

Laforgue *et al.* [51] improved on the work by Knittel *et al.* [49] by producing a heating mat which could reach a high temperature, *ca.* 100 °C, in just a few seconds at 10 V. Laforgue *et al.* produced the heating mat by electrospinning a solution of oxidant, iron (III) tosylate, small amounts of poly(vinyl pyrrolidone) and pyridine to produce a fibre more than 90 wt. % of oxidant and subsequently polymerising PEDOT *via* the use of vapour phase deposition [51].

Shang *et al.* [52] attempted the opposite route to Knittel *et al.* [49] of preparing a poly(pyrrole) coated fabric. Shang *et al.* first soaked the PET fabric in a solution of the $FeCl_3$ dopant and subsequently polymerised the pyrrole monomer *via* vapour phase polymerisation. This achieved surface resistances as low as 200 Ω cm^{-1} which related to a temperature of just below 60 °C at 30 V [52]. Still lower than temperatures achieved by Laforgue *et al.* [51]. Shang *et al.* noted that conductive polymer films deposited *via* the vapour phase provide smoother films than those deposited by the liquid phase deposition [52].

As well as the potential for heating devices, poly(pyrrole) films have been shown to have the potential to be antibacterial and give high temperature resistant properties to the host fabric substrate [53].

1.7.2 Existing methods of achieving textile conductivity

Different methods have been used to render textiles conductive, for circuitry. These methods include weaving conductive metal wires with the non-conductive textile fibres [57], the chemical metallisation of textile fibres [58] and coating of textile fibres with formulations containing conductive particles, such as carbon black or with conductive polymers (or a blend of both) [59-62].

Weaving metal wires together with non-conductive fibres creates a highly conductive textile, but the textile can lose its flexibility [57]. In addition to the material being rigid, the wires themselves are brittle. These brittle wires can easily be broken by simply folding the textile. If the wires are broken conductivity is lost. As the wires can break by folding, washing the textile in a standard washing machine would destroy the interconnected regions of the metal wire.

The chemical metallisation of textile fibres is a process by which metal salts are absorbed by/adsorbed on to a fibre surface and, subsequently chemically reduced to the conductive metallic form by the use of an appropriate reducing agent. This process is generally followed by the provision of a galvanic coating on the surface to connect the absorbed metal particles more effectively. An example of this process is provided by Akbarov *et al.* [58] who metalised a poly(acrylonitrile) (PAN) fibre by immersing the fibre in a bath of nickel (II) chloride and a reducing agent, namely Rongalite ($NaOHCH_2SO_2$). The Ni(II) is absorbed into the fibre and the rongalite subsequently reduces the Ni(II) to Ni(0). The galvanising is provided electrochemically with a solution of nickel sulphate at pH 5-6 and this provided fibres with resistances of the order of 10^{-1} Ω cm^{-1} [58]. Problems can be encountered with this process though; there is not an abundance of reducing agents used to reduce the metals to the metallic form, the reducing agents also can be very pH sensitive, which can cause them to decompose. Some decomposition products can inhibit the reduction reactions further [6]. In addition, some metals can cause allergic reactions to some individuals, nickel in particular so their use must be carefully considered [58].

Thongruang *et al.* [60] designed composites of high density poly(ethylene) (HDPE), ultrahigh molecular weight poly(ethylene) (UHMWPE), graphite and carbon fibre which were dry-mixed, spread into a mould and then subjected to high pressure and temperature to create a thin film of an electrically conductive composite. These films had electrical conductivities over 70 Ω^{-1} cm and were flexible [60]. These can be adhered to the surface of textile fabrics but films of this type will affect the breathability of the textile it will be applied to.

Amongst the examples given previously of electrically conductive polymers being applied to textile fibres, Molina *et al.* [61] electrochemically and chemically polymerised pyrrole on the surface of a polyester (PET) textile with a phosphotungstate ($PW_{12}O_{40}^{3-}$) dopant counter ion. The polyester was immersed in a bath of the monomer and the counter ion for absorption and then iron(III) chloride was added for the polymerisation to occur which provided an electrically conductive textile fabric [61]. A wash test was conducted with this fabric and the surface resistivity doubled.

A disadvantage of immersion of a textile fabric into a polymerisation solution is that the monomer is absorbed indiscriminately, a large area of fabric will become electrically conductive. If circuits are to be made on the surface of a textile with a conductive polymer, a more controlled application is required.

Irwin *et al.* coated single silk threads by dip coating into a mixture of poly(3,4-ethylenedioxythiophene):poly(styrene sulphonate) (PEDOT:PSS) in ethylene glycol [62]. Conductivities achieved were as high as 8.5 S cm^{-1}, ten times less than their silver coated silk thread control. The polymer coated silk threads were successfully used as interconnects for a 555 timer circuit [62].

1.7.3 The use of conductive polymers for textile conductivity

Conductive polymers have been investigated for their use in SMART textiles. These investigations have taken place in the search for a cost effective method of rendering fibres, or certain areas on a textile, electrically conductive [63-65].

In addition to the previous examples, Bashir *et al.* [63] coated polyester (PET) yarns with PEDOT and iron (III) chloride as the dopant. Bashir *et al.* first dipped the polyester yarns into the oxidant and then exposed them to vapours of the EDOT monomer, subsequent polymerisation occurred. The PEDOT coated yarns were finally treated with a 3 wt. % solution of $FeCl_3$ in butanol to dope the conductive polymer. This resulted in an electrically conductive fibre, 1000 Ω over the 150 mm fibre, *i.e.* 75 cm^{-1}, which had comparable mechanical properties measured by observing its elongation at break [63].

Fanous *et al.* melt spun fibres of and coated PET fibres with poly(3-hexylthiophene) doped with $FeCl_3$, they found that melt spinning provides a fibre over twice as conductive as a coated fibre [64]. However, it would be considered more cost effective to coat a PET fibre than melt spin a fibre of poly(3-hexylthiophene) [64].

Seeberg *et al.* reported the application of PEDOT:PSS and poly(aniline) (PANI) to a woven cotton textile surface *via* screen printing to create polymer-polymer thermocouples with a Seebeck coefficient of +10 V K^{-1} [65]. These thermocouples were tested by cycling the temperature from 235 to 350 K and observing the change in voltage, though this voltage drifted and fluctuated [65]. This study raises potential concerns of the use of electrically conductive polymers in harsh environments where temperature can fluctuate quickly.

It is thought the polymers can be used to maintain good mechanical properties and provide high electrical conductivity to the textile surface, unlike the rigid weave of metal wires.

1.7.4 Required properties of conductive polymers

It has been recognised that conductive polymers could be used as flexible films, providing high conductivities, see prior examples. A key requirement would be that the polymer must be able to retain its conductivity and its physical presence on the substrate after creasing and washing, a standard practice with textiles, Molina *et al.* explored this requirement [61]. The polymer would need to be chemically inert once applied to the textile surface and indeed any substrate it was applied, unlike poly(acetylene) films prepared by Akagi *et al.* [26].

1.7.5 Properties provided by existing technologies

The properties of conductive coated textiles can differ according to the conductive polymer type, compare the yarns produced by Bashir *et al.* [63] and Fanous *et al.* [64], different loadings of polymer, different dopants used, compare the differing properties achieved by Irwin *et al.* [62] and Bashir *et al.* [63] with PEDOT applied to textile yarns, and the method of application of polymer to the textile, a direct comparison was made by Fanous *et al.*[64] of melt spinning the conductive polymer or coating a PET fibre.

As the loading of a conductive polymer increases, the conductivity of the fibre should increase. Increasing the loading normally reduces the flexibility of the final material, demonstrated by the loss of elasticity when applying PEDOT to the surface of a viscose fibre [63]. As these conductive polymers are “rigid” molecules, applying them to a supporting fibre surface can improve the flexibilities whilst inducing electrical conductivity. This means that in most cases a compromise should be made between the electrical conductivity of the material and the flexibility of the resulting material.

The methods of application of the conductive polymer to the textile fabric surface can be placed into two categories, *in-situ* polymerisation and post-polymerisation application.

1.7.6 *In-situ* polymerisation on textiles

The term *in-situ* polymerisation on textiles describes the methods in which the monomer or the oxidising agent is first applied to the textile and subsequent polymerisation occurs [52, 58, 61, 63].

Textiles can also be coated electrochemically. If the textiles are immersed in the electrolyte containing the monomer, electropolymerisation can provide coverage of the textile with the polymer as it develops in the solution. Poly(aniline) has been electrochemically deposited onto the surface of cotton, silk and wool fibres [66].

A major *in-situ* method for producing a layer of conductive polymer on a textile surface is that of chemical vapour deposition. This method consists of applying the oxidising agent to the textile fibres with subsequent vapour-phase exposure to the monomer [67].

Cotton fibres can be initially treated with $FeCl_3$ as an oxidant in order to form a layer of poly(pyrrole) on the surface, when the treated fibres are exposed to the vapour of pyrrole [68]. The thickness of the layer can be controlled *via* the changes in the concentration of oxidant on the textile fibre. In this way products with resistances lower than 1000 Ω have been obtained [68].

Many polymers can be “grown” on the surfaces of textile fibres. In one system, the solvent in which the oxidant is solubilised and applied to the fibre needs careful consideration. As the oxidant differs, so does the need for a different optimal solvent [6].

1.7.7 Post-polymerisation application on textiles

Post-polymerisation application concerns the methods by which monomers are polymerised before being applied to the textile substrate.

Some routes of applying a conductive polymer formulation to a textile surface, post-polymerisation, are simple hand-brushing techniques, dipping the textile into the solution, as described earlier [62], and spray deposition [69]. The methods rely on the chemical oxidation, in many cases, of the monomer to achieve the polymer in a suitable solvent. The solution can be applied using the aforementioned methods. Subsequent evaporation of the solvent results in a textile surface that is coated with the conductive polymer. As described previously, it can often be difficult to find a suitable solvent for the conductive polymer.

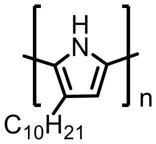


Figure 1.12 Poly(3-decanylpyrrole)

Foitzik *et al.* prepared solutions of poly(3-decanylpyrrole), depicted in Figure 1.12 in chloroform and acetone [69]. This solution was applied to the surface of wool by polymerising in solution with the substrate, spray depositing, vapour deposition and brushing. It was noted that solution polymerisation gave a much less homogeneous surface coating than vapour deposition, for example. Figure 1.13 is a SEM micrograph of the surface of a poly(3-decanylpyrrole) coated wool substrate and pores are clearly present on the surface, this is considered to be due to the evaporation of the chloroform solvent [69].

It is logical, and demonstrated by Foitzik *et al.* that a homogenous coating of conductive polymer on the substrate is desirable for optimum electrical resistance properties [69]. Such a state would provide a greater probability of charge transfer through the textile. Post-polymerisation application methods are more favoured if contact between the strong oxidising agents and the textile substrates would be unfavourable [69].

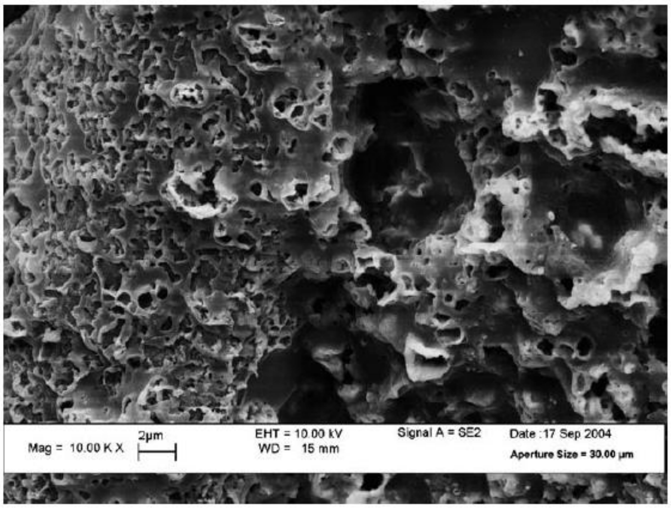


Figure 1.13 Non-homogenous coverage of poly(3-decanylpyrrole) on wool applied by spray deposition [69]

The application of conductive polymers post-polymerisation can result in uneven thicknesses of coating over the textile. Such differences in thicknesses throughout the layer could lead to anisotropic properties throughout. There will be inconsistent electrical conductivities and mechanical properties. Foitzik *et al.* investigated the coating achieved, using chloroform and water as solvents for poly(3-decanylpyrrole) and showed that due to the limited solubility in water, the polymer applies in a much thicker, homogenous layer than provided from chloroform [69]. It is clear that precise control of the application is also required if one is to provide a uniform layer.

1.7.8 Limitations of conductive polymers for textiles

There is no conductive polymer that offers high conductivity which maintains the textile fibres mechanical properties. Conductive polymers can be unstable and can require many processing steps and harsh processing conditions, for example the use of oxidising agents that can damage textile fibres. Some conductive polymers are unstable under atmospheric condition, their conductivities decreasing with time. Conductive polymers need to be tested as routine textiles i.e. wear, folding (creasing) and washing/drying. Different wash conditions can affect each textile polymer differently. Textile polymers have different adhesion strengths and behave differently with abrasion. When textiles are naturally dried they are often subjected to a long exposure to sunlight. The photoconversion that can arise can affect the nature and properties of the textile polymer.

Since there are no conductive polymers on the market that have become mass produced for the SMART textile market, a desirable conductive and flexible polymer has yet to be fabricated.

Many examples of conductive polymers being used to coat textiles have been given previously. These investigations have taken place in the search for a cost effective method of rendering fibres or certain areas of fabrics conductive. It is thought that the polymers can be used to bring both good mechanical properties and high conductivity to the textile surface, avoiding the limitations of the rigid weave of metal wires. A conductive polymer that has become popular in this field is poly(3,4-ethylenedioxythiophene) (PEDOT).

1.8 Poly(3,4-ethylenedioxythiophene) – PEDOT

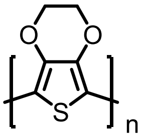


Figure 1.14 Poly(3,4-ethylenedioxythiophene) (PEDOT)

1.8.1 History of PEDOT use

PEDOT, depicted in Figure 1.14, has been heavily investigated in recent years due to the possible, wide array of applications. The uses of PEDOT include organic photovoltaics [70, 71], organic electrodes [71, 72] and in SMART textiles [62, 73, 74].

Younchan *et al.* successfully used PEDOT:PSS as an anode in a flexible organic light emitting diode (OLED) [71]. Examples have been given previously of the use of PEDOT on textiles [62] and Bashir *et al.* have attempted to introduce a standard of measuring electrically conductive fibres so as for easier comparison of electrical conductivities reported by different authors [73].

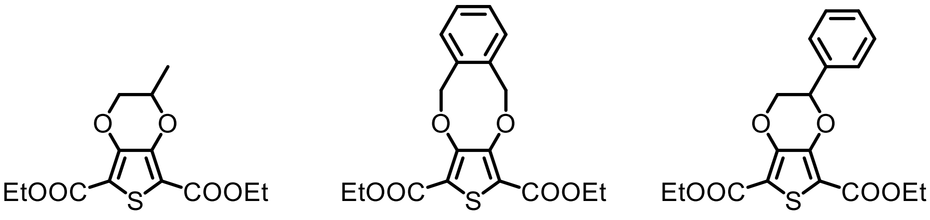
PEDOT is often doped with the polyelectrolyte poly(styrene sulphonate) (PSS) [62, 75, 76]. This doping also modifies the intermolecular structure of PEDOT. PSS chains can lie in between chains of PEDOT, preventing stacking which, as well as the PSS's water solubility enables PEDOT to exist in an aqueous dispersion [77].

There has been research conducted to investigate whether PEDOT can be used as electronic interconnects when mounted on textile fibres for SMART textiles as previously discussed [62, 63, 73, 74]. By preparing the polymer on the surface of a textile fibre, researchers have been able to keep some of the mechanical properties of the fibre while inducing electrical conductivity. This has been successful enough to use PEDOT:PSS coated silk fibres as electrical interconnects for a 555 timer device [62]. The silk fibres in this case had been coated with PEDOT:PSS by *in-situ* polymerisation.

1.8.2 Derivatives of the monomer, EDOT

There are examples of publications regarding derivatives of EDOT [78], specifically derivatives from the oxygen atoms at the 3- and 4- positions of the thiophene ring. Frontana-Uribe *et al.* demonstrated the ability to synthesise derivatives using bulky alkyl dibromides and trialkylamines as a base, see Figure 1.15, in a higher yield than what can be achieved with the respective dichloro- compounds. Some of the derivatives that were reported were, 2,3-dihydro-2-methylthieno[3,4-*b*]-1,4-dioxin-5,7-dicarboxylic acid diethyl ester **8**, 5,10-dihydrothieno[3,4-c][2,5]benzodioxicin-1,3-dicarboxylic acid diethyl ester **9**, 2,3-dihydro-2-phenylthieno[3,4-*b*]-1,4-dioxin-5,7-dicarboxylic acid diethyl ester **10**. These derivatives were not synthesised in order to test their electrical conductivities, instead it was a technical challenge to improve the synthesis of novel thiophene monomers and hence polymers.

Since PEDOT has been so heavily investigated, but not necessarily for this study's purpose, it is thought that there could be a potential to find a conductive polymer, based on PEDOT that can give the properties being searched for.



8 **9** **10**

Figure 1.15 Examples of EDOT derivatives

There has not yet been a publication that describes a highly conductive, highly flexible and stable post polymerisation application of a conductive polymer to a textile surface. Though there are publications [62, 75, 79] regarding the successful coating of fibres *via in-situ* polymerisation, many do not publish attempts at washing the coated the textile in a washing machine.

The textile industry continues to hope that opportunities will occur whereby one can develop a novel conductive polymer that can be applied post-polymerisation, thus increasing the ease of processing. Such polymer formulations could be applied *via* ink jet printing, for example, onto a garment in the pattern required, offering a simple process compared to the coating of single fibres.

1.9 Research Aims

The research presented in this thesis is initially based on the development of a knowledge base for the different routes for the synthesis of 3,4-ethylenedioxythiophene (EDOT). It is intended that research into the varying synthetic routes will highlight the potential stages from where derivatisation could take place.

Experimentation will take place into the development of potentially novel monomers, derivatives of EDOT. The target of derivatisation will be of the "ethylenedioxy bridge" of EDOT, depicted in Figure 1.16. The attempted derivatives must be developed *via* simple synthetic routes, these would be most industrially attractive.

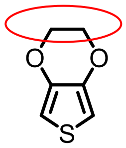


Figure 1.16 "Ethylenedioxy bridge" of EDOT

A commercially available aqueous dispersion of PEDOT:PSS, Clevios FT, will be used as a functional analogue for application trials. This research intends to provide a post-polymerisation application method of electrically conductive textiles which could, in the future, be printed onto textile surfaces. There is a lack of literature information regarding wash testing of conductive polymers applied post-polymerisation. Initially, PEDOT:PSS will be applied to a woven cotton substrate in order to investigate the electrical conductivity of the polymer applied to a fabric textile and to what degree this conductivity is retained post-wash.

Work will begin into the improvement of the physical performance of the electrically conductive polymer on the textile surface. It is expected that PEDOT:PSS alone will be too brittle and be easily damaged during the washing process. The improvement will likely arise from development of blended, or multi-layered, composite. The measured electrical resistances will be compared with published values in order to understand if a benefit has been realised by using a composite structure.

A stretch goal would be to synthesise novel monomers in a great enough quantity to investigate the effects of varying dopants. And further, to attempt application trials of a novel doped electrically conductive polymer *via* the same methods that have been described for PEDOT:PSS.

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Chapter Two

Towards the synthesis of novel monomers based on 3,4-ethylenedioxythiophene (EDOT)

2.1 Aim of experiments

The aim of each of the following experiments was to investigate the synthetic routes for the monomer, 3,4-ethylenedioxythiophene (EDOT). When a reliable and effective method of synthesis was found, it was rationalised that the acquired knowledge would aid investigations into the derivatisation of the monomer, EDOT. When derivatives are found and can be synthesised in high quantities, polymerisation techniques could be investigated in order to potentially generate novel and effective electrically conductive polymers.

2.2 Materials

All of the materials described in the following sections were used as received unless otherwise specified.

2.3 Methods of characterisation

2.3.1 NMR spectroscopy

^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX300 or a Bruker Avance 500 spectrometer using an internal deuterium lock. Chemical shifts are reported in parts per million (ppm), downfield from TMS in δ units and the coupling constants are given in hertz (Hz). TMS is defined as 0 ppm for ^{1}H NMR spectra.

2.3.2 Microanalysis

Microanalyses were carried out using a Sartorius SE2 Ultra-micro balance with a readability of 0.1 µg. Flash combustion was used to analyse carbon, hydrogen, nitrogen and sulphur (CHNS), using a Thermo Flash EA 1112 series. The results for CHNS are a percentage by weight, within the internationally accepted accuracy of ± 0.3% absolute.

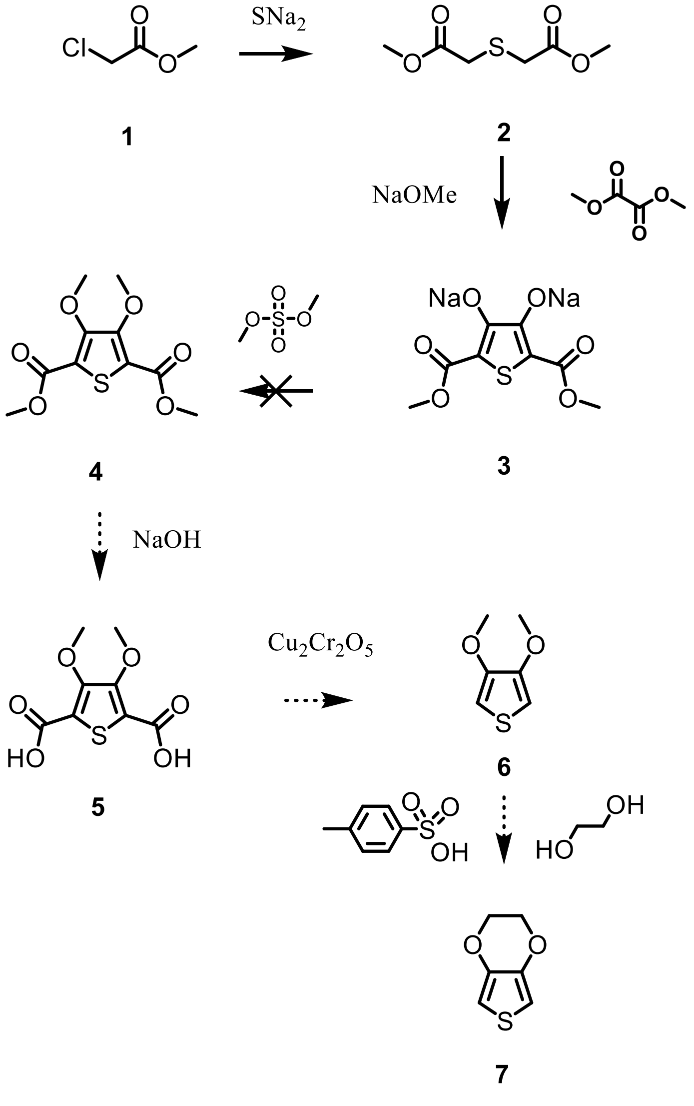
2.4 Synthetic procedures. Results and discussion

2.4.1 Procedure 1

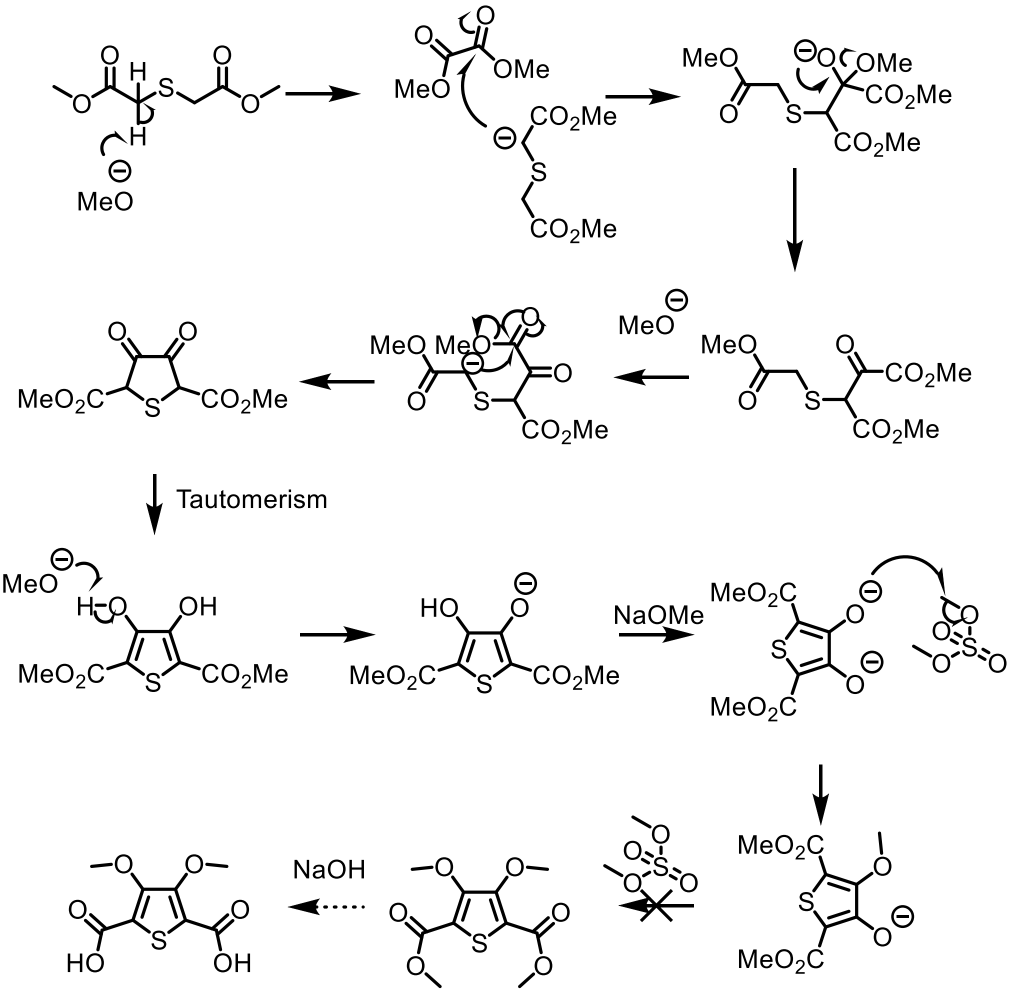
The first procedure followed was one based on three sources [1-3]. This created the initial opportunity to synthesise 3,4-ethylenedioxythiophene (EDOT) from low molecular weight reactants. The synthesis is summarised in Scheme 2.1.

The first step was taken from a patent accepted in 2009, to synthesise dimethyl thiodiglycolate [1]. The reaction is between aqueous sodium sulphide and methyl chloroacetate (**1**), catalysed by sodium dihydrogen phosphate dihydrate. The product dimethyl thiodiglycolate (**2**) was extracted with toluene to give a yield of 36 %. The synthesis was confirmed *via* ^{1}H NMR spectroscopy and by microanalysis.

3,4-Dimethoxythiophene-2,5-dicarboxylate (**3**) can be synthesised from dimethyl thiodiglycolate (**2**), dimethyl oxalate and sodium methoxide to form the disodium salt of 3,4-dioxy-2,5-dicarboxythiophene (**3**), which is then refluxed in dimethyl sulphate to provide the product, dimethyl 3,4-dimethoxythiophenedicarboxylate (**4**) [2]. This resulted in a dark green solution from which it was difficult to separate the desired product (**4**) and so hydrolysis to the acid could not be attempted. The proposed reaction mechanism for this route is shown in Scheme 2.2. An alternative route was investigated for the cyclisation of the diol of the thiophene, Procedure 2.



Scheme 2.1 Procedure 1 - Synthesis of EDOT (7) [1-3]

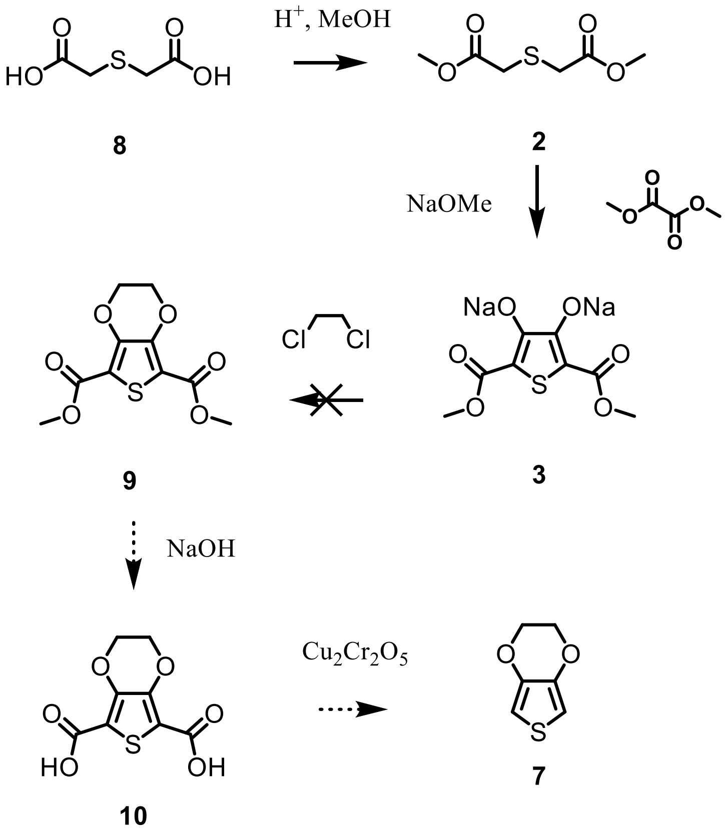


Scheme 2.2 Reaction mechanism of dimethyl thiodiglycolate (2) to dimethoxy 3,4-dimethoxythiophene-2,5-dicarboxylate (4) and further pathway to 3,4-dimethyoxythiophene-2,5-dicarboxylic acid (5)

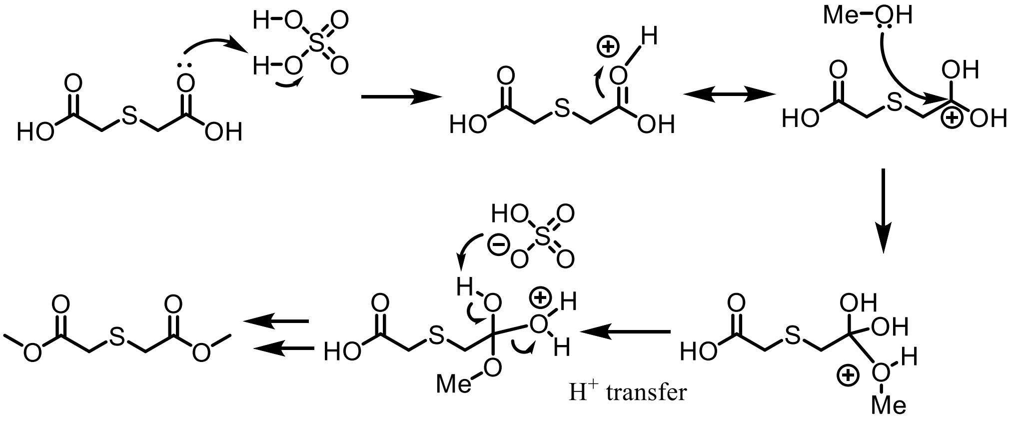
2.4.2 Procedure 2

This procedure is based on that of Pei *et al.* [4] and shown in Scheme 2.3. The starting materials differ, therefore offering an alternative route to provide different thiophene precursors to those identified in Procedure 1.

Dimethyl thiodiglycolate (**2**) was synthesised using a different method to that outlined in Procedure 1, this being the acid catalysed esterification of thiodiglycolic acid (**8**) in refluxing methanol. Once cool, the product was extracted from water with diethyl ether to give dimethyl thiodiglycolate (**2**). This synthetic route was technically simpler, however, it gave the ester in a much lower yield than given in Procedure 1 (17 % in comparison to 36 %). The reaction mechanism can be seen in Scheme 2.4, and the product was confirmed via ^{1}H NMR spectroscopy and by microanalysis.



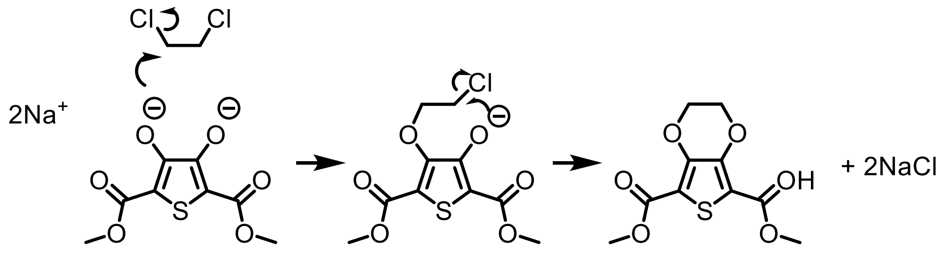
Scheme 2.3 Procedure 2 - Synthesis of EDOT (7) [4]



Scheme 2.4 Reaction mechanism for the conversion of thiodiglycolic acid (8) to dimethyl thiodiglycolate (2)

Dimethyl thiodiglycolate (**2**) was added to diethyl oxalate and methanol. A solution of sodium methoxide, in methanol, was added and the whole refluxed to produce a yellow precipitate of disodium dimethyl-3,4-dioxythiophene-2,5-dicarboxylate (**3**). This method was not always repeatable. When the dimethyl thiodiglycolate (**2**) fraction was added to the sodium methoxide/methanol suspension, the solution began to become so viscous that magnetic stirrers could not agitate the solution. On one occasion, more methanol was added in an attempt to reduce the viscosity, but this was unsuccessful. At the end of the reaction, the precipitate was not the colour expected. Usually, it is a pale yellow. The addition of more methanol caused a burnt orange colour. When this was added to the acidic solution, to protonate the salt, in Procedure 3, no precipitate was formed. On other occasions a mixture of a yellow and a white precipitate forms, which when added to an acidic solution, does not precipitate the desired product either.

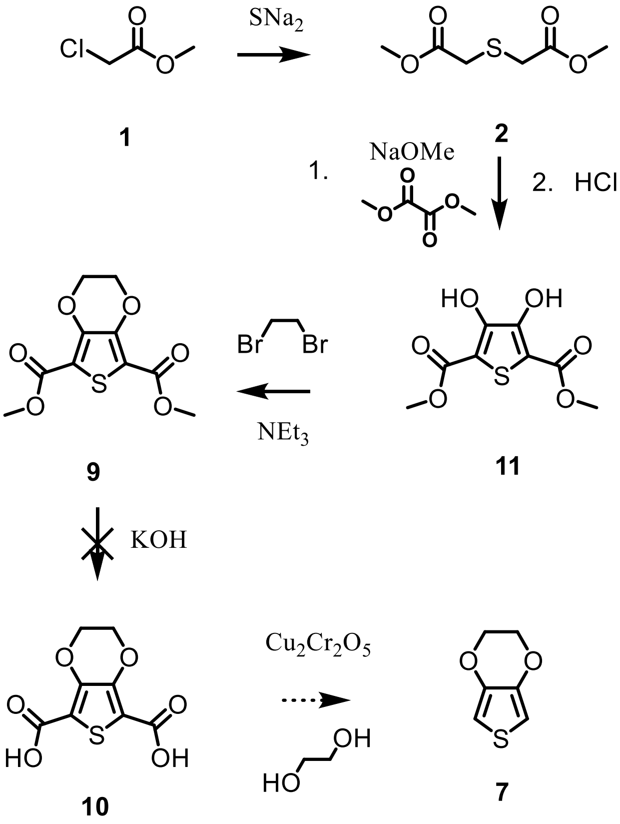
Disodium dimethyl-3,4-dioxythiophene-2,5-dicarboxylate (**3**) was suspended in 1,2-dichloroethane and refluxed. The reaction mechanism is displayed in Scheme 2.5. Once cool, the solution was acidified to produce dimethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (**9**) which was then refluxed in 10 % aqueous sodium hydroxide. Once cool the solution was acidified in order to produce 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid (**10**). However, no precipitate formed for subsequent analysis and further reaction.



Scheme 2.5 Reaction mechanism of disodium dimethyl-3,4-dioxythiophene-2,5-dicarboxylate(3) to dimethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (9) [4]

2.4.3 Procedure 3

This procedure was devised because the synthesis of the dimethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (**9**) was not successful using 1,2-dichloroethane. An alternative reaction, using 1,2-dibromoethane and triethylamine as a base, was attempted (see Scheme 2.6).

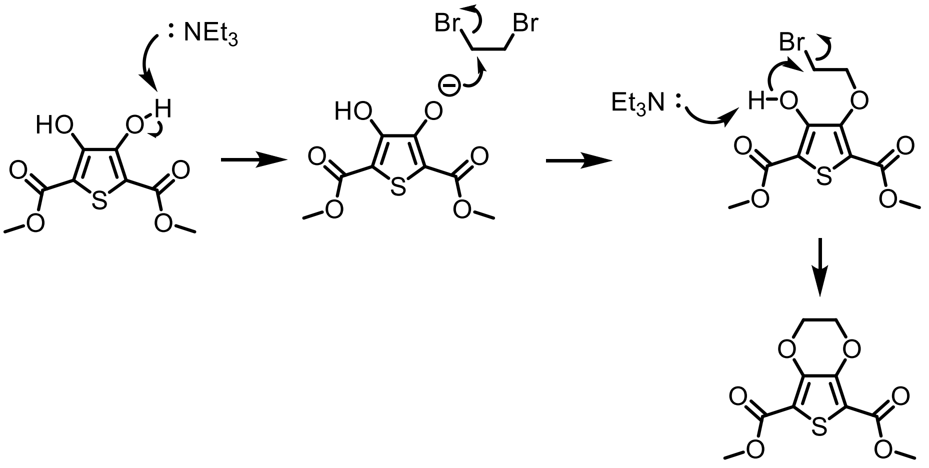


Scheme 2.6 Procedure 3 - Synthesis of EDOT (7) [5-8]

This procedure gave a synthetic route for dimethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**11**) and for dimethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (**9**).

The synthesis for dimethyl-3,4-dihydroxy-2,5-dicarboxylate (**11**) was achieved with varied success in the previous attempts in procedure 2. The method of synthesising dimethyl thiodiglycolate (**2**) from procedure 1 was used along with step 2 from procedure 2. The disodium salt (**3**) in this case, was acidified to produce dimethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**11**), this was confirmed *via* ^{1}H NMR spectroscopy and by microanalysis.

The diol (**11**) was refluxed overnight in DMF, triethylamine and 1,2-dibromoethane. The product, dimethyl 3,4-ethylenedioxythiophene dicarboxylate, (**9**) was extracted from water with diethyl ether. The reaction mechanism is given in Scheme 2.7. This crude product was separated *via* flash chromatography in a 50:50 mix of petroleum ether 40-60 °C/ethyl acetate. This separation was difficult because of low concentrations. The desired product was undetectable when using thin layer chromatography (TLC). Various contrasting agents were used in order to visualise the spot on the TLC plate but these were unsuccessful; permanganate, sulphuric acid and iodine dips.



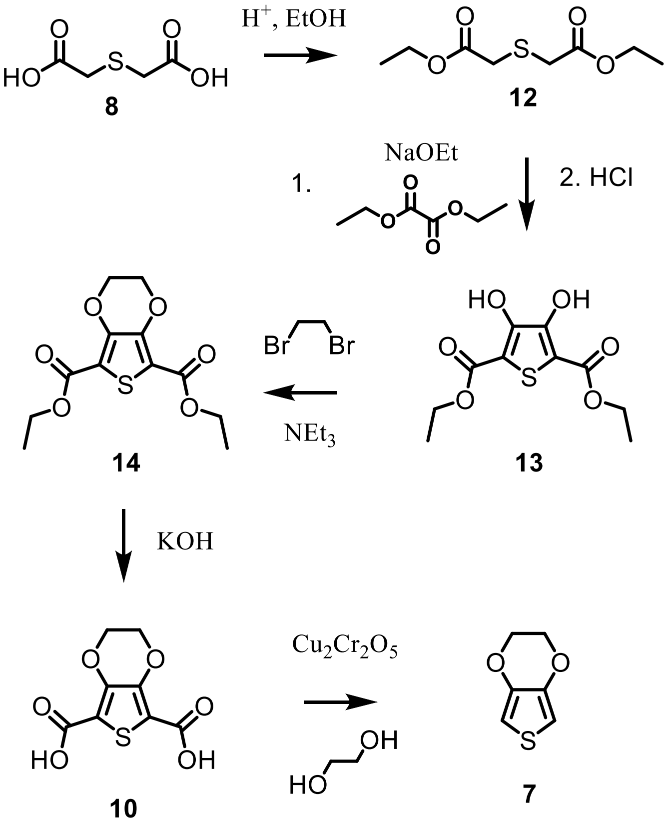
Scheme 2.7 Reaction mechanism of dimethyl-3,4-dihydroxythiophene-2,5-dicarboxylate and 1,2-dibromoethane to dimethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (9)

The chromatographic separation procedure produced one initial fraction early that had a slight yellow colour. Although nothing more came from the column, the upper volume of the silica bed was still brown, suggesting that more product was present. The column was then stripped with methanol to give a darker coloured methanolic fraction. The two fractions were concentrated using a rotary evaporator. The yellow solution gave a yellow oil. The stripped methanol fraction gave a brown coloured oil. The yellow oil contained the desired product, dimethyl 3,4-ethylenedioxythiophene-2,5-dicarboxylate, (**9**) along with DMF. The brown oil was purer product (**9**), with just trace levels of diethyl ether being present from the extraction prior to column separation.

An attempt at the hydrolysis of the dimethyl-3,4-ethylenedioxy-2,5-dicarboxylate (**9**) (fraction one from previous section) using potassium hydroxide in refluxing ethanol. This did not produce the desired diacid product (**10**).

The following procedure was adopted in an attempt to improve this hydrolysis stage.

2.4.4 Procedure 4



Scheme 2.8 Procedure 4 - Synthesis of EDOT (7)

These series of reactions were attempted in order to improve the reaction yields, on the basis that ethyl groups should be better leaving groups than the methyl groups of the previous series, see Scheme 2.8.

The sulphuric acid-catalysed esterification of thiodiglycolic acid (**8**) and ethanol, mixed as described in the earlier example, was a simple and effective reaction. Extraction of the diethyl thiodiglycolate (**12**) with diethyl ether resulted in yields over 96 % compared with less than 20 % from the methyl ester (**2**)

Diethyl thiodiglycolate (**12**) and diethyl oxalate were added to a cooled solution of sodium ethoxide in ethanol. The mixture was refluxed overnight to give a yellow precipitate, the disodium salt of the target molecule. This was filtered, dissolved in water then acidified with concentrated hydrochloric acid to give a white precipitate of the target molecule, diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**), in yields up to 70 %.

The diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**) was subsequently cyclised by refluxing with 1,2-dibromoethane in DMF, catalysed with triethylamine, for 24 hours. The crude mixture was poured into water and extracted with diethyl ether. It was washed and dried to give the pure product, diethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (**14**), in high yields (> 85 %).

Hydrolysis of the dicarboxylate (**14**), in refluxing aqueous sodium hydroxide and the subsequent acidification of the solution provided the brown precipitate of 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid (**10**), with a yield of 47 %.

Finally, the synthesis of 3,4-ethylenedioxythiophene (EDOT) (**7**) was achieved by heating the 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid (**10**) in dry DMF under N_2 with a copper chromite catalyst. The solvent was removed *via* vacuum centrifugation to give a sample of the desired product, EDOT, see Figure 2.1. The NMR spectrum displays the two proton peaks expected at chemical shifts of 4.18 and 6.56.

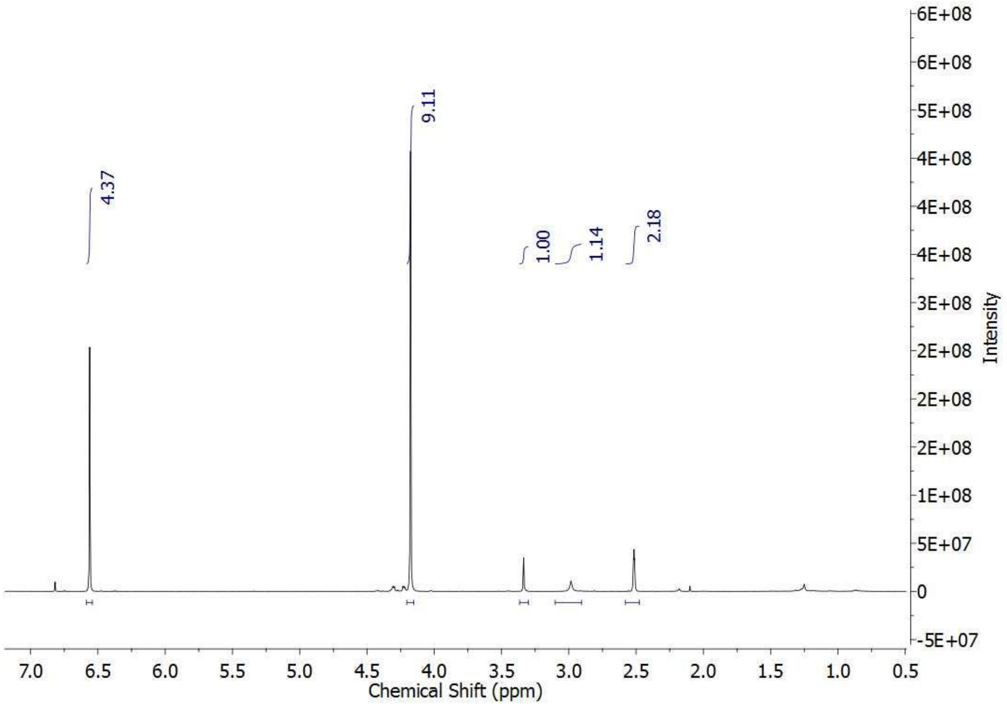


Figure 2.1 NMR spectrum of synthesised EDOT (7)

As described by Frontana-Uribe *et* al. [5], derivatisation of EDOT can begin by reacting diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**) with alternative dibromo-compounds than 1,2-dibromoethane. An attempt was made to synthesise a derivative published by Frontana-Uribe *et* al. [5], diethyl 5,10-dihydro[*f*]thieno[3,4-*b*][1,4]dioxocine-1,3-dicarboxylate, see Figure 2.2 **a** and to synthesise a molecule which has not been reported, Figure 2.2 **b**, diethyl 2,4-dimetyl-3-oxo-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine-6,8-dicarboxylate.

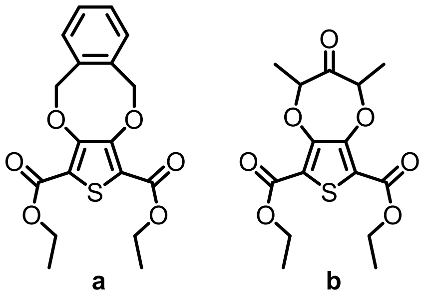


Figure 2.2 Derivatives of diethyl-3,4-ethylenedioxythiophene dicarboxylate attempted *via* use of dibromo compounds

Synthesis of Figure 2.2 **a** was attempted in order to verify the correct experimental procedure. LC-MS analysis showed a peak present with the m/z ratio of 747.1 which equates to 2M+Na. Column chromatography failed to provide a pure sample for analysis.

Subsequently, synthesis of Figure 2.2 **b** was attempted. LC-MS analysis gave two peaks with a m/z ratio of 707.1 which equates to 2M+Na. Despite repeated attempts, using column chromatography, a pure sample could not be obtained.

Hydrolyses of the crude mixtures of the esters were attempted. Unfortunately, analysis showed the final product to be diethyl-3,4-dihydroxythiophene dicarboxylate in both cases. Thus, instead of ester hydrolysis, the believed pendant group attached was cleaved. Attempts to resolve the problem were made by using less protic solvents and alternative bases, including potassium hydroxide and lithium hydroxide. However, either no ester hydrolysis occurred or cleavage of the pendant group occurred.

2.4.5 Procedure 5

This series of reactions were developed as an alternative derivatisation route to the cyclisation route demonstrated previously. The synthesis pathway is identical to that reported as procedure 4 (Scheme 2.8) up to and including the compound diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**), see Scheme 2.9.

In this modification, diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**) was heated in dry DMF, with potassium carbonate and freshly distilled dimethyl sulphate. The crude product was extracted from water with ethyl acetate to give the product, diethyl-3,4-dimethoxythiophene-2,5-dicarboxylate (**15**), in yields of up to 57 %.

The ester (**15**) was subsequently hydrolysed in refluxing aqueous sodium hydroxide to give the dicarboxylic acid (**5**) in high yield (80 %).

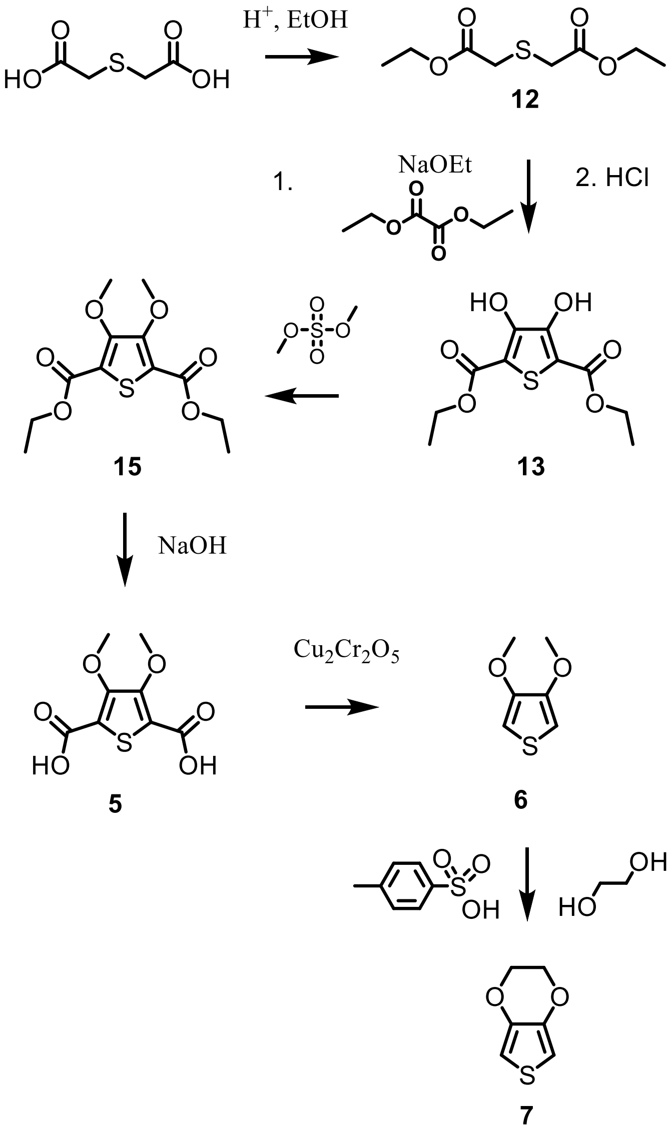
The decarboxylation procedure was completed in quinoline, with a copper chromite catalyst. The crude mixture was vacuum distilled. The distillate was extracted into ethyl acetate, washed with dilute hydrochloric acid and with water to give the desired product, 3,4-dimethoxythiophene (**6**), in high yields, 83 %.

Unlike procedure 4, this method gives a derivatisation point that is further along the synthetic pathway in that the pendant groups are joined as the final step, avoiding potential for the loss of material and any undesired chemical reaction occurring in the subsequent steps.

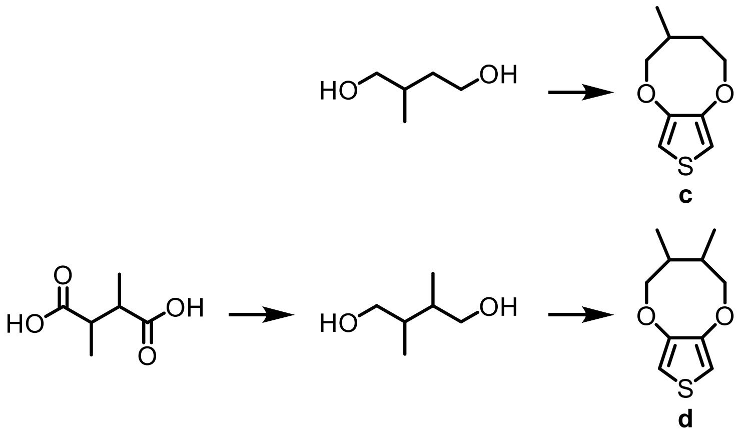
The two novel derivatives expected from this synthesis, can be seen in Scheme 2.10, 3-methyl-2,3,4,5-tetrahydrothieno[3,4-*b*][1,4]dioxocine (**c**) and 3,4-dimethyl-2,3,4,5-tetrahydrothieno[3,4-*b*][1,4]dioxocine (**d**) synthesised from 3,4-dimethoxythiophene (**6**) and 2-methyl-1,4-butanediol and meso-2,3-dimethyl-1,4-butanediol respectively. 2-Methyl-1,4-butanediol can be purchased but 2,3-dimethyl-1,4-butanediol was synthesised by the reduction of meso-2,3-dimethyl succinic acid with lithium aluminium hydride to give a yield of the desired diol, of 56 %.

Each of the diols were reacted with 3,4-dimethoxythiophene (**6**), in dry toluene, under N_2 catalysed by *p*-toluenesulphonic acid. The compound depicted as Scheme 2.9 **c** was synthesised, and detected *via* LC-MS as a peak with a m/z of 391.1, 2M+Na.

Synthesis of the second derivative (Scheme 2.10 **d**) was attempted but no evidence of its presence in the crude reaction mixture was found.



Scheme 2.9 Procedure 5 - Synthesis of EDOT (7)



Scheme 2.10 Derivatives of 3,4-ethylenedioxythiophene attempted *via* the use of 2-methyl-1,4-butanediol (to give c) and 2,3-dimethyl-1,4-butanediol (to give d)

2.5 Discussion

This exploratory synthesis work was conducted to compare the various published pathways to the synthesis of 3,4-ethylenedioxythiophene (**7**) and to establish steps at which derivatisation could be pursued. Procedures 1-5, discussed earlier, differed in one important factor. This factor is whether the derivative of the "ethylenedioxy bridge", described in Research Aims in Chapter 1.9, is created as the final step of the synthesis or if this derivatisation.

Procedures 1 to 3 attempted to create dimethyl esters of the thiophene derivative. But they either struggled to deliver the intended products or gave product in low yields. The final two procedures were attempts to improve on this by creating diethyl esters. At the first stage, the yield of the diethyl thiodiglycolate was up to 94 % in comparison to that of the dimethyl thiodiglycolate (**2**), where yield was 36 %.

The subsequent syntheses of the cyclised dihydroxythiophene esters revealed the advantage of utilising the diethyl ester instead of the dimethyl ester. The dimethyl ester route gave a yield of *ca.* 10 %. The yield of the diethyl ester was 69 %. Procedure 5 differed in that, at this stage of its respective synthesis, a dimethoxythiophene derivative was synthesised with the diethyl ester, with a yield of 57 %. At this respective stage, procedures 2 to 4 were designed to allow derivatisation to occur. However, procedures 1 and 5 required further reactions to occur before derivatisation.

Procedures 2 to 4 involved the use of brominated compounds or chlorinated compounds to cyclise the pendant group of the thiophene derivative. Procedures 2 and 3 involved the attempted synthesis of dimethyl-3,4-ethylenedioxythiophene dicarboxylate (**4**) by the use of 1,2-dichloroethane and 1,2-dibromoethane, respectively. Procedure 4 was an attempt at synthesising diethyl-3.4-ethylenedioxythiophene dicarboxylate (**14**), with 1,2-dibromoethane. The reaction described in procedure 3, utilising 1,2-dibromoethane and triethylamine, produced a sample of the desired product (**14**) for analysis. No viable product was formed from the reaction with 1,2-dichloroethane. Using a combination of steps from procedures 2, 3 and 4, successful synthesis of diethyl-3,4-ethylenedioxythiophene dicarboxylate (**14**) was repeatedly achieved in high yields of up to 85 %. The synthetic route involved the reaction of the diethyl ester (procedure 4) with a dibromo compound (procedures 2 and 3).

Due to the much greater yields obtained following the diethyl ester routes, procedures 1 to 3 were abandoned. Focus was put into procedures 4 and 5. Using procedure 4, derivatisation occurred during the reaction of diethyl 3,4-dihydroxythiophene dicarboxylate (**13**) (step three of five). Using procedure 5 gave derivatisation as the final step in a reaction with 3,4-dimethoxythiophene (**6**).

The basic hydrolysis of the diethyl esters depicted from procedures 4 and 5 gave 3,4-ethylenedioxythiophene dicarboxylic acid (**10**) and 3,4-dimethoxythiophene dicarboxylic acid (**5**) in yields of 50 % and 80 % respectively.

The final stage was decarboxylation of the thiophenyl compounds. The methods used differed with respect to the solvent used, DMF for procedure 4 and quinoline for procedure 5. The removal of the DMF proved difficult because EDOT (**7**) has similar boiling point as DMF. The method chosen for removal was vacuum centrifugation. However, much of the EDOT (**7**) product was also removed. The use of quinoline required vacuum distillation. The products were extracted from the distillate, washed and concentrated. Quinoline was used in further reactions due to the reliability of its separation from the reaction products.

Derivatisation from diethyl-3,4-dihdroxythiophene dicarboxylate (**13**) was attempted *via* the use of dibromo compounds. Of the targeted cyclic compounds described in Figure 2.2, **b** was crudely synthesised. This synthesis gave compounds that could be analysed in a crude mixture during LC-MS with two peaks being close to each other, with a m/z ratio which equated to a mass of 2M+Na. Many attempts were made to separate the desired fractions using flash chromatography. However, the material could not be separated by the use of the common chromatography solvents, and mixtures thereof. The next reaction involved the use of the crude mixture. This was the hydrolysis of the ester and an attempt to isolate the dicarboxylic acid by precipitation from the aqueous medium by acidification of the disodium salt. Unfortunately, the pendant group which was attached in the previous step was cleaved giving the original diethyl 3,4-dihydroxythiophene dicarboxylate (**13**). The use of less protic solvents was attempted in addition to screening alternative bases, sodium hydroxide and lithium hydroxide, in an attempt to "soften" the hydrolysis approach, but to no avail. Either cleavage of the group occurred or no reaction resulted.

As discussed previously, the step prior to derivatisation in procedure 5 was to cleave the carboxylic acid groups from the 3,4-dimethoxythiophene dicarboxylic acid (**5**), in quinoline, catalysed by copper chromite. Work up followed, as discussed, to retrieve the desired product (**6**) in high yields, up to 83 %. It is at this stage that derivatisation can begin. Unlike procedure 4, use of this method involves dihydroxy compounds, catalysed with *p*-toluenesulphonic acid. It was decided that attention should be given to coupling the dioxythiophene with 2-methyl-1,4-butanediol and with 2,3-dimethyl-1,4-butanediol to create two respective derivatives. This would give a basis for investigating the difference in the ultimate electrical resistance of the eventually produced polymer films. Investigations into different physical properties for example, flexibility and electrical resistance and these could be correlated to the inclusion of an extra methyl group of the "ethylenedioxy bridge" derviative.

The synthesis of the derivative with a single methyl group, see Scheme 2.10 **c**, was attempted and the product was detectable *via* LC-MS, as a peak with a m/z ratio of 2M+Na, but a sample could not be separated reliably. The synthesis of the derivative with two methyl groups, Scheme 2.10 **d**, was attempted. No evidence of its presence was found. This synthesis of this derivative was attempted using a diol that had to be reduced from 3,4-dimethyl succinic acid *via* reduction with lithium aluminium hydride.

Separation of these products was difficult and ultimately, unsuccessful. The materials could be separated using LC-MS as for the last portion of analysis, the solvent becomes 100 % methanol which allowed the compounds to move through the column. More, varied attempts at separation would need to be part of future work. Despite difficulty of purification and unsuccessful syntheses of some monomers, with more time and a logical approach of varying concentrations of reagents and catalysts and reaction temperatures and solvents, the optimum reaction conditions would be discovered.

2.6 Conclusions

Various synthesis routes towards 3,4-ethylenedioxythiophene (**7**) and its derivatives were investigated. All of these routes involved protecting the 2 position and the 5 position of the thiophene ring with either a methyl ester or an ethyl ester by firstly synthesising either dimethyl thiodiglycolate (**2**) or diethyl thiodiglycolate (**12**). Diethyl thiodiglycolate (**12**) was synthesised at much greater yields (94 %) than was dimethyl thiodiglycolate (**2**) (36 %).

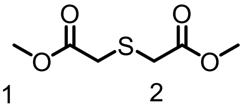
The diethyl ester route is the preferred route when cyclising a thiodiglycolate to create the thiophene ring as the yield of the cyclised product was 69 % while the dimethyl equivalent was only 10 %. This is a stage at which derivatisation could occur, with diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**). It would be advantageous to use the diethyl ester route due to the yields being greater than those achieved using the dimethyl compounds.

The two potential derivatisation routes differ in that one, procedure 4, allows coupling of a pendant group onto diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**) *via* coupling with a dihalide compound. The second, procedure 5, produces diethyl-3,4-dimethoxythiophene-2,5-dicaboxylate (**15**) to continue along a pathway of removing the groups at the 2 and 5 positions of the thiophene to end with a derivatisation step *via* coupling with dihydroxy compounds.

Two novel derivatives of EDOT (**7**) have been synthesised, one from each derivatisation method discussed, and have been identified *via* LC-MS analysis, further purification and isolation has not yet been achieved. The high polarity of the compounds make them difficult to separate using standard flash chromatography. Further work at separation is needed. The derivative formed from the coupling with the dibromo compound could not undergo the process of hydrolysis of the ester. The newly coupled compound was cleaved despite the various conditions used, though there are more conditions to consider for the successful synthesis.

2.7 Experimental

2.7.1 Dimethyl thiodiglycolate (2) [1]



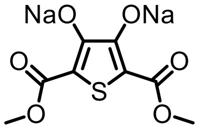
A

Sodium dihydrogen phosphate (2.014 g, 12.9 mmol) was dissolved in water (9.5 mL). The solution was adjusted to pH 6 with aqueous sodium hydroxide (10 wt. %) and then heated (33 °C). An aqueous solution of tributylmethylammonium chloride (1.268 g, 4.0 mmol) and methyl chloroacetate (4.453 g, 41.0 mmol) was added to the phosphate solution. An aqueous solution of sodium sulphide (1M, 56 mL) and methyl chloroacetate (20.202 g, 186.0 mmol) were added over 2 hrs at 33 °C. Aqueous sodium sulphide (1M, 11 mL) was added, at 33 °C, and the mixture stirred for 1 hr. Extraction into toluene (17 mL) followed and the solution was concentrated to give the desired product (**2,** 10.771 g, 60.4 mmol, 36 % yield). Found C, 40.50; H, 5.65; S, 18.25 %, $C_6H_{10}SO_4$ requires C, 40.5; H, 5.6; S, 18 %. ^{1}H NMR δ_H (500 MHz, DMSO), 3.48 (4H, s, H-1), 3.65 (6H, s, H-2). ^{13}C NMR δ_C (125 MHz, DMSO), 33.2, 52.1, 170.0.98.

B

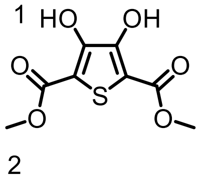
Thiodiglycolic acid (**8**, 4.998 g, 33.3 mmol) was dissolved in methanol (20 mL, 494.9 mmol). Concentrated sulphuric acid (5.7 mL, 106.9 mmol) was added with continuous stirring and then refluxed for 17 hrs. The mixture was poured into water (30 mL) extracted with diethyl ether (20 mL) and concentrated to provide the desired compound (**2**, 1.014 g, 5.7 mmol, 17 % yield). ^{1}H NMR δ_H (500 MHz, DMSO), 3.48 (4H, s, H-1), 3.65 (6H, s, H-2). Found C, 39.45; H, 5.50; S, 18.35 %, $C_6H_{10}SO_4$ requires C, 40.5; H, 5.6; S, 18 %.

2.7.2 Synthesis of disodium dimethyl-3,4-dioxythiophene-2,5-dicarboxylate (3) [2]



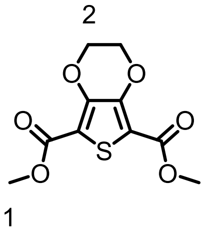
Dimethyl thiodiglycolate (**2**, 1.014 g, 5.7 mmol) and dimethyl oxalate (1.291 g, 8.8 mmol) in methanol (6 mL) were added to sodium methoxide (1.995 g, 36.9 mmol) in methanol (9 mL) and refluxed for 1 hr to form a yellow suspension. The suspension was filtered, washed with methanol (2 x 5 mL) and dried in air to give the disodium salt of the desired compound (**3**, 1.465 g, 5.3 mmol). Analysis completed after further protonation in **2.7.3**.

2.7.3 Synthesis of dimethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (11) [2]



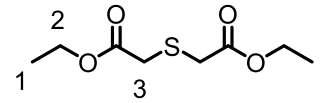
A solution of dimethyl thiodiglycolate (**2,** 1.014 g, 5.7 mmol) and dimethyl oxalate (1.291 g, 8.8 mmol) in methanol (6 mL), was added to sodium methoxide (1.995 g, 36.9 mmol) in methanol (9 mL) and refluxed for 1 hr to form a yellow suspension. This was filtered and washed with methanol (2 x 5 mL) and dried to give the disodium salt (**3**) of the desired compound (1.465 g, 5.3 mmol). The salt (**3**, 0.501 g, 1.8 mmol) was added to sulphuric acid (2M, 10 mL) to produce a white precipitate that was filtered, washed with water (2 x 5 mL) and dried in air to give the desired product (**11**, 0.052 g, 0.2 mmol). Found C, 41.45; H, 3.45; S, 14.1 %, $C_8H_8SO_6$ requires C, 41.4; H, 3.4; S, 13.8 %. ^{1}H NMR δ_H (500 MHz, DMSO), 3.81 (6H, s, H-2), 10.40 (2H, s, H-1). ^{13}C NMR δ_C (75 MHz, DMSO), 52.0, 107.8, 150.0, 162.1.

2.7.4 Synthesis of dimethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (9) [4]



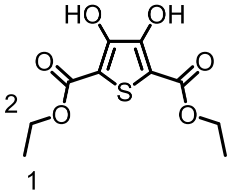
A mixture of dimethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (0.398 g, 1.7 mmol), N,N-dimethylformamide (6 mL), 1,2-dibromoethane (0.376 g, 2.0 mmol) and triethylamine (0.469 g, 4.6 mmol) was heated at 95 °C for 24 hrs. The mixture was poured into diethyl ether (15 mL) and white needles of triethylamine hydrobromide salts were filtered and then rinsed with diethyl ether (10 mL). Water (20 mL) was added and the product was extracted with diethyl ether (20 mL). Once the diethyl ether had evaporated, the insolubles were filtered. This mixture was separated using flash chromatography on a 50:50 mix of petroleum ether 40-60 °C and ethyl acetate to give one fraction and flushing with methanol to provide a second fraction. ^{1}H NMR δ_H (500 MHz, DMSO), 3.153 (6H, s, H-1), 4.035 (4H, s, H-2).

2.7.5 Synthesis of diethylthiodiglycolate (12) [7]



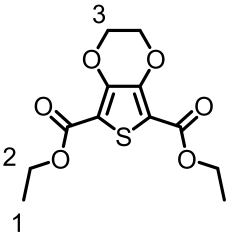
Concentrated sulphuric acid (16 mL) was added to thiodiglycolic acid (**8**, 40.001 g, 266 mmol) in ethanol (120 mL) and the mixture was refluxed overnight. Once cool, the solution was added to water (350 mL) and extracted with diethyl ether (3 x 50 mL) then washed with brine (15 mL) before being dried with magnesium sulphate and concentrated to give a colourless oil (**12**, 51.614 g, 250 mmol, 94 %). ^{1}H NMR δ_H (500 MHz, $CDCl_3$), 1.25 (6H, t, J = 7, H-1), 3.34 (4H, s, H-3), 4.16 (4H, q, J = 7, H-2).

2.7.6 Synthesis of diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (13) [5]



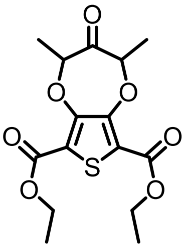
Diethyl thiodiglycolate (**12**, 51.614 g, 250 mmol) was added to diethyl oxalate (95.480 g, 653 mmol). The mix was added slowly to a cooled solution of sodium ethoxide (75.270 g, 1.11 mol), in ethanol (460 mL), and refluxed for 4 hrs and warmed at 60 °C overnight to produce a yellow precipitate. The precipitate was dissolved in water and acidified with hydrochloric acid to give a white precipitate. This was filtered and dried to give a white solid (**13**, 45.076 g, 173 mmol, 69 %). ^{1}H NMR δ_H (500 MHz, CD_3OD), 1.40 (6H, t, J = 7.5, H-1), 4.39 (4H, q, J = 7, H-2).

2.7.7 Synthesis of diethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (14) [7]



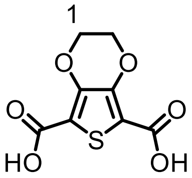
Diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**, 4.014 g, 15.4 mmol) was added to DMF (64 mL) with triethylamine (3.22 mL) and refluxed for 24 hours. The crude mixture was poured into water (50 mL) and extracted with diethyl ether (3 x 35 mL), washed and dried with magnesium sulphate to give the product (**14**, 3.850 g, 13.4 mmol, 88 %). ^{1}H NMR δ_H (500 MHz, $CDCl_3$), 1.38 (6H, t, *J* = 7, H-1), 4.35 (4H, q, *J* = 7.5, H-2), 4.40 (4H, s, H-3).

2.7.8 Attempted synthesis of diethyl 2,4-dimetyl-3-oxo-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine-6,8-dicarboxylate



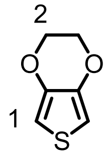
Diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**, 0.535 g, 1.56 mmol) and triethylamine (0.45 mL, 0.59 g) were added to dry DMF (20 mL). 2,4-Dibromo-3-pentanone (0.752 g, 3.08 mmol) was subsequently added and the mixture was heated at 95 °C for 2 days. When cool, the mixture was poured into water and extracted with diethyl ether, washed with brine and concentrated, as **2.7.8**, to give the crude reaction mixture.

2.7.9 Synthesis of diethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylic acid (10) [4]



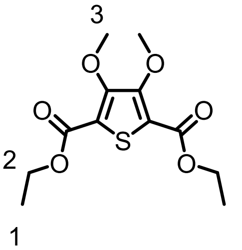
Diethyl-3,4-ethylenedioxythiophene-2,5-dicarboxylate (**14**, 0.250 g, 0.873 mmol) was added to an aqueous solution of sodium hydroxide (0.098 g in 8 mL) and refluxed overnight. The solution was acidified with concentrated hydrochloric acid slowly to produce a brown precipitate of the product (**14**, 0.037 g, 0.161 mmol, 47 %). ^{1}H NMR δ_H (500 MHz, DMSO), 4.36 (4H, s, H-1).

2.7.10 Synthesis of 3,4-ethylenedioxythiophene (7) [4]



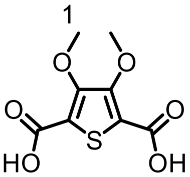
3,4-Ethylenedioxythiophene-2,5-dicarboxylic acid (**10**, 2.210 g, 9.60 mmol) was refluxed in DMF (50 mL) with copper chromite catalyst (2.094 g) overnight under N_2. Unsuccessful attempts were made to separate the product from the solvent leaving trace amounts for analysis. ^{1}H NMR δ_H (500 MHz, DMSO), 4.18 (4H, s, H-2), 6.56 (4H, H-1).

2.7.11 Synthesis of diethyl-3,4-dimethoxythiophene-2,5-dicarboxylate (15) [2]



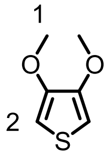
Freshly distilled dimethyl sulphate (50 mL) was added to diethyl-3,4-dihydroxythiophene-2,5-dicarboxylate (**13**, 44.904 g, 173 mmol) and potassium carbonate (63.133 g) in dry DMF (500 mL). The mixture was heated at 160 °C for 2 days. Once cool, the product was poured into water (300 mL) and extracted with ethyl acetate, then concentrated to give the product (**15**, 28.336 g, 98.3 mmol, 57 %). ^{1}H NMR δ_H (500 MHz, CD_3OD), 1.25 (6H, t, *J* = 7 H-1), 2.03 (4H, q, *J* = 7.5 H-2), 4.21 (6H, s, H-3).

2.7.12 Synthesis of diethyl-3,4-dimethoxythiophene-2,5-dicarboxylic acid (5) [2]



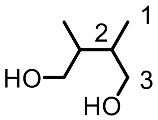
Diethyl-3,4-dimethoxythiophene-2,5-dicarboxylate (**15**, 26.516 g, 92.0 mmol) was added to sodium hydroxide (14.580 g) in water (400 mL) and refluxed overnight. Once cool, the solution was acidified with concentrated hydrochloric acid to precipitate the product (17.186 g, 74.0 mmol, 80 %). ^{1}H NMR δ_H (500 MHz, CD_3OD), 3.86 (6H, s, H-1).

2.7.13 Synthesis of 3,4-dimethoxythiophene (6) [3]



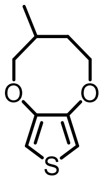
3,4-Dimethoxythiophene-2,5-dicarboxylic acid (**5**, 8.825 g, 38.0 mmol) and copper chromite catalyst (0.705 g) were added to quinoline (45 mL) and heated under N_2, at 160 °C for 2 days. Once cool, the mixture was vacuum distilled. The distillate was extracted with ethyl acetate, washed with dilute hydrochloric acid and dried with sodium sulphate to give 3,4-dimethoxythiophene (4.543 g, 83 %). ^{1}H NMR δ_H (500 MHz, CD_3OD), 3.70 (6H, s, H-1), 6.24 (2H, s, H-2).

2.7.14 Synthesis of 2,3-dimethyl-1,4-butandiol [9]



Lithium aluminium hydride (2.6215 g) was added slowly to a cooled solution of 2,3-dimethyl-1,4-butandioic acid (1.0356 g, 7.09 mmol) in dry tetrahydrofuran (50 mL) in flame dried glassware under N_2. The mixture was allowed to reach room temperature and stirred. The mixture was quenched with methanol, added to water (100 mL) then concentrated hydrochloric acid was added dropwise to dissolve the precipitate. The product was extracted with ethyl acetate (3 x 25 mL) and dried to give the target diol (0.4650 g, 3.93 mmol, 56 %). ^{1}H NMR δ_H (500 MHz, $CDCl_3$), 0.85 (6H, m, H-1), 1.75 (4H, m, H-2), 3.50 (4H, m, H-3).

2.7.15 Attempted synthesis of 3-methyl-2,3,4,5-tetrahydrothieno[3,4-*b*][1,4]dioxocine



3,4-Dimethoxythiophene (**6**, 0.539 g, 3.74 mmol), *p*-toluenesulphonic acid (87.1 mg) and 2-methyl-1,4-butanediol (0.5 mL, 0.496 g, 4.76 mmol) were heated in dry toluene (10 mL) at 80 °C for 48 hrs under N_2. Attempts were made to separate and analyse the mixture. LC-MS identified one fraction with the expected mass peak but this could not be separated *via* flash chromatography. ESI-MS found *m/z* 391.10 $[2M+Na]^+$.

2.8 References

1. Lars, R., et al., *Process for preparing dialkyl thiodiglycolates* 2009. p. 4.
2. Fager, E., *Some derivatives of 3,4-dioxythiophene.* Journal of the American Chemical Society, 1945. **67**(12): p. 2217-2218.
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Chapter Three

Application of an aqueous PEDOT:PSS dispersion to a woven cotton fabric substrate

3.1 Experimental design

This experiment was designed to observe the effect of increasing the amount of PEDOT:PSS on the surface of a textile fabric by way of applying multiple layers. From previous investigation, it was noted that the sample of PEDOT:PSS, purchased from Heraeus Holding GmbH as Clevios FT, to be tested had high water content and when applied to cotton fabric, much of the sample simply ran through the cotton fabric to the substrate behind.

It was hypothesised that as the layers increase, the pores throughout the cotton fabric substrate should effectively get blocked, thus increasing the retention of the amount of PEDOT:PSS on the cotton fabric. As the number of layers increases and the amount of PEDOT:PSS increases, it is expected that the conductivity will increase.

The coated samples had conductivity tested by measuring the electrical resistance using two single point probes over a distance of 10 mm. Crease resistance was analysed by folding and placing under a 5 kg weight and the same analyses were carried out. These samples were observed using a digital 3D microscope to aid description of the conductivity results.

A 1 wt. % aqueous dispersion of PEDOT:PSS was applied to the cotton fabric *via* the use of a K-bar 4. The general technique for application with K-bar is to place the ink at the top of the substrate, then draw the ink forwards using a K-bar 4.

3.2 Sample preparation

3.2.1 Application of PEDOT:PSS to a cotton fabric substrate

15 pieces of cotton were cut from the same part of the fabric sample. They were each applied to the K-bar base and pulled tight to prevent any creases having an effect on the application. The aqueous PEDOT:PSS dispersion (0.1 mL) was applied to the cotton fabric, and a path of polymer dispersion was created, see Figure 3.1. Although a small volume was used, a residue was left on the backing base due to the limited absorption capacity, and the porous nature, of the cotton fabric, see Figure 3.2.

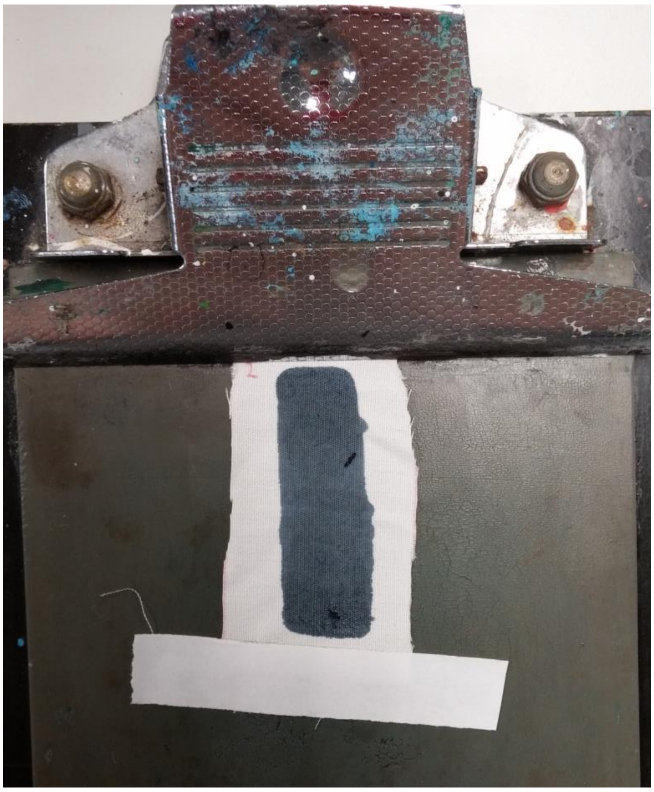


Figure 3.1 Single layer of PEDOT:PSS on cotton

Figure 3.2 Residue remaining after single layer application

The first sample, top left, see Figure 3.3, had 0.5 mL aqueous PEDOT:PSS dispersion applied but this volume was too large, the substrate became saturated and coating uncontrollable, so it is being dried to assess quality alongside this study.

Figure 3.3 Layer 1 before drying. Top row left to right, samples 1-5. Middle row left to right, samples 6-10 and bottom row left to right, samples 11-15

The second layer was applied to samples 2-5, 7-10 and 12-15 and dried, see Figure 3.4. There was a residue remaining after the second application also, see Figure 3.5.

The third layer was applied similarly to the second, but only to samples 3-5, 8-10 and 13-15. It would appear that after two layers, the surface is no longer porous as there is no residue remaining on the plate, see Figure 3.6. This will be investigated with 3D microscopy.

Layer four was applied to samples, 4, 5, 9, 10, 14, 15, see Figure 3.7 and again there was no residue remaining on the base.

Finally layer five was applied only to samples 5, 10 and 15 and left no residue on the backing substrate; see Figure 3.8.

Figure 3.4 Dried second layer applied to samples 2-5, 7-10 and 12-15

Figure 3.5 Slight residue remaining after the application of second layer

Figure 3.6 Third layer applied to samples 3-5, 8-10 and 13-15

Figure 3.7 Fourth layer applied to samples 4, 5, 9, 10, 14 and 15

Figure 3.8 Layer five applied to samples 5, 10 and 15

3.2.2 Creasing samples

In order to assess the crease resistance of PEDOT:PSS, the difference in electrical resistance prior to creasing was compared to that of post-creasing. Electrically conductive polymers can be brittle because of their chemical nature, the conjugated backbone; the application to flexible substrates improves the brittleness but to what degree is not known, it is dependent on many factors including the nature of the substrate that is used and the amount of polymer applied [1-3].

The polymer was applied in the same direction on all samples, this direction will be referred to as the y-axis and the x-axis is perpendicular to this. The first resistance measurements were taken along the application direction, the y-axis. The samples were then folded over the x-axis and then over the y-axis and placed beneath a 5 kg weight for 3 hours to induce a crease, see Figure 3.9.

Figure 3.9 Image of all 15 samples with the creases set

3.2.3 Wash testing

The fabric specimens were washed according to BS EN ISO 6330:2012 using an AEG LAVAMAT 50720 with 500 g of clean ballast and 20 g of the reference detergent (James Heal, Batch CPC6047). The wash sequence was as follows: wash cycle for 15 mins, 3 x rinse for 3 mins, a final rinse for 2 mins and spin for 5 mins. The ballast and fabric samples were dried in a tumble dryer for 30 mins.

3.3 Results and discussion

3.3.1 Thermogravimetric analysis (TGA)

It can be seen from Figure 3.10 that an instant, gradual mass loss occurred until around 270 °C at which point there is a large decrease in gradient which shows a higher rate of degradation over temperature. This analysis shows that the polymer mixture of PEDOT:PSS is stable over the working temperature range envisioned for textile garments.

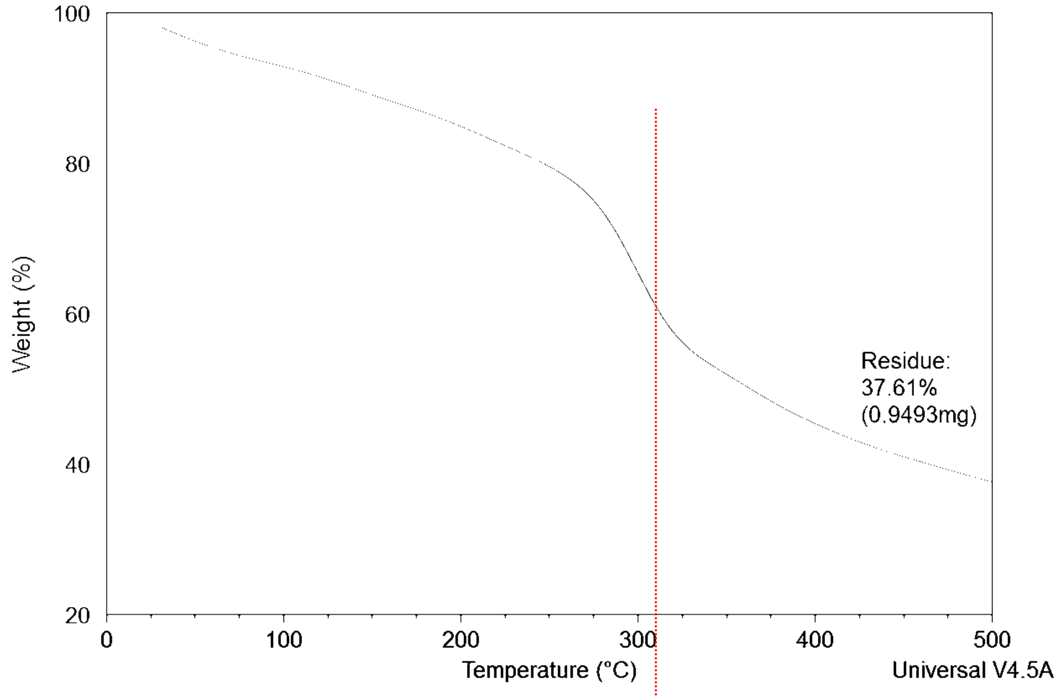


Figure 3.10 TGA of PEDOT:PSS showing degradation over increasing temperature

3.3.2 Differential Scanning Calorimetry (DSC)

The DSC shows three points of interest which have been labelled in Figure 3.11. Point 1 shows an endothermic region which can be related to the water being released from the polymer film. There are two more endothermic regions, 2 and 3, which are due to the two polymers, PEDOT and PSS beginning to change, possibly melting.

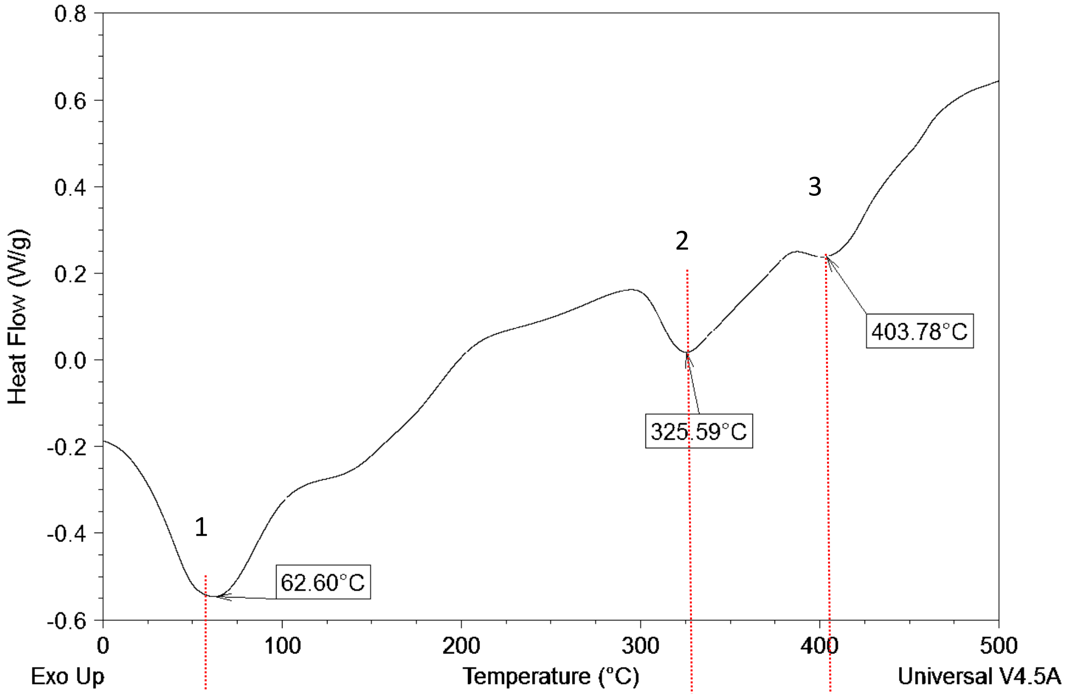


Figure 3.11 DSC of PEDOT:PSS showing heat flow with respect to temperature

3.3.3 Electrical resistance of coated cotton fabric

The masses of each cotton sample were recorded before the PEDOT:PSS dispersion was applied and then recorded when all of the layers had been applied and the composite dried. The resistance was then measured in the direction of polymer application, described previously, over 10 mm. These data are given in Table 3.1.

The electrical resistance of these samples were measured over a distance of 10 mm which strictly gives a unit of measurement as Ω cm^{-1}. Figure 3.12 is a graphical representation of the initial resistance data from the PEDOT:PSS coated cotton fabric. Figure 3.12 **A** shows the rapid decrease in electrical resistance as the mass of polymer on the cotton fabric increases, to what appears to be a minimum *ca.* 300 Ω cm^{-1}. Figure 3.12 **B** displays the data as averages with respect to the mean mass of PEDOT:PSS dispersion applied per layer. One can compare the values given with those from sample 1; this was the sample which had 5 times as much PEDOT:PSS dispersion applied as a single application, 0.5 mL compared to 0.1 mL for each application on samples 2-15. The polymer dispersion spread out across the cotton fabric with less selectivity as to where the polymer would be located on the cotton fabric. The point to note is that there is 8.9 mg of polymer deposited on sample 1 yet sample 1 had the highest resistance of all of the samples in the set, so many smaller applications of polymer are more beneficial to one larger application.

Figure 3.13 shows the reduction of electrical resistance with respect to the mass of polymer ultimately applied to the sample. It is clear to see that samples with one application of the PEDOT:PSS dispersion have high resistances compared to those with more layers. This relationship was expected as Knittel *et al*. reported that they found that layers of PEDOT of less than 2 wt. % had much higher surface resistivities than layers of 3-4 wt. %, which gave much higher conductive textiles [1]. The reason layer one has a lower value is that during application, much of the polymer dispersion passed through the substrate hence not providing subsequent coverage of the cotton fabric, to increase conductivity. This was noted in the Sample Preparation (**3.1**) section previously. The application of the second layer left considerably less residue than the first and the third, fourth and fifth layers left no residue.

Table 3.1 Amount of polymer (PEDOT:PSS) applied to cotton substrates. Single layered samples are # 1, 6 and 11. Double layered samples are # 2, 7 and 12. Triple layered samples are # 3, 8 and 13. 4 layered samples are # 4, 9 and 14. 5 layered samples are # 5, 10 and 15. As noted previously, sample 1 had 0.5 mL aqueous dispersion of PEDOT:PSS applied while all the others received 0.1 mL per application.

#	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Mass Cotton, g	0.2529	0.2292	0.214	0.2425	0.2563	0.2722	0.2579	0.2198	0.2355	0.2683
Total Mass, g	0.2618	0.2338	0.2194	0.2525	0.2664	0.2741	0.2609	0.2247	0.2452	0.282
Mass Polymer, g	0.0089	0.0046	0.0054	0.01	0.0101	0.0019	0.003	0.0049	0.0097	0.0137
Resistance, Ω cm^{-1}	20000	2000	1100	550	500	10000	1000	700	300	300

#	**11**	**12**	**13**	**14**	**15**
Mass Cotton, g	0.3037	0.2891	0.2426	0.268	0.3189
Total Mass, g	0.3048	0.2933	0.2503	0.2791	0.334
Mass Polymer, g	0.0011	0.0042	0.0077	0.0111	0.0151
Resistance, Ω cm^{-1}	8000	900	900	400	350

Layers	**1**	**2**	**3**	**4**	**5**
Samples	1, 6, 11	2, 7, 12	3, 8, 13	4, 9, 14	5, 10, 15

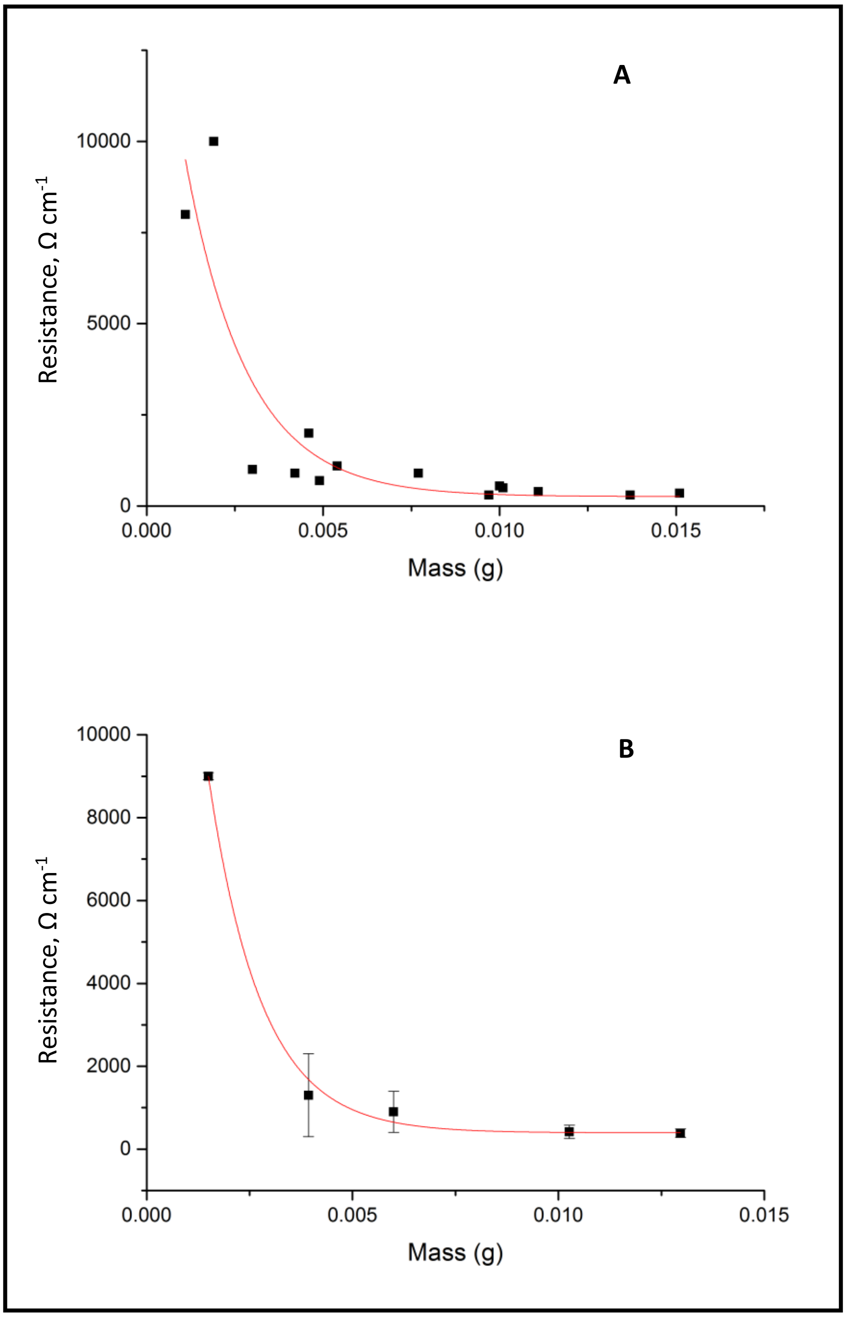


Figure 3.12 The top plot shows the trend that as the total mass of polymer applied to the cotton fabric increases, the resistance decreases while the bottom plot shows the average masses of each layer of PEDOT:PSS applied and their corresponding average resistance; layers 1 to 5 are the points left to right

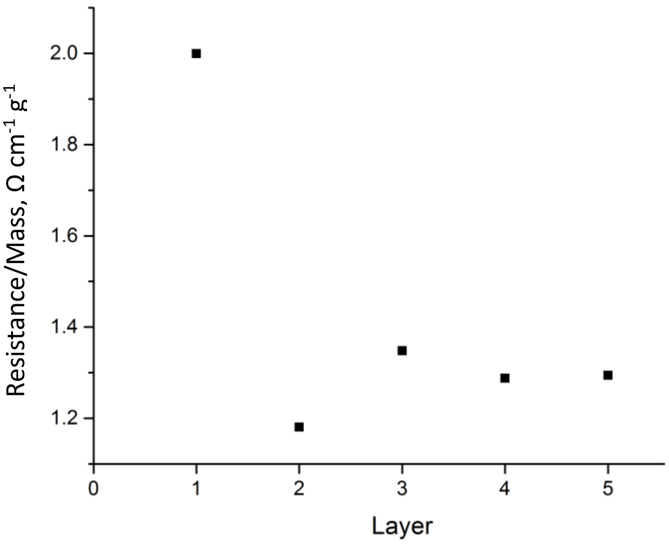


Figure 3.13 The relationship demonstrating that after the application of the first layer, the electrical resistance of the fabrics decreases at a constant rate with increasing applications of PEDOT:PSS

3.3.4 Topology of non-creased PEDOT:PSS coated cotton

3D microscopy was carried out on all of the samples to investigate the layer build up and proposed void filling of the PEDOT:PSS on the cotton substrate.

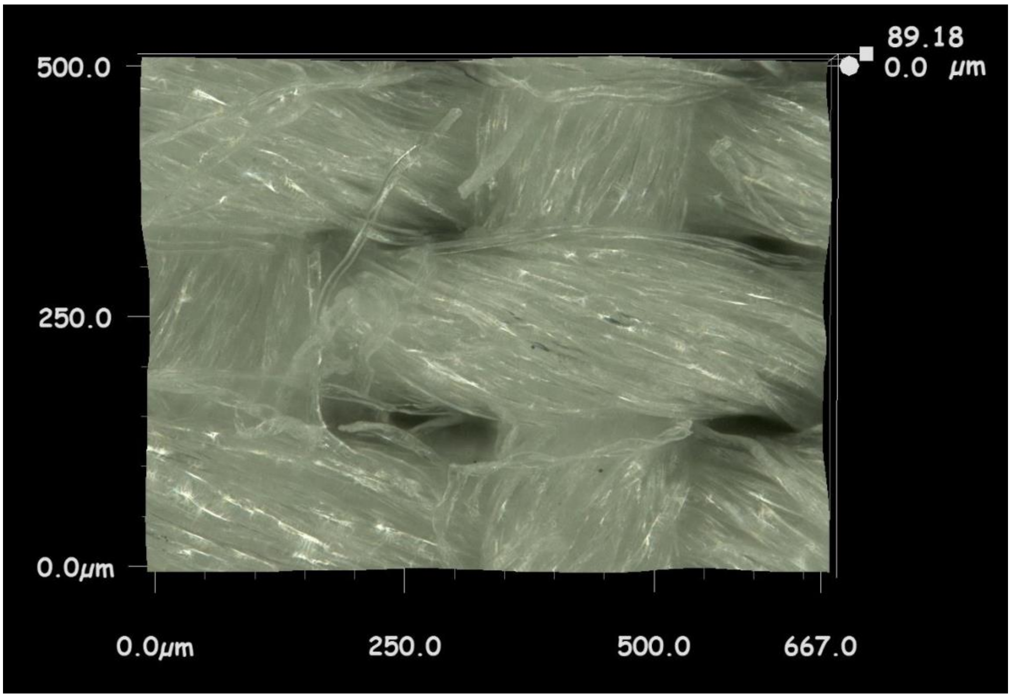


Figure 3.14 3D microscope image of the untreated cotton substrate at 500x magnification

Figure 3.14 shows the 3D microscope image of a sample of an untreated area of the cotton fabric. The cotton fabric is composed of woven threads of *ca*. 300 µm diameter which are further composed of smaller cotton fibres. Voids can be seen as the dark areas between adjacent cotton threads, regions through which a polymer dispersion could flow.

3.3.4.1 Single layer application of PEDOT:PSS

On application of the first layer, it was expected that the cotton fabric would swell and absorb the polymer dispersion since the cotton fabric is hydrophilic and the dispersion contained 99 % water. Figure 3.15 shows there was no coherent layer formation on the majority of the threads. It appears that there is a build up at the intersections between the warp and the weft regions of the substrate.

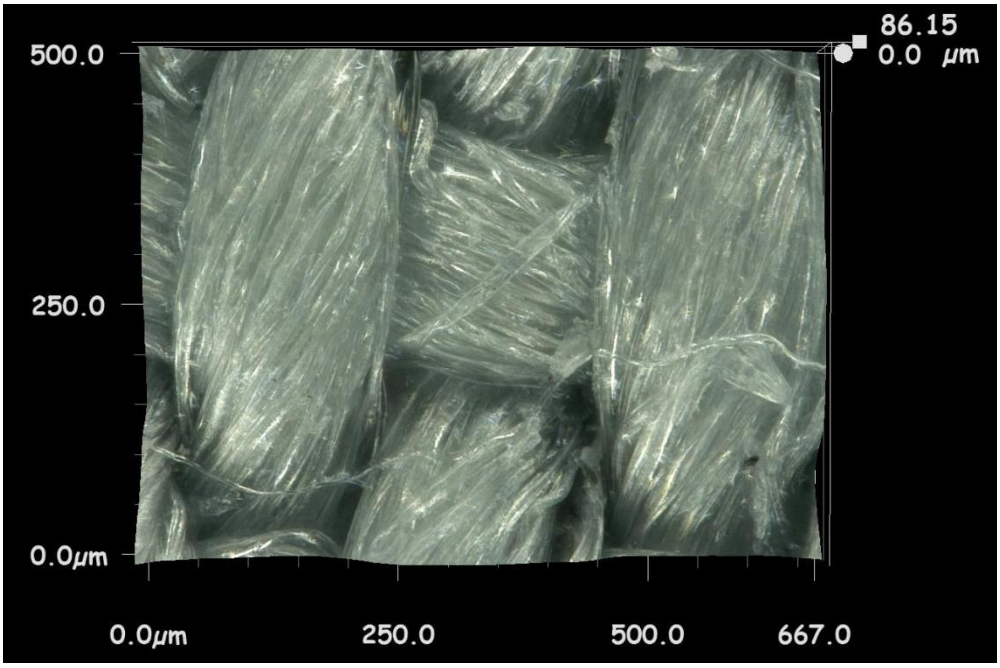


Figure 3.15 3D microscope image following the single application of PEDOT:PSS to the cotton substrate at 500x magnification

The coated fabric was then sectioned to investigate the cross section of the coated area, Figure 3.16. This image confirms that a homogenous layer formation on the surface of the threads had not yet been formed. In some regions of the fabric, a blue colour, characteristic of PEDOT:PSS can be seen.

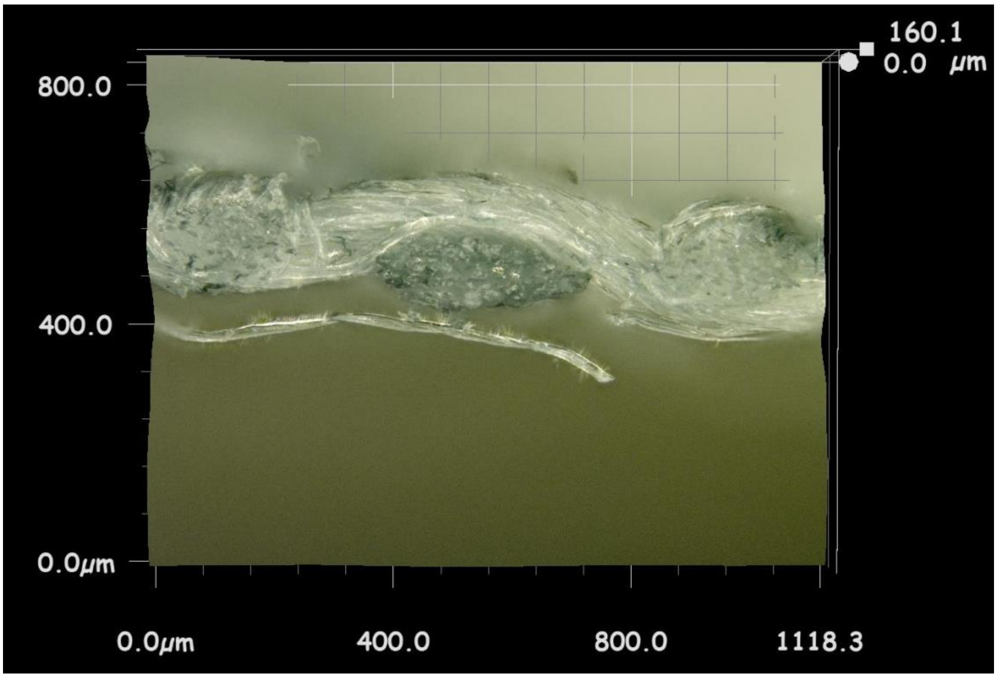


Figure 3.16 3D microscope image of a cross section following single application of PEDOT:PSS to the cotton substrate at 300x magnification

3.3.4.2 Second layer application of PEDOT:PSS

The second application showed a smaller amount of penetration on to the backing during K-bar application. This indicates that the polymer is building up at the intersections of the warp and weft threads. The appearance of the coated threads, Figure 3.17, is very similar to that given by first application, although the colour is slightly darker. This observation fits with the general trend, seen in Figure 3.8 that as the applications increase, the loading of PEDOT:PSS on the surface increases and consequently, the blue colour increases in intensity.

A 3D image was recorded of the cross section of this sample, see Figure 3.18. When compared with the cross section following the single application, Figure 3.16, a darker, blue colour is observable on the surface of the threads.

A blue “speck” was observed on the surface, Figure 3.19, which when investigated under the microscope, appeared to be a piece of precipitated polymer from the dispersion, over 1 mm long and 0.5 mm wide, on the surface of the cotton fabric substrate. The magnification is increased to show the interface of this ordered region with the rest of the coated substrate where it becomes more transparent to show the weave below. This particular bit of polymer will likely have a relatively higher electrical conductivity than the surrounding areas but due to its small area, measurements could not be made.

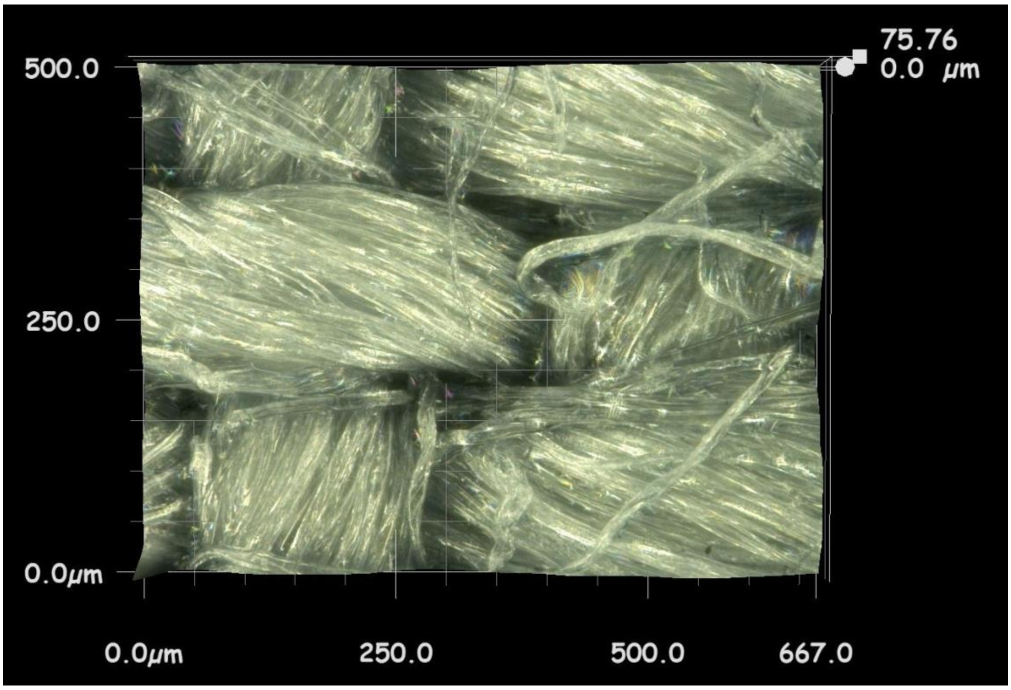


Figure 3.17 3D microscope image of a fabric sample following the second application of PEDOT:PSS to the cotton substrate at 500x magnification

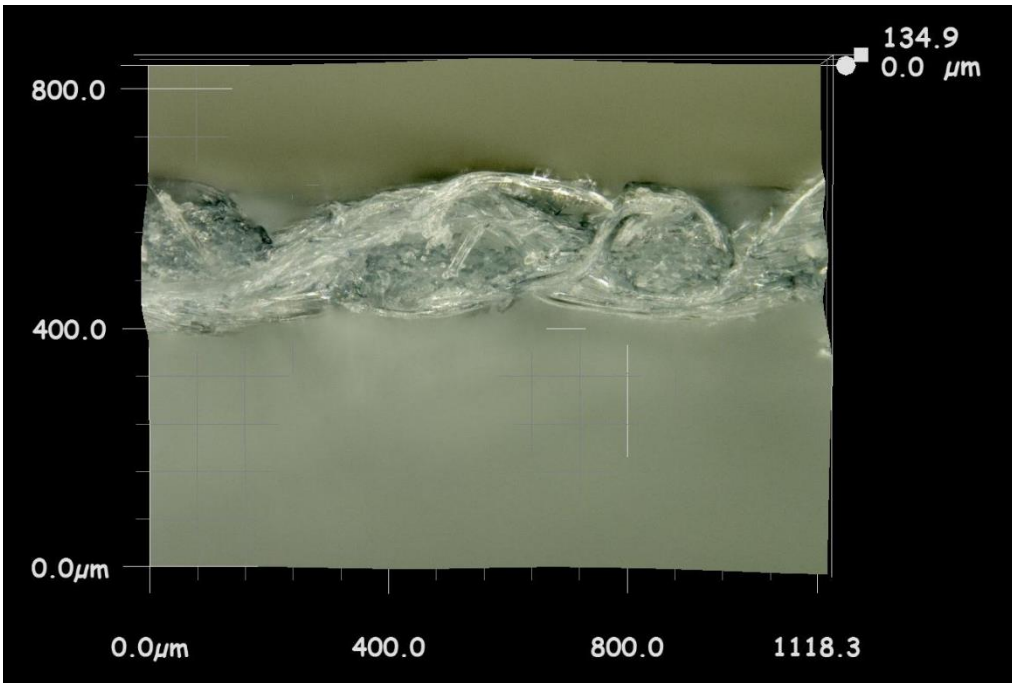


Figure 3.18 3D microscope image of a cross section of a fabric sample following the second application of PEDOT:PSS at 500x magnification

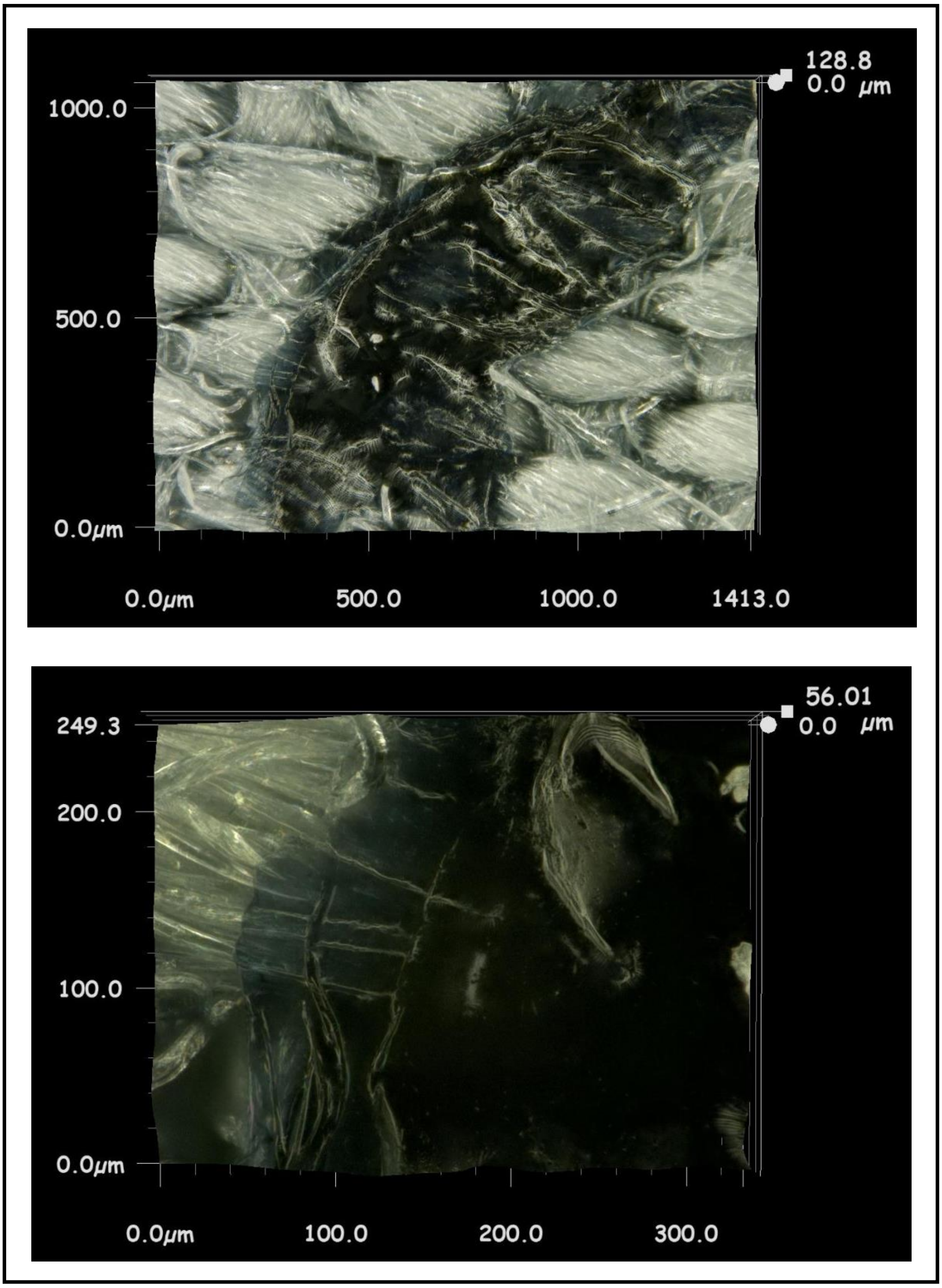


Figure 3.19 3D microscope images of a precipitated region of PEDOT:PSS on the surface of the cotton fabric substrate. Upper image at 250x and the lower image at 1000x magnification

3.3.4.3 Third layer application of PEDOT:PSS

The third application of the aqueous dispersion of PEDOT:PSS to the cotton fabric resulted in no residue remaining on the backing plate from the K-bar deposition. Thus the PEDOT:PSS is building up on the previous layers. Figure 3.20 shows the polymer build up where the warp and weft meet. The dark blue areas indicate that the PEDOT:PSS loading is increasing on the threads, visualised by the increasing intensity of the blue colour also.

Figure 3.21 is a 3D image of the cross section and fortunately, the cut has been made through a thread, the centre of this is white while the outsides are blue in colour, showing the build-up of PEDOT:PSS on the surface.

On the surface of the three layer sample are some specks of polymer, Figure 3.22 shows one of these, bottom right area, it is easy to see the level of polymer is much higher in this region than to the top left of the image due to the darker blue colour that can be seen.

Figure 3.23 shows the interface between the printed area and the non-printed area of the cotton substrate; left side has PEDOT:PSS applied. Comparing where the warp and weft meet, it can be seen that polymer is building up giving a darker colour in these areas while the untreated cotton has a lot lower contrast of these areas.

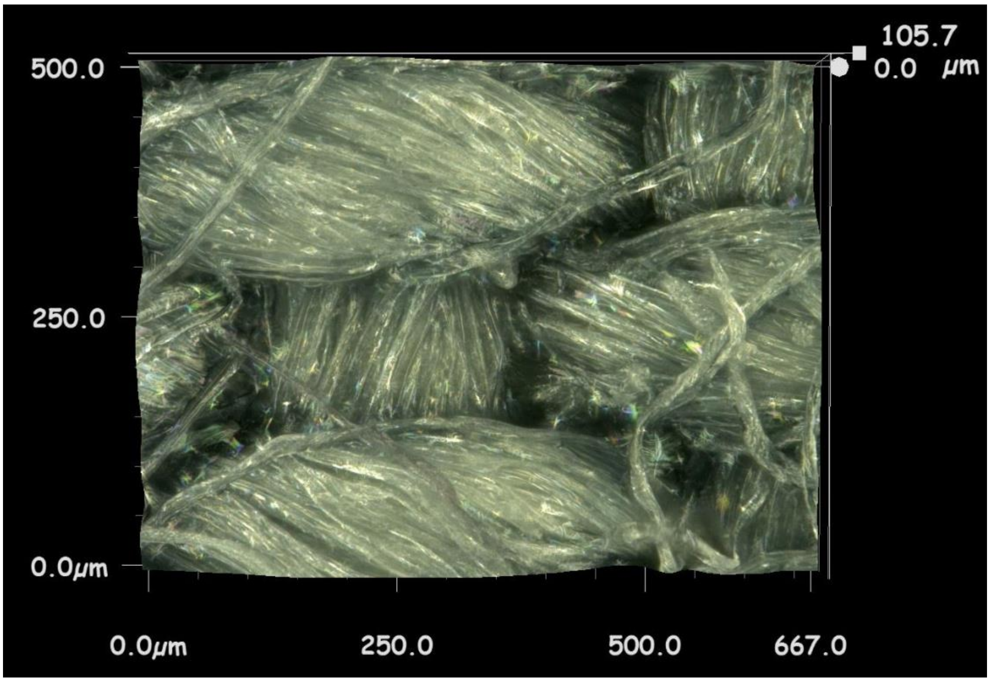


Figure 3.20 3D microscope image following the third application of PEDOT:PSS to the cotton fabric substrate and the build-up of polymer at the warp and weft junctions

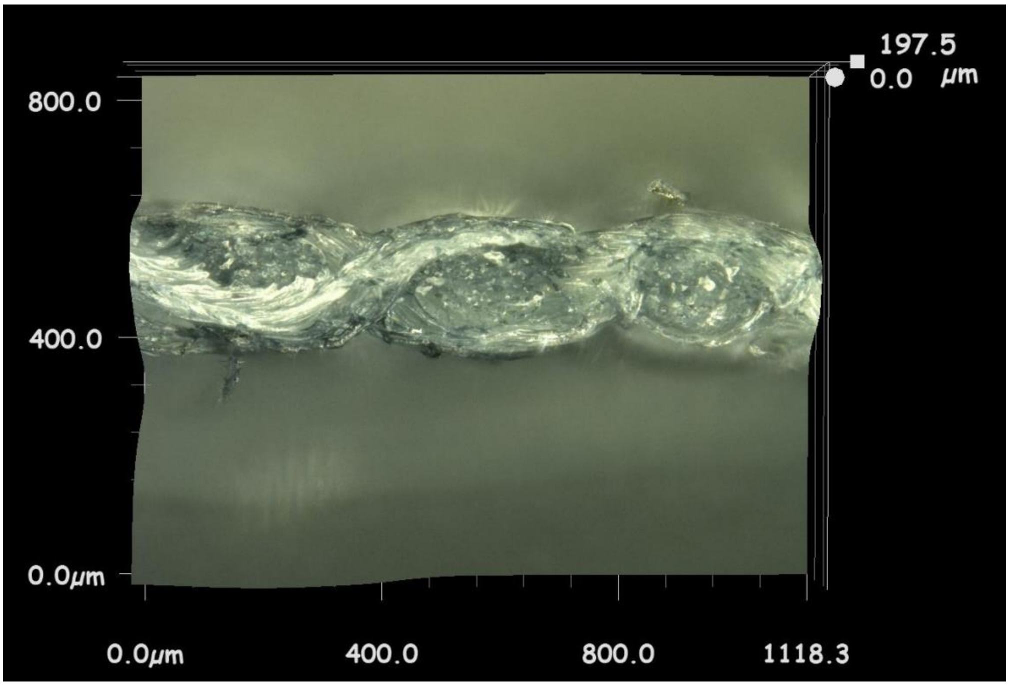


Figure 3.21 3D microscope image of a cross section following the third application of PEDOT:PSS to a cotton fabric sample

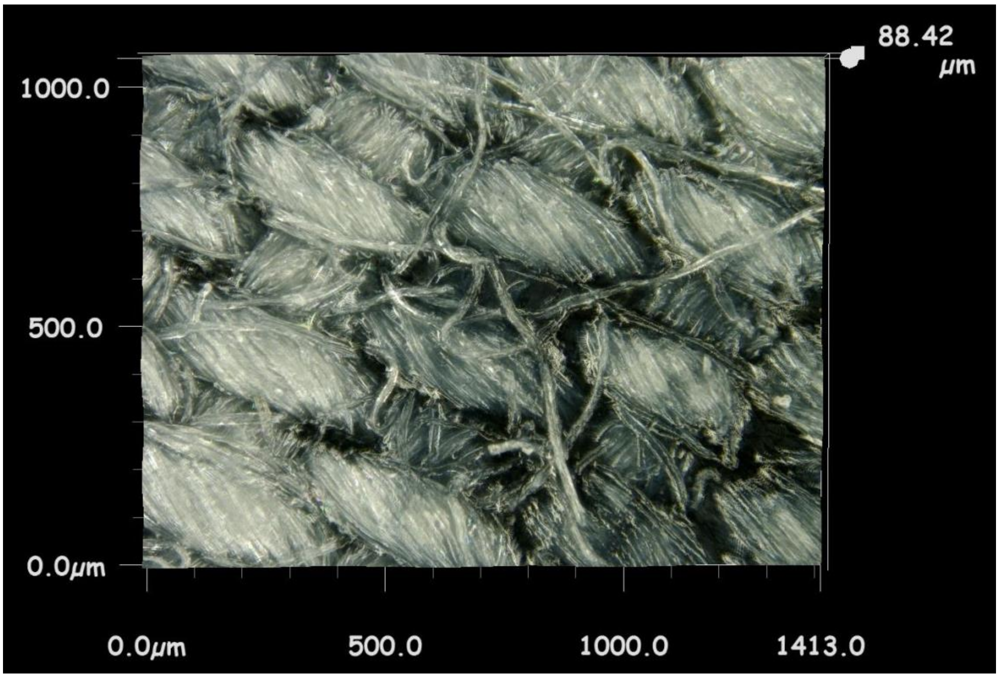


Figure 3.22 3D microscope image of a speck of polymer present on the surface of the cotton fabric following the application of the third layer of PEDOT:PSS at 250x magnification

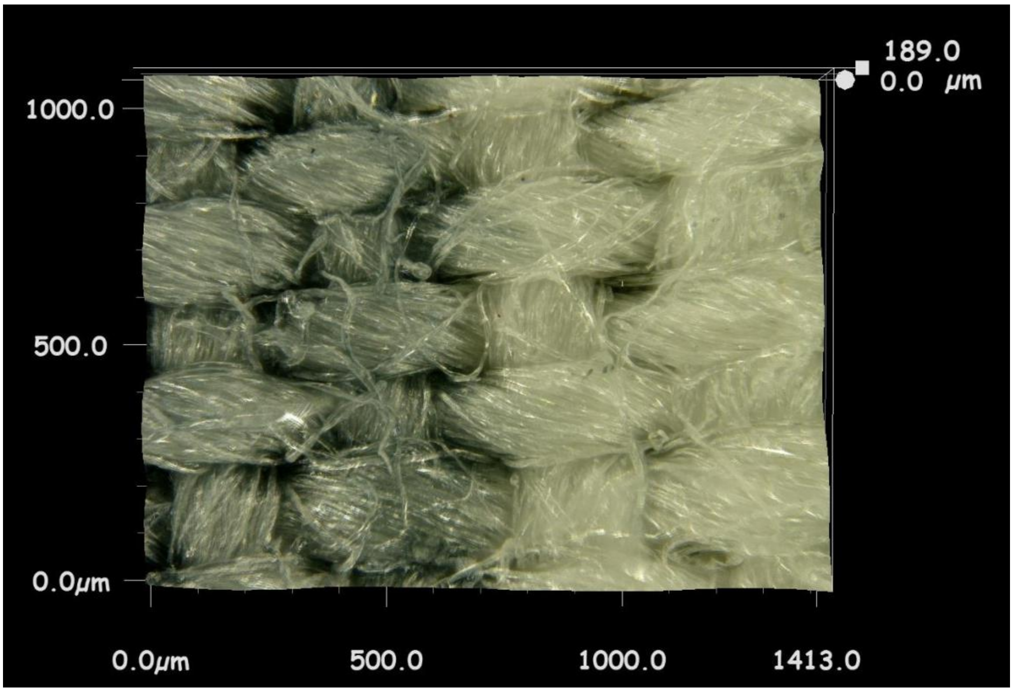


Figure 3.23 3D microscope image of the interface between three applications of PEDOT:PSS coated cotton fabric, left, and untreated cotton fabric, right, at 250x magnification

3.3.4.4 Fourth layer application of PEDOT:PSS

The cotton fabrics, after the fourth application of the aqueous dispersion of PEDOT:PSS, look similar to those following the third application but with more of a build-up of the polymer, see Figure 3.24, the dark blue regions. The coating of the threads can be seen in the image of the cross section, Figure 3.25, the amount of blue colour is a good indication as to whether there is more or less polymer on the surface of a substrate.

The average mass of polymer that has been applied to the cotton fabric with two applications was 3.9 mg, the mass applied from three applications was 6.0 mg and the average mass of polymer on the fabric with four applications was 10.2 mg. The application of the third layer increased the mass by 35 %. The fourth application resulted in a polymer mass increase of 41 % from the third application. This demonstrates that with each subsequent application of the aqueous dispersion of PEDOT:PSS, a higher proportion of the conductive polymer is being deposited onto the surface to provide a more electrically conductive surface.

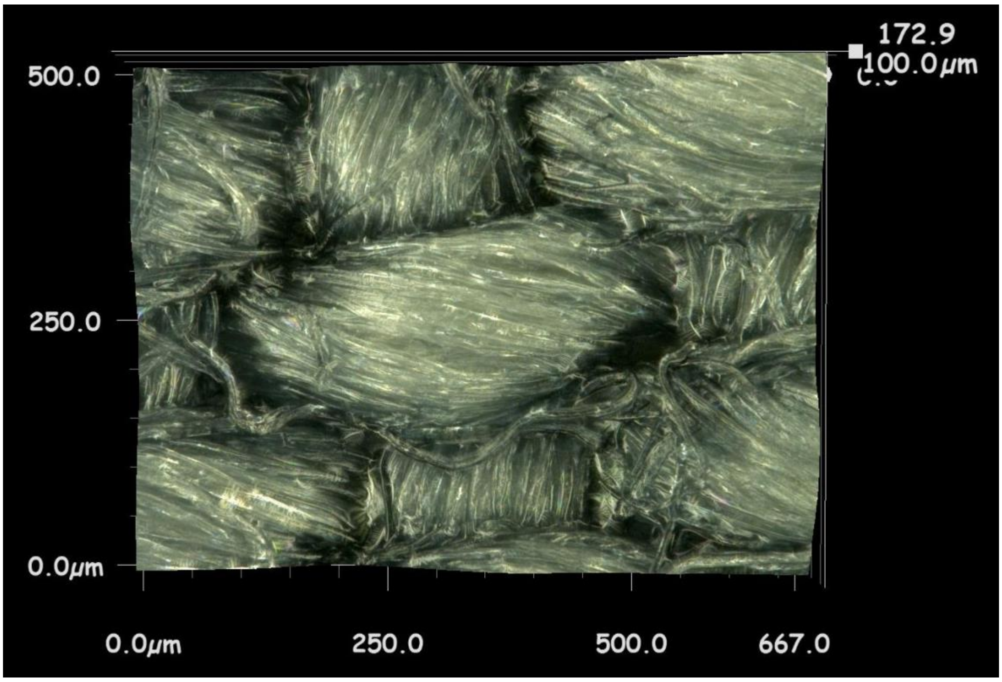


Figure 3.24 3D microscope image of a cotton fabric following four applications of PEDOT:PSS at 500x magnification

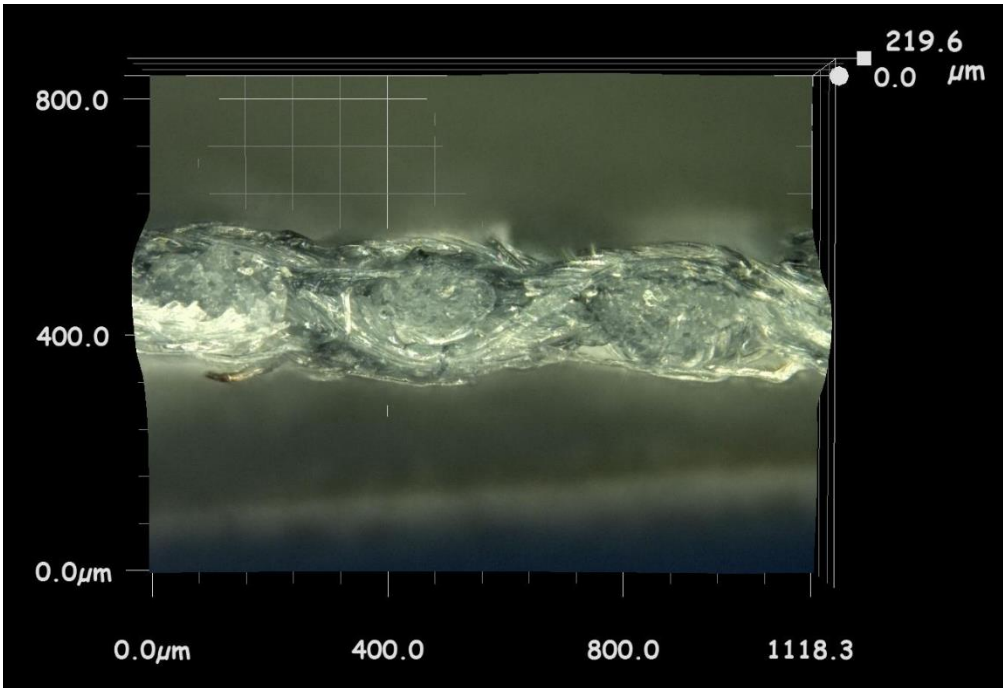


Figure 3.25 3D microscope image of the cross section of a cotton fabric following four applications of PEDOT:PSS at 300x magnification

3.3.4.5 Fifth layer application of PEDOT:PSS

The deposited fifth layer, after drying, shows the most intense blue colour, see Figure 3.26. Samples with five layers of PEDOT:PSS applied proved to be the least electrically resistive. This image shows the accumulation of polymer at the intersections which obscures the view of the threads travelling below it.

There was a speck on the surface which was also investigated at 500x magnification, the speck appears to be a crystalline area of PEDOT:PSS which is situated on the surface of the cotton substrate, see Figure 3.27.

The image of the cross section, Figure 3.28, shows clearly the build-up of polymer on the surface, this is concluded due to the darker blue colour. The more polymer on the surface of the substrate, the higher the electrical conductivity of the sample.

Foitzik *et al*. [2] and Bashir *et al*. [3] are amongst many who have investigated the application of conductive polymers on to textile substrates. Foitzik *et al*. showed that post-polymerisation application of conductive polymers can lead to more homogenous coatings of fibres [2]. Smooth, homogeneous coatings lead to overall lower electrical resistance. Figure 3.26 shows a very smooth surface coating of PEDOT:PSS and, excepting few specks witnessed, it appears homogeneous to provide low electrical resistance.

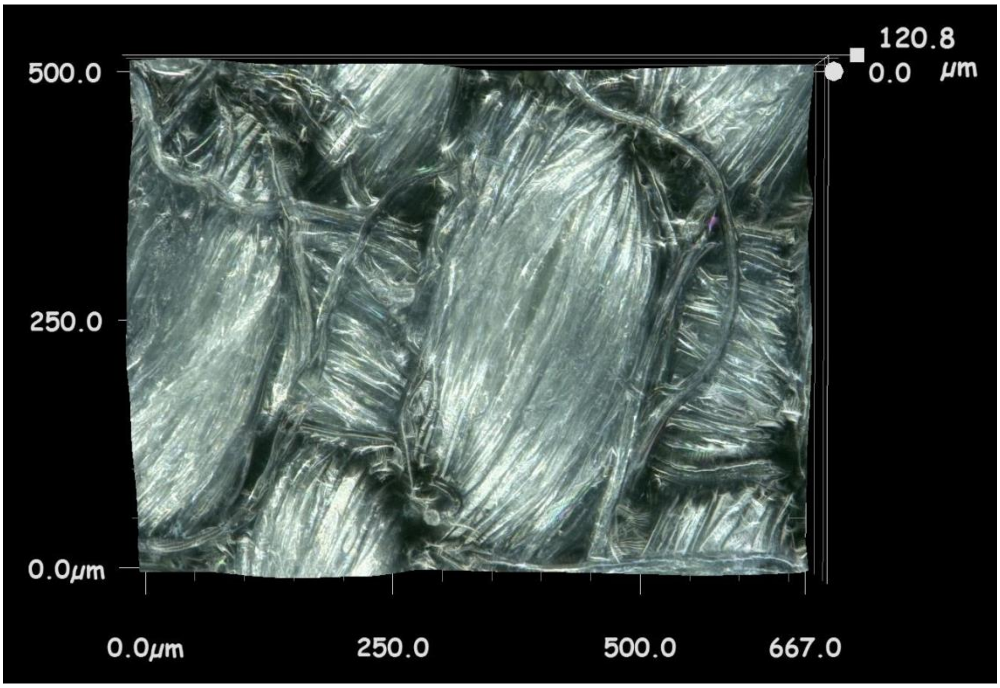


Figure 3.26 3D microscope image of a cotton fabric following five applications of PEDOT:PSS at 500x magnification

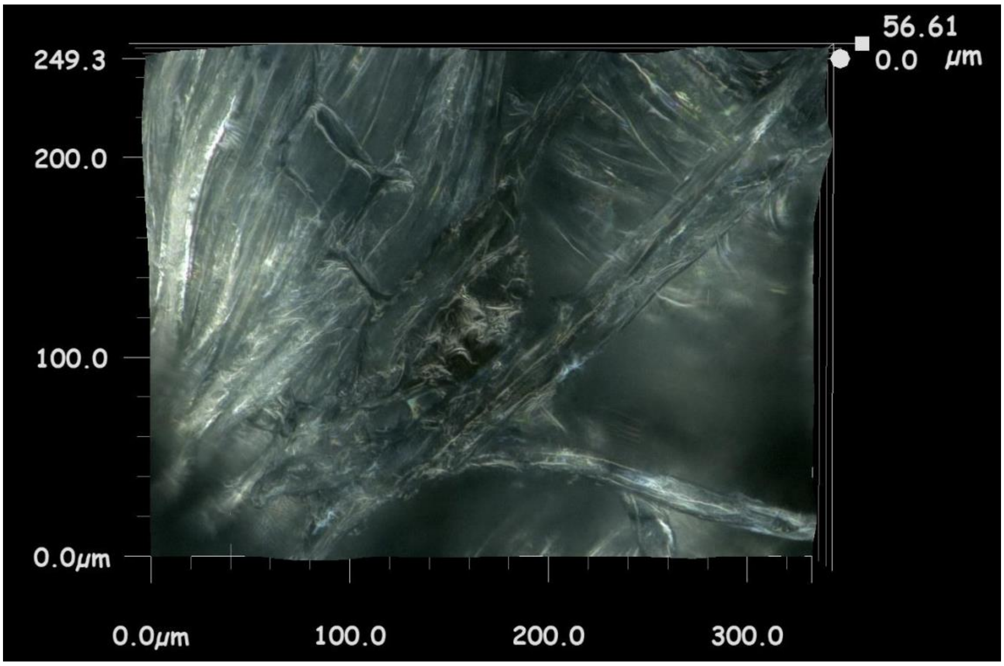


Figure 3.27 3D microscope image of a cotton fabric following five applications of PEDOT:PSS at 500x magnification. A speck on the surface looks glassy, sitting above the cotton weave

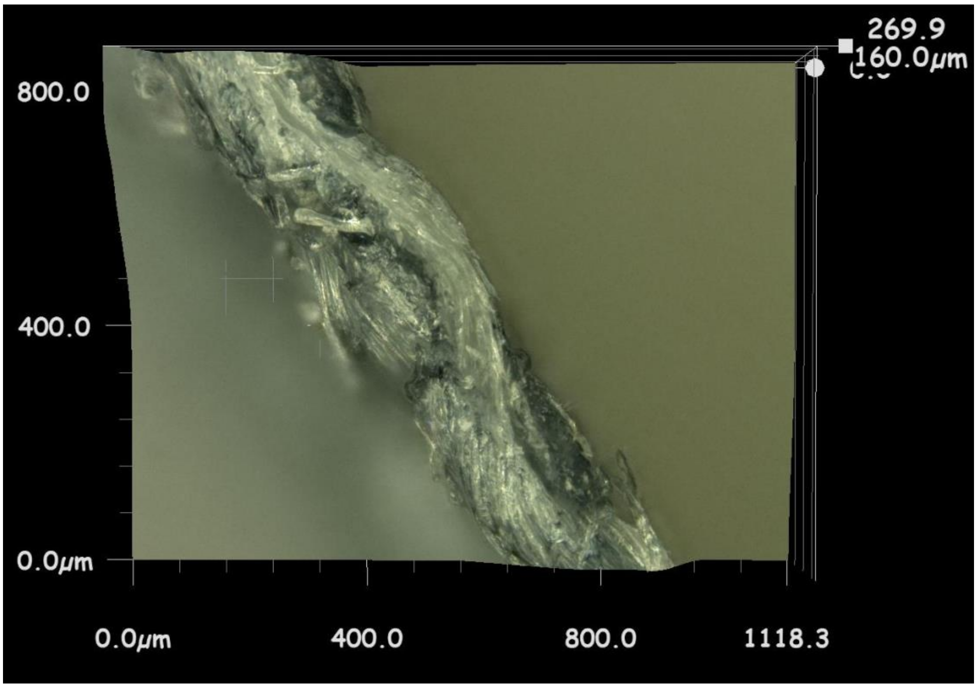


Figure 3.28 3D microscope image of a cross section of a cotton fabric following five applications of PEDOT:PSS at 500x magnification

3.3.5 Electrical resistance of creased coated cotton fabrics

Four resistance measurements were taken. Two measurements were taken over the x-axis crease and either side of the y-axis crease (A and B); and two measurements were taken over the y-axis crease and on either side of the x-axis crease (C and D), see Figure 3.29. The acquired data are given in Table 3.2.

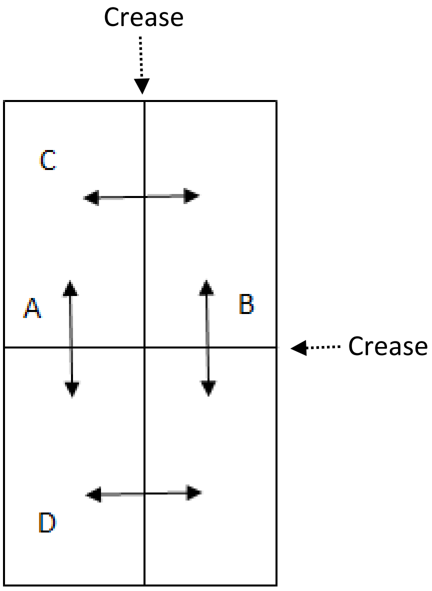


Figure 3.29 Directions electrical resistance was measured of the creased coated cotton fabric samples

Table 3.2 Resistance measurements of samples 1-15; A and B are taken over the x-axis crease on each side of the y-axis crease; C and D are taken over the y-axis crease on each side of the x-axis crease, all over 10 mm

Zone	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
A, Ω cm^{-1}	20000	2000	600	500	400	30000	1100	900	500	700
B, Ω cm^{-1}	19000	3000	650	550	500	30000	1400	950	1100	650
C, Ω cm^{-1}	20000	1600	500	500	450	11000	1000	1050	550	500
D, Ω cm^{-1}	19000	1500	500	600	450	10000	800	400	400	550

Zone	**11**	**12**	**13**	**14**	**15**
A, Ω cm^{-1}	20000	1000	1400	600	600
B, Ω cm^{-1}	20000	950	1400	550	750
C, Ω cm^{-1}	10500	800	1400	600	500
D, Ω cm^{-1}	14000	900	1100	650	500

Layers	**1**	**2**	**3**	**4**	**5**
Samples	1, 6, 11	2, 7, 12	3, 8, 13	4, 9, 14	5, 10, 15

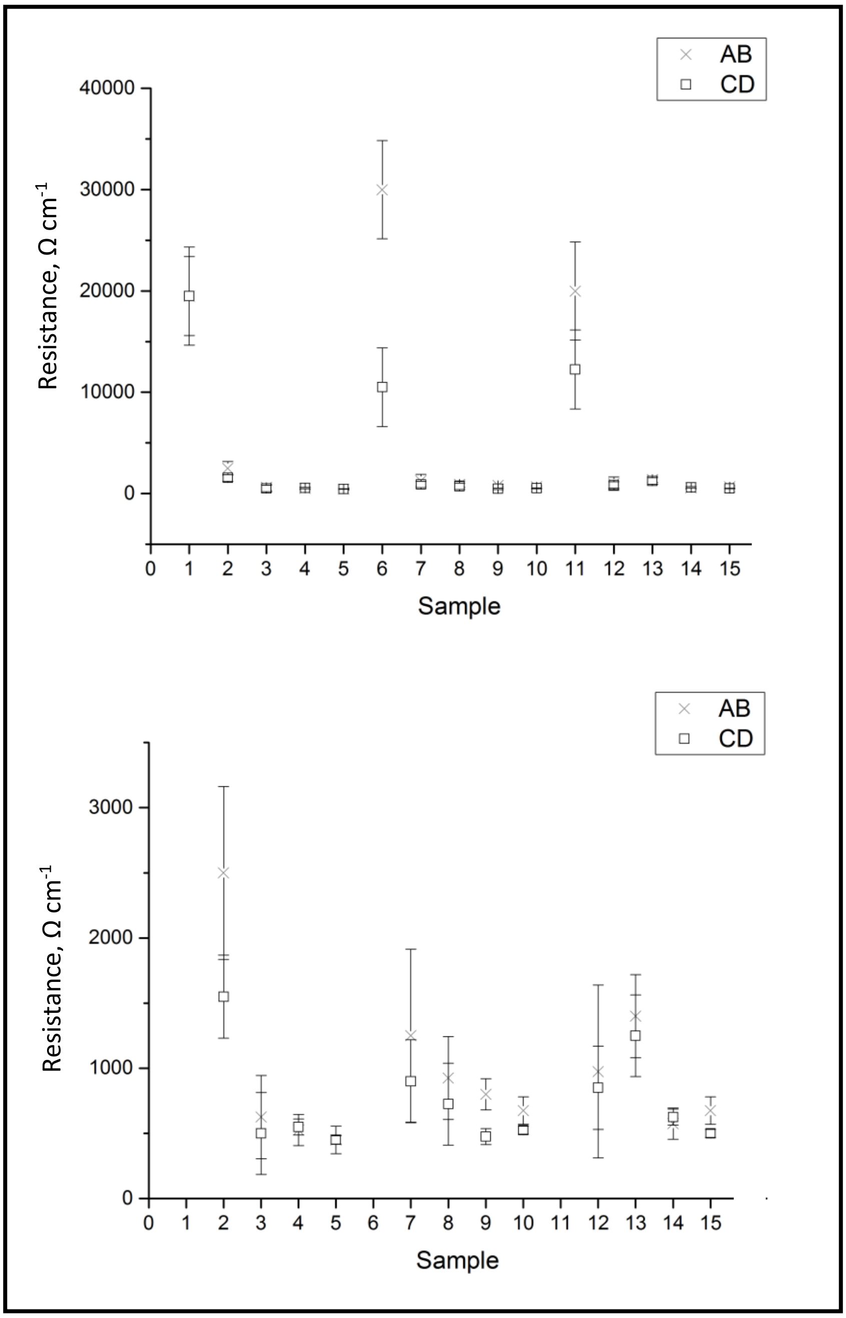


Figure 3.30 Resistance measurements of the creased coated cotton fabrics. The top plot compares all values while the bottom plot omits values from samples 1, 6 and 11 to visualise the differences at the lower resistance values

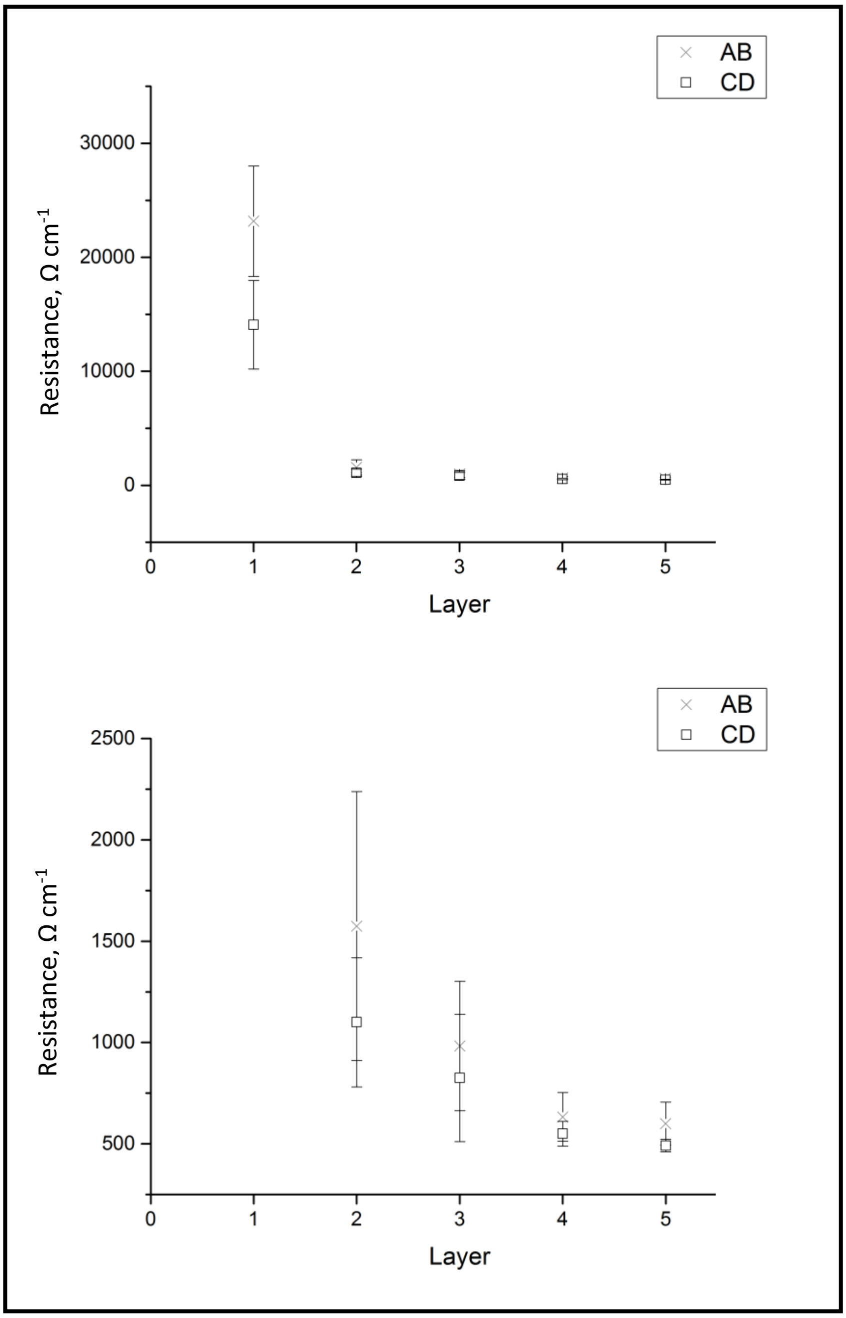


Figure 3.31 Average resistance measurements with respect to applied layers of PEDOT:PSS after creasing the sample. The top plot compares all values while the bottom plot omits layer 1 to compare the lower resistance values

The general trend as seen with the initial electrical resistance measurements is preserved, see Figure 3.31. That with the increase in layer application of PEDOT:PSS, the electrical resistance decreases and thus, conductivity increases. Discounting samples with one layer of PEDOT:PSS applied, there are no differences in electrical resistance with respect to the direction of measurement across the creases. Due to the nature of application with a K-bar, there is a possibility to induce linearity in the direction of application but this has not occurred.

Figure 3.32 is a direct comparison between the resistance measurements recorded prior to, and post creasing, of the coated cotton fabrics. The average electrical resistances remain the same for samples with one to three layers of PEDOT:PSS applied, post creasing. But the electrical resistance of samples with four and five layers of PEDOT:PSS applied suffered, post creasing. The electrical resistance of samples with four and five layers of PEDOT:PSS showed a 34 % and 35 % increase in resistance respectively, over 10 mm.

This increase in resistance and hence, loss of conductivity, shows that when more than a total of 10 mg of PEDOT:PSS is applied, over an area of *ca*. 70 x 30 mm, creasing can reduce the conductivity of the PEDOT:PSS coating. Thus, the resulting coating has a lower level of flexibility than cotton fabric samples with one to three layers of conductive polymer applied.

3.3.6 Electrical resistance of the washed, coated cotton fabrics

Two resistance measurements were made for each washed sample; one along the y-axis and one along the x-axis. The averages of these readings are reported in Table 3.3.

Figure 3.34 is a graphical representation of the data in Table 3.3 which shows a differing trend to what has been seen previously (Figure 3.31 and Table 3.1). The trend of increasing conductivity as the number of layers increase was not as clear. The bottom plot of Figure 3.34 shows the average readings against the number of layers that were applied, the trend observed is that electrical resistance decreases with increasing application up to four layers, with the electrical resistance increasing for samples with five layers of PEDOT:PSS applied.

Before washing these coated fabric samples, it was difficult, if not impossible, to predict how the electrical resistance would be affected. It could be suggested that at low mass loadings of polymer, despite the number of applications, washing would affect the polymer films similarly due to the strong physical bond between the fabric threads and the polymer film. As the polymer film thickness increases, there is a higher susceptibility to cracking which, with leverage, could peel the film from the fabric surface.

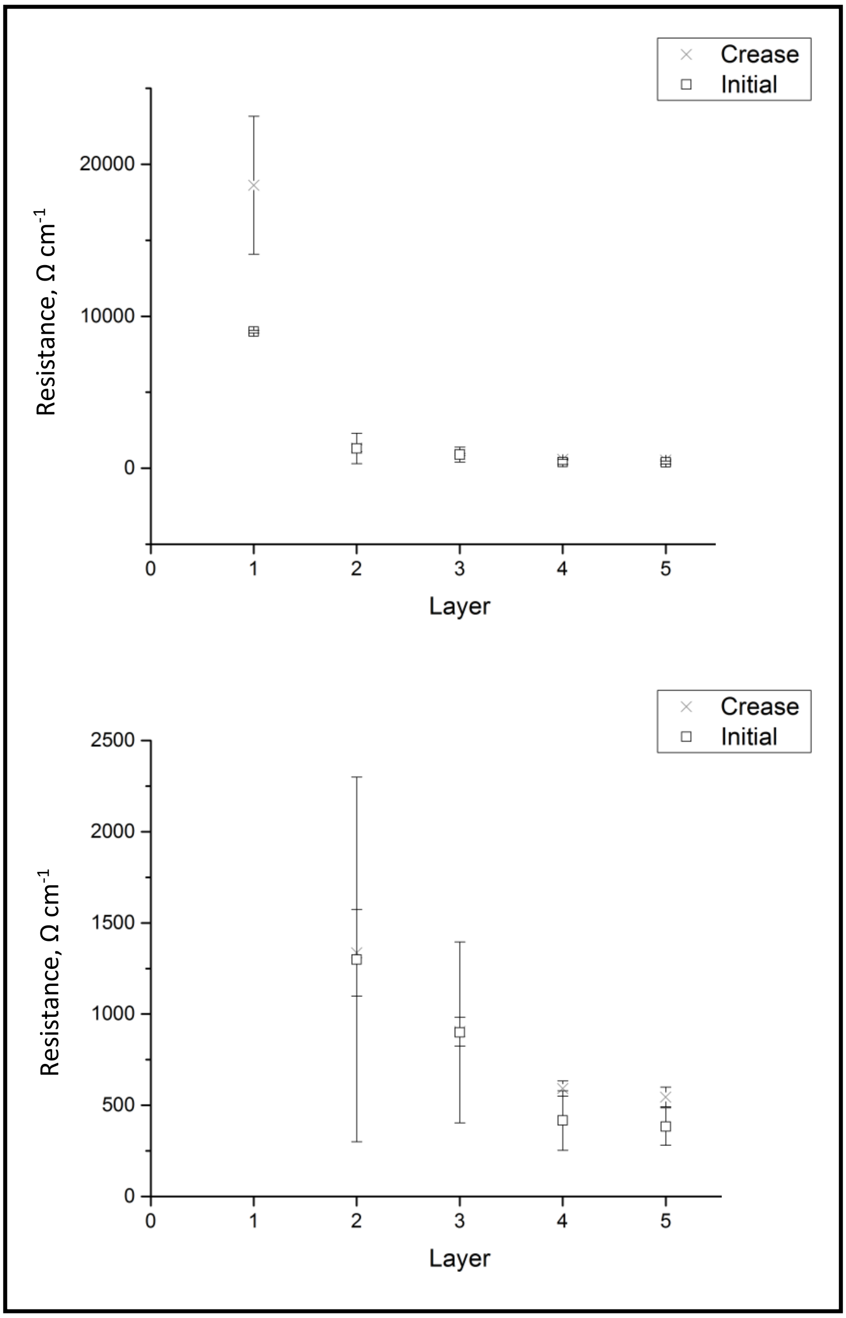


Figure 3.32 A comparison of the resistances of the coated cotton fabrics initially and post creasing, the top plot shows average values for each layer while the bottom plot omits layer 1 to display the differences at lower resistance values

Table 3.3 Resistance readings of the coated cotton fabric samples post washing and drying

#	1	2	3	4	5	6	7	8	9	10
y-axis, Ω cm^{-1}	60000	14000	4000	4000	4000	200000	6500	10000	4000	5000
x-axis, Ω cm^{-1}	60000	12000	4000	3500	3500	80000	6000	5000	3500	6500
Average, Ω cm^{-1}	60000	13000	4000	3750	3750	140000	6250	7500	3750	5750

#	11	12	13	14	15
y-axis, Ω cm^{-1}	90000	9500	10000	6500	4000
x-axis, Ω cm^{-1}	50000	6000	10000	4000	4500
Average, Ω cm^{-1}	70000	7750	10000	5250	4250

Layers	1	2	3	4	5
Samples	1, 6, 11	2, 7, 12	3, 8, 13	4, 9, 14	5, 10, 15

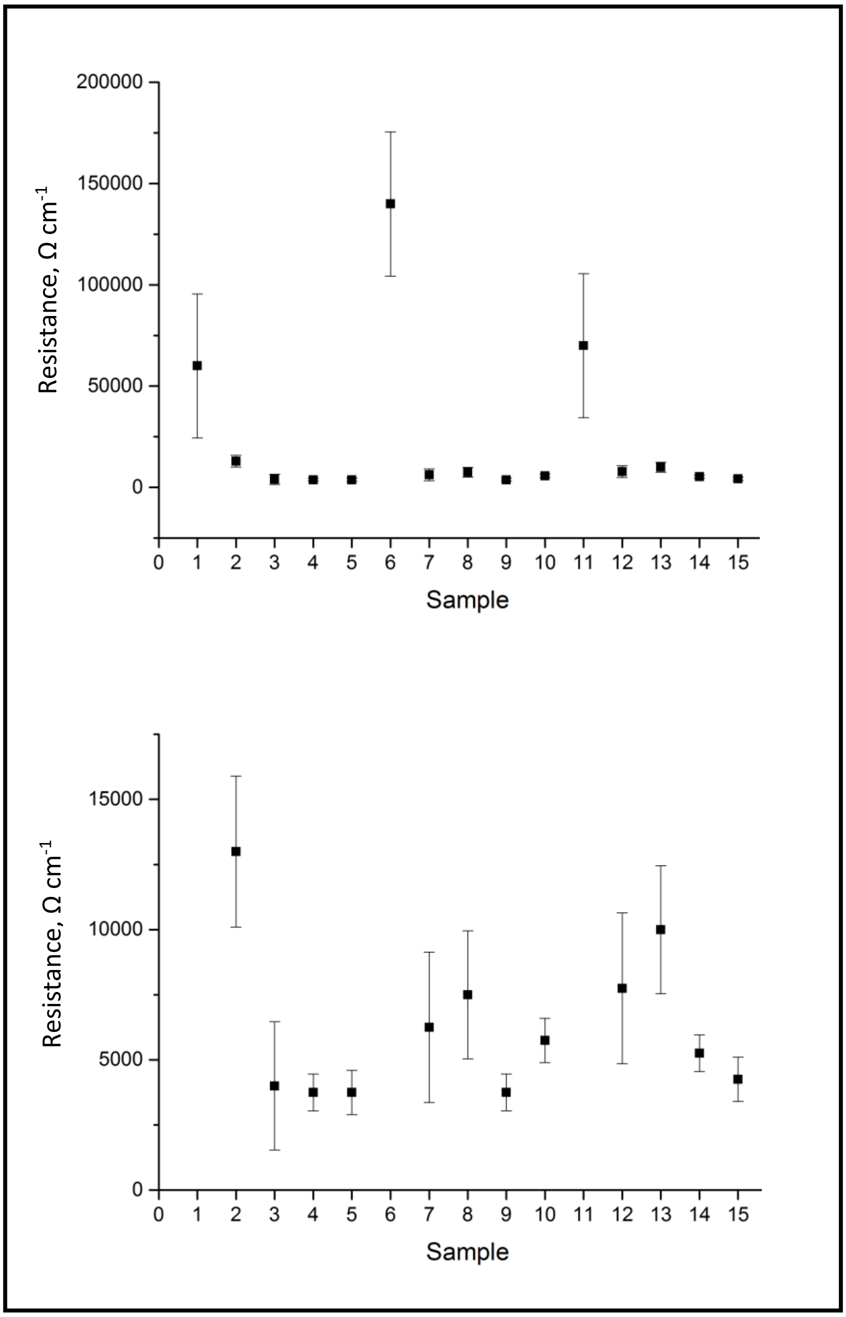


Figure 3.33 Resistance measurements of washed coated cotton samples. The top plot displays all data while the bottom plot omits samples 1, 6 and 11 to compare the lower resistance values

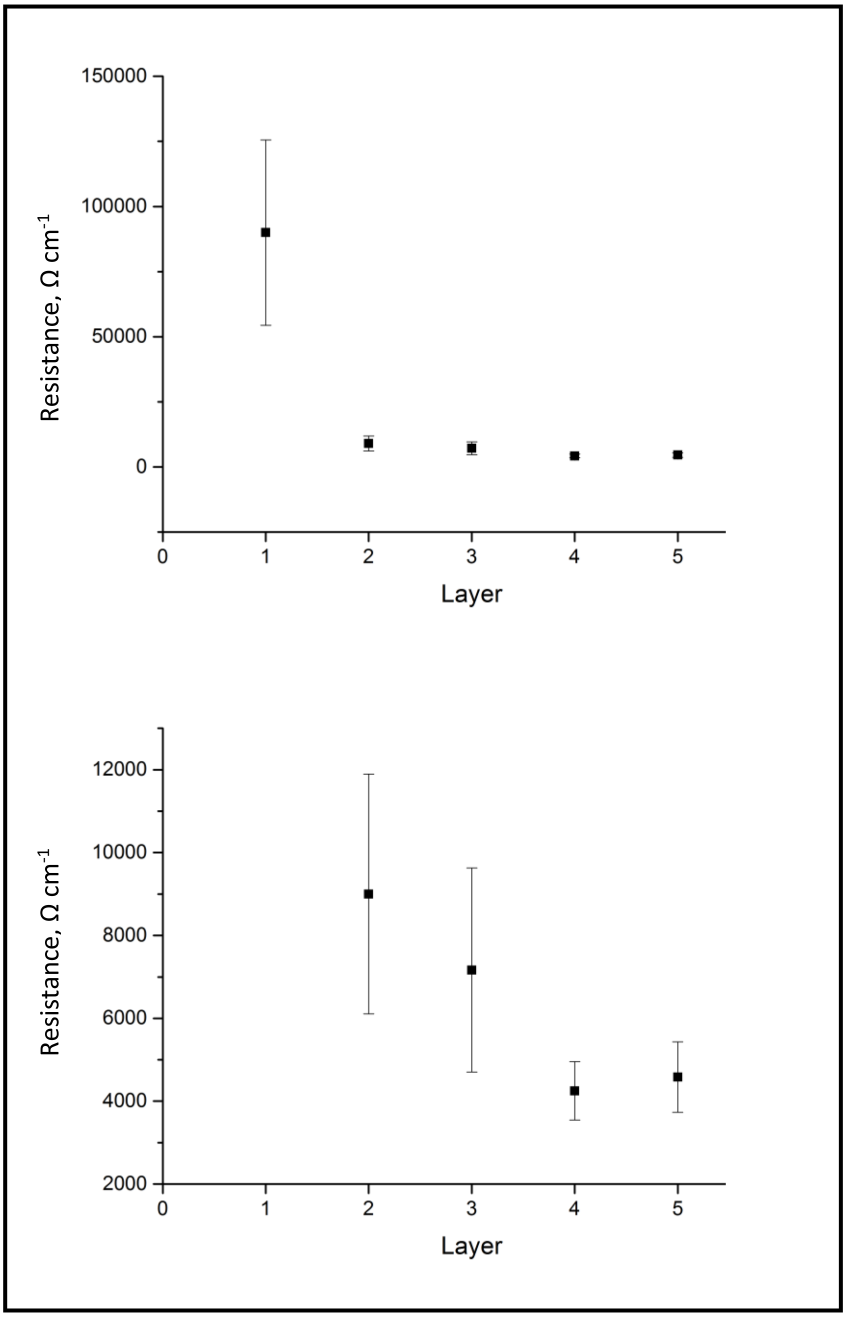


Figure 3.34 Average resistance measurements of washed coated cotton fabrics with regard to the number of layers of PEDOT:PSS applied, the top plot displays all values while the bottom plot omits layer 1 to observe the lower resistance values

Figure 3.35 is the graphical representation of the average electrical resistances of each layer after each treatment step. After washing, it can be seen that there is a significant increase of electrical resistance, for layers one to five, the percentage increase of electrical resistance from the post creasing measurements are 483, 672, 793, 718 and 840% respectively.

One major destructive force that is experienced by the fabrics in the washing process is abrasion. The PEDOT:PSS film is insoluble in water and is also relatively chemically inert, with respect to the conditions present during washing. Foitzik *et al.* conducted abrasion tests on poly(3-decanylpyrrole) coated fabrics and witnessed an increase in electrical resistance of *ca*. 33 % [2]. Despite the larger increase in electrical resistance, the resistances presented in this body of work are better. Foitzik *et al*. achieved a resistance of *ca.* 20,000 Ω cm^{-1} [2] compared to the average resistance of a cotton fabric with five layers of PEDOT:PSS applied, post wash, 4,500 Ω cm^{-1}.

Despite this apparent improvement over a value presented in the literature, this is a catastrophic loss of conductivity which would lead to the conclusion that simple application of PEDOT:PSS to cotton in this way would not suffice. A circuit would need to be devised with a specified resistance value in mind and this would have to remain constant throughout its lifetime for optimum operation. The end user would not be able to treat this as a regular garment. The work presented highlighted the potential issues with washing electrically conductive polymer films that was previously unknown. Further chapters of this thesis describe methods to improve this behaviour to minimise this negative effect.

3.3.7 Topology of washed coated cotton fabric

Figure 3.36 is a 3D microscopic image of an untreated cotton sample after the washing cycle. Comparing this image with an image taken before washing, Figure 3.14, it is clear that the fabric sample is not as smooth, there are many threads which have been untwined. This might be expected of a cotton sample that has been washed in washing machine, due to the “abrasive” environment experienced.

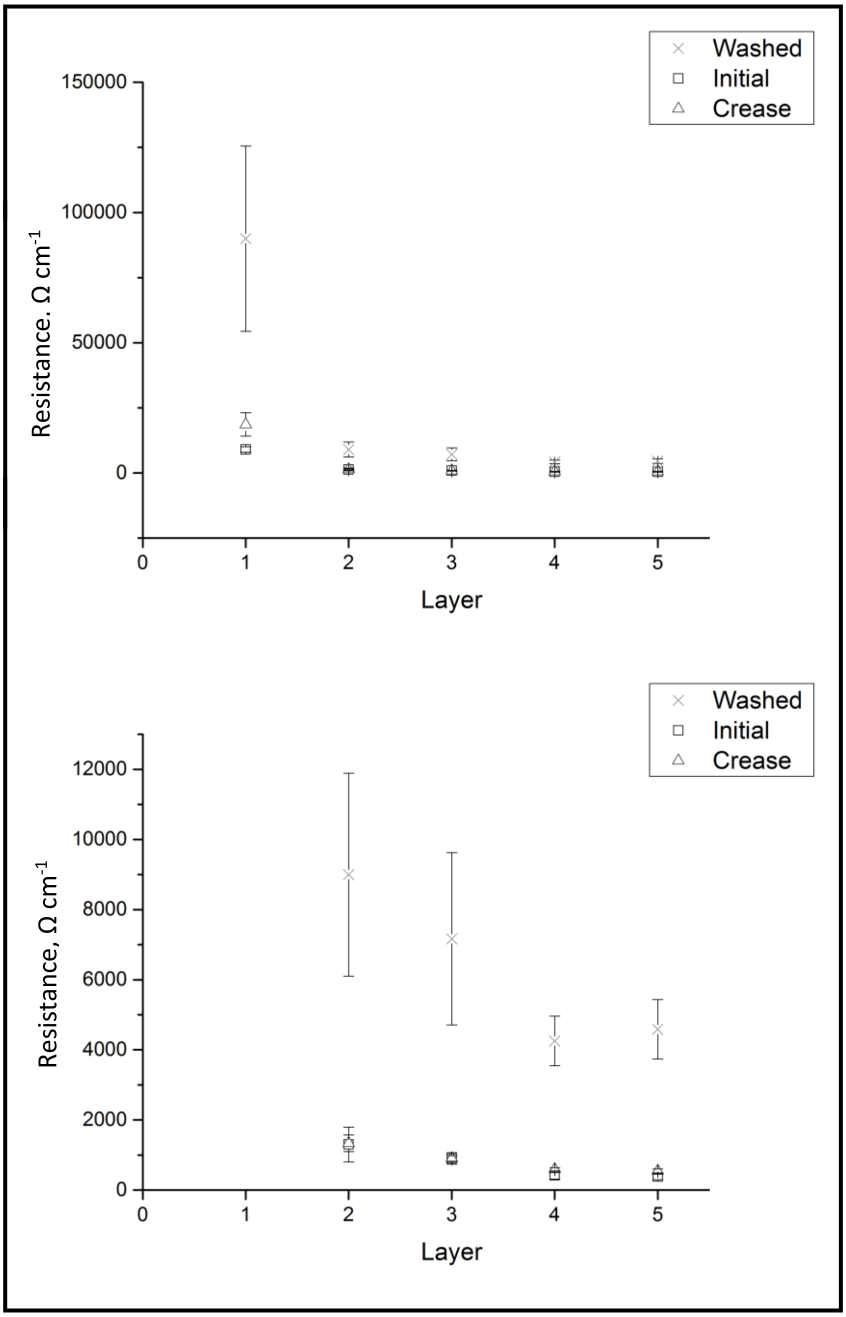


Figure 3.35 Comparison of electrical resistance of coated cotton initially, post crease and post wash, the top plot displays all data while the bottom plot omits layer 1 to compare the lower resistance values

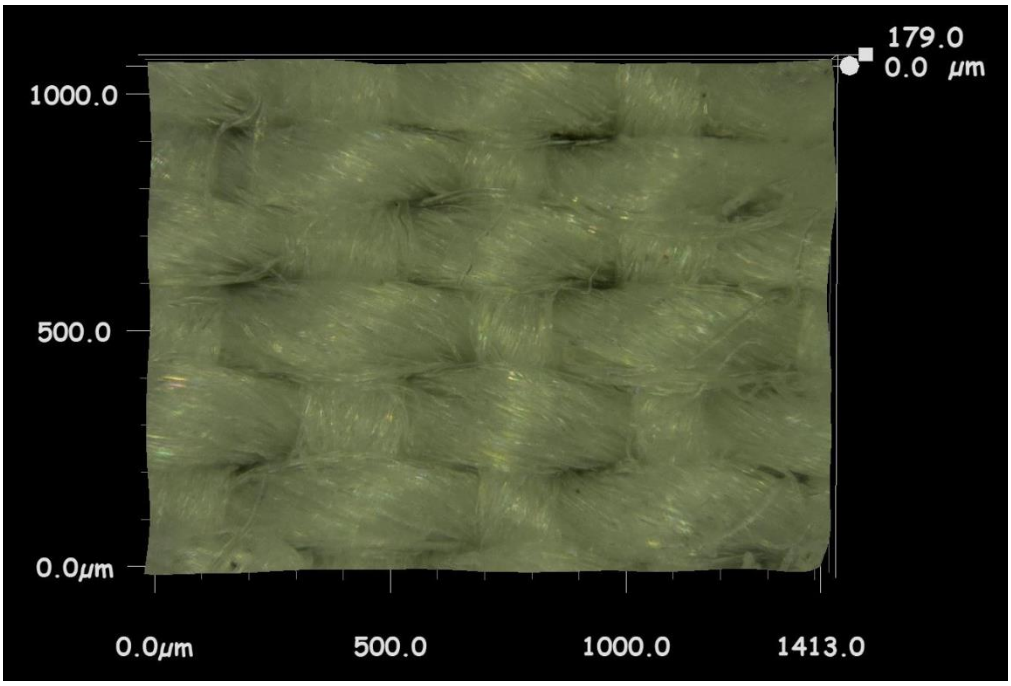


Figure 3.36 3D microscope image of a washed control cotton fabric sample, at 250x magnification

3.3.7.1 Single layer application of PEDOT:PSS

As with the untreated sample of cotton, the treated area had many untwined areas; the contrast provided by the blue colour of the coating highlights this, see Figure 3.37.

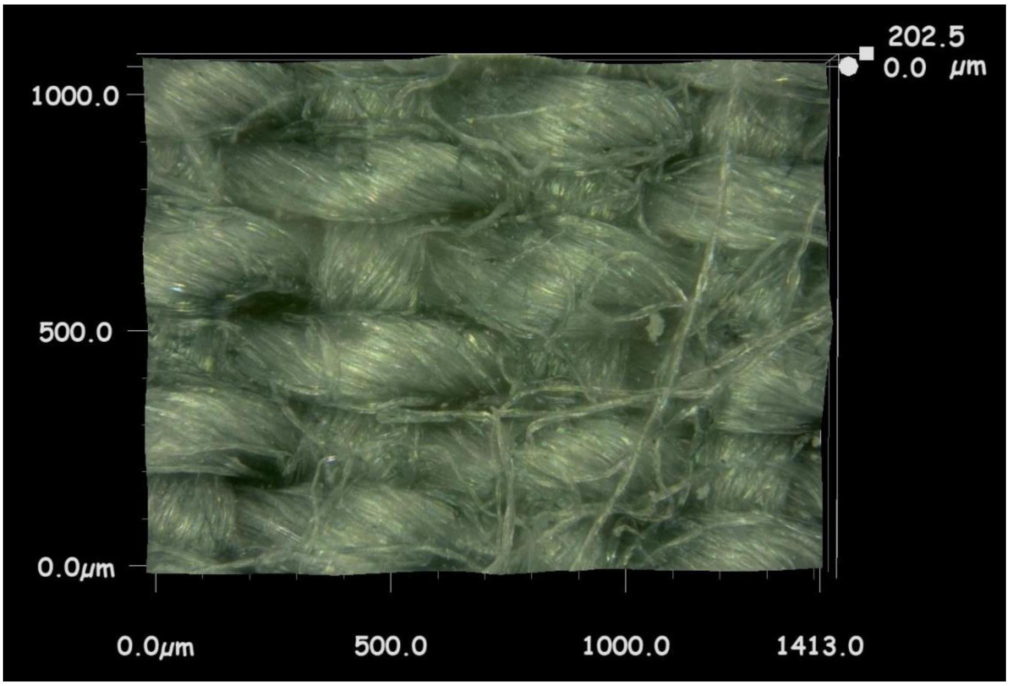


Figure 3.37 3D microscope image of a washed fabric sample with a single layer of PEDOT:PSS applied at 250x magnification

3.3.7.2 Second layer application of PEDOT:PSS

The microscope image of the sample that had received two layers of PEDOT:PSS is very similar to that with the single layer of PEDOT:PSS, Figure 3.38. No actual damage is seen to the coating surface. It appears that the loss in electrical conductivity is due to the untwining of the cotton threads.

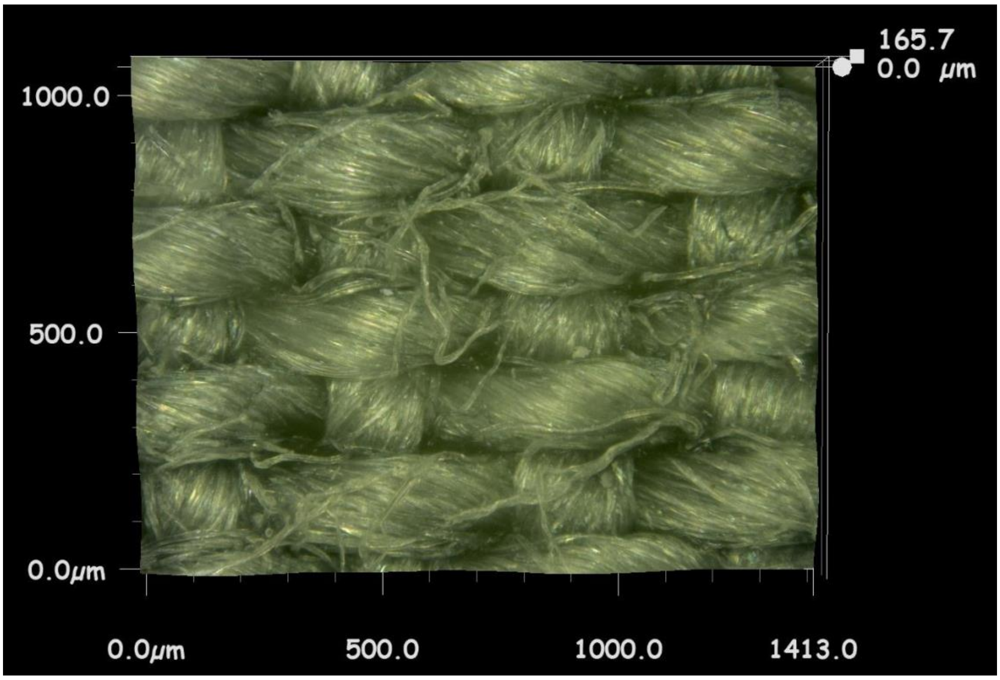


Figure 3.38 3D microscope image of a washed cotton sample with two layers of PEDOT:PSS applied at 250x magnification

3.3.7.3 Third layer application of PEDOT:PSS

Figure 3.39 shows a section of a cotton fabric sample that had been treated with three layers of PEDOT:PSS. This image depicts a surface that is very much deformed. At the centre of the image, the thread direction is not discernible. The threads are no longer tightly held together meaning that the connections between threads would be poor, decreasing the conductivity.

A point to note is also that in some sections of some samples there is white precipitate on the surface, as seen in Figure 3.40. These are thought to be either salts or undissolved washing powder that has not been washed away during the rinsing stages of the washing cycle.

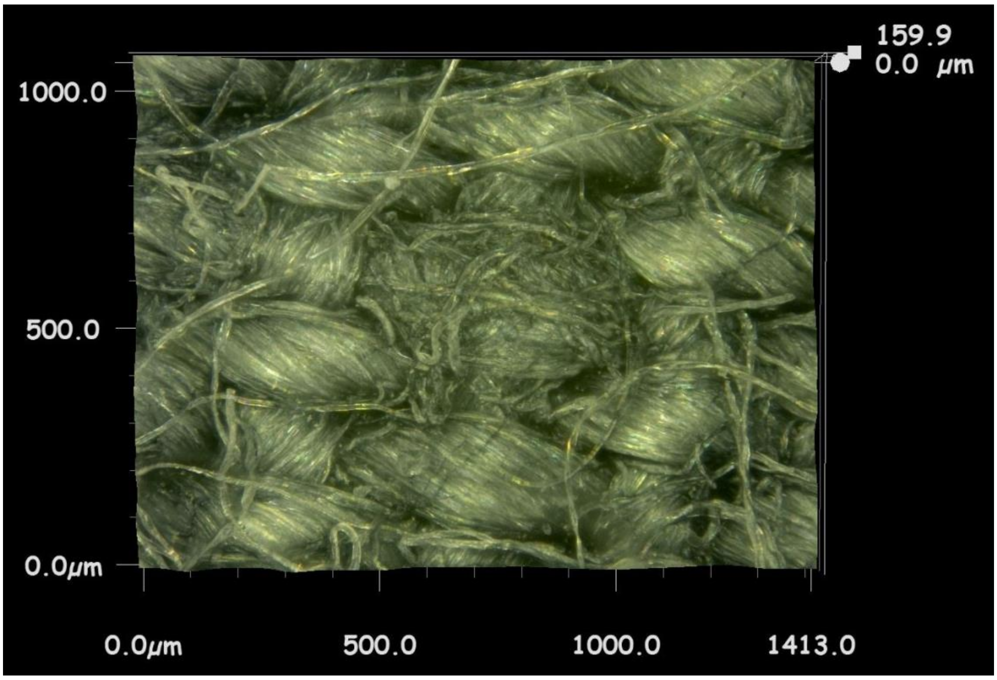


Figure 3.39 3D microscope image of a washed cotton sample treated with three layers of PEDOT:PSS applied, at 250x magnification

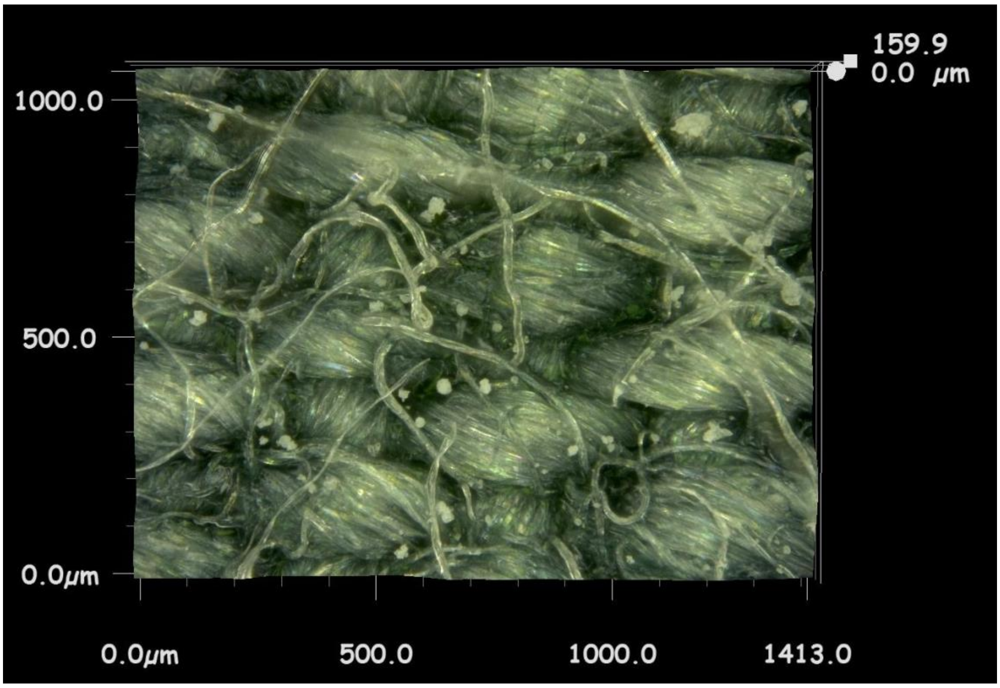


Figure 3.40 3D microscope image of a washed cotton sample treated with three layers of PEDOT:PSS but with precipitate on the surface, at 250x magnification

3.3.7.4 Fourth layer application of PEDOT:PSS

The cotton fabric samples that received four applications of PEDOT:PSS show some sections of the weave which have no discernible direction, see the centre of Figure 3.41. These samples also had some precipitate build up on the surface. Thus, a greater magnification image was taken at 1000x magnification, see Figure 3.42. This precipitate appears to be a colourless, crystalline solid, similar to what would be expected from salt precipitation or washing powder precipitation.

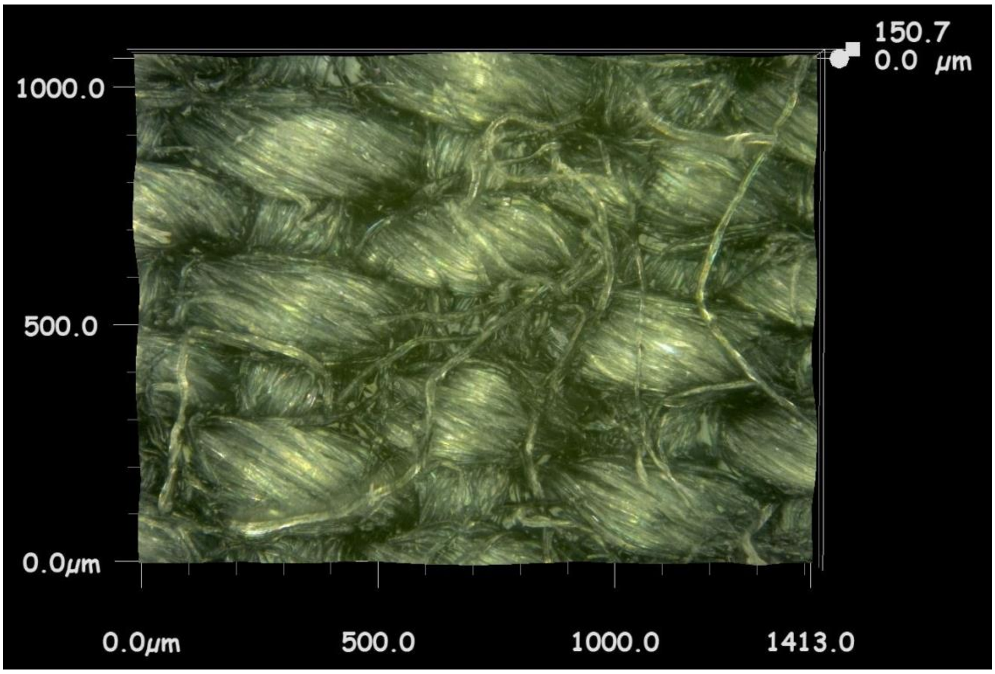


Figure 3.41 3D microscope image of a washed sample treated with four layers of PEDOT:PSS, at 250x magnification

Figure 3.42 3D microscope image of precipitation formation on a thread at 1000x magnification

3.3.7.5 Fifth layer application of PEDOT:PSS

The samples coated with five layers of PEDOT:PSS increased in resistance by the highest amount, compared to the resistances measured of the creased samples, after washing. The resistance had increased by almost 840 %, an increase to 4500 Ω cm^{-1} from 545 Ω cm^{-1}. To aid explanation, with the greater the number of layers of polymer applied, the flexibility reduces. Samples with four or five layers increased in electrical resistance by over 40% by creasing alone, while samples with three layers or fewer, remained almost the same.

Figure 3.43 shows untwined threads of a fabric sample, as seen previously but in the areas between threads there is light scattering, as if the polymer has created a solid layer between some of the threads. Nevertheless the electrical resistance has increased by a large margin.

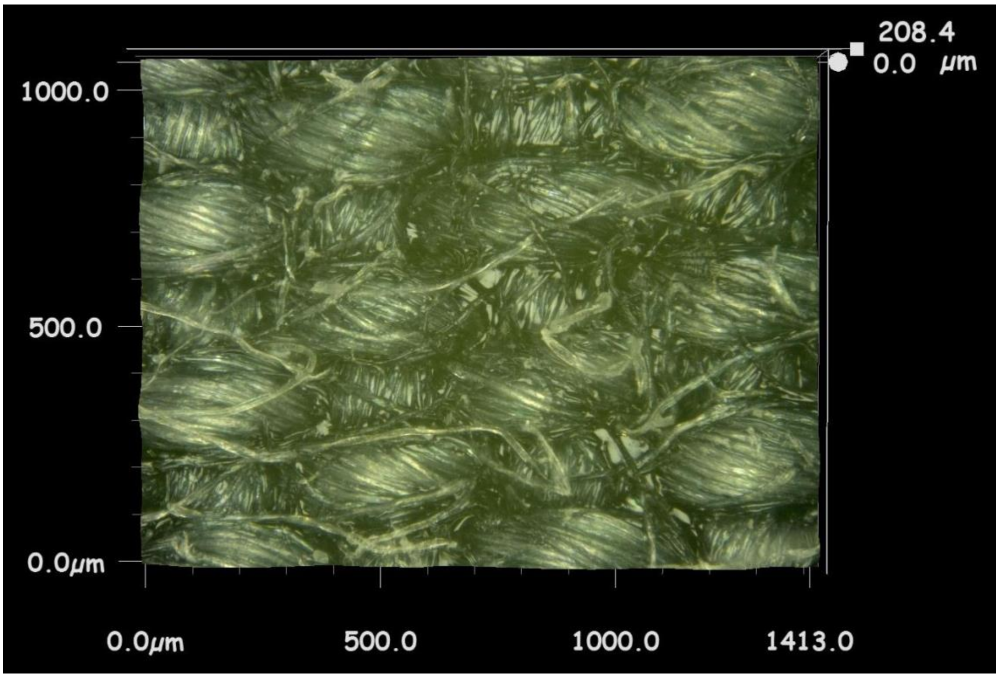


Figure 3.43 3D microscope image of a washed cotton fabric sample treated with five layers of PEDOT:PSS, at 250x magnification

This microscopy work provides an alternative method as to how the electrically conductivity of a coating could reduce on a fabric substrate. Initially, it was thought that the polymer would break away with abrasion or be degraded. It is apparent that another failure mode would be due to the cotton weave unravelling which physically pulls coated threads away from each other. This reduces the number of quality connections of the polymer across the sample thus reducing electrical conductivity.

3.4 Summary

An aqueous dispersion containing 1 % PEDOT:PSS, as Clevios FT, was applied to a cotton fabric substrate in an increasing number of layers. These layers were applied in single applications of the PEDOT:PSS solution (0.1 mL) and dried between each application. The samples were measured for their weight uptake of PEDOT:PSS and their electrical resistance initially, after creasing and after washing. These samples were then subjected to 3D microscopy to view the quality of the surface coating.

This study was an exploration of the ability of PEDOT:PSS to produce an electrically conductive textile fabric, giving an understanding of any limitations with respect to the expected treatment of a textile fabric garment *i.e.* creasing and washing.

Initial resistances were measured as 9000, 1300, 900, 416 and 383 Ω cm^{-1} for samples treated with one to five layers of PEDOT:PSS, respectively. The 3D microscope showed an increase in polymer coating the fibres which coincided with increasing layers of polymer the resistance will decrease. The polymer first filled the voids between the cotton weave and slowly increased coverage from that point.

Each sample was creased along the x- and y-axes and the electrical resistance was measured. The difference in resistance for layers one to three compared to the initial values are negligible whereas layers four and five had an increase of resistance of *ca.* 70 %. This shows the ability of the polymer to withstand creasing is lost after four layers have been applied to a woven cotton fabric. The 3D microscope did not give any visual indication of the crease damaging the polymer on the surface. It is considered that some of the coating on the threads would have cracked due to the inherent stiffness of intrinsically conductive polymers.

The coated samples were then washed in a washing machine; this caused a catastrophic loss of conductivity/increase in electrical resistance. Increases in resistances of 483, 673, 793, 718 and 840 % were observed for layers one to five, respectively, compared to the resistances measured after creasing. The lowest resistance observed, post washing, was that of cotton fabric samples treated with four layers of PEDOT:PSS, 4250 Ω cm^{-1}, more than twice as resistive as the initial resistance measured for samples treated with just one layer of conductive polymer. 3D microscopy proved valuable, showing the roughing of the surface of the coated threads, many had untwined which must reduce the contact between adjacent threads, thus, reducing electrical conductivity.

3.5 Conclusion

This study provided information on the properties of a PEDOT:PSS coated textile fabric which can be used as a benchmark to be compared to when designing improvements. Resistance values that were obtained after applying to the cotton fabric substrate were compared with published resistance values achieved from conductive polymer coated textiles, post polymerisation. The resistances reported in this Chapter improve on published values directly after application with resistances as low as 383 Ω cm^{-1}.

This application of PEDOT:PSS has showed that the conductive polymer alone, applied to a fabric substrate will not withstand the expected fabric treatment set out in the aims of the research. Creasing and washing of the coated fabric severely increases the electrical resistance. Despite the reported electrical resistances being as good as some published values, consistency of electrical resistance is a requirement to build a reliable electronic circuit. A method of protecting the conductive polymer surface coating will be addressed in the subsequent Chapters.

Concerns were raised with the method that the electrical resistances were measured using a two point probe. The resistance differed with varying pressure applied to the electrodes, this will be addressed in the subsequent Chapters.

3.6 References

1. Knittel, D. and E. Schollmeyer, *Electrically high-conductive textiles.* Synthetic Metals, 2009. **159**(14): p. 1433-1437.

2. Foitzik, R.C., A. Kaynak, and F.M. Pfeffer, *Application of soluble poly (3-alkylpyrrole) polymers on textiles.* Synthetic Metals, 2006. **156**(7-8): p. 637-642.

3. Bashir, T., M. Skrifvars, and N.K. Persson, *Synthesis of high performance, conductive PEDOT-coated polyester yarns by OCVD technique.* Polymers for Advanced Technologies, 2012. **23**(3): p. 611-617.

Chapter Four

Application of a composite of PEDOT:PSS and a latex to a carton board substrate

4.1 Experimental design

This section was designed to provide an assessment on the creation of a PEDOT:PSS multilayer assembly that consisted of a base layer of latex (poly(butyl acrylate)-co-(styrene)) applied to a carton board substrate, an electrically conductive polymer and a final layer of latex. This work aimed to provide a solution to the challenges highlighted in Chapter Three, that the surface can be abraded

The carton board was used as the substrate to examine differences due to the use of latex without having to take into account the behaviour of a textile substrate. Also, the carton board substrate was expected to enable the printed films to dry more quickly than the cotton as it will not absorb as much water from the latex or conductive polymer dispersions, enabling a quicker sample generation and screening. The rationale was that if this multilayer assembly functioned, was electrically conductive, this method would be transferred to a woven cotton substrate for wash testing, as Chapter Three.

4.2 Sample preparation

4.2.1 Synthesis and application of the aqueous latex dispersion to the carton board substrate

4.2.1.1 Carton board substrate

Supplied by Incada Exel, Proctor Paper & Board Ltd., Westland Square, Leeds. The paper card has a density of 240 gm^{-2}, thickness of 400 µm, good smoothness and uniform ink adsorption characteristics.

4.2.1.2 Synthesis of latex

Butyl acrylate (9.4 mL), styrene (3.1 mL) and AIBN (0.167 g) were added to dodecyl sulphonic acid (1.080 g) in water (100 mL) then sonicated in an ice bath for 30 mins. The mixture was stirred overnight at 65 °C under N_2. The resulting suspension was used without further purification.

4.2.1.3 Application of latex to the carton board substrate

The aqueous latex dispersion (*ca.* 2 mL) was applied to the substrate using a K-bar 4. The substrate was then placed in an oven at 40 °C until dry.

4.2.2 Application of PEDOT:PSS layers to the latex coated carton board

The aqueous dispersion of PEDOT:PSS (0.05 mL) was applied to the latex treated carton board using a K-bar 4. The samples were dried in an oven at 40 °C until dry and then another treatment of PEDOT:PSS was applied to samples and the process repeated to give a range of samples having one to five layers of PEDOT:PSS in triplicate.

4.2.3 Application of copper wire electrodes to the PEDOT:PSS and latex coated carton board

Four copper wire electrodes were placed *ca.* 10 mm apart in the x- and y-directions in a rhombus shaped configuration. An electrically conductive epoxy, namely CircuitWorks® Conductive Epoxy CW2400 manufactured by ITW Chemtronics, is a two-part epoxy containing silver particles that when mixed and cured, provides a hard, electrically conductive bonding layer. The two parts were mixed according to the instructions and was applied to the base of the copper wire at the interface with the PEDOT:PSS treated surface.

The glued samples were placed in a 40 °C oven to cure.

4.2.4 Application of the latex top layer to the PEDOT:PSS-latex-carton board composite

The synthesised latex dispersion was applied to the surface of the structure, over the subsequent treatments, using a small brush as standard coating techniques could not be used over the electrodes. The electrodes protrude from the surface hence, a K-bar 4 would not be able to run down the surface. The dispersion was brushed on until the surface was wetted and allowed to dry. This process was repeated until the surface was electrically insulating (electrical resistance > 100 M Ω) by testing with a two point probe.

4.3 Results and discussion

4.3.1 Topology of the initial latex layer on the carton board

On the surface of the carton board substrate, after it had received the latex base layer, see Figure 4.1, globules of polymer could be seen on the surface. These globules, when drying, have mostly joined to form a continuous thin film across the substrate, with the exception of a few larger deposits of latex.

This thin film of latex was applied so as to remove any interaction between the subsequent layers of PEDOT:PSS with the substrate. It was reassuring to view a created film as the latex will eventually be used on a textile substrate as a means of filling pores and providing a more even surface on which the PEDOT:PSS film could form.

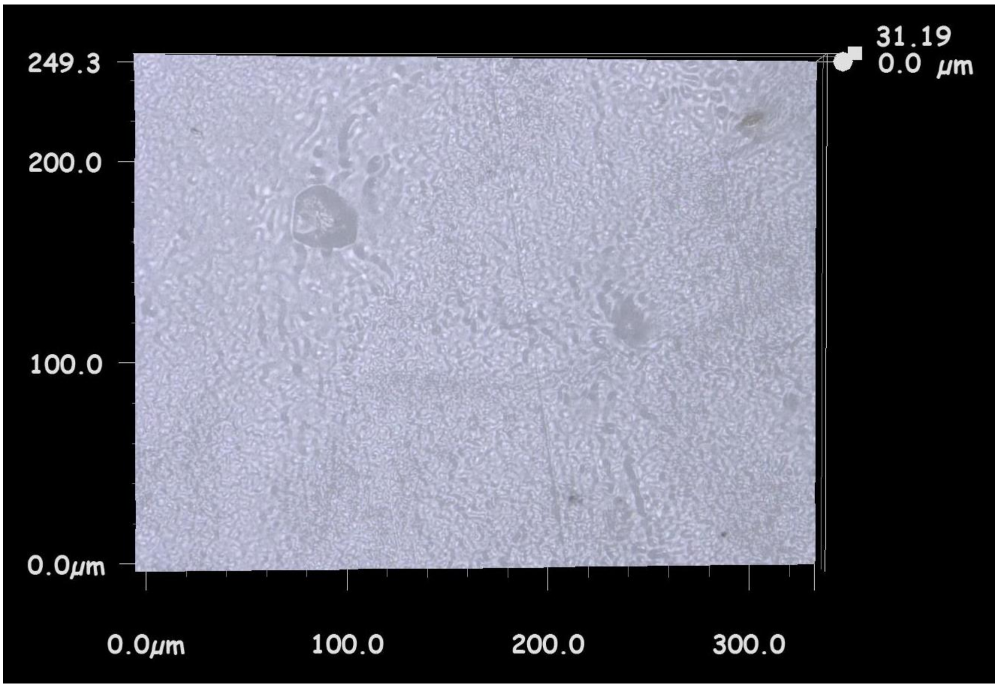


Figure 4.1 A 3D microscope image of the latex base layer on the carton board substrate at 1000x magnification

4.3.2 Electrical resistance of PEDOT:PSS layers

4.3.2.1 Ambient electrical resistance measurements

Once the PEDOT:PSS layers were dried, a two point probe was used to measure the electrical resistance of the samples in the x- and y-directions. The resistance varied proportionally with pressure applied to the surface using the probes. This is a potential source of error in the measurements which is overcome by the use of the electrodes, described later. The work presented describes ambient and post drying electrical resistances. In this case the term ambient refers to samples that have been dried, as described previously, but left to stand at room temperature overnight. The measurements made post drying were measured immediately on the removal of the samples from the oven.

It was found that the ambient surface resistances of the PEDOT:PSS layers were much greater than those reported in Chapter Three for samples with PEDOT:PSS applied to a cotton substrate. The lowest resistance measured was *ca.* 4 k Ω cm^{-1}, Figure 4.2. There was a general trend of a slight decrease in resistance after each additional layer of PEDOT:PSS was applied to the carton board surface, as expected on the basis of observations given in Chapter Three.

Figure 4.3 shows the average electrical resistances with respect to the number of layers of PEDOT:PSS applied. The lowest electrical resistance measured was 5.2 ± 2 k Ω cm^{-1}. Because of the planar surface of the substrate, increased conductivity hence, lower electrical resistance, should be expected. However, the hydrophobic latex layer appears to allow only a small amount of conductive polymer to be retained on the surface. At most, *ca.* 56 mg of conductive polymer was deposited onto the surface after five applications. The samples created in Chapter Three had only 13 mg of conductive polymer deposited. Due to the non-porous and hydrophobic treated surface of the latex treated carton board, the aqueous PEDOT:PSS dispersion spread across the sample when drawn down with the K-bar 4. This could relate to the low conductivity, high resistance, of the samples created, in comparison to the resistances identified in Chapter Three. The samples created in Chapter Three were targeted to only coat a small area while coating onto the latex treated carton board was less specific.

Another point to consider with regard to the low conductivity of the samples is the limitation in the use of the two point probes for measurement. Having a small contact area between the probe and material, as will be described in the following microscopy section, the probes could lie on a small area with less conductive polymer present. Logically, increasing pressure might increase the contact area giving a more reliable reading.

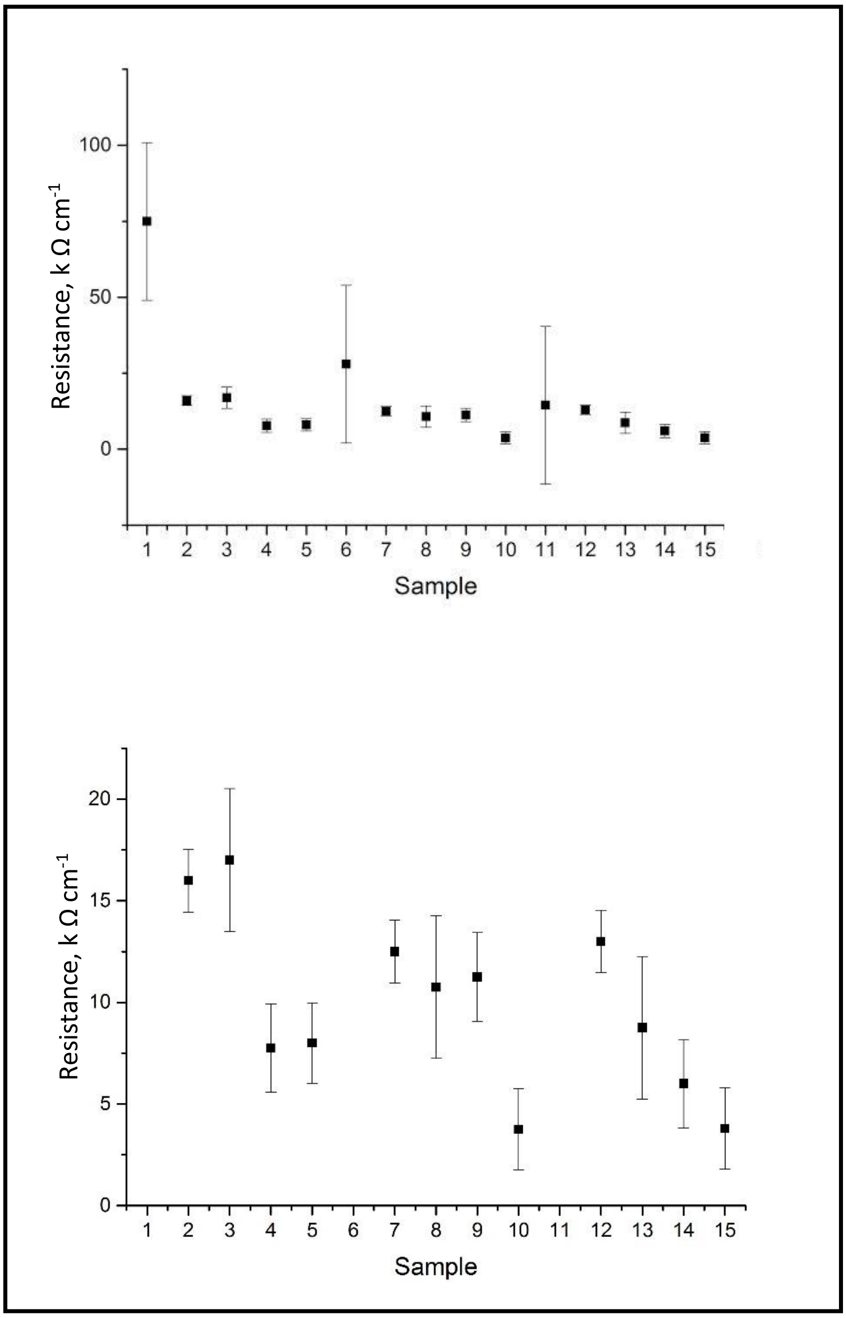


Figure 4.2 Resistance measurements recorded with a two point probe of the PEDOT:PSS coated and latex treated carton board substrate. The top plot shows all data while the bottom plot omits samples with one layer of PEDOT:PSS for clarity

Table 4.1 Mass of conductive polymer applied and resistances measured at ambient conditions and after drying measured with the two point probe and average values with respect to the number of applications of PEDOT:PSS applied

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Mass of PEDOT:PSS, g	0.0113	0.0438	0.0376	0.0347	0.0423	0.0123	0.0628	0.0566	0.0511	0.0455
Ambient Resistance, k Ω cm^{-1}	75	16	17	7.75	8	28	12.5	10.75	11.25	3.75
Post Drying Resistance, k Ω cm^{-1}	67.5	32	20	12.5	9.75	40	27	15.5	8	3.25

Sample	**11**	**12**	**13**	**14**	**15**
Mass of PEDOT:PSS, g	0.0174	0.0562	0.0283	0.0141	0.0365
Ambient Resistance, k Ω cm^{-1}	14.5	13	8.75	6	3.8
Post Drying Resistance, k Ω cm^{-1}	67.5	20	13	10	5

Layer	**1**	**2**	**3**	**4**	**5**
Mass of PEDOT:PSS, g	0.0137	0.0543	0.0408	0.0333	0.0414
Ambient Resistance, k Ω cm^{-1}	39.17	16.17	13.58	9.67	5.58
Post Drying Resistance, k Ω cm^{-1}	58.33	29.50	17.75	10.25	6.50

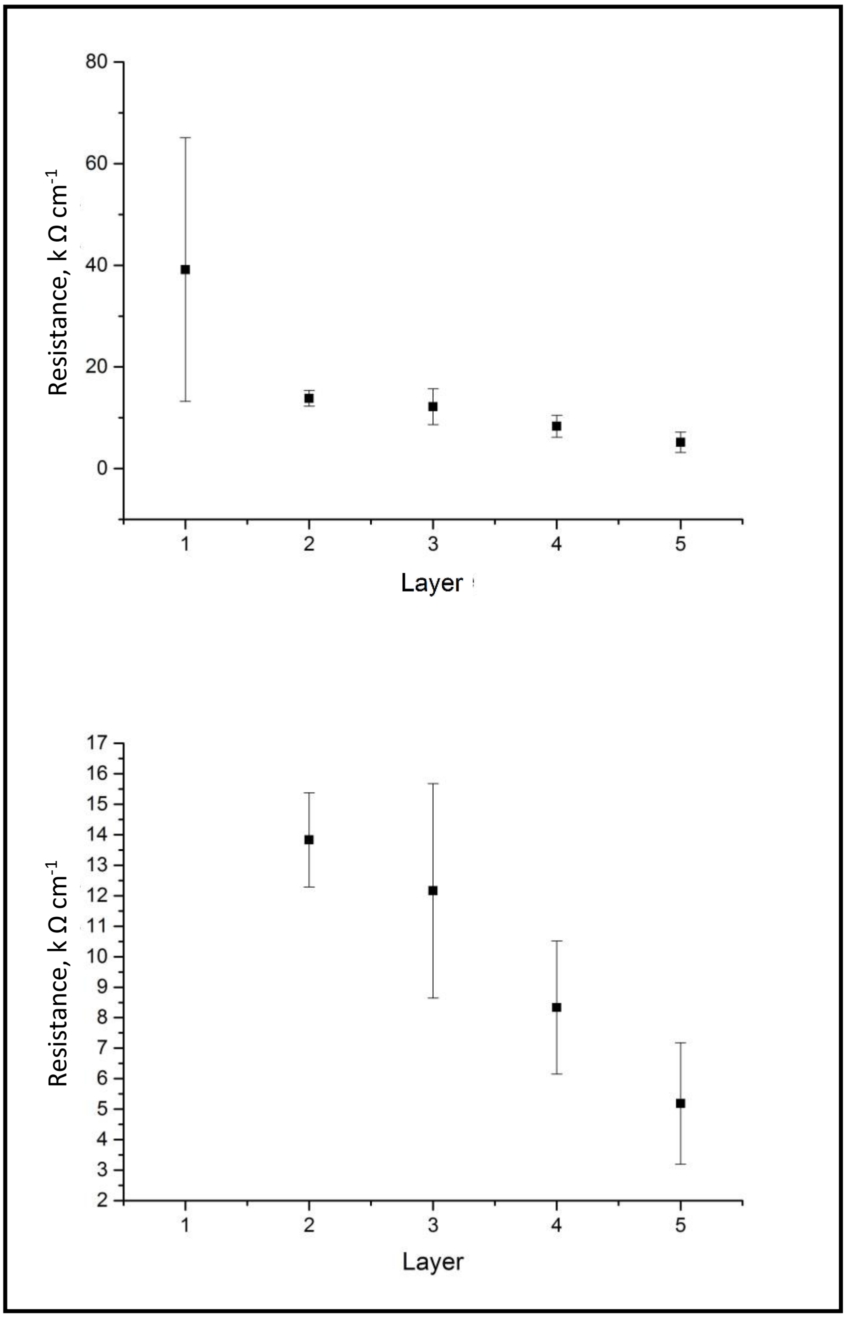


Figure 4.3 Average resistance measurements with respect to number of layers of PEDOT:PSS applied to the latex treated card substrate. The top plot shows all data while the bottom plot omits layer 1 for clarity

4.3.2.2 Electrical resistance measurements of the samples post drying

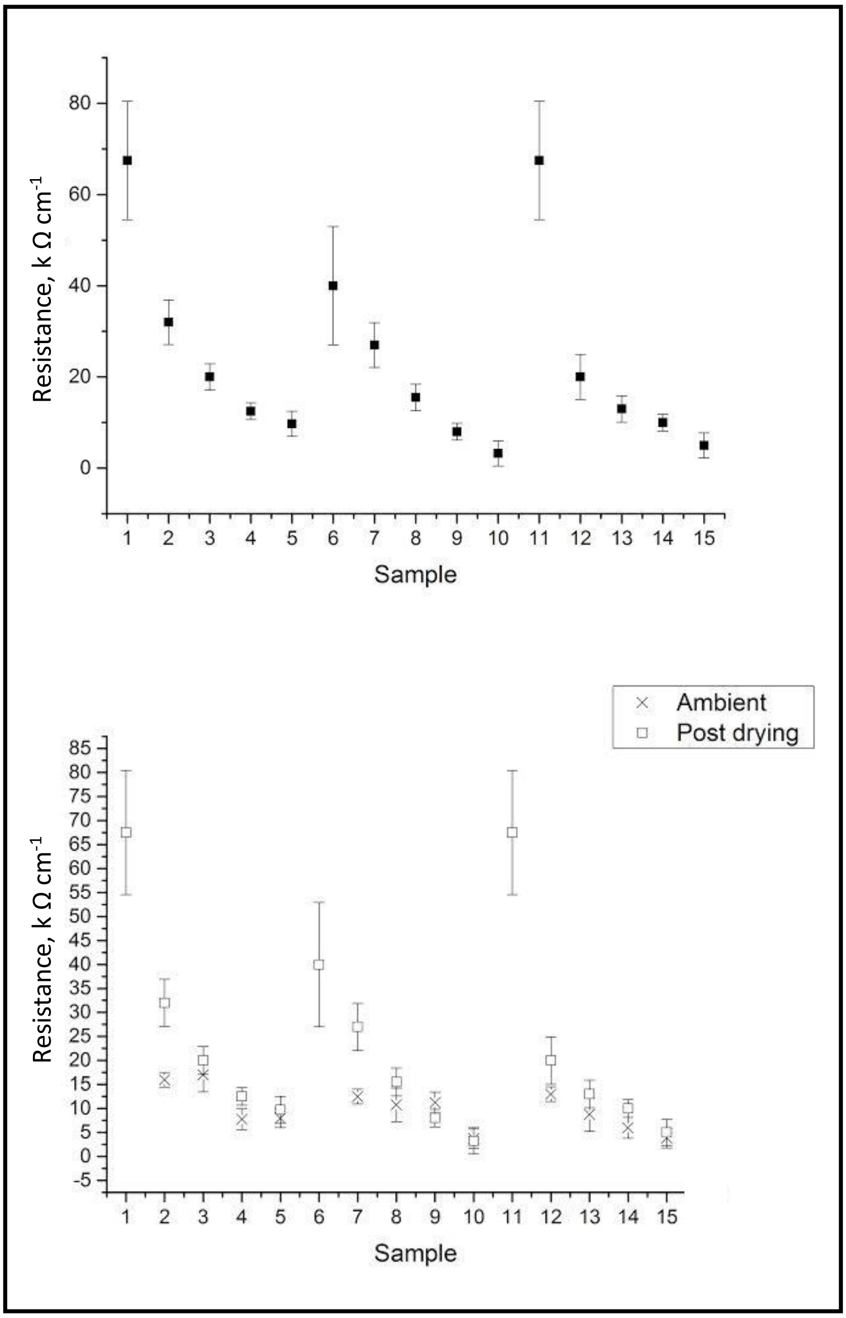


Figure 4.4 Resistance measurements recorded of the samples after they had been dried in the oven. The top plot shows only dried resistance while the bottom plot displays the comparison to the ambient resistance

When weighing the samples of latex treated and PEDOT:PSS coated carton board substrate, it was noted that there was a significant mass gain after the samples had been left at room temperature. Mass increases of as much as 2.31 % were reported after allowing the samples to rest at room temperature overnight. This effect is due to the absorption of moisture from the atmosphere.

This presence of water, reduced the electrical resistance of the samples. The electrical resistance in almost all of the samples increased once the samples were dried, see Figures 4.4-4.6. As the amount of water gain and removal appears to be regardless of the number of PEDOT:PSS applications, the source of this variation could be considered to be primarily due to the card substrate with a small portion being adsorbed onto the conductive polymer surface.

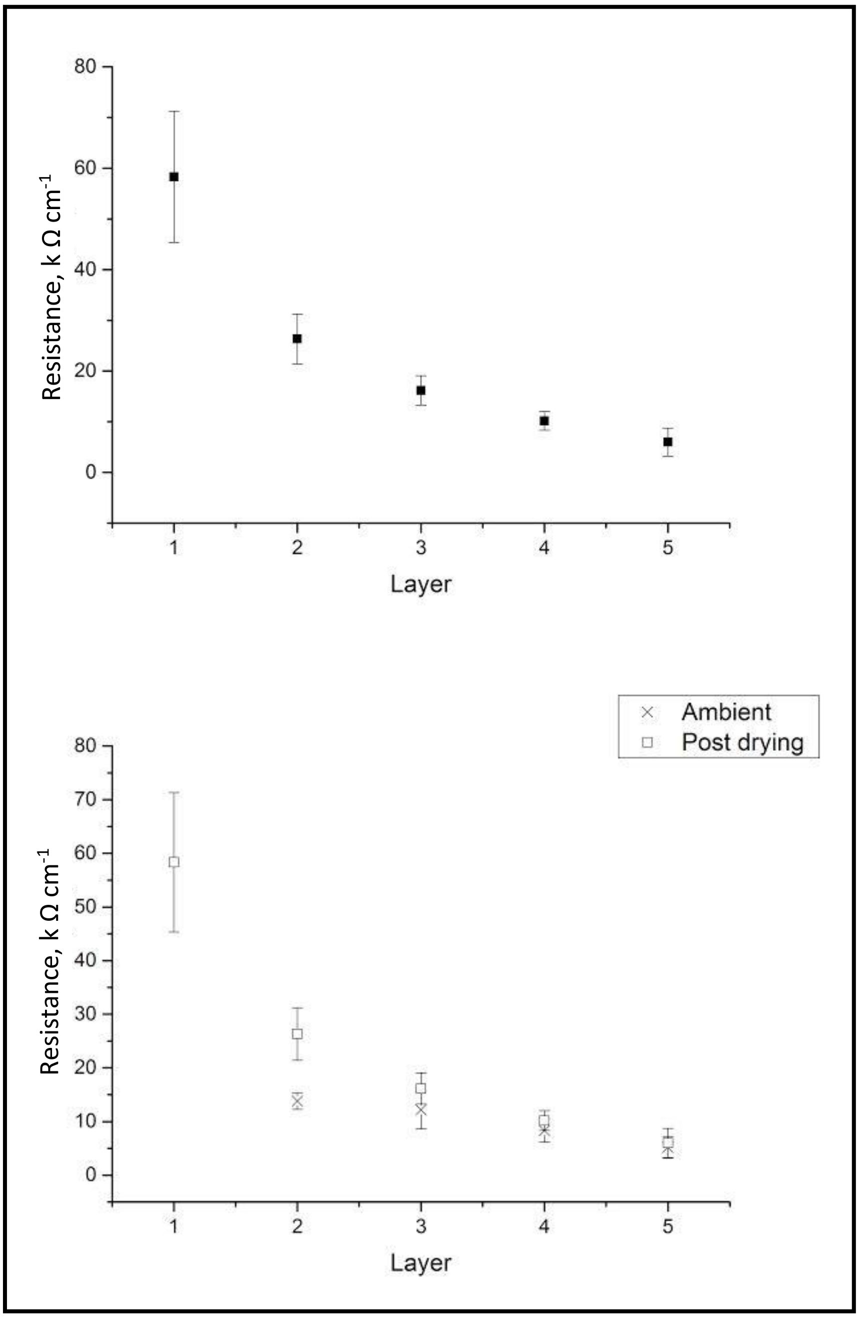


Figure 4.5 Average resistance measurements recorded of the samples after they had been dried in the oven. The top plot shows only post dried resistance while the bottom plot displays the comparison to the ambient resistances. Layer 1 of the ambient measurements was omitted for better comparison of the later samples

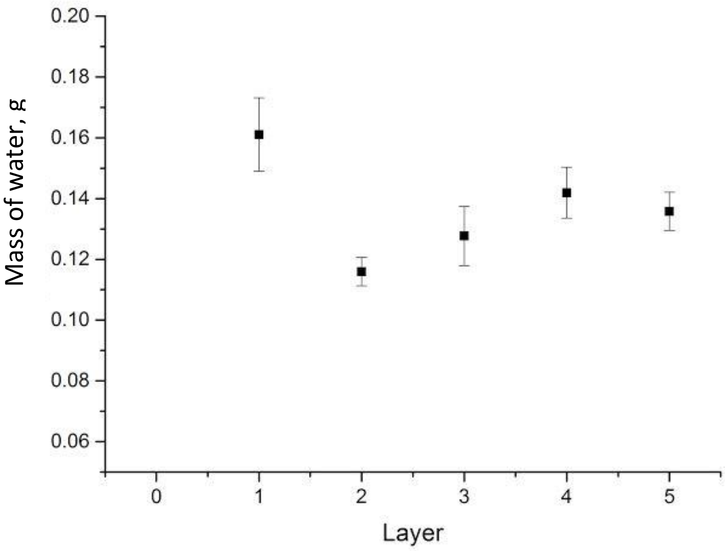


Figure 4.6 The increased mass of the sample attributed to moisture with respect to the number of layers of PEDOT:PSS applied

4.3.3 Topology of PEDOT:PSS layers applied to the latex coated carton board

This work was undertaken to evaluate the physical appearance of the conductive polymer and to relate this appearance to the performance of the conductive polymer assembly.

The carton board substrate provides a more planar surface onto which the conductive polymer can form a film than would be provided by textile substrates. After one application of PEDOT:PSS to the latex treated carton board, discrete areas of conductive polymer were seen, see Figure 4.7, as darker blue areas across the surface. These would describe the very high electrical resistance of these zones since, in order to conduct electricity, there has to be at least one, unbroken pathway across the surface. The greater the number of pathways, the greater the conductivity would be.

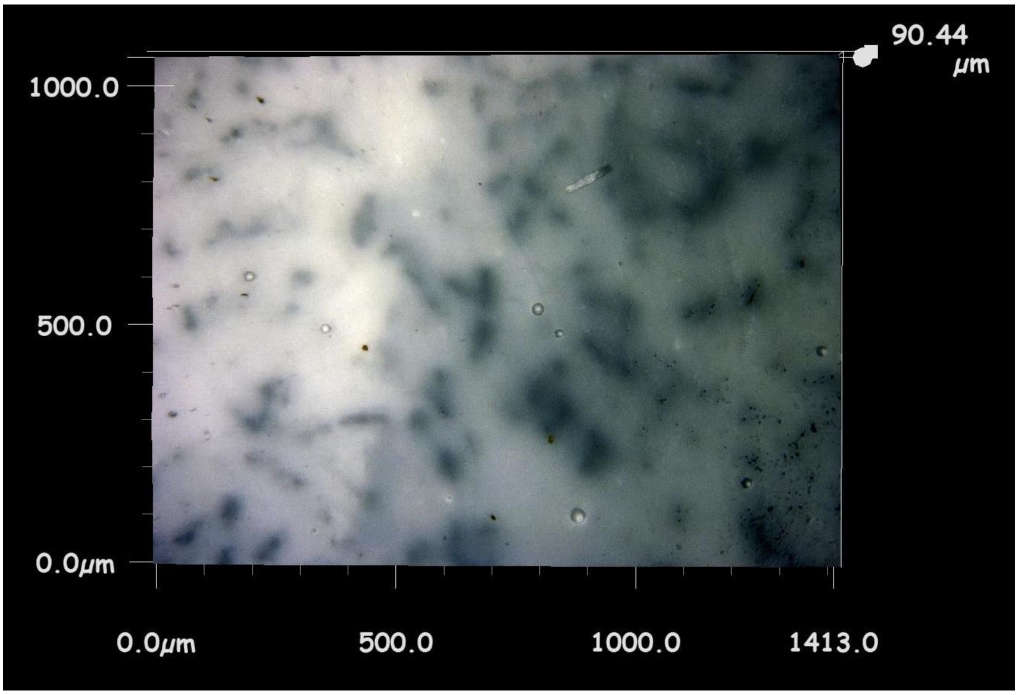


Figure 4.7 3D microscope image after one layer of PEDOT:PSS has been applied to the latex coated carton board substrate at 250x magnification

Once two layers of PEDOT:PSS were applied, a coherent film formed across the surface with K-bar lines displayed, see Figure 4.8. These lines are minutely raised from the rest of the surface and are due to the construction of the K-bar. As the K-bar is a wire wrapped rod, the gaps between each wrap of the wire give this extra height of a small portion. These lines continued across the whole sample and mostly throughout its length. Such irregularities could potentially impact the electrical conductivity of the sample due to the uneven surface coverage of the conductive polymer. It is intended that with subsequent applications of polymer, an equal amount of polymer would be retained at each point of the film to produce a thicker film with a lower electrical resistance. If these raised sections occur, there would be areas of the film highly conductive in one direction, along the direction of the line and ideally, the film should be equally conductive in all directions. Notably, these raised lines did not present themselves on the fabric substrate in Chapter Three, so would not pose an issue for application to textile substrates.

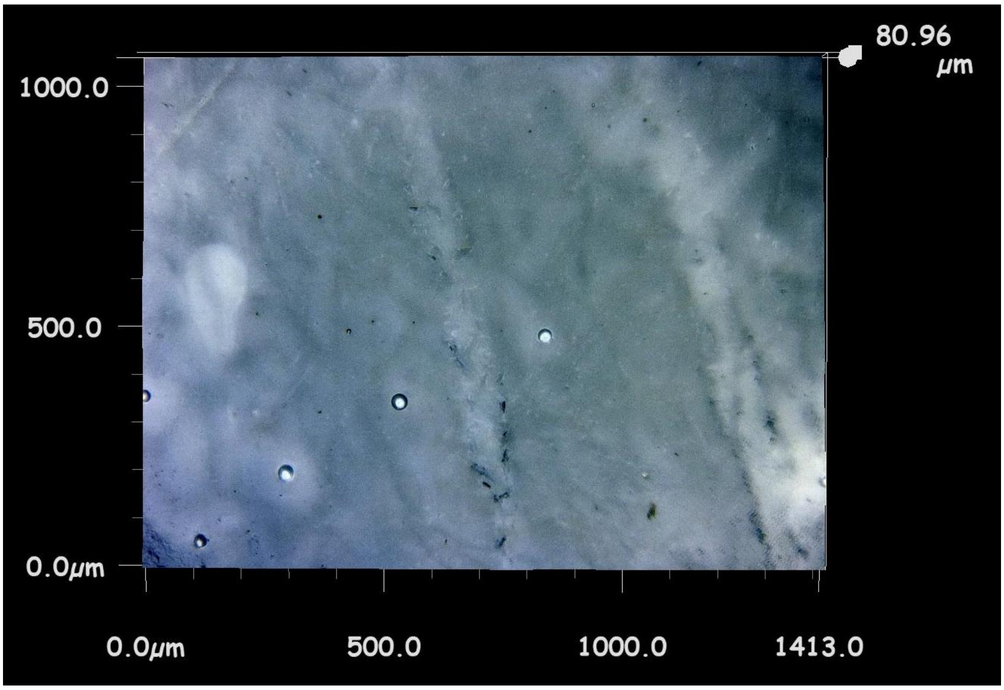


Figure 4.8 3D microscope image of a sample with two layers of PEDOT:PSS applied to the latex treated carton board substrate displaying the lines from application with a K-bar at 250x magnification

Magnification of the surface after three layers of PEDOT:PSS were applied showed a surface with a greater build-up of conductive polymer, again, the lines are due to the use of the K-bar, see Figure 4.9.

In some samples, trapped air bubbles occurred in the PEDOT:PSS matrix, see Figure 4.10. These bubbles will most likely be due to air captured by surfactant in the aqueous PEDOT:PSS dispersion when mixing prior to application.

As increasing layers of PEDOT:PSS were applied, the polymer film became more prone to physical damage. Figure 4.11 shows some damage caused by the two point probe. The two point probes were contacted with the surface with some pressure to achieve the good connection needed for reliable resistance measurements. This adversely affects the surface structure which will ultimately increase the electrical resistance which can be measured at these points. The “damage” arises as indentations of *ca.* 600 µm in diameter.

The brittle nature of the PEDOT:PSS is further displayed in Figure 4.12. This is chipped away or it could have cracked during the drying stage, some samples coming away from the polymer-latex-carton board composite.

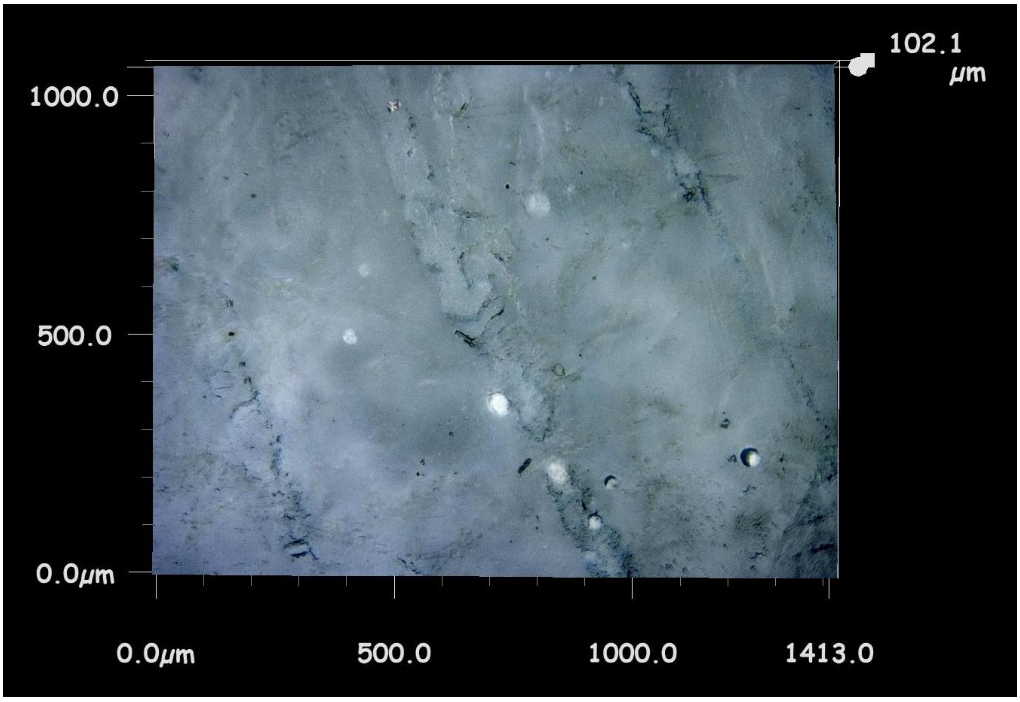


Figure 4.9 3D microscope image of a sample with three layers of PEDOT:PSS applied to the latex treated carton board substrate at 250x magnification. Lines due to the K-bar are present once more

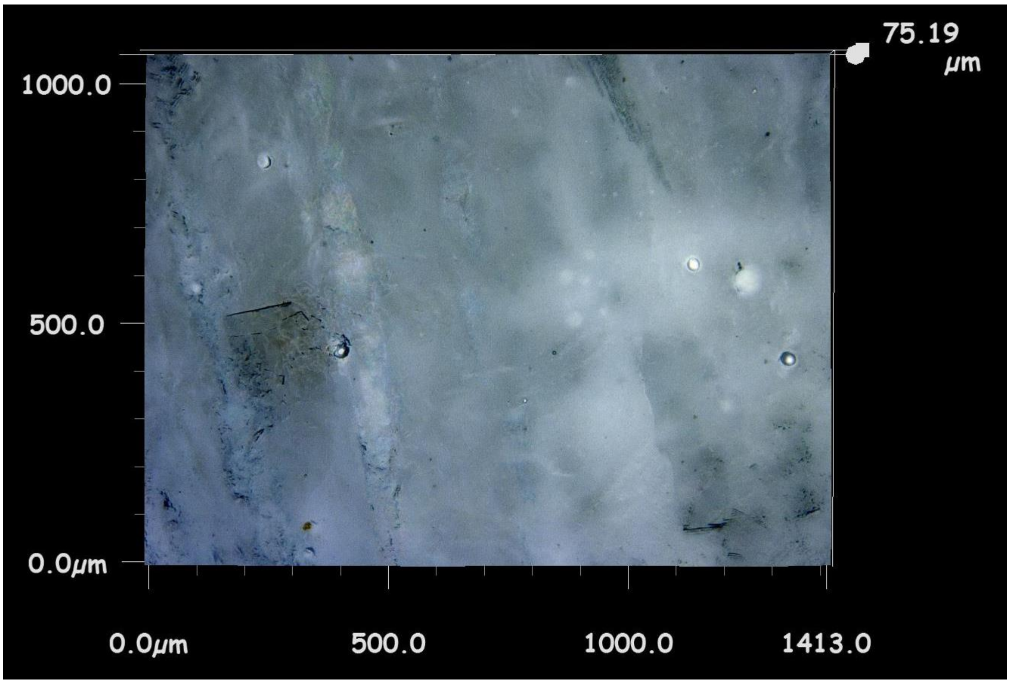


Figure 4.10 3D microscope image of a sample with four applications of PEDOT:PSS on a latex treated carton board substrate

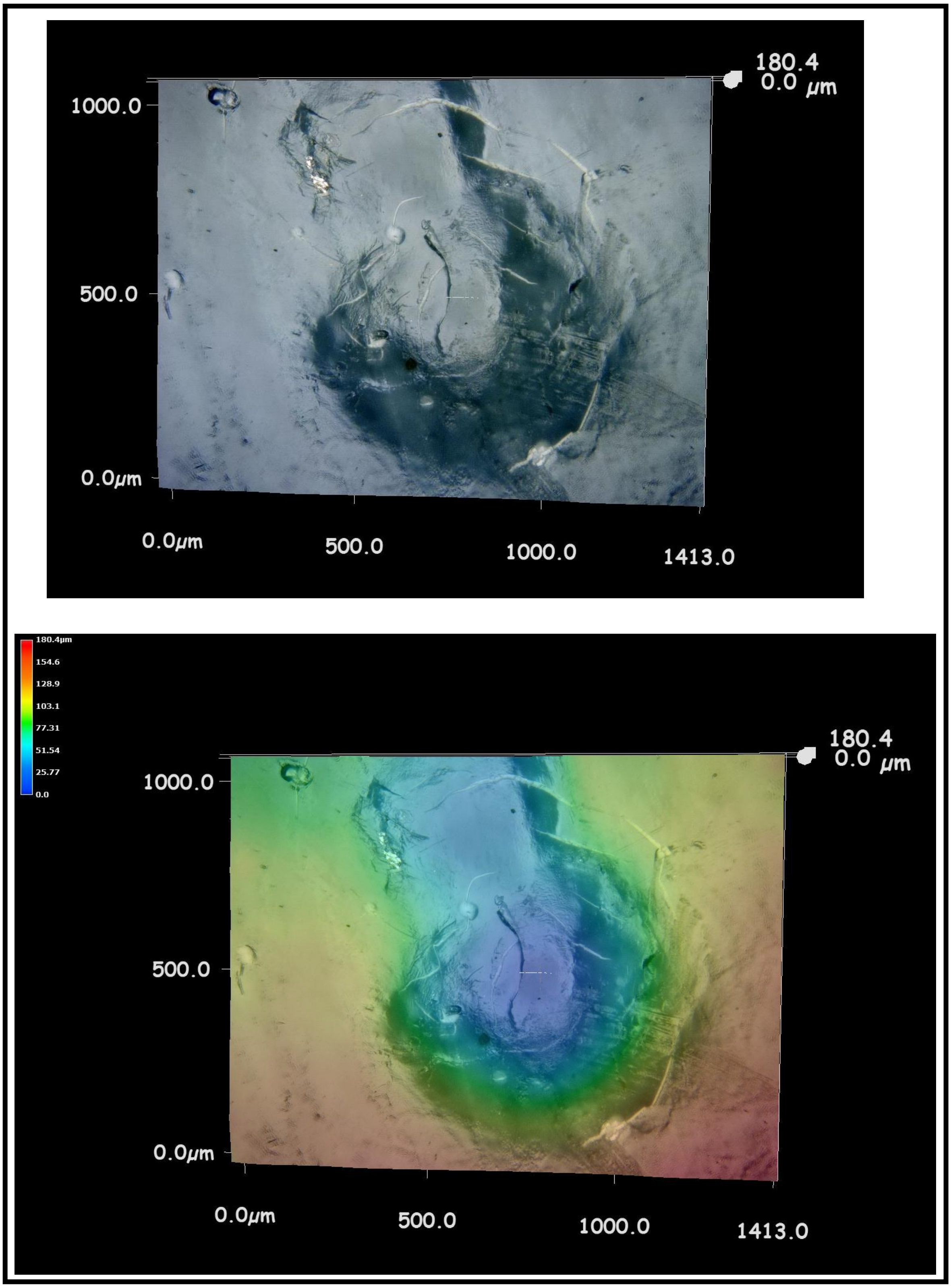


Figure 4.11 3D microscope images of a sample with five layers of PEDOT:PSS applied to a latex treated carton board substrate, at 250x, which show the damage caused to the surface due to the use of the two point probe. The top image shows the sample normally while the bottom image has colours to show the relative height of the areas, blue is low while red is high

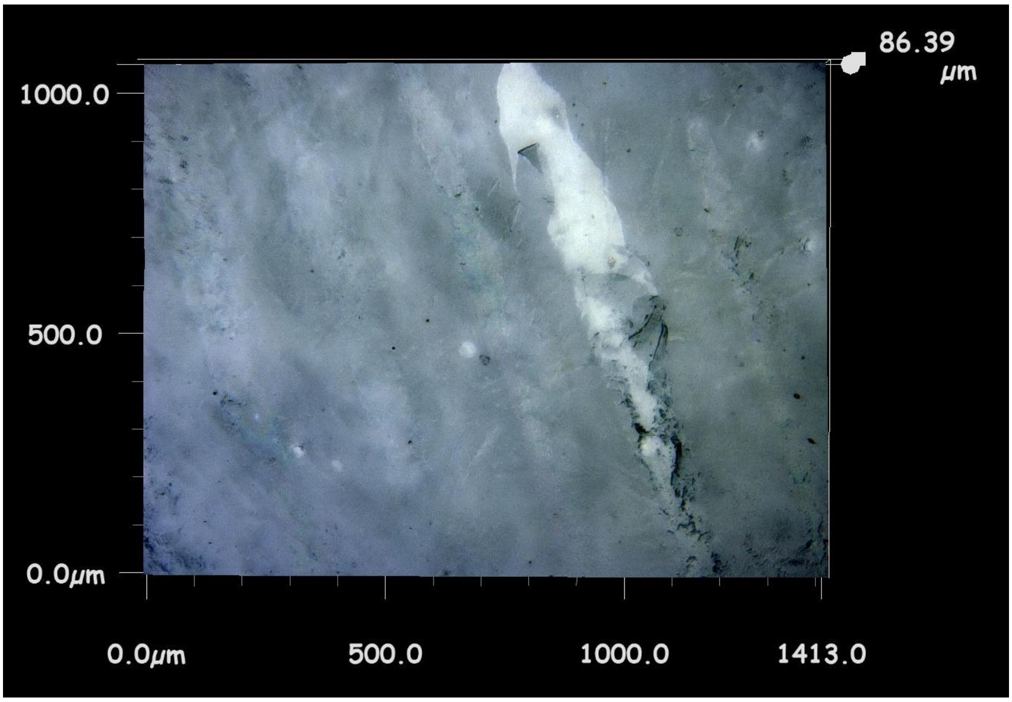


Figure 4.12 3D microscope image of a sample with five applications of PEDOT:PSS to a latex treated carton board substrate, at 250x magnification, displaying the brittleness of the surface coating

Figure 4.13 Photograph of the PEDOT:PSS coated samples. Samples are numbered 1-15 from top left to bottom right. Increasing number of applications of PEDOT:PSS from one to five layers from left to right in triplicate

Figure 4.13 shows an overall picture of the PEDOT:PSS coated latex treated samples. It was intended to form homogeneous layers on each of the samples but this did not happen. The conductive polymer accumulated in some areas while leaving other areas partially uncovered. This could explain the relatively high resistances that were observed compared to the data presented in the earlier Chapter Three, in addition to the wider coverage described earlier. This behaviour could be caused by the repulsion of the aqueous dispersion of the conductive polymer by the latex treated surface of the carton board substrate. The damage which can be caused to the PEDOT:PSS displays the importance of using a top latex layer in order to protect it, described later.

4.3.4 Electrical resistance measurements of the composite with copper wire electrodes

4.3.4.1 Ambient electrical resistance measurements

The nickel coated copper electrodes were applied to the surface using an electrically conductive epoxy to give a better surface contact area to improve upon the earlier two point probe method. This method reported very similar values of resistance with the lowest being *ca.* 4.4 ± 16 k Ω cm^{-1} but the standard deviations of the readings were much larger than using the two point probe. This deviation is not wholly due to the electrodes but the water absorption described earlier.

4.3.4.2 Electrical resistance measurements post drying

Unlike the previously discussed example, when the samples with copper electrodes were dried in the oven their resistance values became comparable to those of the samples when at ambient conditions. The effect that the drying does have though was to reduce the standard deviation of the readings, see Figures 4.15 and 4.16.

The ambient example described previously has an electrical resistance of 4.4 ± 16 k Ω cm^{-1} while after drying, the equivalent value is 3.55 ± 4.8 k Ω cm^{-1}. Despite the epoxy being allowed to react and set for a number of days, it is thought that the oven treatment has furthered and finalised the cure which ultimately gave a better contact with the PEDOT:PSS surface.

Table 4.2 Resistances measured of samples with copper electrodes both at ambient conditions and after drying and average values with respect to the number of applications of PEDOT:PSS applied. $^{+}$ Outlier, * average taken disregarding outliers.

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ambient Resistance with copper electrodes, k Ω cm^{-1}	38.2	24.35	20.1	27.9	41.65	57.7	12.15	6.05	4.4	4.35
Post Drying Resistance with copper electrodes, k Ω cm^{-1}	32.1	22.7	17.45	23.8	300^{+}	51.3	10.6	4.95	3.2	3.55

Sample	**11**	**12**	**13**	**14**	**15**
Ambient Resistance with copper electrodes, k Ω cm^{-1}	18.25	10.35	20.5	11	8.5
Post Drying Resistance with copper electrodes, k Ω cm^{-1}	12.85	8.35	18.5	7.25	13.1

Layer	**1**	**2**	**3**	**4**	**5**
Ambient Resistance with copper electrodes, k Ω cm^{-1}	38.05	15.62	15.55	14.43	18.17
Post Drying Resistance with copper electrodes, k Ω cm^{-1}	32.08	13.88	13.63	11.42	8.33*

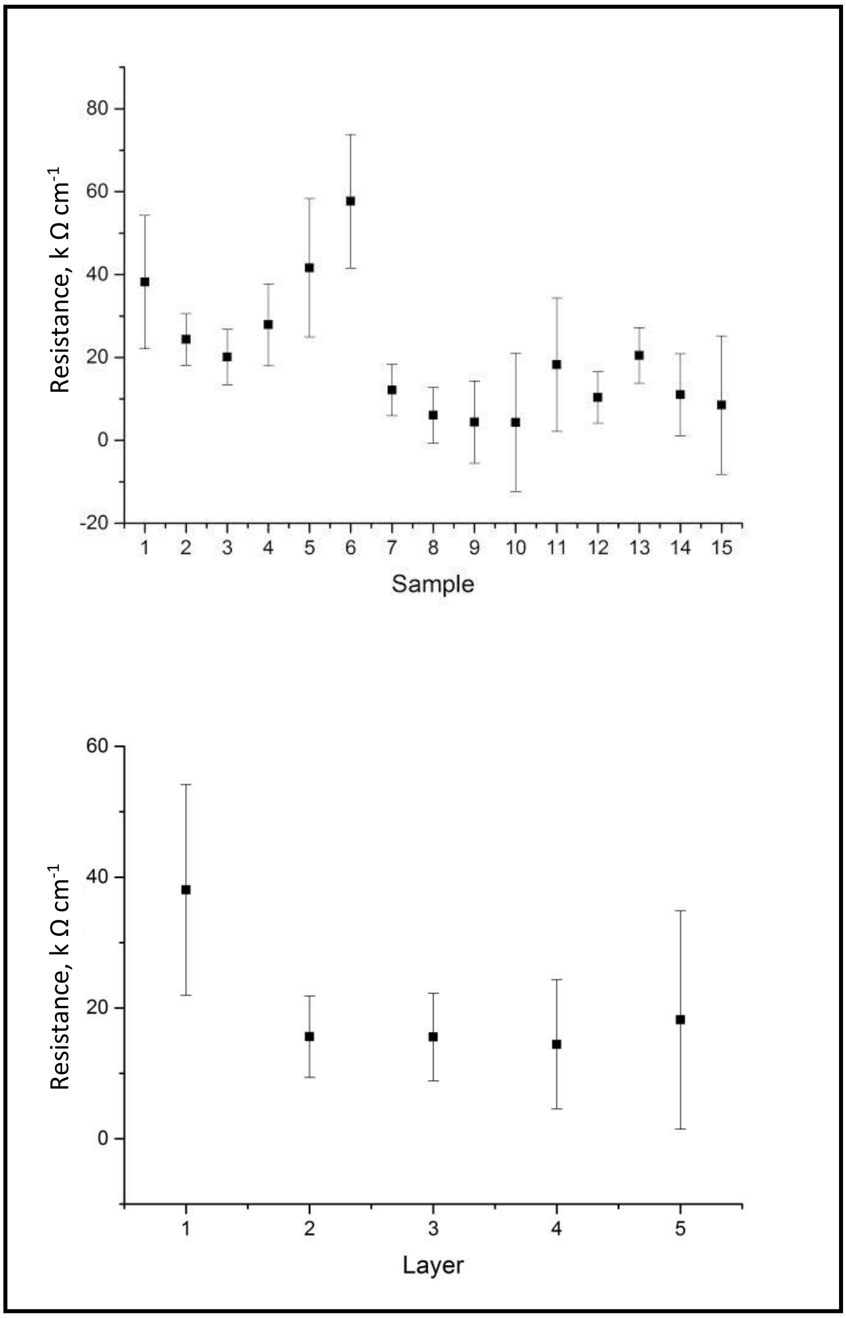


Figure 4.14 Ambient resistance measurements of the samples after nickel coated copper electrodes were attached to the conductive polymer surface. The top plot shows resistances of individual samples while the bottom plot shows average readings with respect to the number of layers of PEDOT:PSS applied

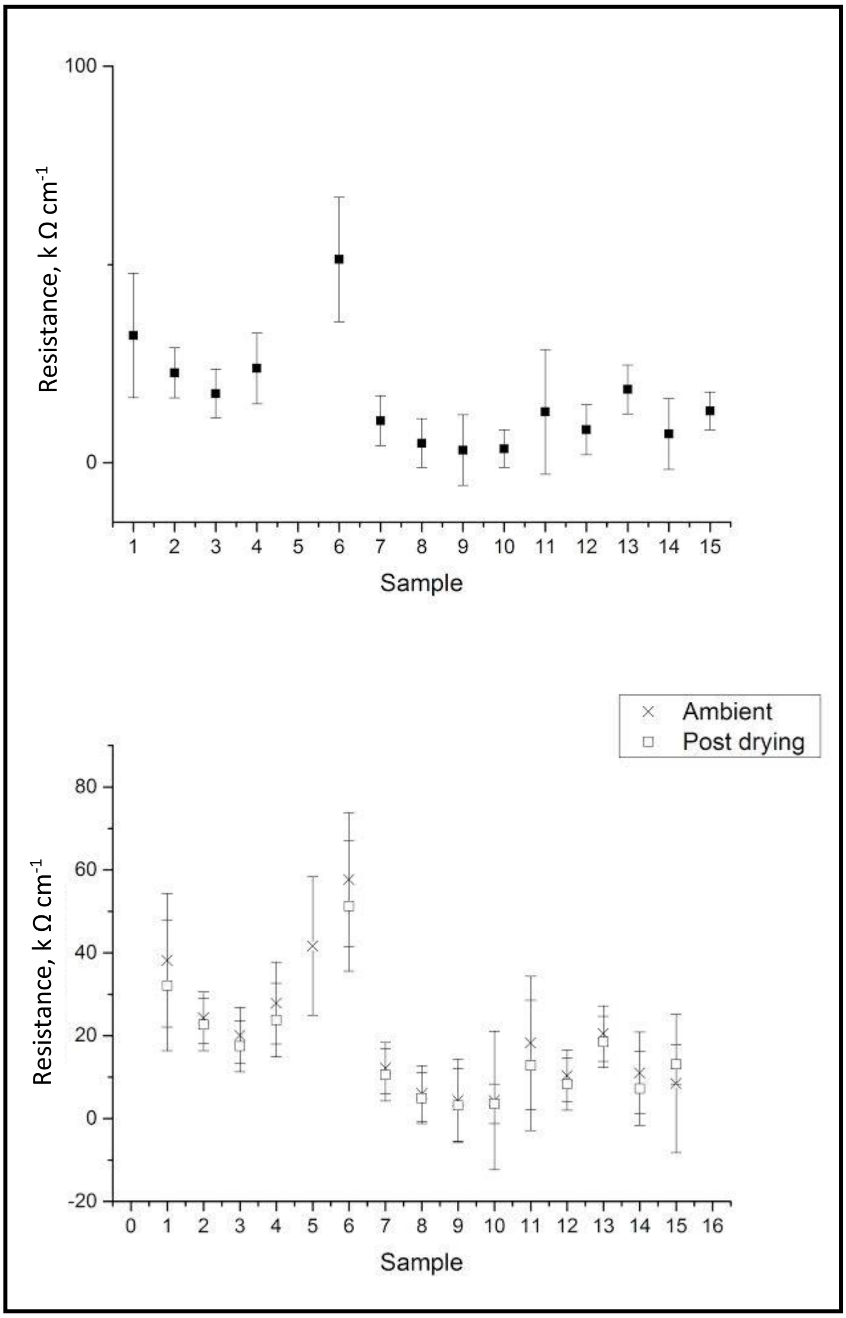


Figure 4.15 Resistance measurements taken of the samples with copper electrodes after they had been dried in the oven. The top plot shows only dried resistance while the bottom plot displays the comparison to the ambient resistances

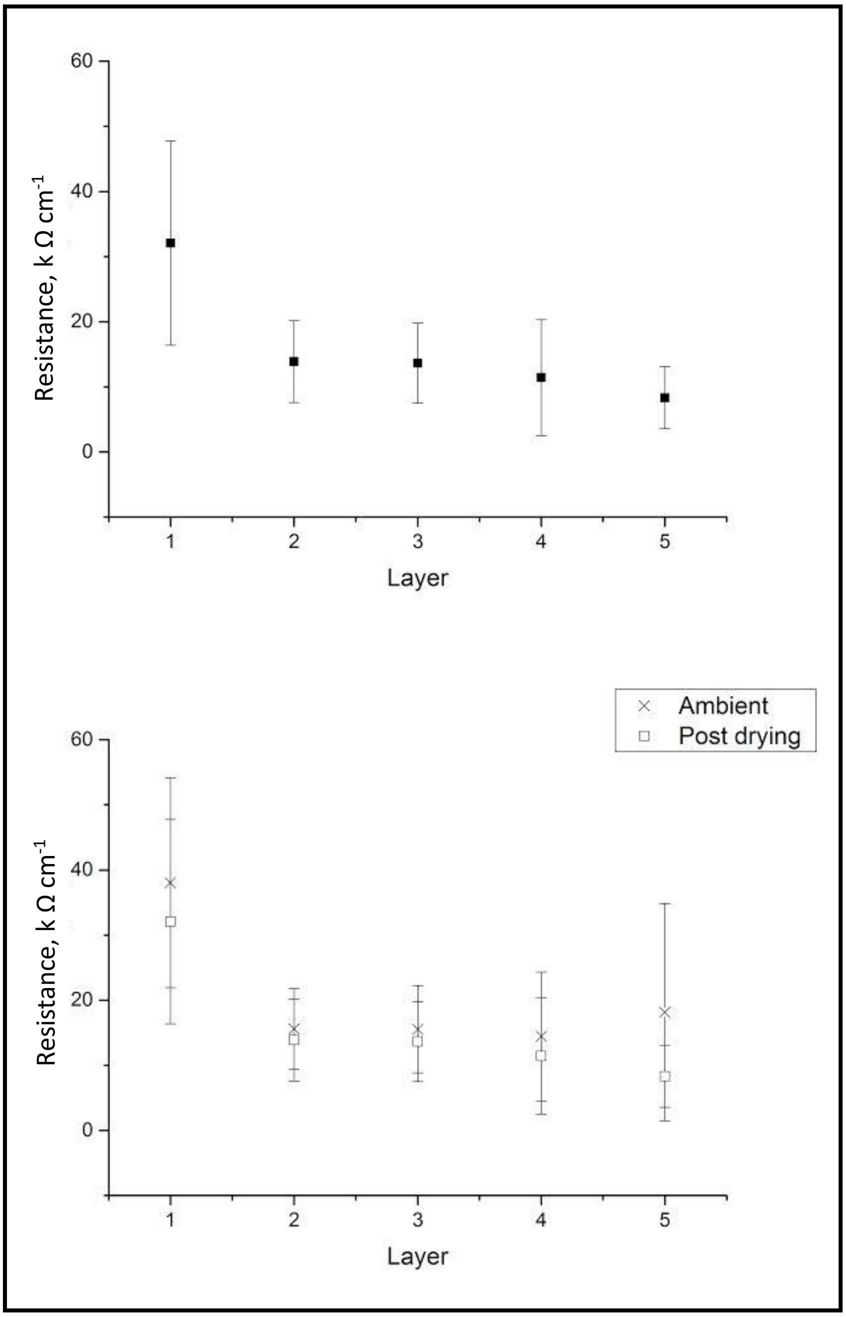


Figure 4.16 Average resistance measurements taken of the samples with copper electrodes after they had been dried in the oven. The top plot shows only dried resistance while the bottom plot displays the comparison to the ambient resistances

Figure 4.17 shows the arrangement of nickel coated copper electrodes used on the samples with the electrically conductive epoxy applied at the base of them. The electrodes were cut to *ca.* 50 mm, such a length so crocodile clips could be used to connect them with the ohmmeter without damaging the epoxy-electrode-surface bonding as the epoxy is relatively brittle.

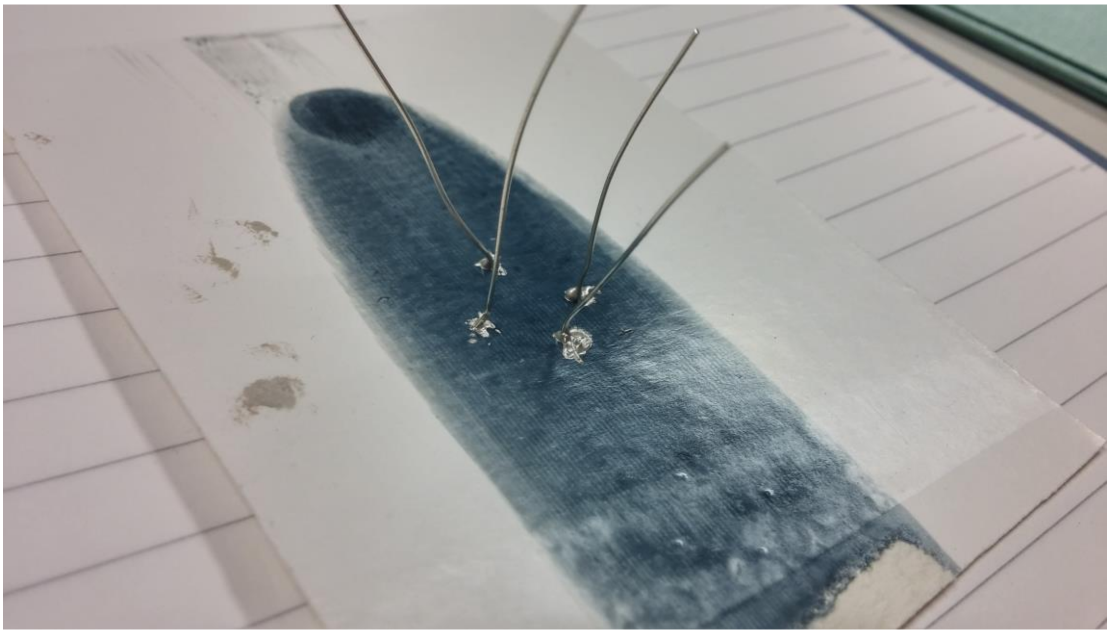


Figure 4.17 Photograph of the copper electrodes that have been attached to the conductive polymer surface

4.3.5 Electrical resistance measurements of the composite with electrodes and the latex top layer

The final top layer of latex was brushed onto the surface of the sample with a small brush and allowed to dry. This process was repeated until the surface was electrically insulating (resistance > 100 M Ω) measured by the two point probe. This latex top layer is intended to form a barrier to protect the PEDOT:PSS coated surface from scratching and from the high amount of friction present during a wash cycle in a washing machine.

4.3.5.1 Ambient electrical resistance measurements

In the previous sections, the lowest resistance that has been measured has been of sample 10. At the previous stage, this resistance, at ambient conditions, was 4.4 ± 16 k Ω cm^{-1}. After drying the latex top layer and allowing the sample to reach ambient conditions, this resistance was lower still, at 2.0 ± 0.93 k Ω cm^{-1}. The electrical resistances measured are presented in Figure 4.18 and Table 4.3.

A possible explanation of this phenomenon is that the latex dispersion is aqueous and as the dispersion is dried it begins to film form which could trap moisture at the interface between the latex film and the PEDOT:PSS coated surface. This thin layer of water could aid the electrical conductivity of the composite.

Table 4.3 Resistances measured of samples with copper electrodes and a latex top layer both at ambient conditions and after drying and average values with respect to the number of applications of PEDOT:PSS applied. $^{+}$ Outlier, * average taken disregarding outliers.

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ambient Resistance with copper electrodes, k Ω cm^{-1}	45.95	23.45	15.9	16.2	61.4^{+}	26	9.55	4.6	17.4	2
Post Drying Resistance with copper electrodes, k Ω cm^{-1}	33.1	16.5	8.75	9.35	28.05	26.6	7.15	3.55	1.45	1.4

Sample	**11**	**12**	**13**	**14**	**15**
Ambient Resistance with copper electrodes, k Ω cm^{-1}	13.05	12.15	10.6	4	5.7
Post Drying Resistance with copper electrodes, k Ω cm^{-1}	9.45	7.35	5.95	2.35	3.2

Layer	**1**	**2**	**3**	**4**	**5**
Ambient Resistance with copper electrodes, k Ω cm^{-1}	28.33	15.05	10.37	12.53	3.85*
Post Drying Resistance with copper electrodes, k Ω cm^{-1}	23.05	10.33	6.08	4.38	10.88

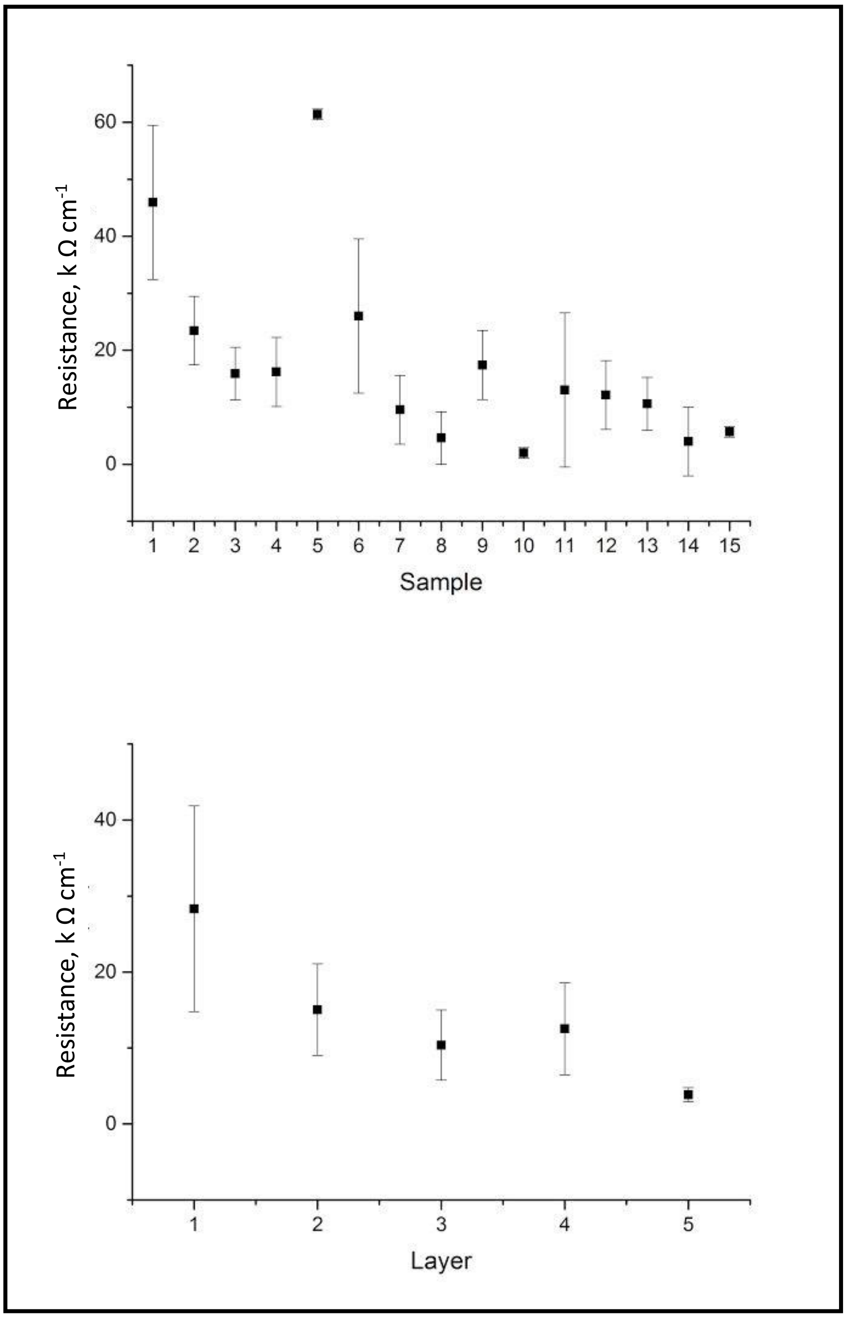


Figure 4.18 Ambient resistance of samples with a final application of latex after application of the copper electrode and PEDOT:PSS coating. The top plot shows values for each sample, the bottom plot shows average resistance values with respect to the number of applications of PEDOT:PSS applied to the sample

4.3.5.2 Electrical resistance measurements recorded post drying

Once more the effect of drying in the oven was investigated by measuring the resistances of the samples. As is displayed in Table 4.3 and Figures 4.19 and 4.20, a reduction of electrical resistance has been witnessed for all samples. Sample 10 in particular has an improved resistance of 1.4 ± 0.9 k Ω cm^{-1}.

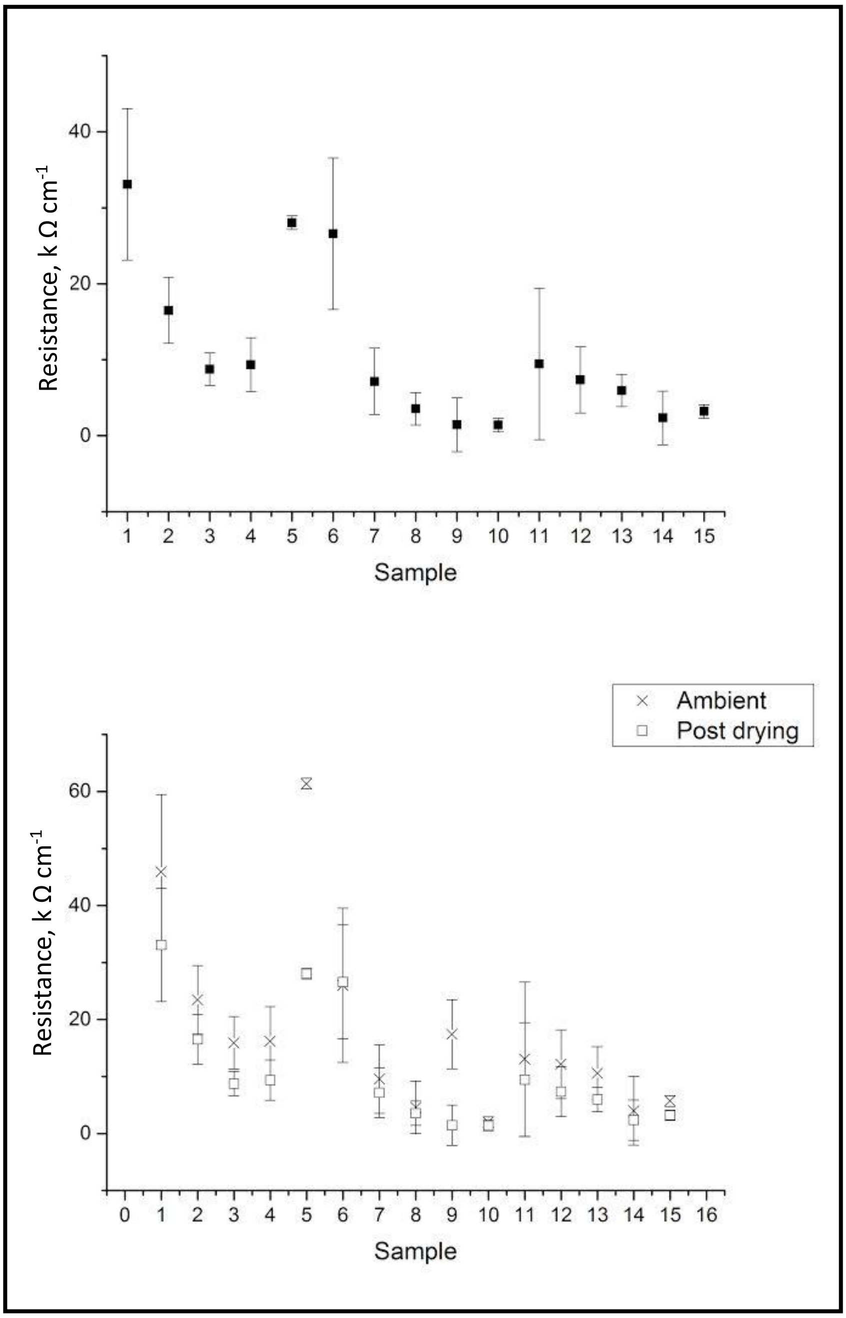


Figure 4.19 Electrical resistances of the samples with a latex top layer and copper electrodes after they had been dried. The top plot shows only the data post drying while the bottom plot compares ambient and post drying resistances

The resistances measured shows that when the samples have a lower moisture content, the sample is more electrically conductive. As described previously, it is proposed most of the moisture is lost by the substrate rather than the polymer coated surface layers. The card substrate could be swelling when absorbing water so the opposite would occur when drying. This could cause the substrate to shrink thus bringing the areas of the conductive polymer closer to conduct charge more efficiently. If this was the case, the same effect would be present without the latex top layer but perhaps the latex top layer is amplifying the effect. This phenomenon needs closer examination during further study.

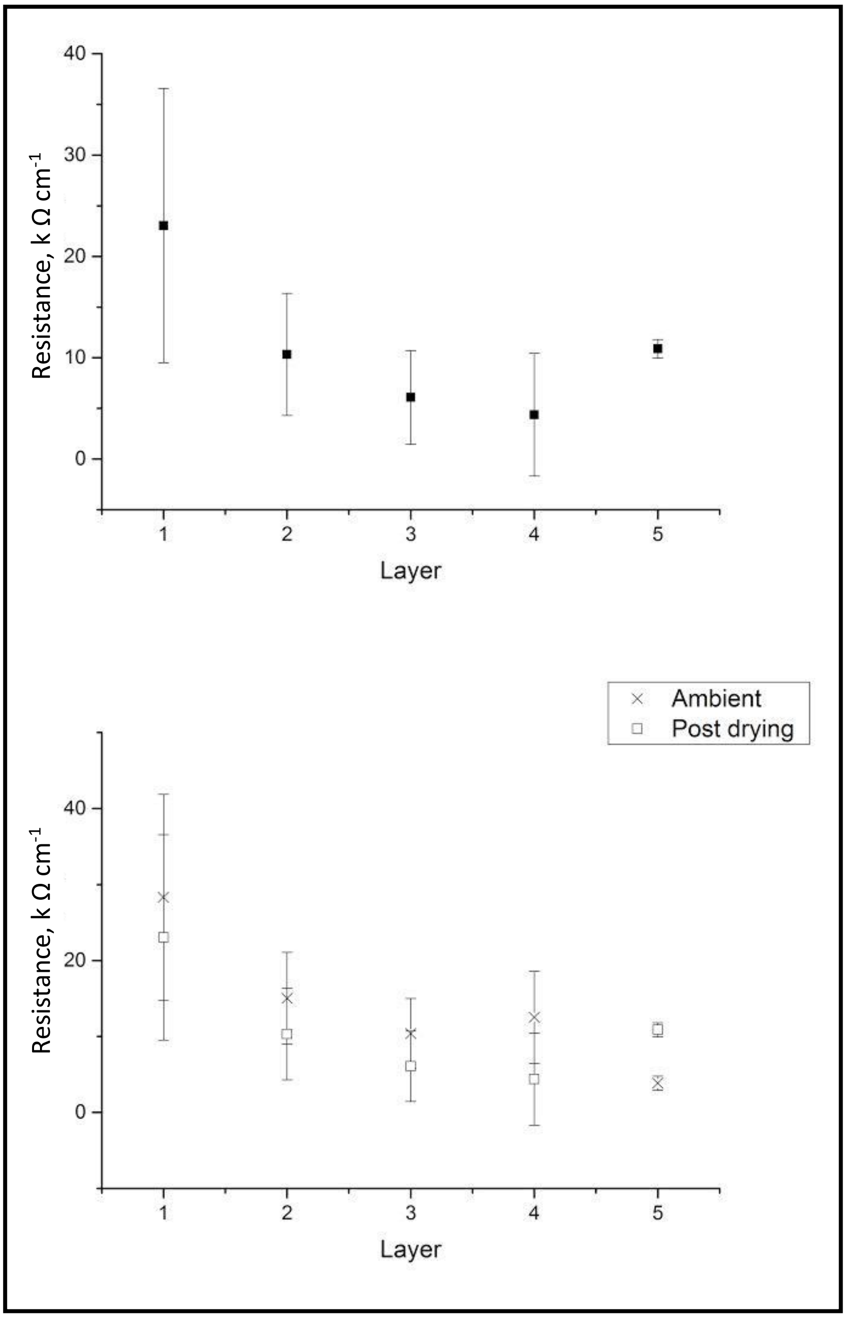


Figure 4.20 Average resistance measurements with respect to the number of layers of PEDOT:PSS applied, of the samples with the latex top layer and copper electrodes after they were dried. The top plot shows only the data post drying while the bottom plot compares ambient and post drying resistances

4.3.6 Discussion

This section aims to discuss all of the data presented in this chapter collectively in order to understand any potential additive effect of each of the process steps.

It was noted previously that after each process step namely, application of PEDOT:PSS, application of nickel coated copper electrodes and the application of the latex top layer, the lowest electrical resistance measured decreased, therefore the samples had a higher electrical conductivity. This single value monitored over three processes, does not alone accurately reflect the overall effect of the processing steps on measured resistance.

Figure 4.21 displays the data that is provided in Table 4.4 to demonstrate that, there is no discernible difference or improvements of the measured electrical resistances when the samples are allowed to reach ambient conditions. There are some examples of reduced variability of the measure, but when viewing the average resistance value with respect to the number of layers of PEDOT:PSS applied, a similar resistance value is returned.

The same is also true regarding the resistance measurements recorded post drying. Disregarding the obvious outliers, there is no discernible difference between the measured resistances, see Table 4.5 and Figure 4.22.

These results display that the idea to use a copper electrode with a conductive epoxy in order to measure electrical resistance through an electrically insulating top layer of latex will return the same electrical resistance as the use of the two point probe. It was shown earlier that the two point probe can damage the surface of the PEDOT:PSS film. The use of these electrodes removes that potential of damage completely. This work suggests that this method to use a latex top layer to protect the electrically conductive polymer will not adversely affect the electrical conductivity of the created samples.

There are some noted differences in measured electrical resistance which appear to be due to the water content of the composite sample. The difference in measurements appears to be regardless of the process that has taken place on the sample so therefore would be inherent with the substrate. This effect would have to be investigated when attempting tests on other substrates to understand the possible effects of moisture absorption from the atmosphere.

Table 4.4 Resistance measurements of the samples after PEDOT:PSS has been applied, after application of the nickel coated copper electrodes and after the final layer of latex had been applied. Bottom shows the average resistance measurements with respect to the number of PEDOT:PSS applications made to the latex treated substrate. These measurements were taken at ambient conditions. $^+$ Outlier, * average taken disregarding outliers.

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
PEDOT:PSS, k Ω cm^{-1}	75	16	17	7.75	8	28	12.5	10.75	11.25	3.75
Copper electrode, k Ω cm^{-1}	38.2	24.35	20.1	27.9	41.65	57.7	12.15	6.05	4.4	4.35
Latex top layer, k Ω cm^{-1}	45.95	23.45	15.9	16.2	61.4$^+$	26	9.55	4.6	17.4	2

Sample	**11**	**12**	**13**	**14**	**15**
PEDOT:PSS, k Ω cm^{-1}	14.5	13	8.75	6	3.8
Copper electrode, k Ω cm^{-1}	18.25	10.35	20.5	11	8.5
Latex top layer, k Ω cm^{-1}	13.05	12.15	10.6	4	5.7

Layer	**1**	**2**	**3**	**4**	**5**
PEDOT:PSS, k Ω cm^{-1}	39.17	16.17	13.58	9.67	5.58
Copper electrode, k Ω cm^{-1}	38.05	15.62	15.55	14.43	18.17
Latex top layer, k Ω cm^{-1}	28.33	15.05	10.37	12.53	3.85*

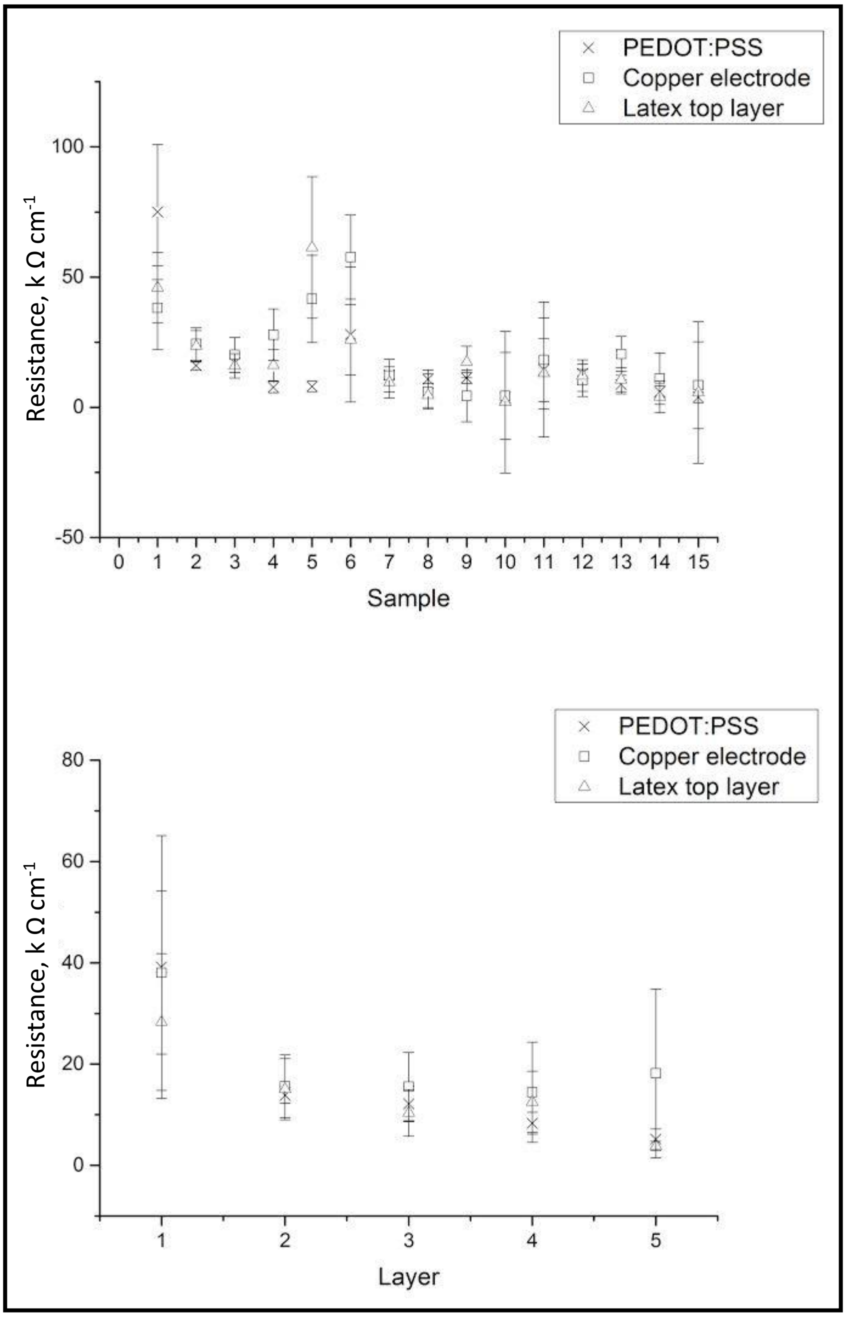


Figure 4.21 A comparison of all the resistance measurements taken when the samples were left to reach ambient conditions. The top plot shows resistance measurements of all samples while the bottom plot displays average resistance measurements with respect to the number of applications of PEDOT:PSS to the card substrate

Table 4.5 Resistance measurements of the samples after PEDOT:PSS has been applied, after application of the nickel coated copper electrodes and after the final layer of latex had been applied. Bottom shows the average resistance measurements with respect to the number of PEDOT:PSS applications made to the latex treated substrate. These measurements were taken directly after treatment in the oven. $^{+}$ Outlier, * average taken disregarding outliers $^{+}$ Outlier, * average taken disregarding outliers.

Sample	1	2	3	4	5	6	7	8	9	10
PEDOT:PSS, k Ω cm^{-1}	67.5	32	20	12.5	9.75	40	27	15.5	8	3.25
Copper electrode, k Ω cm^{-1}	32.1	22.7	17.45	23.8	300^{+}	51.3	10.6	4.95	3.2	3.55
Latex top layer, k Ω cm^{-1}	33.1	16.5	8.75	9.35	28.05	26.6	7.15	3.55	1.45	1.4

Sample	11	12	13	14	15
PEDOT:PSS, k Ω cm^{-1}	67.5	20	13	10	5
Copper electrode, k Ω cm^{-1}	12.85	8.35	18.5	7.25	13.1
Latex top layer, k Ω cm^{-1}	9.45	7.35	5.95	2.35	3.2

Layer	1	2	3	4	5
PEDOT:PSS, k Ω cm^{-1}	58.33	29.50	17.75	10.25	6.50
Copper electrode, k Ω cm^{-1}	32.08	13.88	13.63	11.42	8.33*
Latex top layer, k Ω cm^{-1}	23.05	10.33	6.08	4.38	10.88

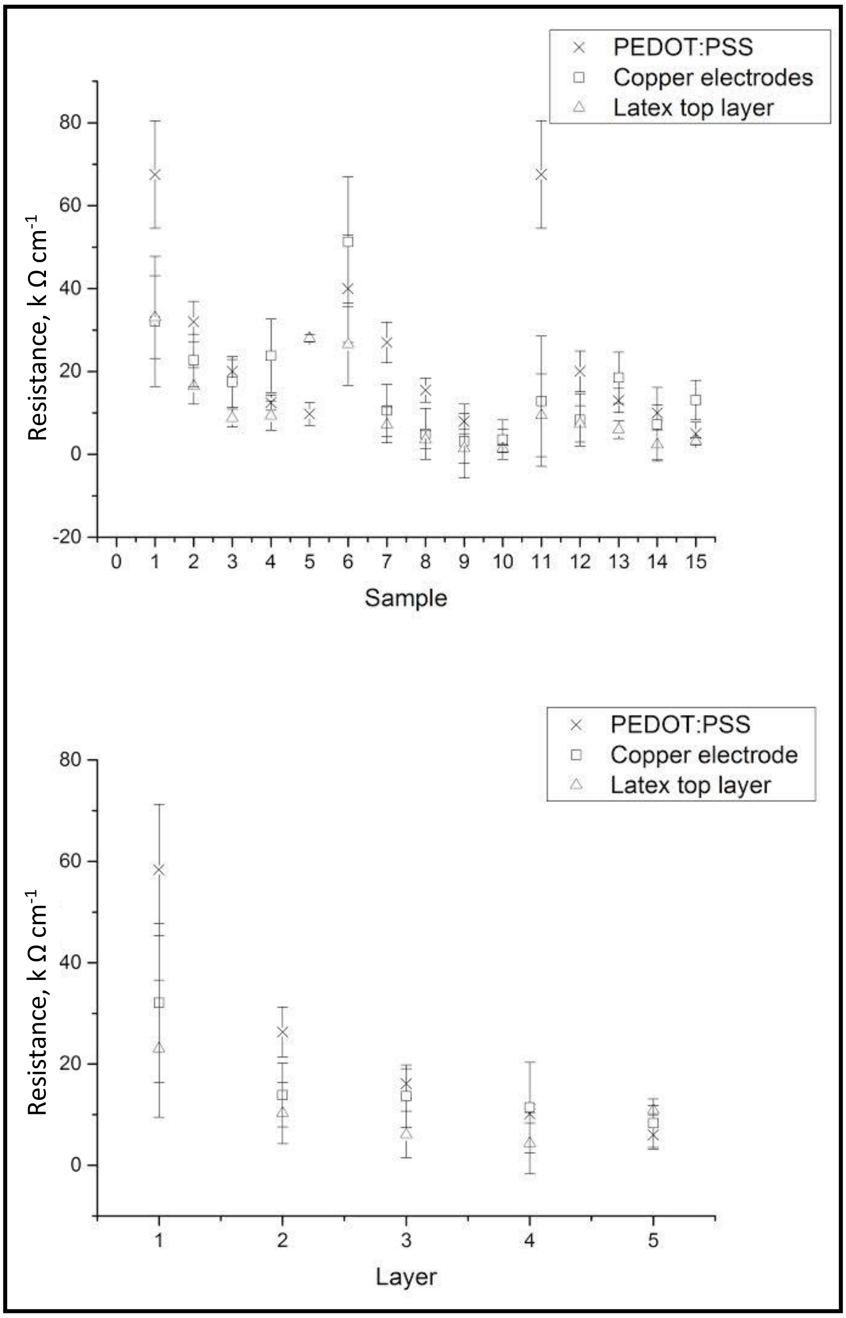


Figure 4.22 A comparison of all the resistance measurements of the samples post drying. The top plot shows resistance measurements of all samples while the bottom plot displays average resistance measurements with respect to the number of applications of PEDOT:PSS to the card substrate

4.4 Conclusions

It has been demonstrated that a synthesised latex dispersion can be applied to a carton board surface to provide a thin film of latex on the surface. Subsequently, an aqueous dispersion of PEDOT:PSS can be applied to the hydrophobic, latex film. Electrical resistances can be measured with using a two point probe but the associated error can be large due to the measured resistance being directly proportional to pressure, to an extent.

The surface layer of PEDOT:PSS was shown to be brittle and prone to damage. The two point probe left impressions and was shown to crack the PEDOT:PSS layer. Damage to the layer could also be inflicted by friction with evidence of a portion of the sheet breaking away from the surface.

Nickel coated copper electrodes were applied to the PEDOT:PSS layer using a two part, electrically conductive epoxy. This successfully provided a means to measure the resistances without applying pressure, thus not damaging the surface coating, while also reducing the error associated with the measurements.

Application of the top layer of latex can provide an electrically insulating surface (resistance > 100 M Ω). Despite the electrically insulating surface, the latex does not affect the electrical resistance of the PEDOT:PSS layers beneath, measured using the aforementioned electrodes.

The study conducted discovered a potential issue which existed throughout the experiment and which should be considered when planning further trials. The electrical resistance of the samples were measured after being allowed to reach ambient conditions, described previously, and also immediately after the samples were removed from the oven (post drying), the measured resistances differed. This variation was considered to be due to the substrate absorbing water from the atmosphere. During this study, the differences were not significant yet this variability could be present and should be considered in future experiments. The total mass of moisture per sample in this particular study was up to around 2.31 % but this mass will differ with respect to different substrates.

The electrical resistances reported from this study would be too low for the intended purpose but the ultimate resistance values that have been attained are not intended to represent those which can be achieved on a fabric substrate. Due the planar nature of the carton board substrate, the hydrophobicity of its surface treatment and the aqueous state the polymer is in, the film that can be formed *via* application with a K-bar will be thin as the polymer is forced down and away from the sample. A cotton substrate has the ability for the polymer dispersion to swell the cotton fibres which would lead to a higher loading of conductive polymer from each subsequent addition. This study was intended to understand the limitations of, and the effect that, a multi layered assembly would have on the electrical resistance of an electrically conductive polymer.

This study provides a basis on which to build further study to investigate fabric substrates. This multi layered approach was used in an attempt to deliver a crease resistant and wash resistant electrically conductive textile fabric, described in Chapter Five.

Chapter Five

Application of a composite of PEDOT:PSS and a latex to a woven cotton fabric substrate

5.1 Experimental design

The electrical resistance of the multi-layered system of PEDOT:PSS – latex on a woven cotton fabric substrate was investigated. Initially, a layer of latex, poly(butyl acrylate)-co-(styrene), was applied as a base layer, intended to fill the voids of the woven cotton fabric, then PEDOT:PSS was applied in layers, as described in Chapters 3 and 4, using a K-bar 4, giving fabric samples with up to 5 layers of PEDOT:PSS. An application of the latex to the surface of the conductive polymer resulted in an electrically resistant surface. Thus, prior to this application, an electrode was applied using an electrically conductive epoxy.

The electrical resistances of the PEDOT:PSS coated cotton fabrics were measured prior to the application of the top layer of latex, post application of the electrically conductive epoxy electrodes and post application of the top layer of latex. Creasing the sample had only a small detrimental effect on electrical conductivity so these samples did not undergo creasing but were examined for wash resistance.

5.2 Sample preparation

5.2.1 Synthesis and application of latex to a woven cotton fabric substrate

5.2.1.1 Synthesis of latex

Please refer to Chapter Four for the synthesis of latex.

5.2.1.2 Application of latex to the woven cotton fabric substrate

Due to the high water content of the produced latex dispersion, application using a K-bar was not possible due to the pores present in the woven cotton material. The cotton samples were immersed into the dispersion and then laid out to dry. This was repeated, providing 2 dips in total.

5.2.2 Application of PEDOT:PSS layers

PEDOT:PSS was applied to the latex-coated cotton fabric using a K-bar 4. A 1 wt. % aqueous dispersion of PEDOT:PSS (*ca.* 1 mL) was applied across the top of the sample and the K-bar 4 was drawn down to give a coating on the surface. Each sample was placed in the oven at 40 °C to dry after each application of PEDOT:PSS. This process was repeated to give samples with one to five layers of PEDOT:PSS in triplicate.

5.2.3 Application of electrically conductive epoxy electrodes

The electrically conductive epoxy, namely CircuitWorks® Conductive Epoxy CW2400 manufactured by ITW Chemtronics, is a 2 part epoxy containing silver which when mixed, provides a hard, electrically conductive bonding. The 2 parts were mixed and then applied to the PEDOT:PSS coated samples as 4 small globules in a rhombus shape separated by *ca.* 10 mm in the x- and y-direction, see Figure 5.1.

Figure 5.1 Electrically conductive epoxy on the surface of the PEDOT:PSS and latex coated cotton fabric substrate

5.2.4 Application of latex top layer

The final layer of latex was brushed atop the PEDOT:PSS layer. This process was repeated until the surface was no longer electrically conductive (resistance > 100 M Ω).

There was some covering of latex onto the conductive epoxy electrodes. A sufficient amount was removed by very light filing of the surface with an emery board, until the electrical resistance could be measured.

5.3 Results and discussion

5.3.1 Application of latex to the woven cotton fabric substrate

The cotton samples were immersed into the latex dispersion and subsequently dried, twice. Figure 5.2 displays the percentage mass increase of the cotton fabrics after the latex was applied. The average increase in mass of these samples was 13.7 ± 0.6 %.

5.3.2 Application of PEDOT:PSS Layer

PEDOT:PSS was applied to the cotton fabrics as described in Chapter Four. Refer to Table 5.2 for the mass increases due to PEDOT:PSS.

5.3.2.1 Resistance Measurements

Resistances were measured using a 2 point probe over 2 cm to obtain values over a larger distance. PEDOT:PSS was applied in the same fashion as described in Chapter Three. Due to the application of latex to the substrate, more polymer was retained on the surface as the voids were closed, see Figure 5.2. Due to the lack of penetration of the conductive polymer through the cotton fabric, lower resistance values were expected. The resistances obtained for the material after treatment with PEDOT:PSS were as low as 200 Ω cm^{-1}. Figure 5.3 shows the relationship between the amount of polymer added and the degree of resistance obtained. After adding the first layer, there is a regular decrease in the electrical resistance with increased addition of PEDOT:PSS.

The sheet resistance is a common measurement that is used in relation to electrically conductive inks or coatings. The method employed for these measurements was the use of a pair of copper electrodes, 20 mm wide and 30 mm long, separated by 30 mm to give a 30 mm x 30 mm square of sample measured between the electrodes. The resistance did not improve after the application of four layers as seen in the fact that the samples having four and five layers, of PEDOT:PSS applied, gave sheet resistance values of 1.47 and 1.46 k Ω sq^{-1}, respectively (where sq relates to the 30 mm^2 of sample between the electrodes).

Table 5.1 Masses of the woven cotton fabrics before and after application of latex

#	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Mass of Cotton, g	1.441	1.5279	1.3135	1.2276	1.2726	1.4865	1.4688	1.3701	1.4486	1.4306	1.3583	1.039	1.0729	1.0872	1.3934
Mass with latex, g	1.6358	1.7482	1.4778	1.3964	1.4514	1.6781	1.66	1.5486	1.6487	1.6281	1.5514	1.1779	1.2313	1.2391	1.5868
Mass of latex, g	0.1948	0.2203	0.1643	0.1688	0.1788	0.1916	0.1912	0.1785	0.2001	0.1975	0.1931	0.1389	0.1584	0.1519	0.1934
% Mass Increase	13.52%	14.42%	12.51%	13.75%	14.05%	12.89%	13.02%	13.03%	13.81%	13.81%	14.22%	13.37%	14.76%	13.97%	13.88%

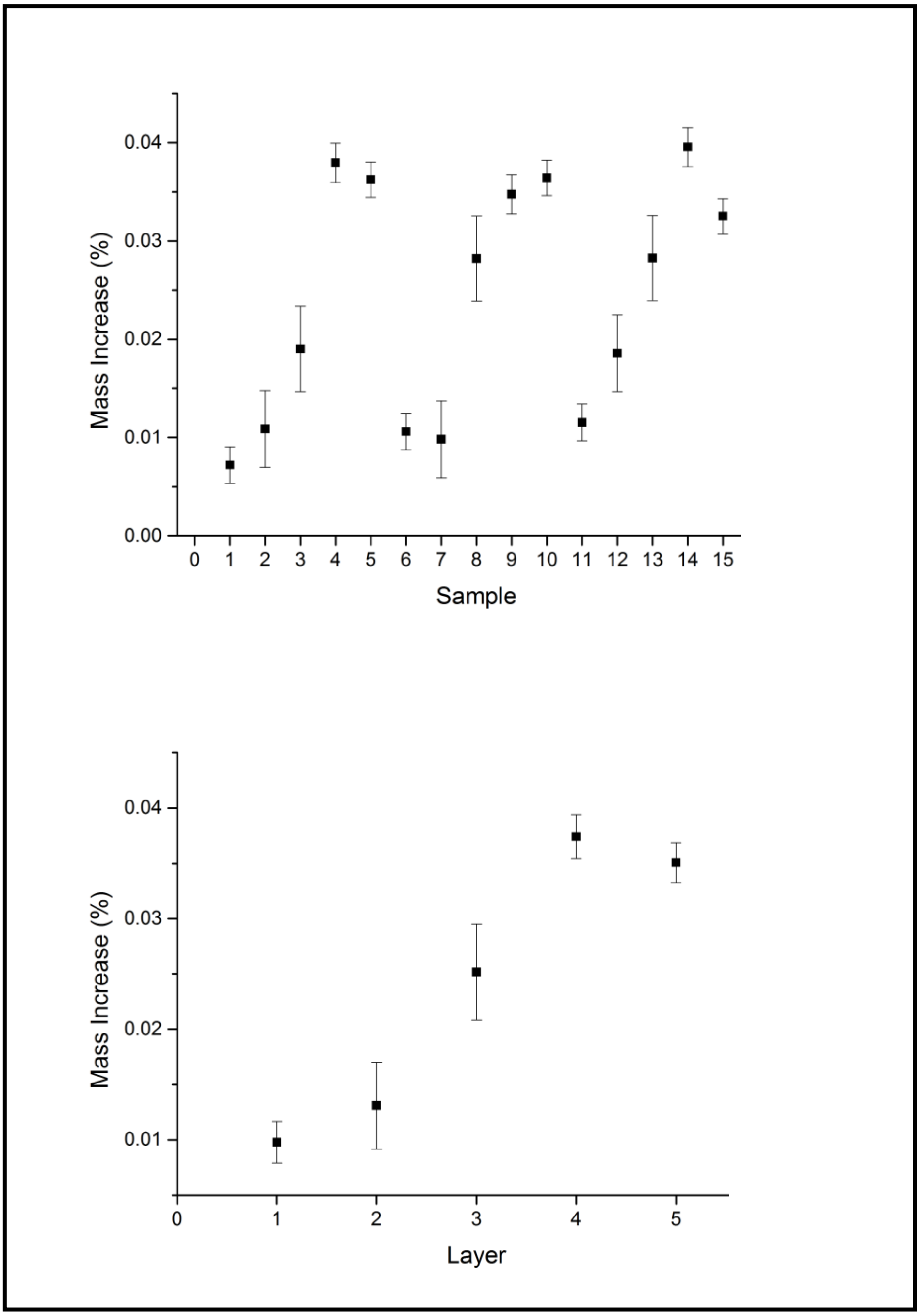


Figure 5.2 The amount of PEDOT:PSS that is applied to the latex coated cotton fabric substrate after each application. The top plot is individual samples and the bottom plot is averages with respect to the number of layers applied.

Table 5.2 Mass of PEDOT:PSS applied to the latex treated cotton fabric substrate and the percentage mass increase, to which this equates, and the measured electrical resistances of the samples and layer averages

	1	2	3	4	5	6	7	8	9	10
Mass PEDOT:PSS, g	0.0118	0.019	0.0281	0.053	0.0526	0.0178	0.0163	0.0437	0.0573	0.0593
% Mass increase	0.72%	1.09%	1.90%	3.80%	3.62%	1.06%	0.98%	2.82%	3.48%	3.64%
Resistance, x-direction, Ω cm^{-1}	3250	750	550	225	225	2000	1000	375	225	190
Resistance, y-direction, Ω cm^{-1}	5250	600	600	200	300	1750	700	600	150	140
Average Resistance, Ω cm^{-1}	4250	675	575	212.5	262.5	1875	850	487.5	187.5	165

	11	12	13	14	15
Mass PEDOT:PSS, g	0.0179	0.0219	0.0348	0.049	0.0516
% Mass increase	1.15%	1.86%	2.83%	3.95%	3.25%
Resistance, x-direction, Ω cm^{-1}	5500	550	350	175	275
Resistance, y-direction, Ω cm^{-1}	3250	400	275	150	225
Average Resistance, Ω cm^{-1}	4375	475	312.5	162.5	250

Layer	1	2	3	4	5
Mass PEDOT:PSS, g	0.0158	0.0191	0.0355	0.0531	0.0545
% Mass increase, Ω cm^{-1}	0.98%	1.31%	2.52%	3.74%	3.51%
Average Resistance, Ω cm^{-1}	3500	666.6	458.3	187.5	225.8

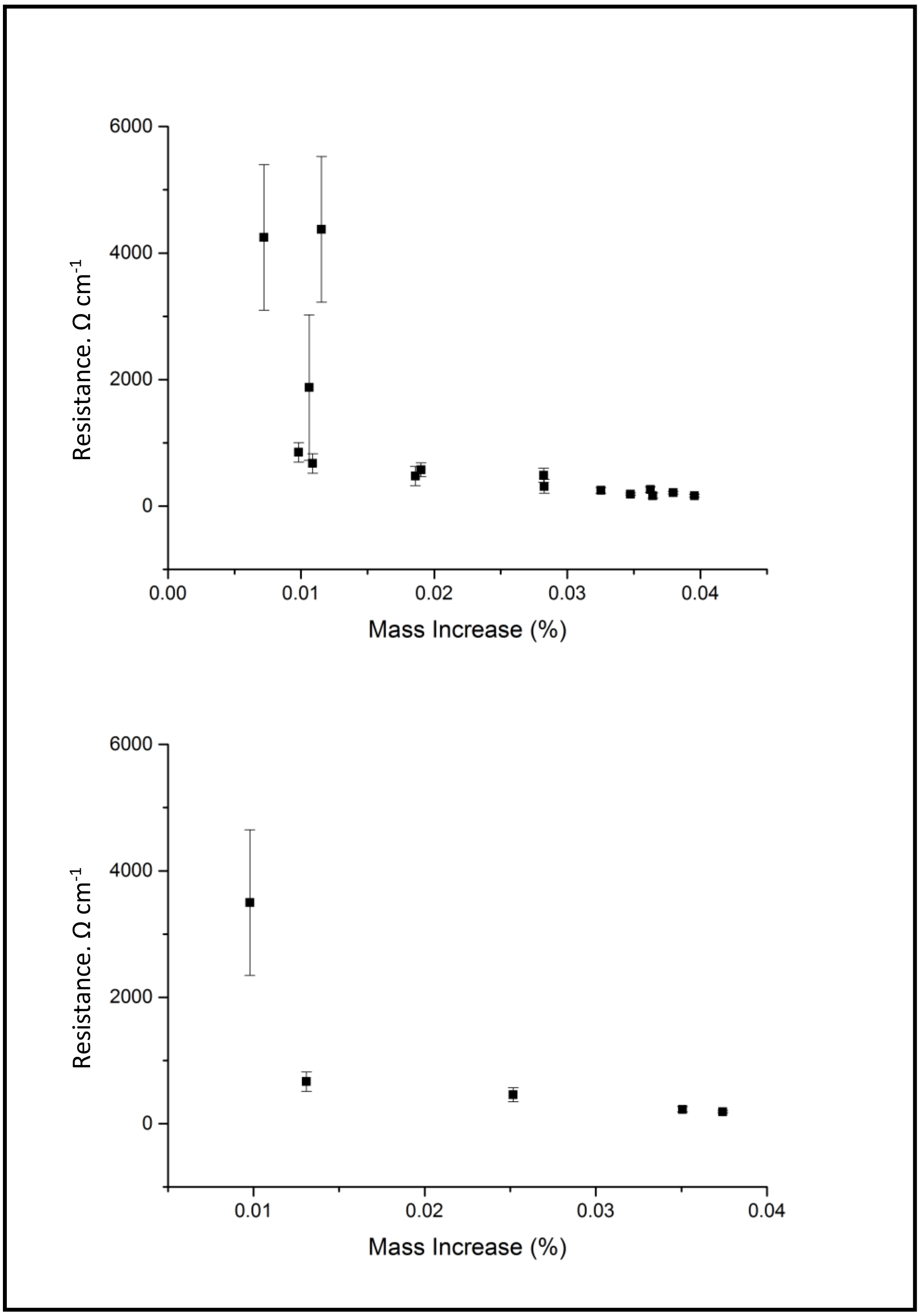


Figure 5.3 The relationship between the amount of PEDOT:PSS applied to the substrate and the resistance over 10 mm. The top plot is of individual samples, the bottom plot is averages with respect to the number of layers applied.

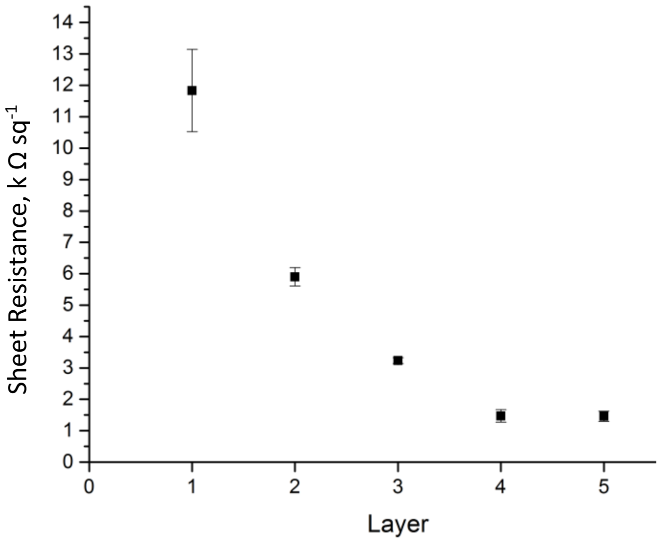


Figure 5.4 Sheet resistance of layer averages of PEDOT:PSS on the latex treated cotton substrate

5.3.2.2 Topology of the PEDOT:PSS coated, latex treated woven cotton fabric

This application of PEDOT:PSS differed to that described in Chapter Three due to the cotton having a latex layer on the surface. Figure 5.5 shows the surface after one coating of PEDOT:PSS. It is noteworthy that there was no residue of PEDOT:PSS on the backing plate post application with the K-bar 4, in contrast to Chapter Three, in that there was a residue on the backing plate up to and including the second application of PEDOT:PSS. This leads to the conclusion that the pores between the weaves of the cotton fibres have been filled by the prior immersion application of latex, allowing more PEDOT:PSS to form on the surface of the material.

Increasing the amount of conductive polymer on the surface to two layers, see Figure 5.6, caused pool like formations to occur. This pool formation was not observed until after the third application on the cotton fabric substrate in Chapter Three. Figure 5.6 also shows the solid layer being formed on the surface at this early stage.

Figures 5.7-5.9 depict the consequences of increasing the application of conductive polymer to the surface from three to five layers. It is apparent, visually, that much more PEDOT:PSS has been applied to the surface when compared to similar samples from Chapter Three.

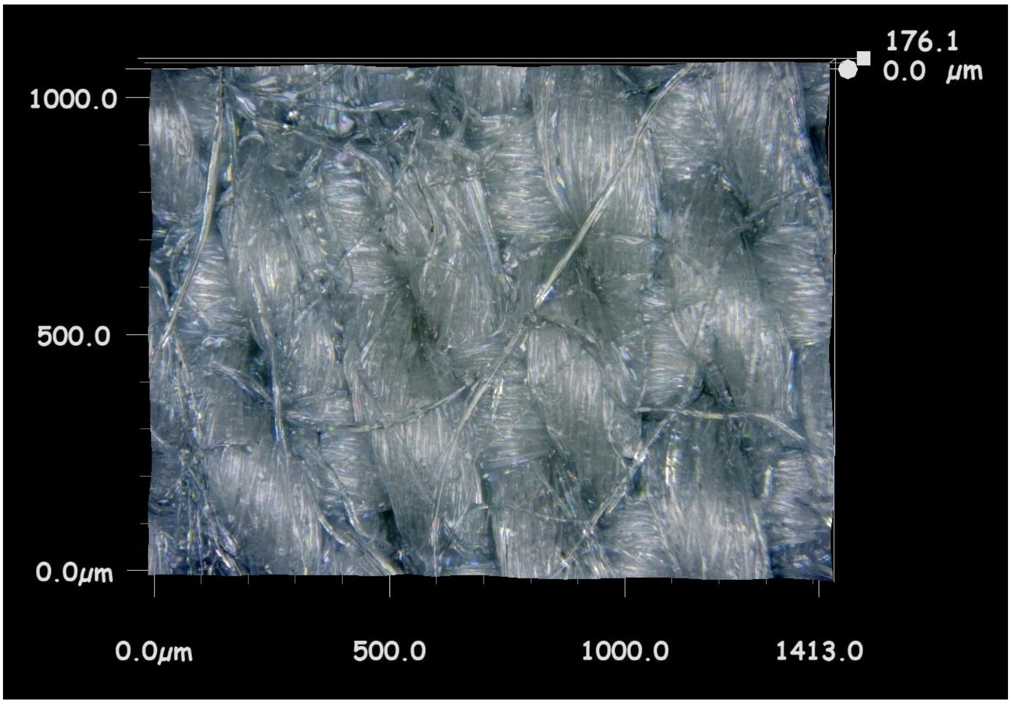


Figure 5.5 3D microscope image of a latex treated cotton fabric sample with one application of PEDOT:PSS at 250x magnification

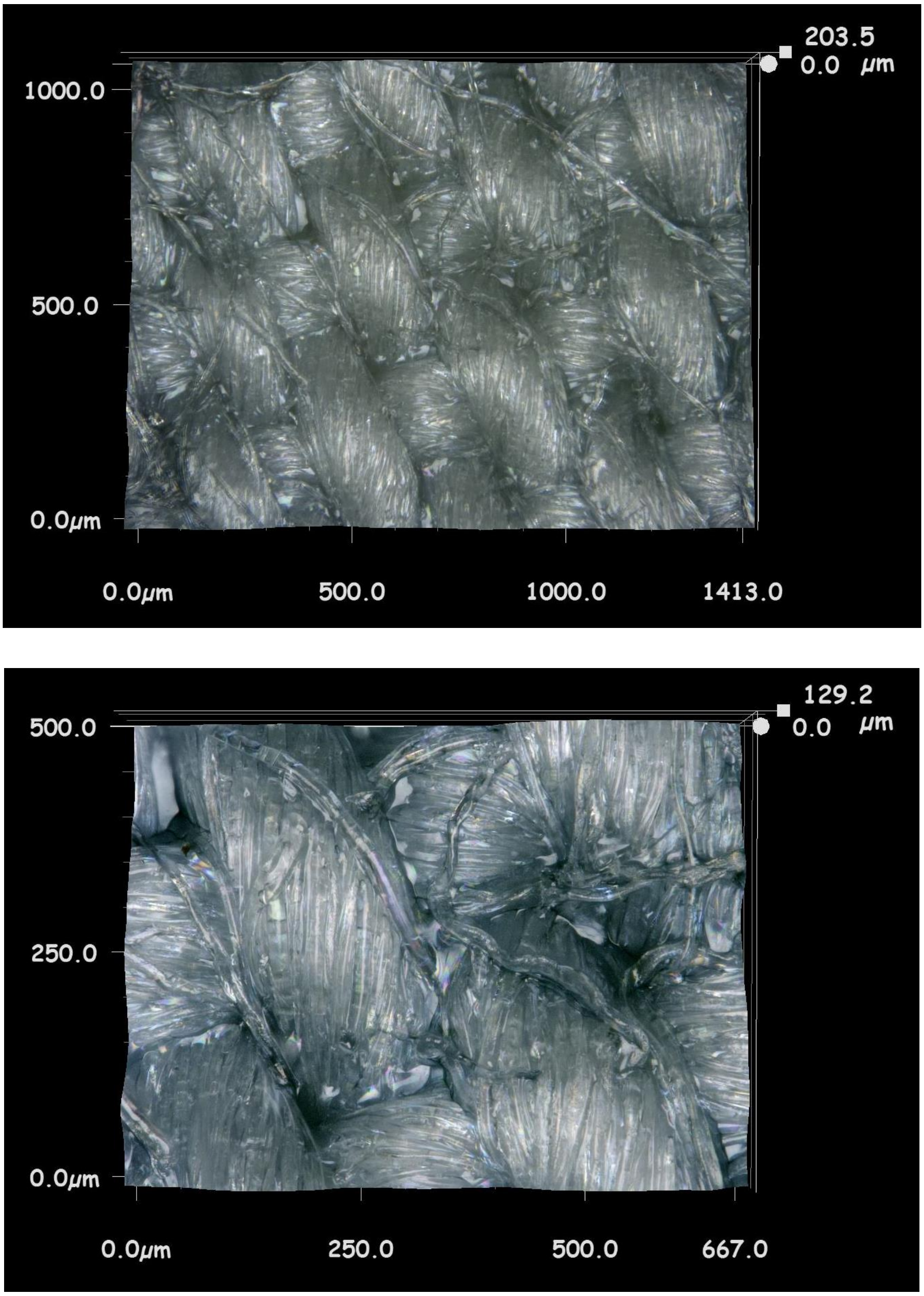
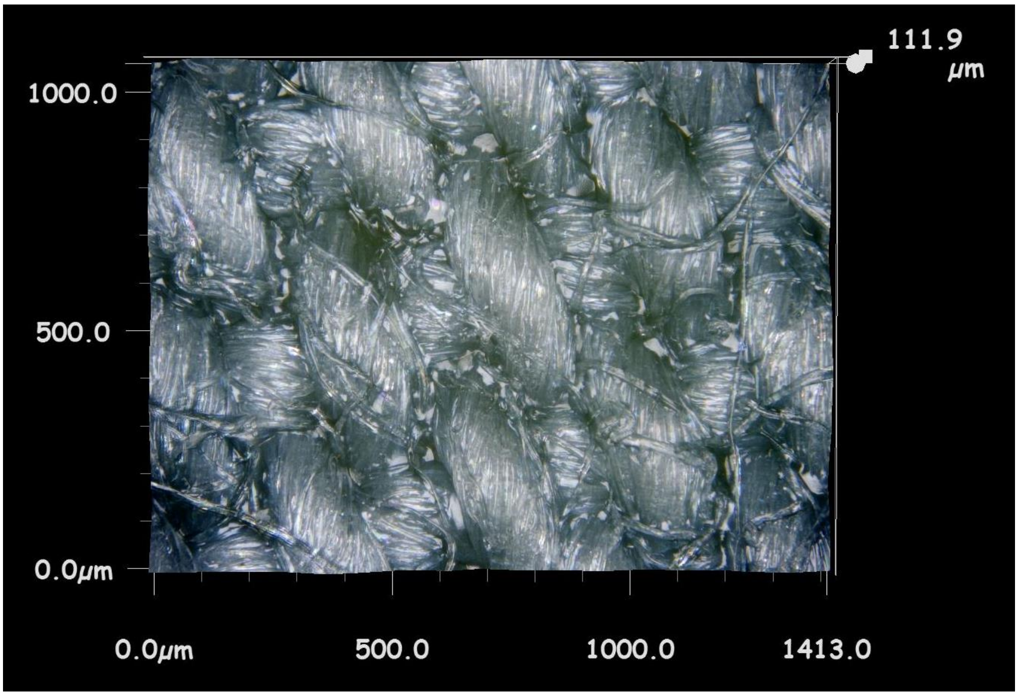


Figure 5.6 3D microscope images of a latex treated cotton fabric with two applications of PEDOT:PSS, the top image at 250x magnification and the bottom image at 500x magnification



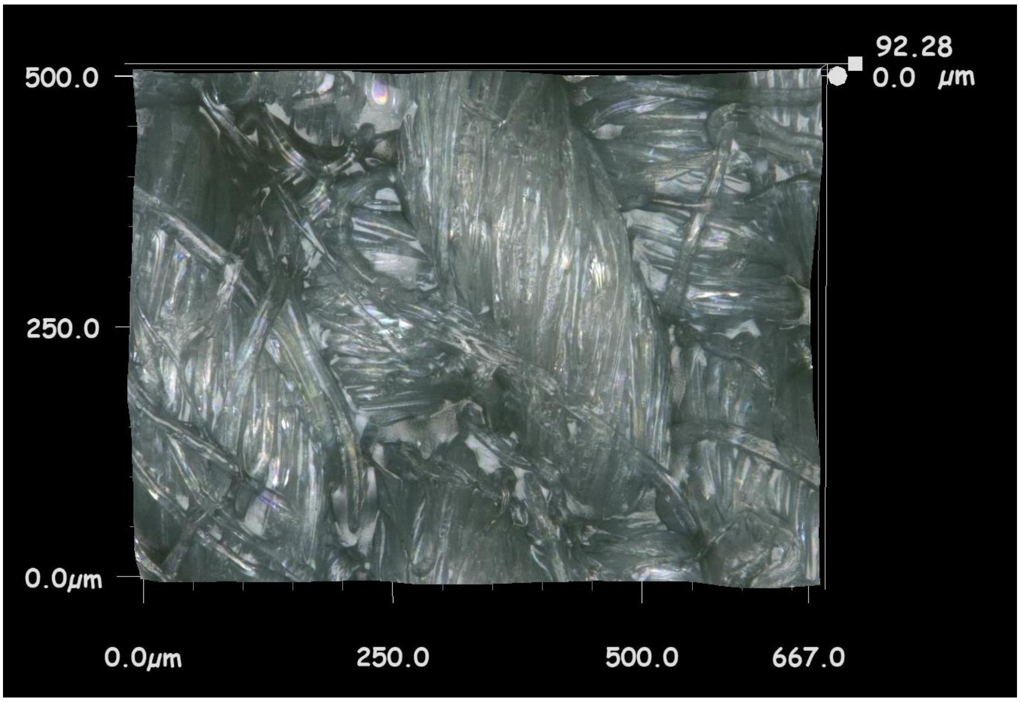


Figure 5.7 3D microscope images of a latex treated cotton fabric with three applications of PEDOT:PSS, the top image at 250x magnification and the bottom image at 500x magnification

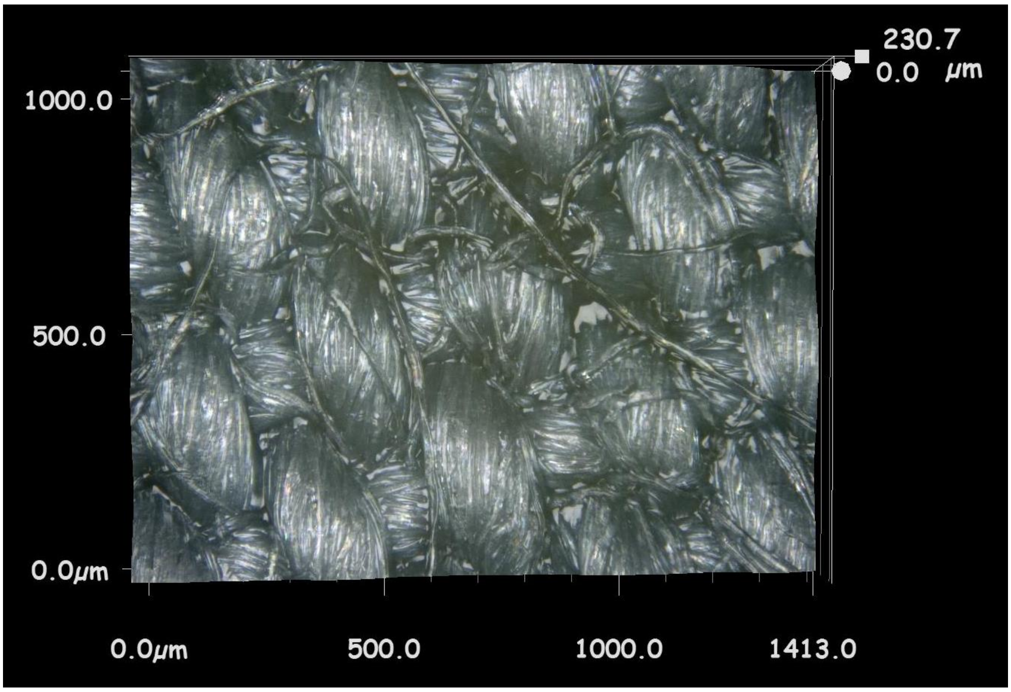


Figure 5.8 3D microscope image of a latex treated cotton fabric with four applications of PEDOT:PSS at 250x magnification

Figure 5.10 depicts the individual mass gains of PEDOT:PSS against the mass increases obtained in Chapter Three. It is worth noting that in Chapter Three, the highest amount of PEDOT:PSS applied to the samples was 15.1 mg, at five applications, which equates to a mass increase of 4.74 % due to PEDOT:PSS. On this occasion, at five applications, the mass of polymer applied to the surface was as high as 59.3 mg but only equates to a mass increase of 3.64 %. The coatings in Chapter Three were subject to the conductive polymer passing through the cotton substrate to the backing plate until two layers had been applied, which limited the total amount of conductive polymer when compared to the coatings on the latex treated cotton substrate. Due to the latex coating applied to the current samples, less conductive polymer passed through the cotton fabric. The latex coating allowed the PEDOT:PSS to create a wider surface coating than described in Chapter Three. This describes the lower percentage mass increase due to the PEDOT:PSS applications.

As mentioned previously, the lowest average resistance measured was 200 Ω cm^{-1}, which coincides with an average mass of conductive polymer of 54.5 mg across the sample or a mass increase of 3.51 %. In Chapter Three, the lowest reported resistance was 300 Ω cm^{-1} with an average mass of conductive polymer of 9.7 mg or a mass increase of

4.12 %. Thus, the use of the latex treatment of the cotton fabric allows less conductive polymer to be applied to the surface for lower electrical resistances to be obtained.

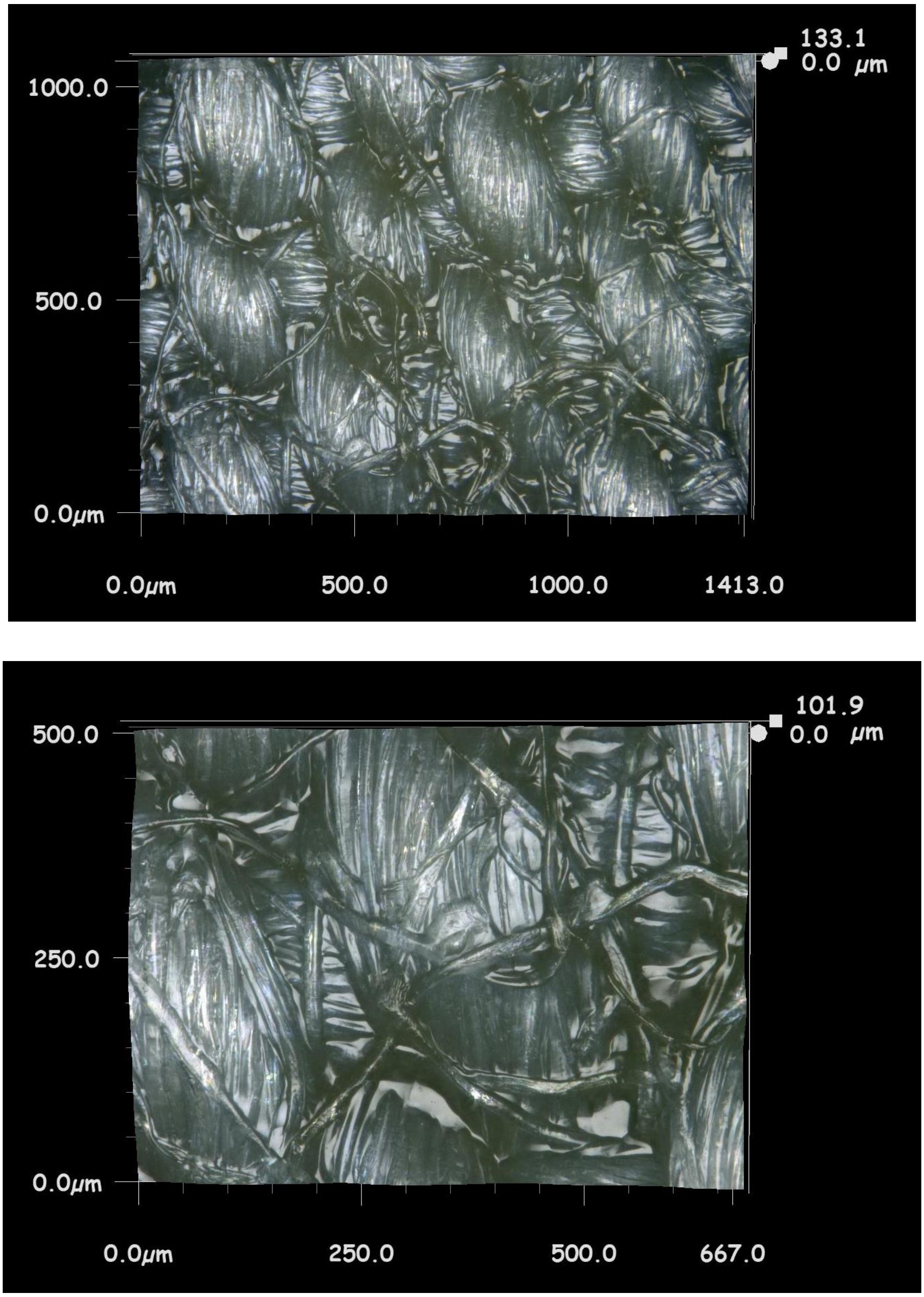


Figure 5.9 3D microscope images of a latex treated cotton fabric with five applications of PEDOT:PSS, the top image at 250x magnification and the bottom image at 500x magnification

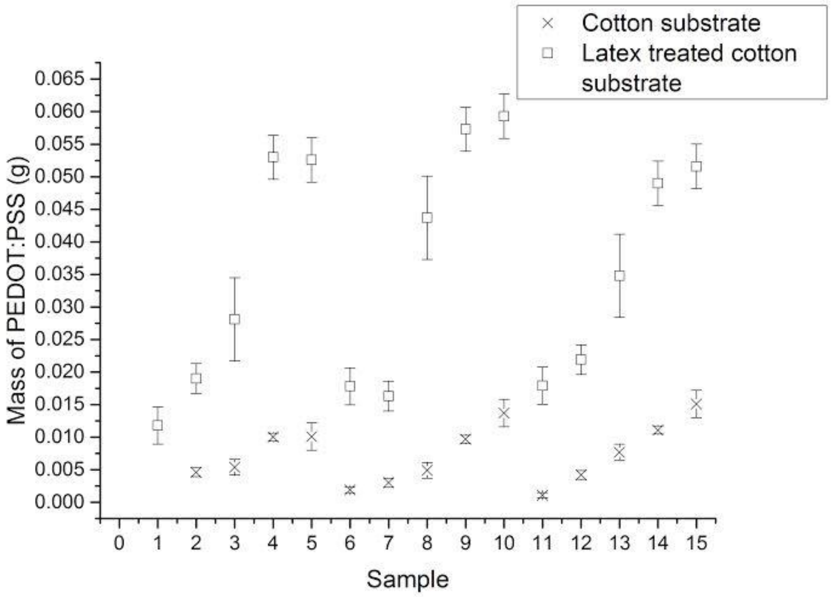


Figure 5.10 A comparison of the amount of PEDOT:PSS applied to the latex treated substrate and the untreated cotton substrate described in Chapter Three

5.3.3 Application of electrically conductive epoxy electrodes

The two part epoxy was mixed as prescribed by the instructions. The epoxy was applied to the PEDOT:PSS surface using the supplied applicator. Each spot of conductive epoxy was applied *ca.* 10 mm apart, as depicted earlier in Figure 5.1.

5.3.3.1 Resistance measurements with electrically conductive epoxy electrodes

The electrical resistance was measured once more in order to compare against the resistances measured with the two point probes of the PEDOT:PSS layers. It was expected that the resistance would be lower than measured previously. This is due to the improved contact of the probe with the conductive medium. Previously, the resistance was directly proportional to the pressure with which the probes were applied to the polymer surface. In this case, the probes were in contact with a metal epoxy with high electrical conductivity which had physically bonded with the polymer surface.

Figures 5.11 and 5.12 depict the electrical resistance values obtained which shows the resistance measured of the sample with electrically conductive epoxy is lower than the use of the two point probes directly onto the PEDOT:PSS layer. The lowest measured electrical resistance was 180 Ω cm^{-1}. If this technology was to be used in an electrical circuit, the PEDOT:PSS would have to be connected to sensors and other components, this conductive epoxy could be used to make these connections.

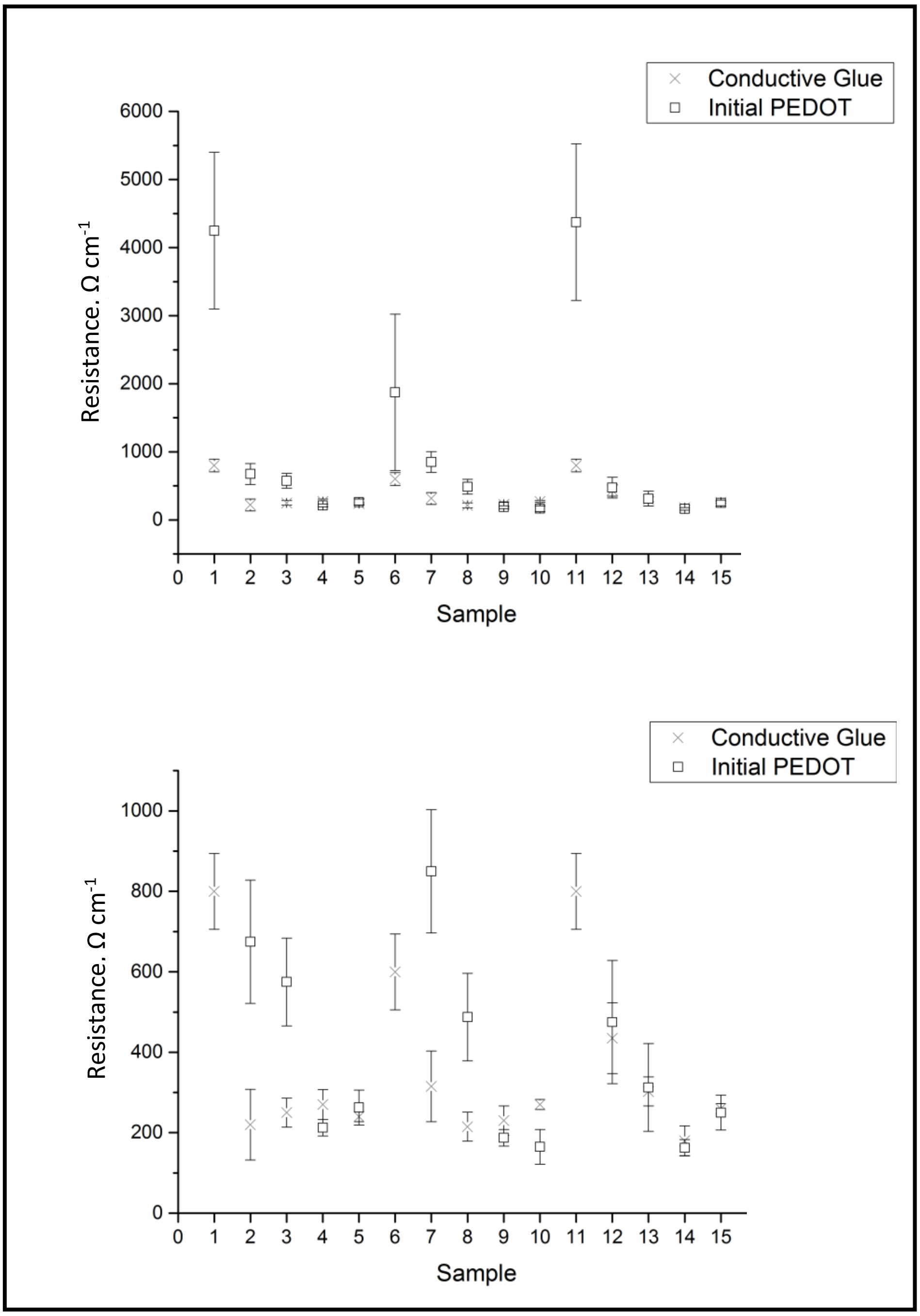


Figure 5.11 A comparison of the measured resistances after the application of the electrically conductive epoxy. The top plot displays all data while the bottom plot has omitted the resistance values of the initial PEDOT:PSS of samples 1, 6 and 11.

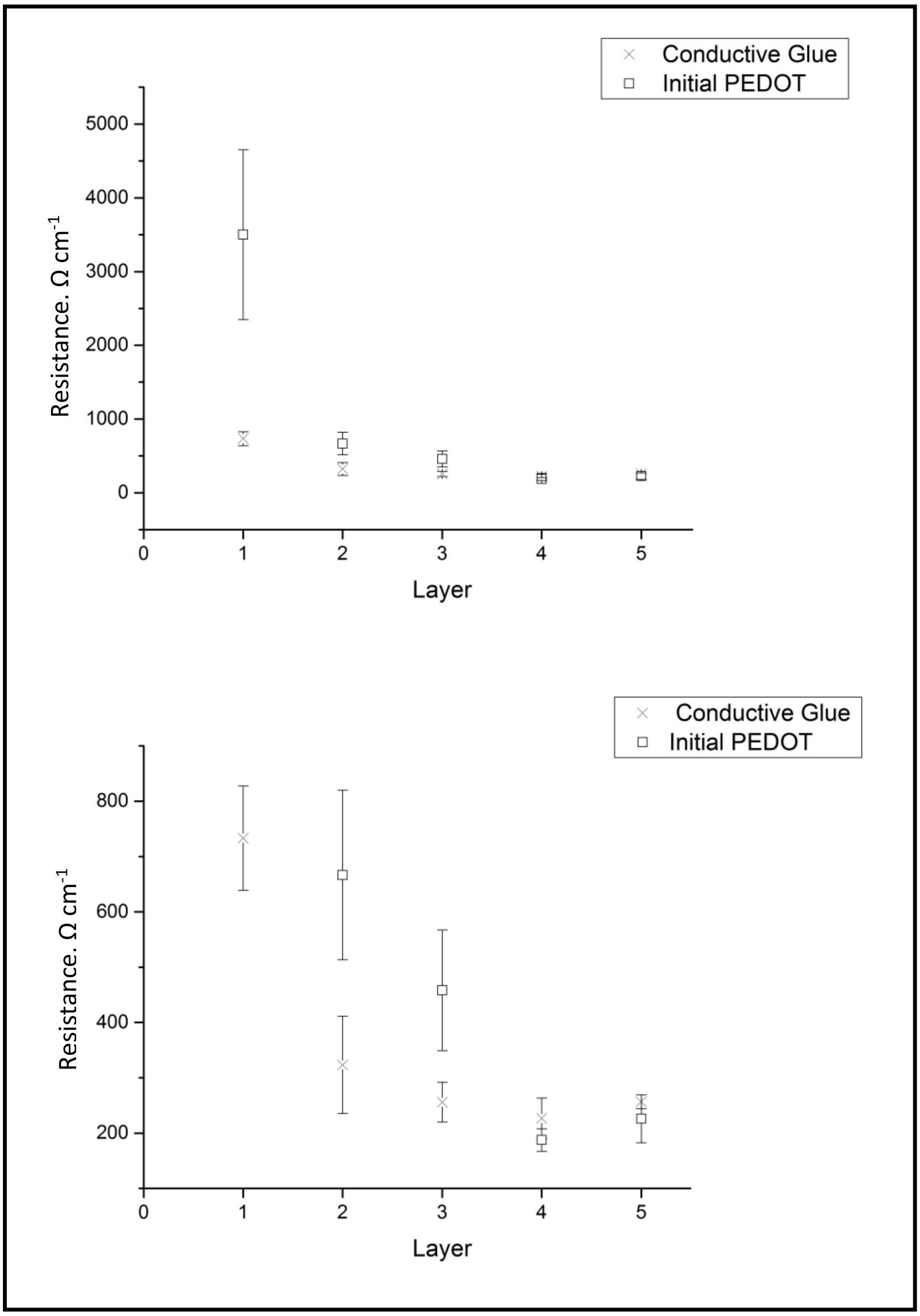


Figure 5.12 A comparison of the measured resistances after the application of the electrically conductive epoxy. The top plot displays average resistances of the number of layers applied and the bottom plot omits the initial value for layer one for greater clarity of difference between the layers

5.3.3.2 Topology of the electrically conductive epoxy on the surface of the PEDOT:PSS layers

The images captured by the 3D microscope, see Figure 5.13, shows the connection made between the conductive epoxy and the PEDOT:PSS treated cotton. The epoxy has bonded to the full surface of the cotton which will give a much truer representation of the electrical resistance due to the lack of reliance on the pressure the probes are applied with.

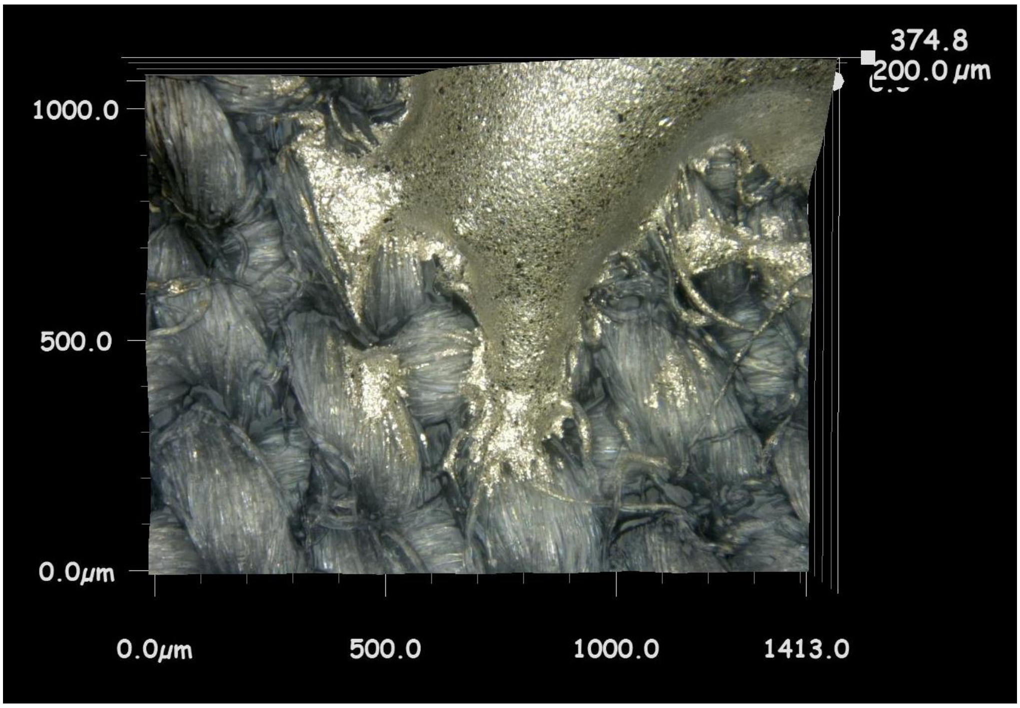


Figure 5.13 3D microscope image of the electrically conductive epoxy on the surface of a PEDOT:PSS and latex treated cotton fabric at 250x magnification

5.3.4 Application of the latex top layer to the treated cotton fabric

The further application of latex as a top layer was done using a small brush until the surface was wetted and allowed to dry. This was repeated a further two times for a total of three latex applications resulting in an electrically non-conductive (insulating) surface.

Inevitably, the latex had covered some of the conductive epoxy electrodes which increased the measured electrical resistance. Light abrasion with an emery board removed the surface coating of the latex to reveal a conductive surface once more.

5.3.4.1 Electrical resistance measurements with the latex top layer

The resistance probes were placed onto the electrically conductive epoxy electrodes where they had been filed slightly. The resistances were measured and have been presented in

Figures 5.14, 5.15 and Table 5.3. It can clearly be seen that the application of the latex top layer had slightly hindered the conductivity of the surface. This difference is more visible for samples with three to five layers of PEDOT:PSS applied. Previously, the resistances were as low as 180 Ω cm^{-1} whereas after the application of latex, the lowest electrical resistance measured was 825 Ω cm^{-1}.

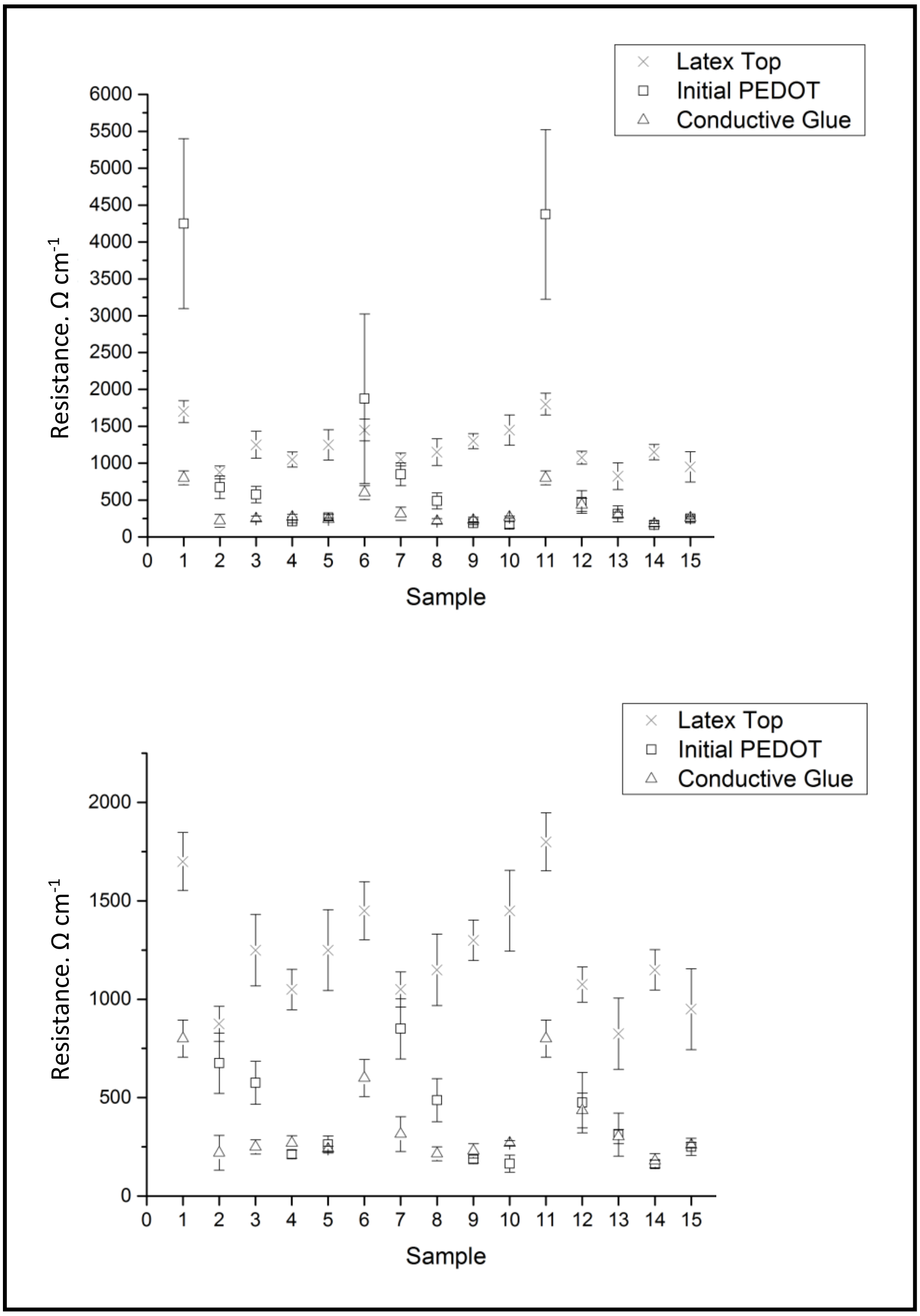


Figure 5.14 Comparison of the resistance initially after application of PEDOT:PSS, application of conductive epoxy and after the application of the latex top layer to the cotton fabrics. The top plot shows all data for comparison and the bottom plot has removed the resistance value for the initial resistance after application of PEDOT:PSS for samples 1, 6 and 11.

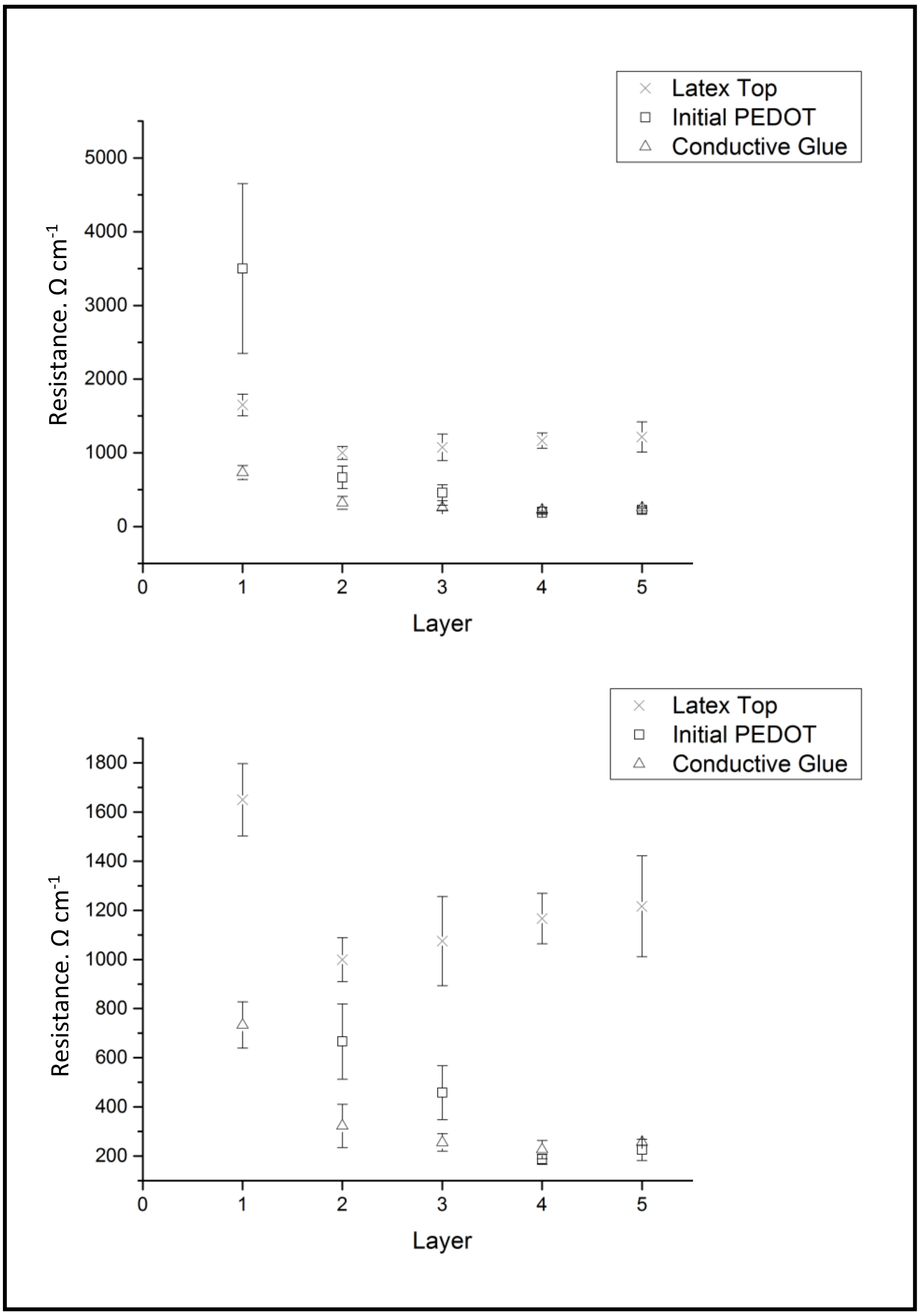


Figure 5.15 Comparison of the average layer resistance initially after application of PEDOT:PSS, application of conductive epoxy and after the application of the latex top layer to the cotton fabrics. The top plot shows all data for comparison and the bottom plot has removed the resistance value for the initial resistance after application of PEDOT:PSS for layer 1.

The difference in resistance could be due to the insulating latex *co*-polymer interfering with the conductive pathways set by the application of PEDOT:PSS. As the latex is an aqueous dispersion, this could have swelled the cotton substrate allowing some particles of latex to be drawn between adjacent PEDOT:PSS coated fibres.

Table 5.3 Mass of latex applied as a top layer and the measured electrical resistance and layer averages

	1	2	3	4	5	6	7	8	9	10
Mass Latex, g	0.0519	0.07	0.0455	0.0445	0.0532	0.0713	0.0714	0.0564	0.0577	0.0534
Resistance, x-direction, Ω cm^{-1}	1700	950	1500	1000	1200	1500	1100	1300	1500	1800
Resistance, y-direction, Ω cm^{-1}	1700	800	1000	1100	1300	1400	1000	1000	1100	1100
Average Resistance, Ω cm^{-1}	1700	875	1250	1050	1250	1450	1050	1150	1300	1450

	11	12	13	14	15
Mass Latex, g	0.0635	0.052	0.0564	0.0525	0.0587
Resistance, x-direction, Ω cm^{-1}	1700	950	700	1100	1100
Resistance, y-direction, Ω cm^{-1}	1900	1200	950	1200	800
Average Resistance, Ω cm^{-1}	1800	1075	825	1150	950

Layer	1	2	3	4	5
Mass Latex, g	0.0622	0.0645	0.0528	0.0516	0.0551
Average Resistance, Ω cm^{-1}	1650	1000	1075	1166.6	1216.6

The latex top layer had affected the measured electrical resistance, the lowest resistance measured was 825 Ω cm^{-1} and it must be acknowledged that samples in Chapter Three have resistances as low as 300 Ω cm^{-1} prior to washing, as the current samples are presently.

5.3.4.2 Topology of the latex top layer

The latex was applied to the PEDOT:PSS film with a brush on this occasion due to the presence of the electrodes on the surface of the conductive polymer. The latex was applied until a thin film had wetted the surface and allowed to dry. This was repeated until the surface was electrically insulating.

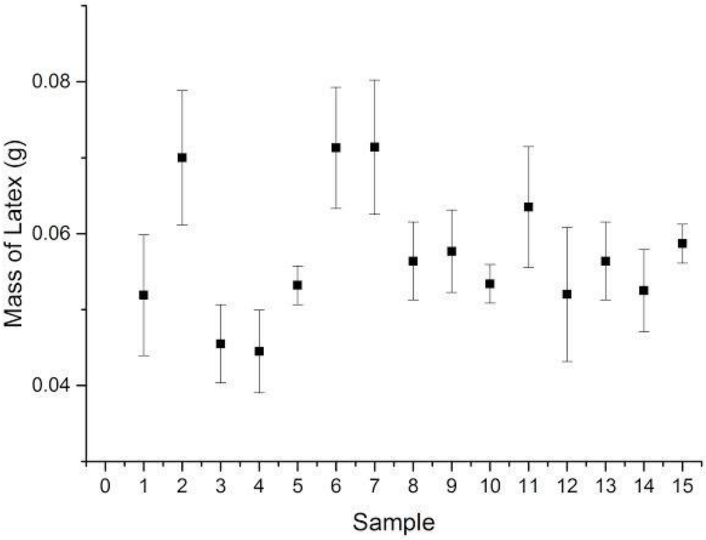


Figure 5.16 Mass of latex applied as a top layer

Figure 5.16 shows the mass of latex applied to the samples. Considering the possibility of variability of the applications, each sample had a similar amount of latex applied to the surface. The average amount of latex required to provide an insulating surface was 57.2 ± 8.2 mg.

3D microscopy was utilised on this occasion to investigate whether a film of latex had been applied to the surface. Figures 5.17-5.20 are attempts to visualise this layer, each with increasing layers of PEDOT:PSS applied to the surface. Figures 5.17 and 5.18 display some highly reflective fibres and in some areas, globules can be seen, similar to the original application of latex to the cotton substrate. Figure 5.19 is a comparison of the PEDOT:PSS coated and uncoated area of the substrate with a latex top layer, both areas exhibit the reflective nature seen previously but a film still cannot be visualised. Finally, Figure 5.20 shows a sample with five layers of PEDOT:PSS and a latex top layer. Due to the dark colour of the PEDOT:PSS it is difficult to see added reflectivity which appears evident on the earlier images in the series.

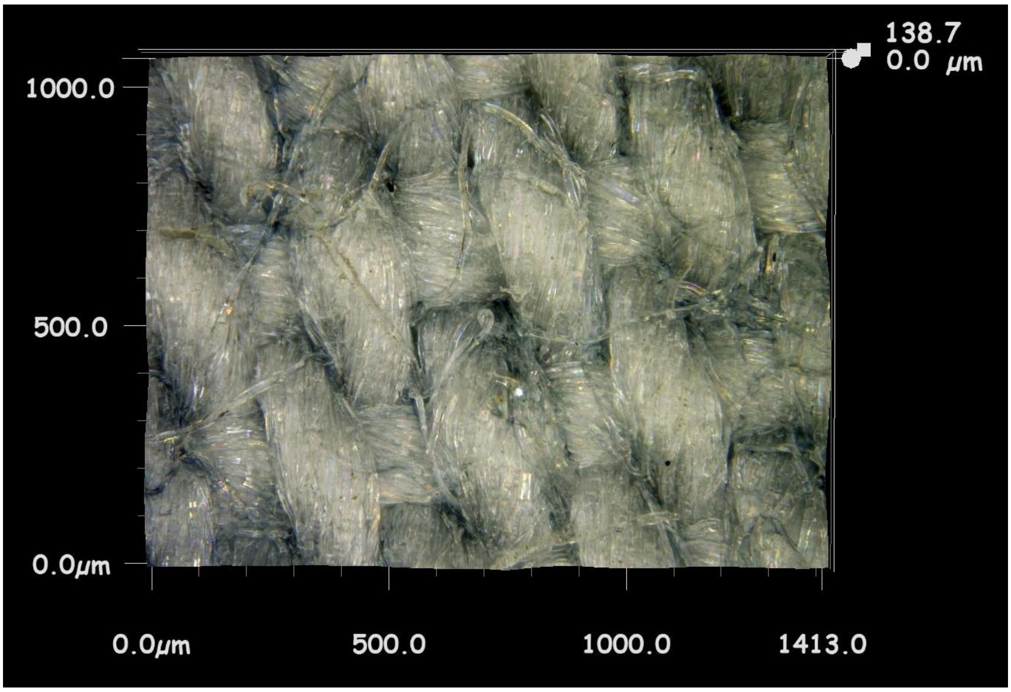


Figure 5.17 3D microscope image of a sample with a latex top layer above one application of PEDOT:PSS at 100x magnification

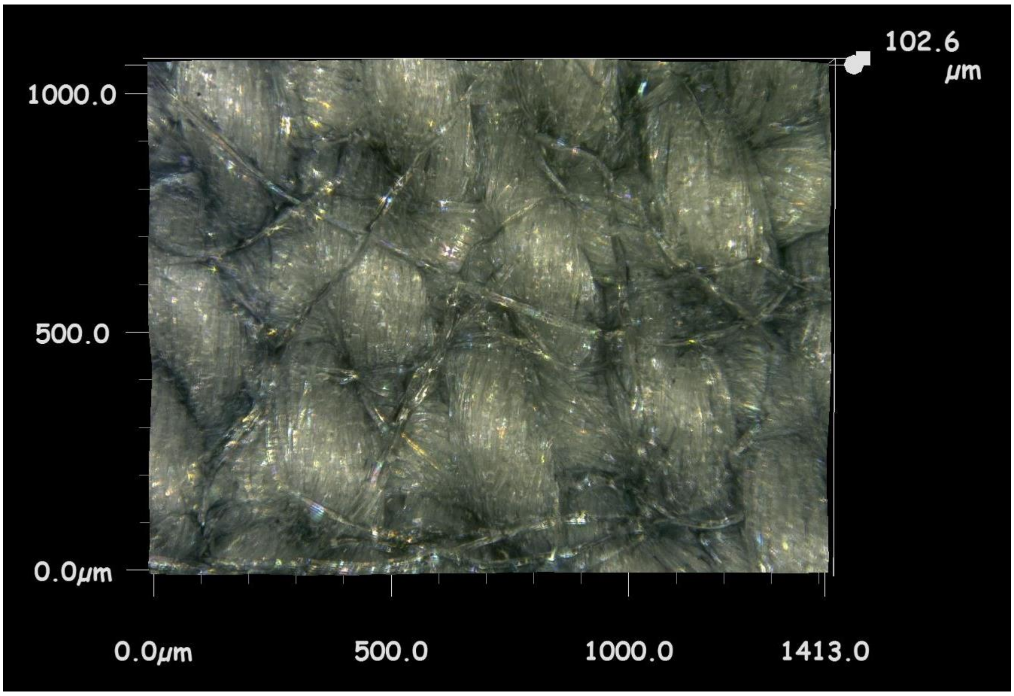


Figure 5.18 3D microscope image of a sample with a latex top layer above two applications of PEDOT:PSS at 100x magnification

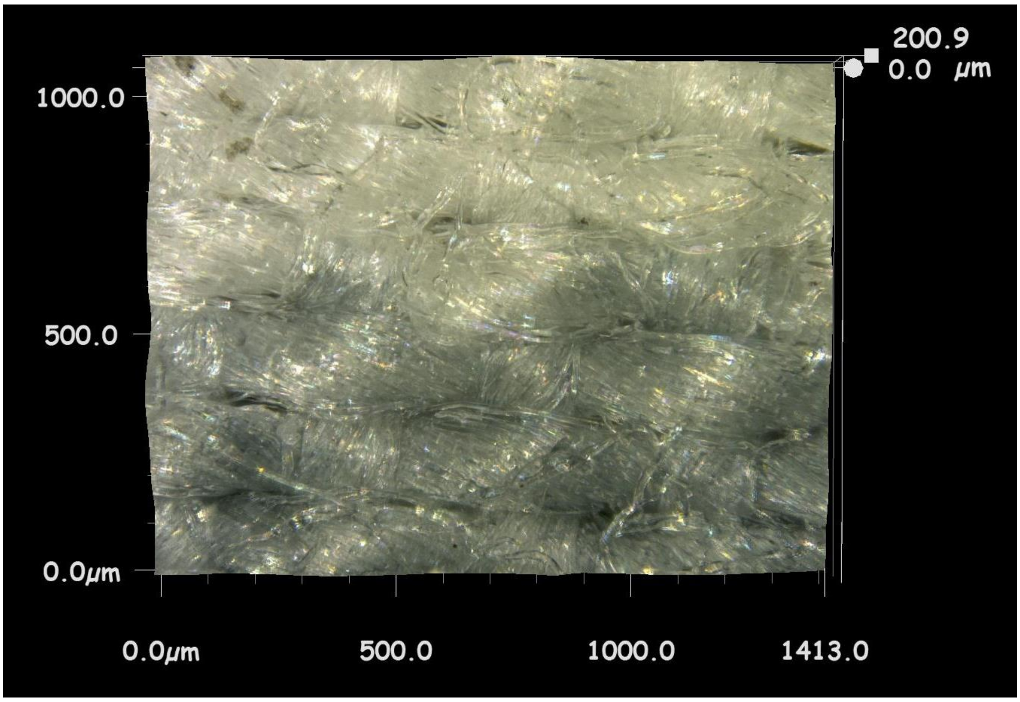


Figure 5.19 3D microscope image of a sample with a latex top layer above three applications of PEDOT:PSS at 100x magnification

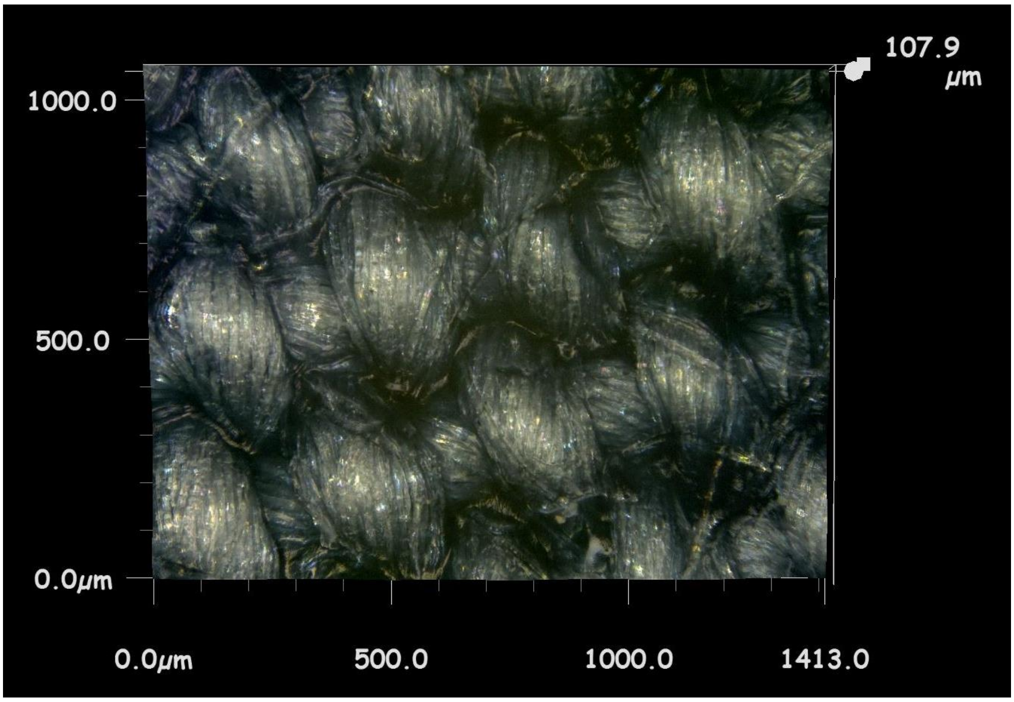


Figure 5.20 3D microscope image of a sample with a latex top layer above five applications of PEDOT:PSS at 100x magnification

5.3.5 Wash Testing

The samples were washed according to BS EN ISO 6330:2012 as described in Chapter Three.

5.3.5.1 Electrical resistance measurements post washing

In order to measure the electrical resistance, the probes were placed onto the electrically conductive epoxy “electrodes”. Some of these had been damaged during the washing process, with cracks appearing or by the removal of the electrode from the surface. Where damage had been made to electrodes, the probes were placed firmly onto the PEDOT:PSS coating to obtain a measurement.

The cotton fabric samples with fewer layers of PEDOT:PSS applied, suffered most with respect to electrical resistance. Figure 5.21 shows that samples 1, 6 and 11, those with one layer of PEDOT:PSS applied had very high resistances, a minimum of 7000 Ω cm^{-1}, and also that samples 2, 7 and 12, those with two layers of PEDOT:PSS, had a large uncertainty associated with the readings. This is due to broken electrodes on the samples which lead to unrepeatable resistance measurements being recorded.

When the reader looks to the bottom of Figure 5.21, the resistances of samples with one layer and the error bars of those with two layers have been removed to give greater clarity of the rest of the data. Samples with three layers of PEDOT:PSS now had the largest uncertainty, relatively. Importantly, samples with four and five layers of PEDOT:PSS had a low error associated with them and the lowest resistance maintained was 260 Ω cm^{-1}, lower than the respective resistance measured after the latex top layer was applied.

Figure 5.22 shows similar data as discussed previously but with average resistance measurements with respect to the number of layers of PEDOT:PSS applied. As discussed, samples with four or five layers of PEDOT:PSS return the lowest resistance measurements, 400 ± 304 Ω cm^{-1} and 512 ± 29 Ω cm^{-1} respectively. These resistance values are both lower than the average values measured after the application of the latex top layer.

The electrical resistance data of the samples after application of the electrically conductive epoxy, the latex top layer and washing have been compiled into Figure 5.23. Due to the data discussed prior, the samples with one layer of PEDOT:PSS applied are included in the top plot for the reader's interest but have been omitted from the bottom chart for improved comparison and discussion.

A general observation can be made instantly, that the resistances measured after washing are much closer to the electrical resistance measured after the conductive epoxy was applied, rather than after the latex top layer was applied.

Average resistance measurements, with respect to the number of layers of conductive polymer, have been depicted in Figure 5.24 in a similar method as previously, firstly displaying all data while the bottom chart has removed some values and error bars. Cotton fabric samples with one and two layers of PEDOT:PSS showed an increase in electrical resistance after washing the samples when compared with the resistance measured after the latex top coat was applied. Samples with three layers have the large uncertainty due to the damage described previously but those with four and five layers can be seen to have an electrical resistance part way between the resistances measured after the electrically conductive epoxy was applied and after the latex top layer.

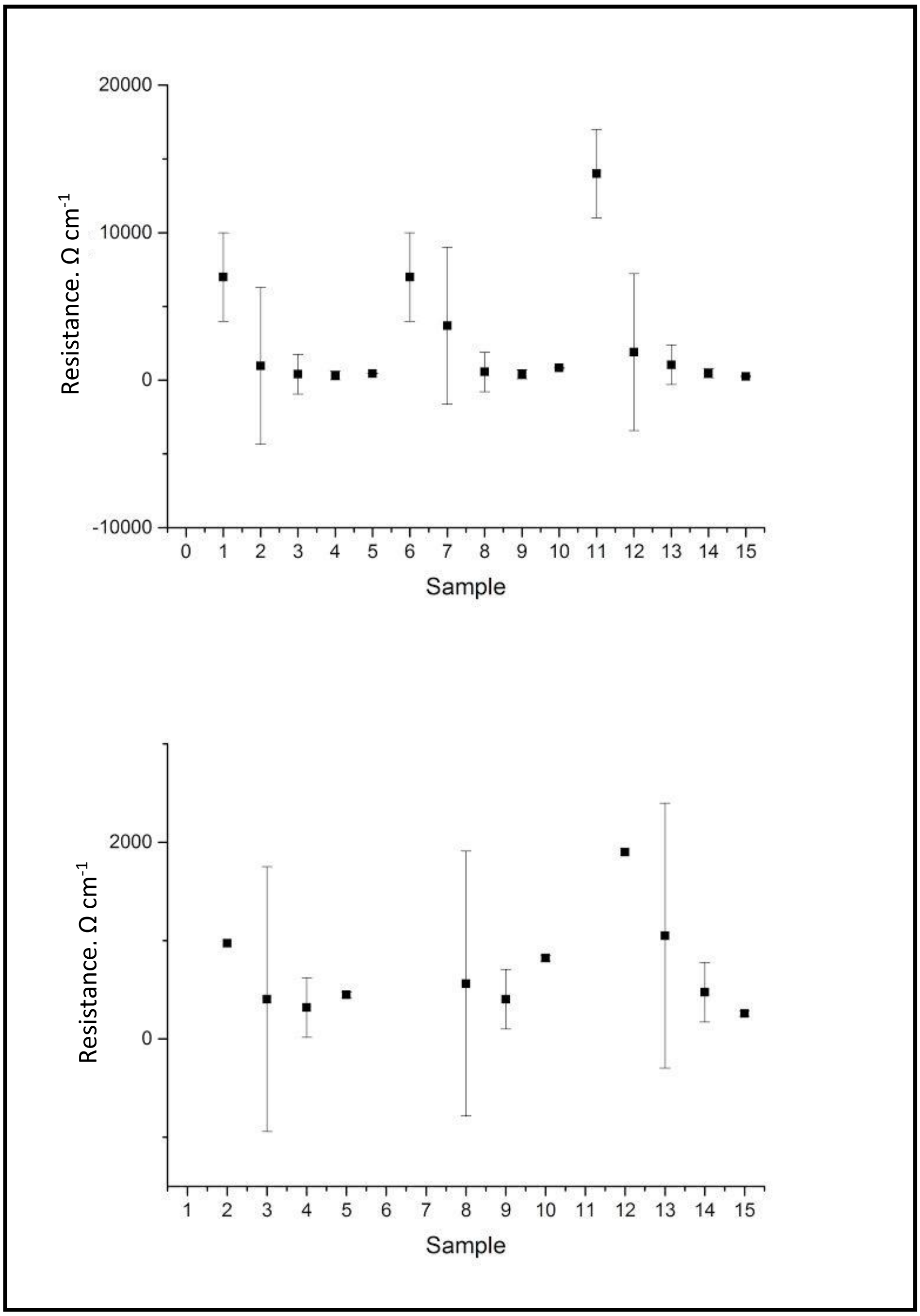


Figure 5.21 Resistance measurements of the samples after a wash cycle. The top plot shows all data while the bottom plot has removed samples 1, 6, 7 and 11 and removed the error bars on samples 2, 7 and 12 for greater clarity.

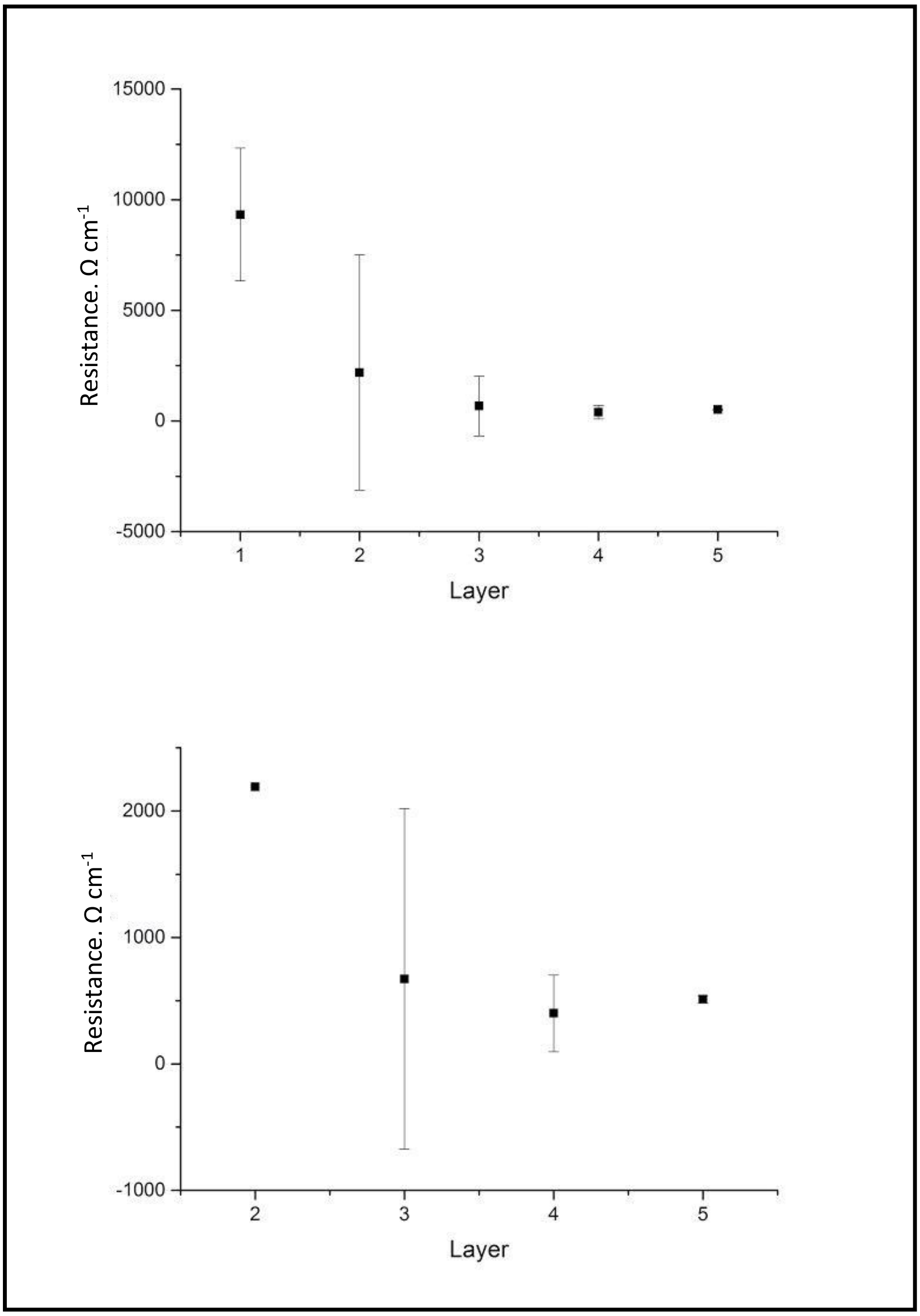


Figure 5.22 Average resistance measurements with respect to the number of layers of PEDOT applied to the surface after a wash cycle. The top plot shows all data while the bottom plot has removed layer 1 and the error bars of layer 2 for clarity.

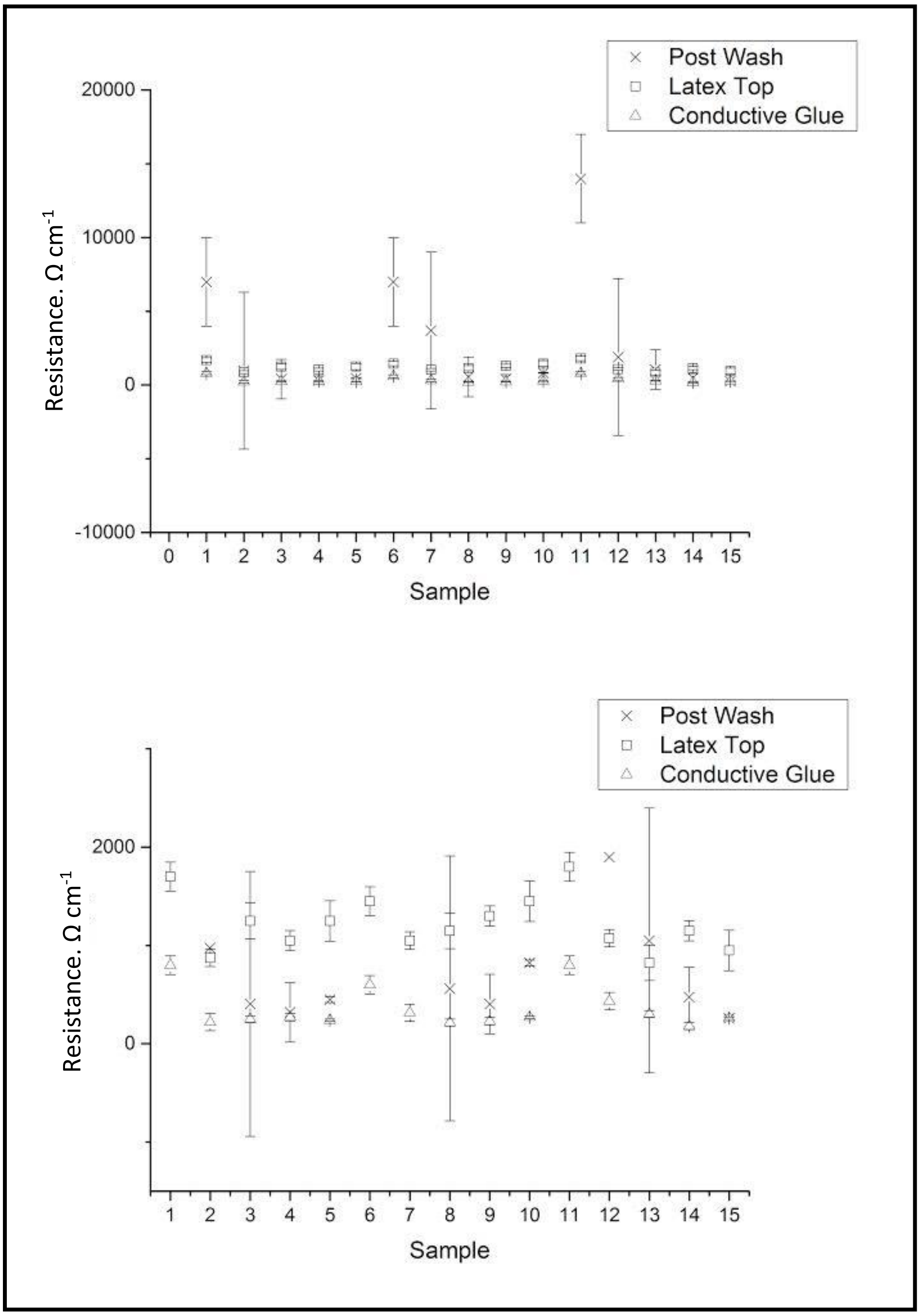


Figure 5.23 A comparison of the resistance values of the samples post wash, after the latex top coat and after the application of the conductive epoxy alone. The top plot shows all data while the bottom plot omits data similar to Figure 5.22.

Table 5.4 Mass losses of the samples during washing, their respective measured electrical resistance and layer averages

	1	2	3	4	5	6	7	8	9	10
Mass loss, g	0.0714	0.0808	0.0583	0.0595	0.0918	0.0843	0.0834	0.0871	0.0939	0.1176
Resistance, x-direction, Ω cm^{-1}	6000	850	450	340	600	7500	4000	600	450	550
Resistance, y-direction, Ω cm^{-1}	8000	1100	360	300	300	6500	3400	525	360	1100
Average Resistance, Ω cm^{-1}	7000	975	405	320	450	7000	3700	562.5	405	825

	11	12	13	14	15
Mass loss, g	0.0795	0.0583	0.0672	0.0853	0.0859
Resistance, x-direction, Ω cm^{-1}	13000	2000	1100	500	240
Resistance, y-direction, Ω cm^{-1}	15000	1800	1000	450	280
Average Resistance, Ω cm^{-1}	14000	1900	1050	475	260

Layer	1	2	3	4	5
Mass loss, g	0.0784	0.0742	0.0709	0.0796	0.0984
Average Resistance, Ω cm^{-1}	9333.3	2191.7	672.5	400.0	511.7

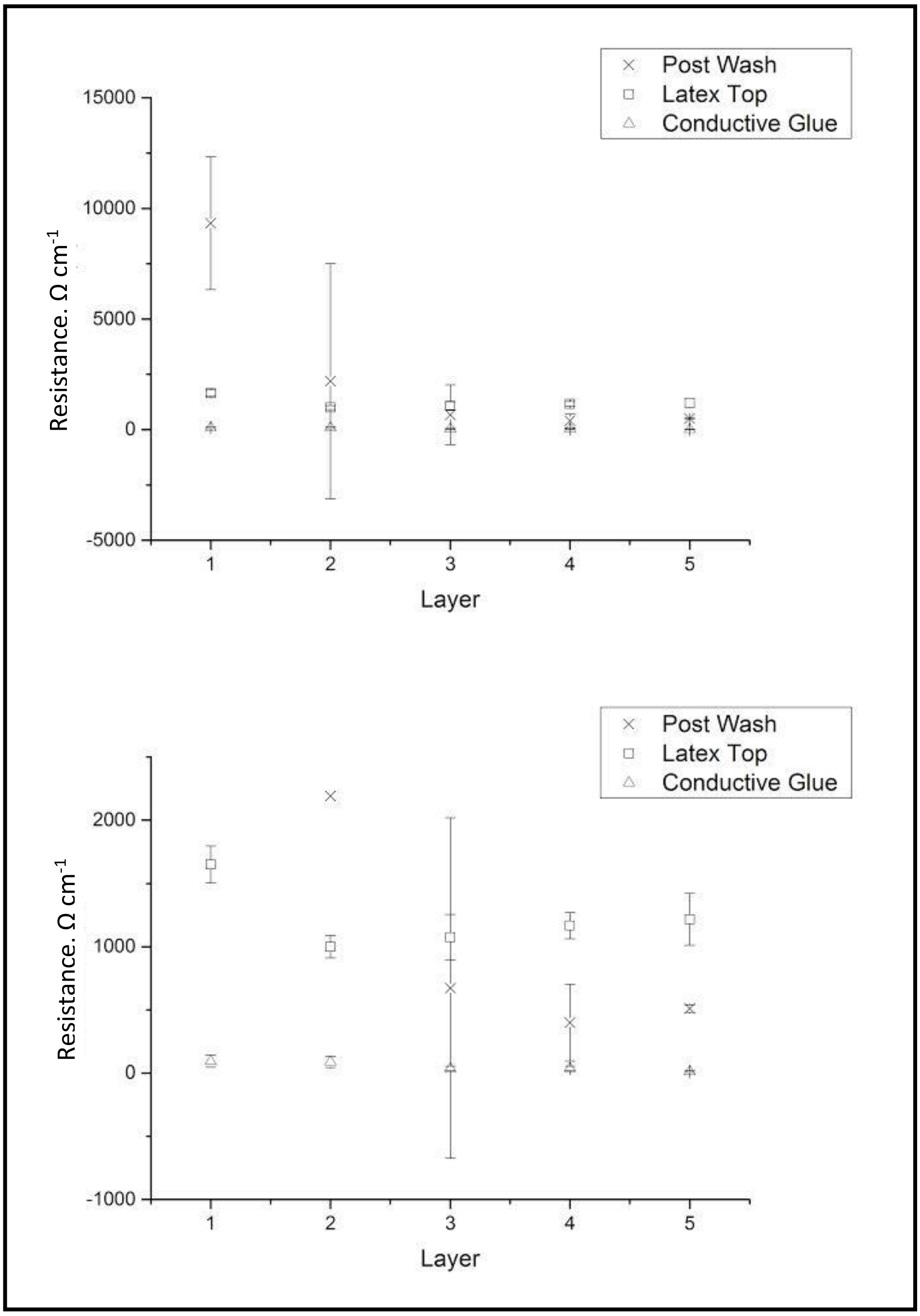


Figure 5.24 A comparison of the average resistance values with respect to the number of layers post wash, after the latex top coat and after the application of the conductive epoxy alone. The top plot shows all data while the bottom plot omits data similar to Figure 5.22

5.3.5.2 Topology of the fabric polymer composite post wash

After the washing process, the electrical resistances were measured which also enabled a visual observation of the samples. The overview of the condition of the samples can be seen in Figure 5.25. In many of the samples were small creases and abrasion of the surfaces, though in certain samples, the creases had a high amount of wear, some samples even had holes worn through the surface, some closer images can be seen in Figure 5.26.

Figure 5.25 An image of the samples after washing and drying. Damage can be seen on a number of samples in the form of creases and even holes.

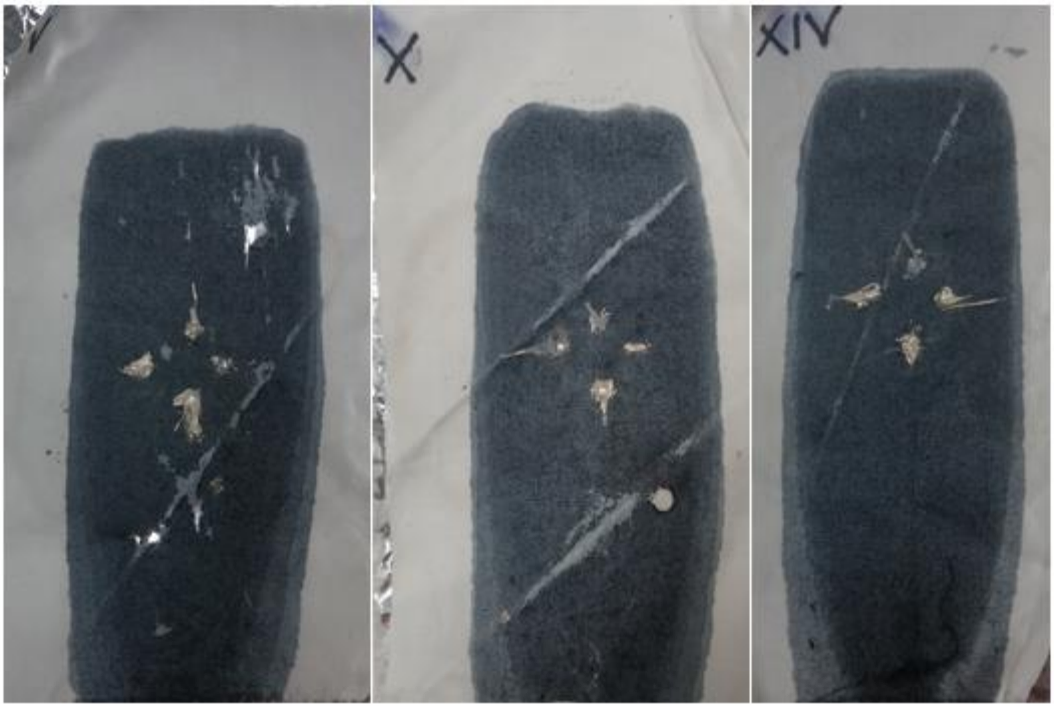


Figure 5.26 Closer inspection of the more damaged samples show the extent of the damage. Electrodes have been removed and the conductive polymer looks to have been removed from the surface by friction.

As the number of layers of PEDOT:PSS applied increased, the substrate became stiffer which increased its susceptibility to damage from creases. The creases break the polymer film which in, turn reduces the electrical conductivity, increasing the resistance, of the sample. From this study, it is apparent that the latex top coat, at the levels applied, does not protect the PEDOT:PSS layer from abrasion to a large extent as the creases and the lighter blue colour along them can be seen to pass through the area where there is a latex top layer. This could be improved by simply applying more latex to the surface therefore more investigation would be required. This extent of apparent damage was not seen in the previous wash testing of only PEDOT:PSS coated cotton fabrics in Chapter Three. The fabric samples in this study were considerably larger than those of Chapter Three but more wash testing of similar samples would be required to investigate whether this physical damage is repeatable. Despite the physical damage witnessed, the electrical resistances measured were similar to those measured prior to washing.

Figure 5.27 is a representative 3D microscope image, of a sample with one layer of PEDOT:PSS, to compare any differences that may be seen from using a latex top layer through a wash test. These particular samples show little to no differences, the cotton weave appears to be becoming unwound and broken similar to the previous experiments with no latex treatment. Figure 5.28 is a comparison of cotton fabric samples with two layers of conductive polymer and latex treatments and a sample with two layers of conductive polymer but no latex applied. The cotton weave, still, appears to become unwound yet the colour of the substrate appears darker. This darker colour is due to the higher amount of PEDOT:PSS that has been applied due to the latex treatment of the substrate, this extra loading of conductive polymer leads to improved electrical resistances when compared to the sample with no latex treatments.

As the number of applications of PEDOT:PSS increased, up to four and five layers, the woven substrate appeared to get less unwoven throughout the washing and drying process, this is apparent when comparing Figure 5.29 and 5.30 with Figure 5.27 and 5.28. Due to the initial latex coating, more PEDOT:PSS was allowed to remain on the surface of the fibres. This in conjunction with the applications of latex has strengthened the cotton fibres to remain tightly packed to result in the improved electrical resistance, compared with the resistances described in Chapter Three, post wash.

Figure 5.29 shows the comparison between a latex treated sample with four layers of conductive polymer and a sample without the latex treatments. It is easier to see a difference in shade between the samples, the darker colour belonging to the sample with latex treatment. As mentioned in Chapter Three, there are areas at the intersections of individual fibres which appear to have “pools” of polymer which appear much deeper and fuller than previous. Figure 5.30 is a similar comparison but of five layers of PEDOT:PSS. The darker colour and deep pools of polymer are present also which lead to the explanation behind the improved electrical resistance, post wash, on a latex treated sample.

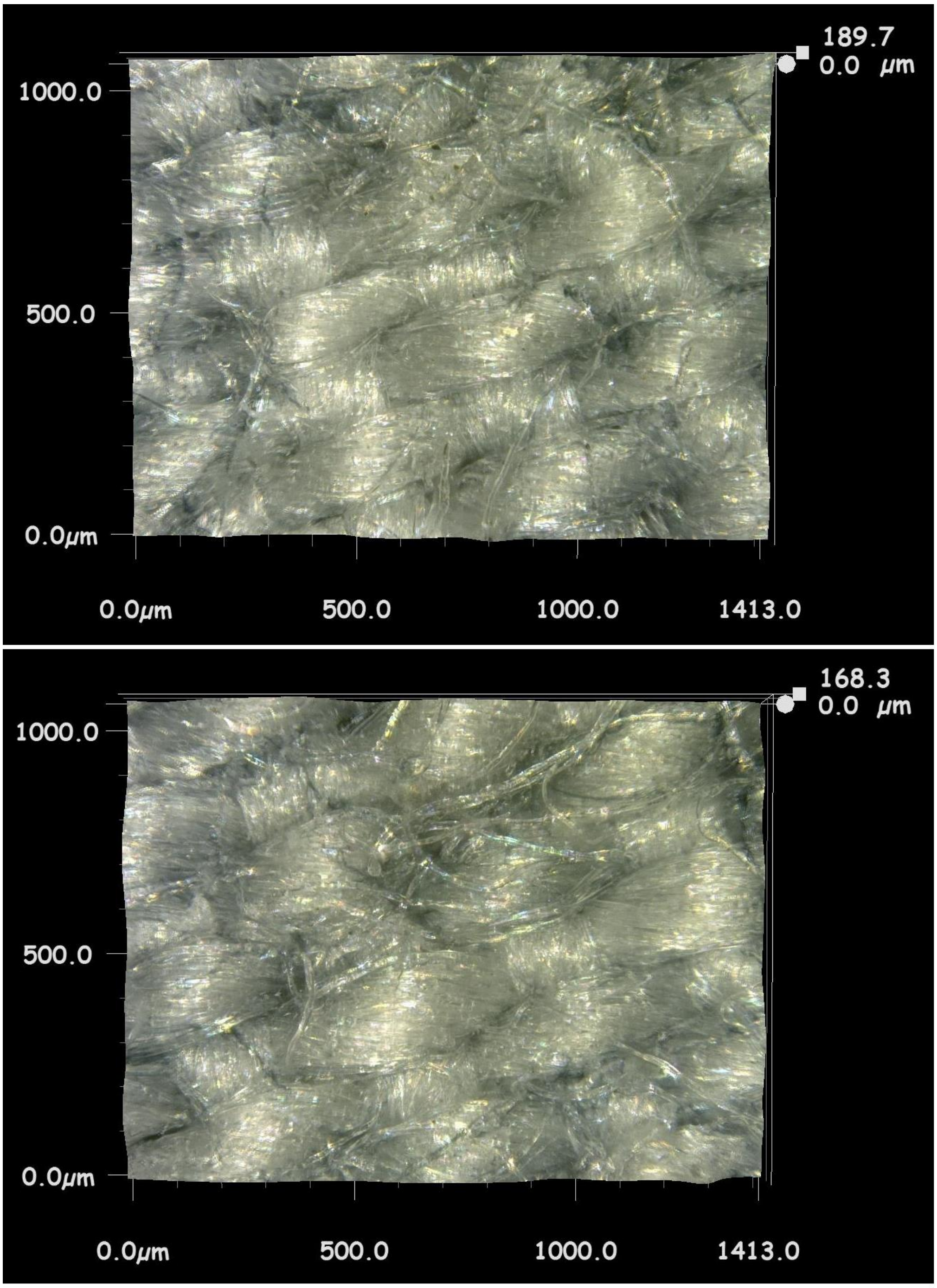


Figure 5.27 3D microscope images for a comparison of the parts of a sample, with one layer of PEDOT:PSS, which had a latex top layer (top image) and which did not (bottom image) at 250x magnification.

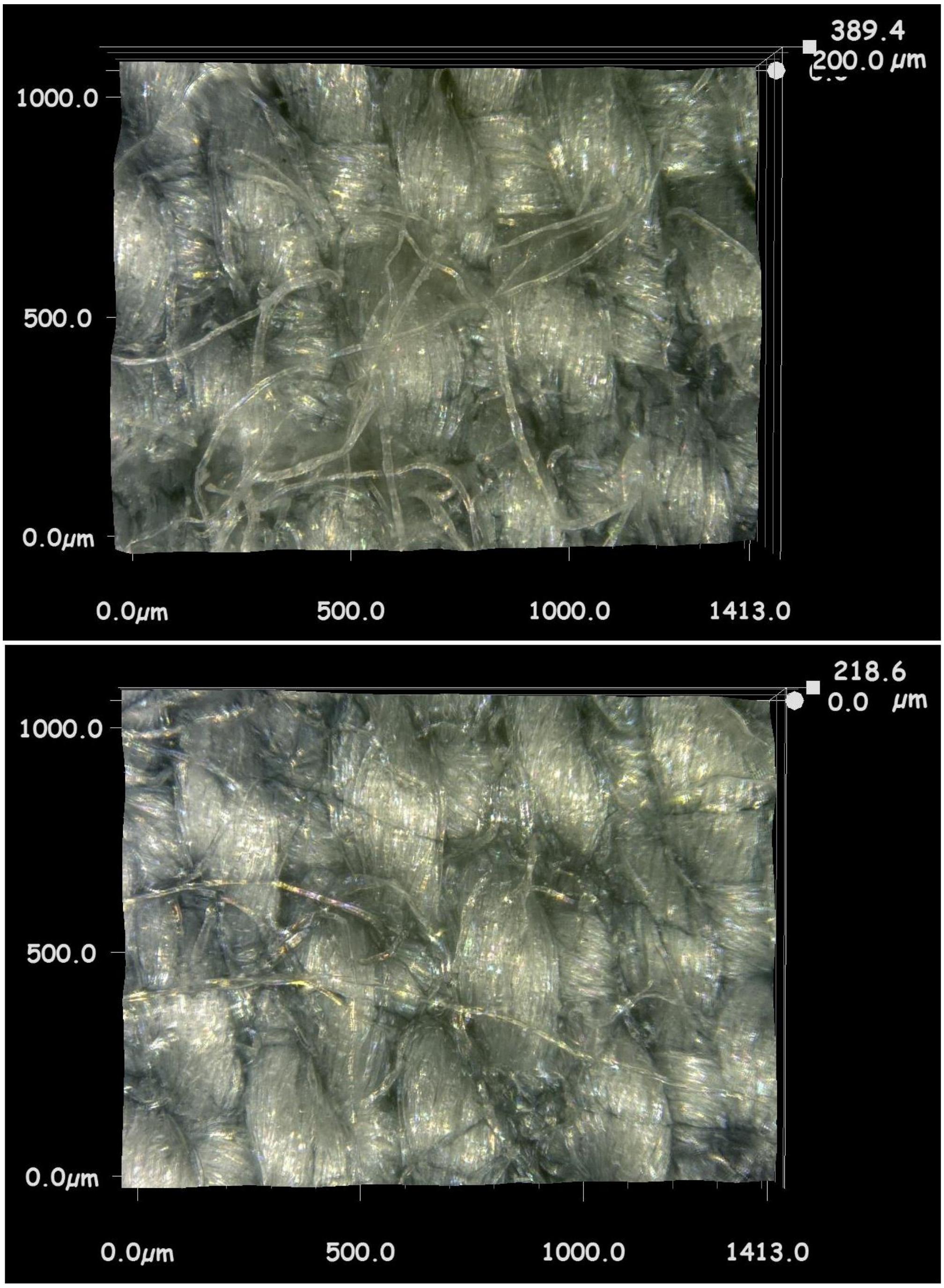


Figure 5.28 3D microscope images for a comparison of the parts of a sample, with two layers of PEDOT:PSS, which had a latex top layer (top image) and which did not (bottom image) at 250x magnification.

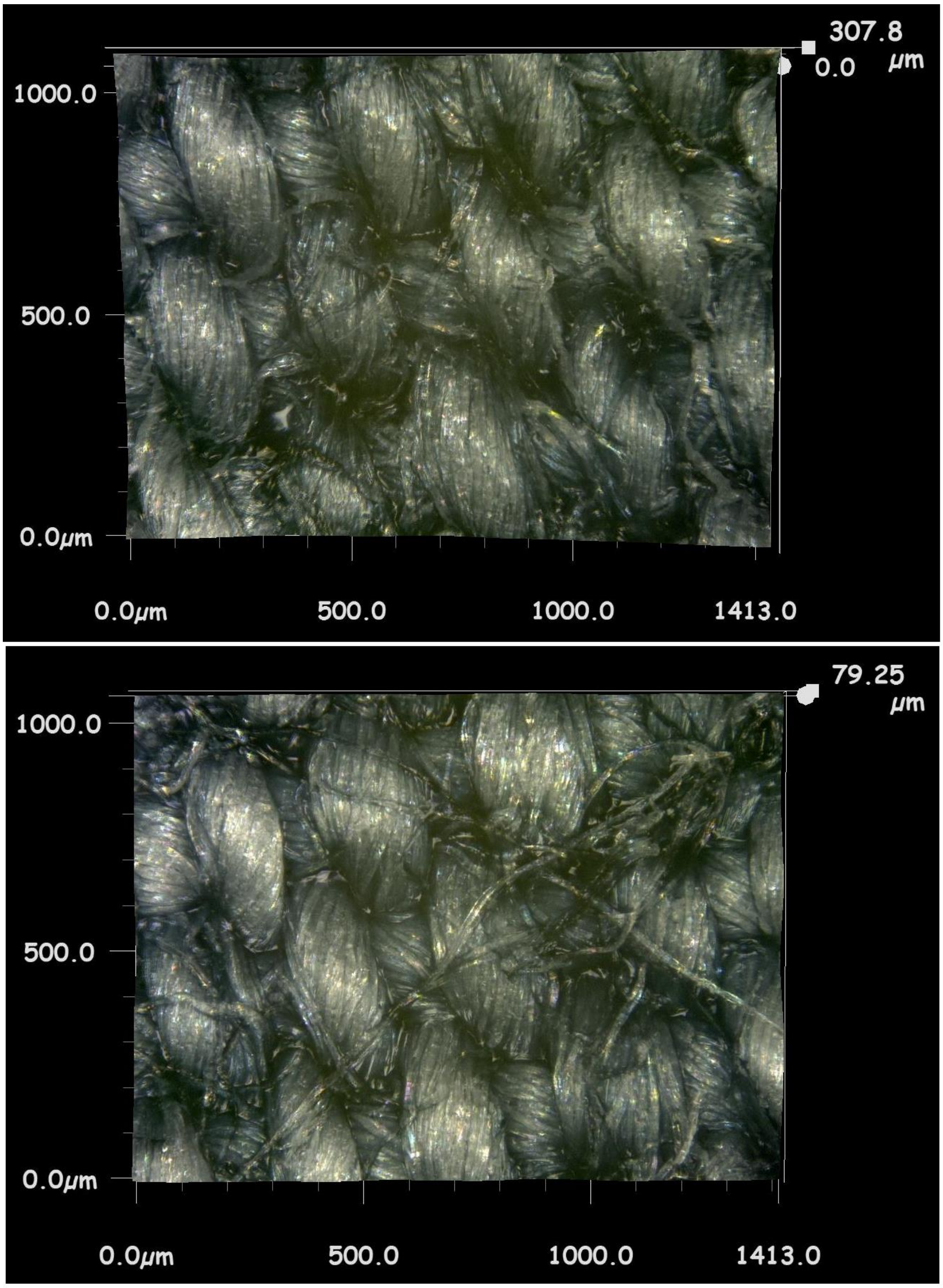


Figure 5.29 3D microscope images for a comparison of the parts of a sample, with four layers of PEDOT:PSS, which had a latex top layer (top image) and which did not (bottom image) at 250x magnification. The woven fabric appears to be becoming less unwoven during the wash and drying processes.

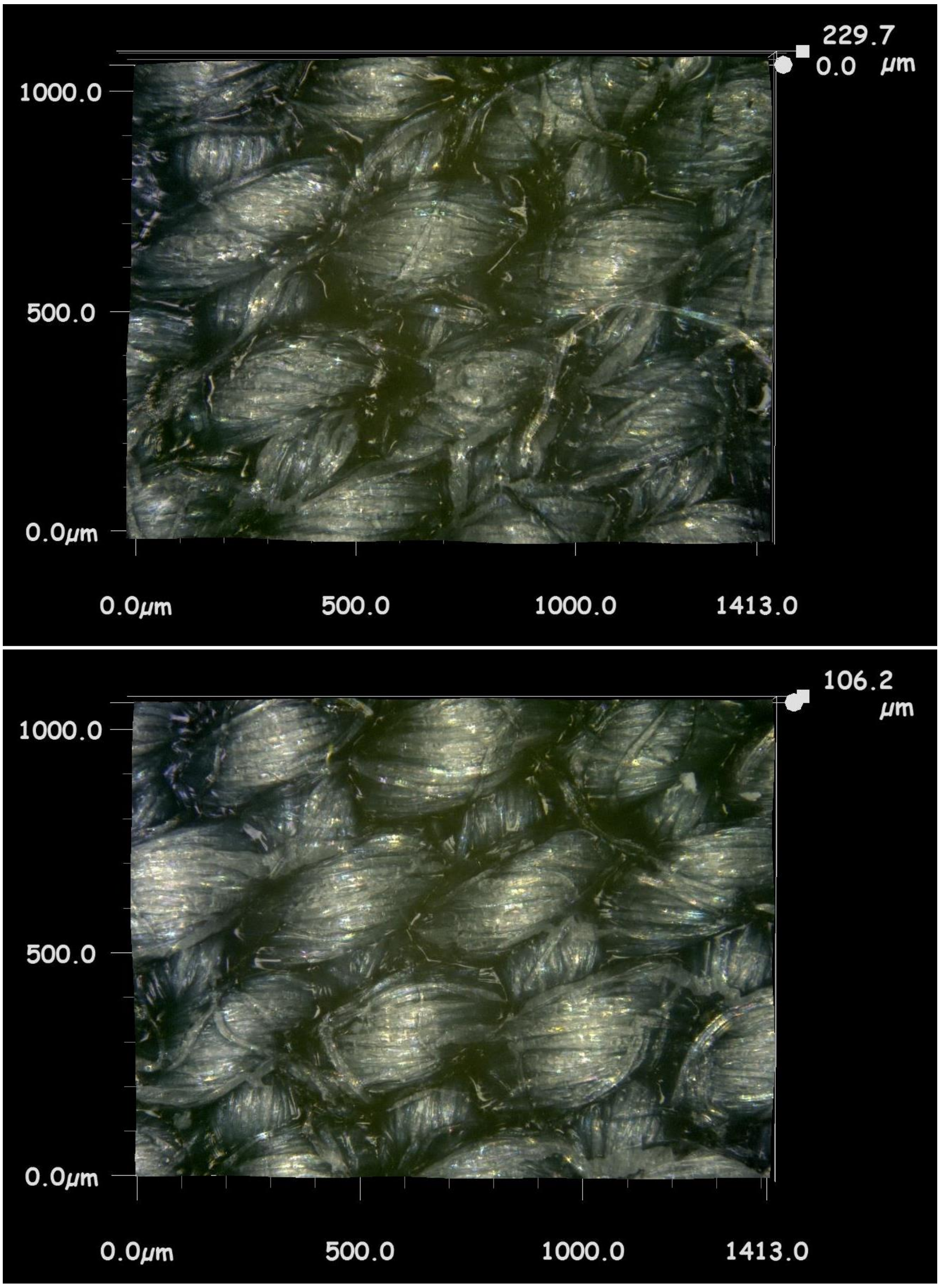


Figure 5.30 3D microscope images for a comparison of the parts of a sample, with five layers of PEDOT:PSS, which had a latex top layer (top image) and which did not (bottom image) at 250x magnification. The woven fabric appears to be becoming less unwoven during the wash and drying processes.

5.4 Discussion

In order to compare the absolute electrical resistance values with those achieved in Chapter Three, it is useful to provide some charts to compare them graphically. These charts are present in this section so as not to detract from the conversation of the results found in the previous sections.

The two stages to be compared are pre and post wash. Chapter Three had samples with one to five layers of PEDOT:PSS applied directly to a cotton substrate while this work had a layered composite of a latex treated cotton, PEDOT:PSS, electrically conductive electrodes and a final top layer of latex. Figure 5.31 displays a comparison of the resistance values measured at this stage. An instant difference can be seen regarding samples with one layer of PEDOT:PSS applied. The average resistance is much lower for the latex composite than just the PEDOT:PSS coated cotton, 1.65 ± 0.15 k Ω cm^{-1} and 9 ± 1 k Ω cm^{-1} respectively. The presence of the latex film on the substrate enabled a better application of PEDOT:PSS to the surface for a lower instant electrical resistance.

At two and three layers of PEDOT:PSS applied, it can be seen that the resistance measured of the latex composite has a much reduced associated error to those of Chapter Three. This was due to the PEDOT:PSS still passing through the substrate during application. At three layers, the electrical resistances can be argued to be statistically identical. The difference to be considered is that for the latex composite, the surface was coated with 35.5 mg of PEDOT:PSS, a mass increase of 2.52 % and the sample from Chapter Three had a mass of PEDOT:PSS of 6.0 mg, a mass increase of 2.64 %.

At four and five layers, the pure PEDOT:PSS coated cotton fabric samples have lower electrical resistances than those of the latex composites, 417 Ω cm^{-1} to 1167 Ω cm^{-1} and 296 Ω cm^{-1} to 1217 Ω cm^{-1} respectively. The resistances of the latex composites increased dramatically when a top layer of latex was applied which would raise the question that if these electrically conductive materials were to be used without the requirement to be washed, would a three layer PEDOT:PSS composite be better than a five layer composite? Further testing would be required to investigate if this impact of the latex top layer could be mitigated.

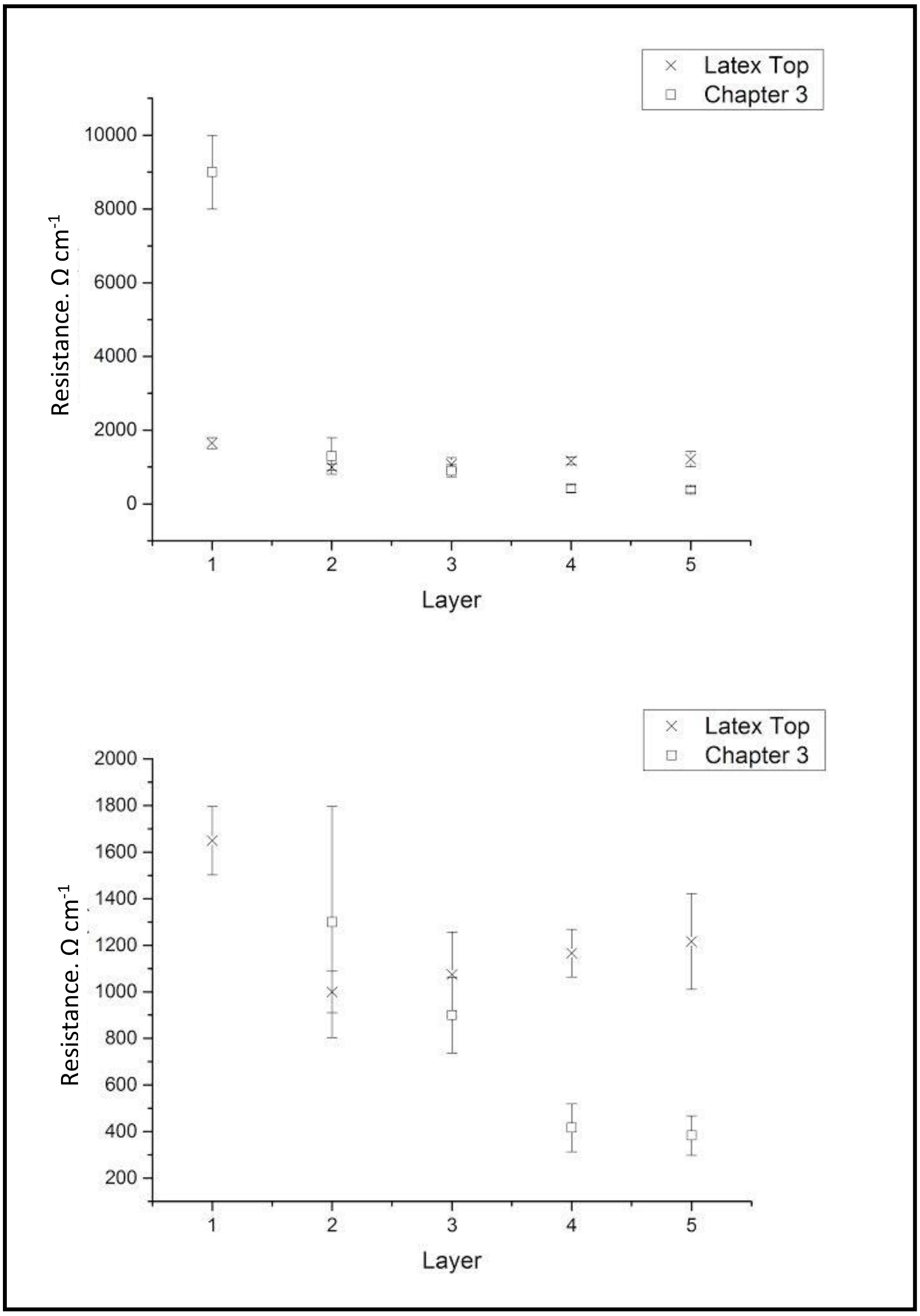


Figure 5.31 A comparison of the average electrical resistance with respect to the number of layers of PEDOT:PSS applied after the latex top layer and the PEDOT:PSS treated cotton from Chapter Three. The top plot shows all data while the bottom plot omits layer 1 of Chapter Three data for clarity

After the washing process it is clear to see in Figure 5.32 that the latex composites have lower electrical resistances, on average, than the samples with just PEDOT:PSS coated cotton, from Chapter Three. The greatest difference can be seen when comparing samples with one layer of PEDOT:PSS. Chapter Three samples' resistances have increased from 9 ± 1 k Ω cm^{-1} to 90 ± 36 k Ω cm^{-1} whereas the latex composite increased from 1.65 ± 0.15 k Ω cm^{-1} to 9.3 ± 3 k Ω cm^{-1}. The latex composite sample was more resilient to the washing process, though both are relatively poor results.

Cotton fabric samples with two layers of PEDOT:PSS show better results for both sample types, though the latex composite provided resistance values almost an order of magnitude lower. The Chapter Three samples' resistance increased from 1.3 ± 1.1 k Ω cm^{-1} to 9 ± 3 k Ω cm^{-1} whereas the latex composites increased from 1 ± 0.089 k Ω cm^{-1} to just 2.2 ± 5.3 k Ω cm^{-1}. The error is due to the electrodes breaking during the washing process giving a varying degree of contact with the PEDOT:PSS layer.

At increasing layers of PEDOT:PSS past this point, strange behaviour occurred which was discussed earlier, the post wash electrical resistance values, of the latex composite samples, were measured to be lower than resistances recorded pre wash. At three layers of PEDOT:PSS, the samples from Chapter Three returned average resistances of 7.2 ± 2.9 k Ω cm^{-1} while the latex composite returned 672 ± 1350 Ω cm^{-1}. Before the wash process, the samples with three layers of PEDOT:PSS were comparable in electrical resistance, this example shows the benefit of the latex composite for wash resistance.

Four layers of PEDOT:PSS post wash had resistances of 4.25 ± 0.7 k Ω cm^{-1} and 400 ± 300 Ω cm^{-1} for the PEDOT:PSS coated cotton and the latex composite respectively. Prior to washing, these differing samples had a difference of just 600 Ω cm^{-1} although, as discussed previously, the latex composite's electrical resistance reduced by over 600 Ω cm^{-1} while expectedly, the PEDOT:PSS coated cotton increased by an order of magnitude.

A similar statement can be made for fabric samples with five layers of PEDOT:PSS as four. The latex composite resistance decreased by over 600 Ω cm^{-1} during the washing and drying processes to return a resistance value of 512 ± 29 Ω cm^{-1} while the sample from Chapter Three increased by an order of magnitude to 4.6 ± 0.85 k Ω cm^{-1}. It was observed that cotton fabrics coated with the composite became much less unravelled during the wash process, compared with the observations in Chapter Three. This increased retention of structure of the coated cotton is the key improvement which produced the impressive post wash electrical resistance measurements.

This data provides evidence that creating a latex-PEDOT:PSS composite is an effective method to build wash fastness into a PEDOT:PSS layer on a woven cotton substrate. The electrically conductive bridge through the top layer of latex should be improved with a more durable material which would return resistance measurements with less error associated.

5.5 Conclusion

It has been successfully demonstrated that a latex-PEDOT:PSS composite with an electrically insulating surface can be applied to a woven cotton fabric and the electrical resistance measured. An artefact witnessed during the process was that after applying the top layer of latex, the electrical resistance of the samples increased. Prior to the application of the latex top layer, peak conductivities were achieved with electrical resistances of less than 200 $\Omega\ cm^{-1}$. Once the latex top layer was applied, the respective resistance was 1150 $\Omega\ cm^{-1}$. This negative interaction after applying the top layer requires more research to better understand and minimise this effect.

The electrical resistances measured prior to washing are mostly similar to results reported in Chapter Three. This method of creating an electrically conductive multi-layered composite has demonstrated that the final insulating layer does not negatively affect the electrical conductivity of the virgin electrically conductive polymer. Also the method of measuring the electrical resistance with conductive epoxy electrodes through this surface provides repeatable measurements.

Application of the conductive polymer as part of a latex composite presented improvements when comparing the post wash electrical resistances of the composite and the samples described in Chapter Three. Direct comparison displays that the resistances achieved in Chapter Three and from the current multi-layered composite, the samples with just PEDOT:PSS on the cotton substrate lost much of their conductivity, evidenced by large increases in electrical resistance, for example an increase in resistance for one sample from 300 to 5750 $\Omega\ cm^{-1}$. The composite samples, conversely, decreased in electrical resistance pre to post washing. For example 950 to 260 $\Omega\ cm^{-1}$ in a representative sample.

The choice of electrically conductive electrode, in this study provided by a silver containing 2 part epoxy, should be reconsidered for a more durable substitute. The electrodes were easily damaged during the wash process which introduced error for some measurements recorded post wash.

This study has provided an electrically conductive polymer based composite with equal electrical resistance values prior and post wash treatment. Bashir *et al.* provided a PEDOT coated fibre, prepared by *in-situ* polymerisation, with resistances in the region of 350 Ω cm^{-1} [1]. *In-situ* polymerisation, arguably, provides the most electrically conductive threads but the work presented in this Chapter has provided a highly electrically conductive cotton fabric following a post polymerisation application of the electrically conductive polymer. Molina *et al.* attempted to wash a poly(pyrrole) coated polyester fabric but witnessed a doubling of the surface resistance [2]. The electrical resistances reported within this work describe post wash electrical resistances that are similar to those prior to washing.

Consequently, this body of work lends itself to the potential of further work; to substitute the 2 part epoxy with a material which can be mechanically bonded to the electrically conductive polymer coated substrate, potentially riveting to reduce error in measurement post wash and to investigate the behaviour of latex as a top layer and throughout the wash process to improve the pre wash electrical resistance of the samples. This multilayer configuration of latex and conductive polymer should be translatable with any such conductive polymer so future electrically conductive polymers could be applied in this manner for direct comparison.

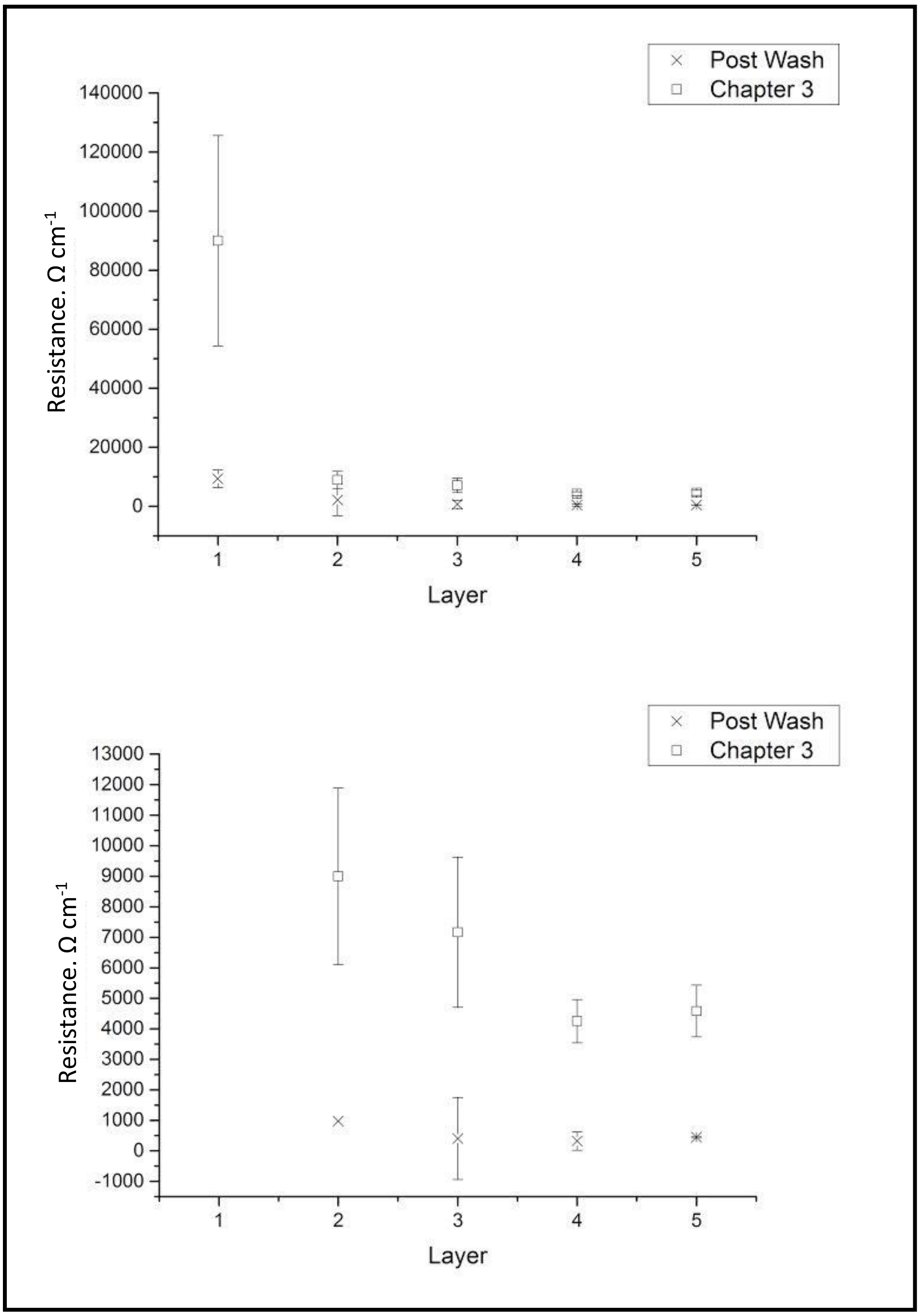


Figure 5.32 A comparison of the average electrical resistance measured with respect to the number of layers of PEDOT:PSS applied, post wash of the latex treated samples and the PEDOT:PSS treated cotton from Chapter Three. The top plot shows all data while the bottom plot omits layer 1 data for clarity

5.6 References

1. Bashir, T., et al., *Electrical resistance measurement methods and electrical characterization of poly(3,4-ethylenedioxythiophene)-coated conductive fibers.* Journal of Applied Polymer Science, 2012. **124**(4): p. 2954-2961.

2. Molina, J., et al., *Chemical and electrochemical polymerisation of pyrrole on polyester textiles in presence of phosphotungstic acid.* European Polymer Journal, 2008. **44**(7): p. 2087-2098.

Chapter Six

Summary
and future work

6.1 Summary

SMART textiles are envisaged to be utilised for improving the efficiency of health care providers. These textiles will harbour electronics and sensors which could monitor the vital signs of a patient and transmit the data, in real time, for remote monitoring. This ease of monitoring would allow patients to be discharged sooner, freeing up limited bed space in hospitals. The patients, despite being at home, can still be monitored remotely and the services notified of any changes. The electronics in a textile are traditionally interconnected with metal wires which can increase the weight of the textile making them less comfortable for the wearer. Electrically conductive polymers could potentially provide the electrical conductivity required for these electrical interconnects but would remain light, flexible and comfortable. A potential disadvantage of electrically conductive polymers would be poor wash fastness to the textile surface, hence losing electrical conductivity meaning the SMART textile could not be washed by conventional methods.

The synthetic routes to the monomer of the well-regarded electrically conductive polymer, PEDOT were investigated. It is known that varying the appendage groups from the conjugated thiophene backbone can affect the inherent flexibility, and electrical conductivity, of the polymer. For this reason, the synthesis routes were investigated for potential points from which derivatives of EDOT could be made. Two of these such points were highlighted and experimented. One point included derivatisation early in the synthetic procedure, requiring further synthetic steps to produce the EDOT derivative while the second point described the derivatisation as the final step of the synthesis procedure. The first route provided impure samples of potential EDOT, diethyl ester derivatives but these could not be isolated for further use or analysis. Mass directed HPLC only provided 5 mg of a sample for analysis. The second route also delivered impure samples of a novel derivative, which could not be separated *via* conventional chromatographic techniques. It was considered that the second route would be a more economic route since the novel derivative would not be lost through subsequent synthetic steps. This work also showed that synthetic routes utilising ethyl ester groups at the 2- and 4- positions on the thiophene were much more successful than methyl ester groups.

For application trials, a commercial sample of PEDOT:PSS was used as an analogue of any future derivatives of thiophene based electrically conductive polymers. Unlike *in-situ* polymerisation techniques, the aim of this investigation was to selectively coat certain areas of a textile, for electrical circuitry. So initially, PEDOT:PSS was applied to a woven cotton fabric with a K-bar 4 to investigate the electrical resistance of the resulting coatings with respect to the number of PEDOT:PSS applications to the surface. For the first few applications there was a high degree of penetration of the polymer dispersion through the fabric, until the coating had filled the pores. Electrical resistances of as low as 300 Ω cm^{-1} were achieved. It was noted that the electrical resistances of samples with two or three PEDOT:PSS layers were largely unaffected from creasing but samples with four and five layers recorded increases of *ca*. 42 %. After wash testing, the electrical resistances were recorded as much as 8.4 fold greater than pre washed. This displayed the poor wash resistance of the PEDOT:PSS film.

Chapter Four then describes the prototyping of a method conceived to improve the wash performance of the electrically conductive polymer. The concept consisted of using a synthesised latex copolymer as a base layer to fill the voids present in the cotton fabric. Upon this, the PEDOT:PSS layers were applied. Prior to the final application of latex as a top layer, metal electrodes were applied to the surface of the PEDOT:PSS as latex is electrically insulating. This composite, created on a carton board substrate, provided an electrically insulating surface yet the electrodes allowed resistance measurements. The electrical resistances measured in this section were very high but the absolute resistances measured were not the subject of investigation. Instead, it was important to note that, post application of the latex top layer, the same electrical resistance could be measured of the PEDOT:PSS layers as prior to the latex application. It was intended that the top layer of latex would provide an effective wear protective layer to the conductive polymer beneath.

Chapter Five translated the composite created in Chapter Four on a carton board substrate to the woven cotton fabric used in Chapter Three. The cotton fabric was immersed in the latex dispersion for application due to the ability of the cotton to absorb the aqueous dispersion before a layer could be formed with the K-bar. Layers of PEDOT:PSS were applied to the latex treated cotton fabric and subsequent application of electrodes were provided by an electrically conductive epoxy. Final application of the latex top layer was with a brush due to the electrodes' prominent position on the surface. The samples were washed and the electrical resistances, pre- and post-wash, were compared. The electrical resistances measured post wash were as low as 260 Ω cm^{-1} for a sample with five layers of PEDOT:PSS within the composite. The comparable resistances recorded from Chapter Three, post wash, are in the region of 10 fold greater than the composite. This study provided an electrically conductive polymer composite which retained a low electrical resistance after washing in a washing machine.

6.2 Future work

Since a wash resistant electrical composite has been created, the highest priority would be to renew effort in the synthesis of novel derivatives of PEDOT. The unsuccessful attempts at derivatisation thus far are not because their synthesis is impossible, it is simply because the ideal conditions for their syntheses have not been found. Purification of the synthesised derivatives could perhaps be achieved by attempting to crystallise them from solution. Conducting experiments in a systematic method of, varying concentrations of reactants and catalysts, investigating differing solvents and temperatures will yield these ideal conditions required for successful synthesis and purification.

Once novel monomers have been synthesised, polymerisation experiments can be conducted. Oxidative polymerisation is widely reported in the literature and varying dopants should be investigated, iron (III) chloride and poly(styrene sulphonate) for example, to compare relative electrical resistances of films cast from these dispersions. Further, the use of sorbitol as a secondary dopant is described in the literature by applying the aqueous solution to the surface to improve the electrical resistance measurement.

The synthesised novel polymers would be applied to cotton fabrics as the aforementioned composite and compared to that of PEDOT:PSS for wash resistance. Composites would also be created to include surface treatments of the conductive polymer, such as sorbitol, to understand if this can decrease the measured electrical resistance, and if the composite retains this post wash.

The composites could also be improved. The wash testing showed that the electrically conductive epoxy is brittle and cracked or came away from the surface of the conductive polymer. The electrodes could be improved by applying rivets to the conductive polymer surface. These rivets, though not bonded to the surface to the degree of the epoxy, would be tightly pressed against the polymer layer for a secure contact. This pressure must be balanced so as to not break the conductive polymer layer.

The use of the latex as the upper wear layer of the composite could potentially be improved. Poly(urethanes) are used in some industries as functional protective layers which can prevent plasticiser migration, for example, and could even be used to imbue the surface of the composite with a better “handle”. This could be examined while also understanding the potential for breakdown under UV radiation and yellowing with application of visible light. With the intended function in mind, the SMART textile would likely be worn beneath another garment so this effect may not be a priority.