

**STUDIES ON VAPOUR PHASE POLYMERISATION OF
PYRROLE AND ELECTROCONDUCTIVE TEXTILES
PREPARED THEREFROM FOR SENSING APPLICATION**

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PYRROLE AND ELECTROCONDUCTIVE TEXTILES
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by

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Submitted

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to the



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CERTIFICATE

This is to certify that the thesis entitled “**Studies on Vapour Phase Polymerisation of Pyrrole and Electroconductive Textiles Prepared Therefrom for Sensing Application**”, being submitted by **Mr Ankur Shukla** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by the candidate in the Department of Textile and Fibre Engineering, IIT Delhi. He has worked under our guidance and supervision, fulfilling the requirements for the submission of the thesis, which has attained the standard required for a Ph.D. degree at this institute.

The research work carried out to complete the thesis has not been submitted for the award of a degree or diploma in any institute in part or full.



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ABSTRACT

Electroconductive textiles or e-textiles are a group of promising new materials that are becoming very important for their potential use in the areas of electromagnetic shielding, electrothermal generators, electrostatic dissipation, sensors and actuators, and data transfer, to name a few. The current research work explores electrochemical polymerisation and vapour phase polymerisation methods in depth with the aim to develop a fast and industrially scalable process for large-scale fabrication of flexible and non-metallic electroconductive textiles.

In electrochemical polymerisation, the rate of polymerisation and the polymer deposition can be controlled quite precisely by controlling the applied voltage or system current during polymerisation. The solution used for electrochemical polymerisation typically contains one or more compounds in addition to the monomer. These compounds are added with the aim to either achieve low electrical resistance polymer deposition or to obtain a higher polymer add-on. However, there has been an ambiguity in the role of the compounds. Understanding the actual role of the compounds, as to whether they function as a dopant or an electrolyte, is crucial. The current study compared sodium nitrate, sodium 2-anthraquinone sulfonate (AQSA-Na), p-toluene sulfonic acid (pTSA) and oxalic acid to understand the role of different compounds in electrochemical polymerisation. A metric called charge utilization factor (CUF) was defined to characterise each chemical. A suitable combination of a low CUF compound with a high CUF compound turned out to be a better option for achieving low electrical resistance when applied over a polyester fabric. The only hindrance is that it requires a conductive substrate connected with a metallic back electrode.

Vapour phase polymerisation (VPP) is another method used to develop electroconductive fabric. It is a single-step process and does not require a solvent for the dissolution of pyrrole, which makes it eco-friendly. A glass setup was designed and fabricated in-house to perform VPP on fabric under a controlled environment. The setup consisted of separate sections for boiling pyrrole and for vapour deposition on the sample. The effect of oxidant (FeCl_3) concentration, dopant (pTSA) concentration, polymerisation time and pyrrole temperature were studied. The experimental data revealed that oxidant concentration and the rate of vapour formation played a decisive role in determining the surface resistance of polypyrrole-coated fabric. Quite interestingly, a suitable selection of process parameters yielded an electroconductive fabric with a surface resistance of around $220\ \Omega$. Ultrasonication was carried out to assess the surface adherence of polypyrrole to the fabric. After 10 min of sonication, the fabric resistance increased sharply due to the removal of polymer from the surface, as confirmed also by air permeability and spectrophotometry. The fabric, due to its flexible nature, did not show significant change in resistance during bending and slight turning up to 20° along its axis.

A new process was developed to obtain a faster process by combining electrochemical polymerisation and vapour phase polymerisation. This novel process, which has been named electrically assisted chemical vapour polymerisation (eCVP), offered the flexibility of applying a voltage (up to 12 V) during polymerisation to boost the formation of polypyrrole. The glass setup used for VPP was modified, and a power supply was connected in series to the fabric sample. Experimental data showed a decrease in resistance with increasing polymerisation time and the applied voltage. The oxidant (FeCl_3) concentration also played an equally important role. This novel process resulted in a higher polypyrrole add-on and over 50 % reduction in surface resistance compared to the VPP

method within 3 min time. It also showed the possibility of scale-up for large-scale continuous production of electroconductive fabric.

The polypyrrole-coated fabric prepared by using eCVP was used for the fabrication of interdigitated capacitive sensors (IDS). Different designs were prepared to obtain an efficient design of the sensor by changing the width and the number of fingers. Thus, multiple designs with varying capacitance were obtained. The capacitive behaviour of IDS was evaluated at different frequencies from 20 Hz to 2 MHz, and the most stable and cost-effective design was selected. The prepared IDS was then used for RH sensing and compared with commercially available sensors. The polypyrrole-coated fabric also showed a change in resistance when exposed to acetone and ammonia vapours. Since the behaviour of textile fabrics often depends on the environment, one sensor was prepared with polyethylene lamination to protect it from environmental changes. The capacitance vs frequency behaviour of laminated and unlaminated sensors showed that lamination did not affect the working of the IDS for humidity sensing.

Finally, a prototype machine was designed and developed for the preparation of electroconductive fabric continuously. The machine was used to polymerise polypyrrole over nylon, cotton, and polyester fabrics at different speeds. The pre-treated fabric was dipped in the oxidant solution, followed by squeezing. This oxidant-rich fabric was exposed to pyrrole vapours in the reaction chamber. During the exposure of the fabric to pyrrole vapours, an electrical voltage was applied simultaneously to the fabric. The successful preparation of electroconductive fabric by employing the prototype machine demonstrated the possibility of scaling up the eCVP process for large-scale production of electroconductive textiles.

सार

इलेक्ट्रोकंडक्टिव टेक्सटाइल या ई-टेक्सटाइल आशाजनक नई सामग्रियों का एक समूह है जो इलेक्ट्रोमैग्नेटिक परिरक्षण, इलेक्ट्रोथर्मल जनरेटर, इलेक्ट्रोस्टैटिक अपव्यय, सेंसर और एक्चुएटर्स और डेटा ट्रांसफर जैसे क्षेत्रों में अपने संभावित उपयोग के लिए बहुत महत्वपूर्ण होते जा रहे हैं। वर्तमान शोध कार्य इलेक्ट्रोकेमिकल बहुलकीकरण और वाष्प चरण बहुलकीकरण विधियों की गहराई से खोज करता है, जिसका उद्देश्य लचीले और गैर-धातु इलेक्ट्रोकंडक्टिव टेक्सटाइल के बड़े पैमाने पर निर्माण के लिए एक तेज़ और औद्योगिक रूप से मापनीय प्रक्रिया विकसित करना है।

इलेक्ट्रोकेमिकल बहुलकीकरण में, बहुलकीकरण की दर और पॉलीमर डिपोजिशन को बहुलकीकरण के दौरान लागू वोल्टेज या सिस्टम करंट को नियंत्रित करके काफी सटीक रूप से नियंत्रित किया जा सकता है। इलेक्ट्रोकेमिकल बहुलकीकरण के लिए उपयोग किए जाने वाले विलयन में आमतौर पर एकलक के अलावा एक या अधिक यौगिक होते हैं। इन यौगिकों को या तो कम विद्युत प्रतिरोध वाले बहुलक जमाव को प्राप्त करने या उच्च बहुलक ऐड-ऑन प्राप्त करने के उद्देश्य से जोड़ा जाता है। हालाँकि, यौगिकों की भूमिका में एक अस्पष्टता रही है। यौगिकों की वास्तविक भूमिका को समझना, जैसे कि वे डोपेंट या इलेक्ट्रोलाइट के रूप में कार्य करते हैं, महत्वपूर्ण है। वर्तमान अध्ययन में इलेक्ट्रोकेमिकल बहुलकीकरण में विभिन्न यौगिकों की भूमिका को समझने के लिए सोडियम नाइट्रेट, सोडियम 2-एंथ्राक्विनोन सल्फोनेट (AQSA-Na), पी-टोल्यूनि सल्फोनिक एसिड (pTSA) और ऑक्सालिक एसिड की तुलना की गई। प्रत्येक रसायन को डोपेंट या इलेक्ट्रोलाइट के रूप में चिह्नित करने के लिए चार्ज यूटिलाइजेशन फैक्टर (सीयूएफ) नामक एक मीट्रिक परिभाषित किया गया था। एक उच्च सीयूएफ यौगिक के साथ कम सीयूएफ यौगिक का एक उपयुक्त एक पॉलिएस्टर कपड़े पर लागू होने पर कम विद्युत प्रतिरोध प्राप्त करने के लिए एक बेहतर विकल्प निकला। एकमात्र बाधा यह है

कि इसके लिए एक प्रवाहकीय सब्सट्रेट की आवश्यकता होती है जो एक धात्विक बैक इलेक्ट्रोड से जुड़ा होता है।

वाष्प चरण बहुलकीकरण (वीपीपी) एक अन्य विधि है जिसका उपयोग इलेक्ट्रोक्रोमिक फ़ैब्रिक विकसित करने के लिए किया जाता है। यह एक एकल-चरणीय प्रक्रिया है और इसमें पायरोल के विघटन के लिए किसी विलायक की आवश्यकता नहीं होती है, जो इसे पर्यावरण-अनुकूल बनाता है। नियंत्रित वातावरण में कपड़े पर वीपीपी निष्पादित करने के लिए घर में ही एक ग्लास सेटअप डिजाइन और निर्मित किया गया। सेटअप में पाइरोल को उबालने और नमूने पर वाष्प जमाव के लिए अलग-अलग अनुभाग शामिल थे। ऑक्सीडेंट (FeCl_3) सांद्रता, डोपेंट (pTSA) सांद्रता, बहुलकीकरण समय और पाइरोल तापमान के प्रभाव का अध्ययन किया गया। प्रयोगात्मक डेटा से पता चला कि ऑक्सीडेंट की सांद्रता और वाष्प गठन की दर ने पॉलीपाइरोल लेपित कपड़े की सतह प्रतिरोध को निर्धारित करने में निर्णायक भूमिका निभाई। काफी दिलचस्प बात यह है कि प्रक्रिया मापदंडों के उपयुक्त चयन से लगभग 220Ω के सतह प्रतिरोध के साथ एक इलेक्ट्रोक्रोमिक कपड़ा प्राप्त हुआ। कपड़े पर पॉलीपाइरोल की सतह के जुड़ाव का आकलन करने के लिए अल्ट्रासोनिकेशन किया गया। 10 मिनट के सोनिकेशन के बाद, सतह से बहुलक हटने के कारण कपड़े का प्रतिरोध तेजी से बढ़ गया, जैसा कि वायु पारगम्यता और स्पेक्ट्रोफोटोमेट्री द्वारा भी पुष्टि की गई है। कपड़ा, अपनी लचीली प्रकृति के कारण, झुकने और अपनी धुरी पर 20° तक मामूली मोड़ के दौरान प्रतिरोध में महत्वपूर्ण परिवर्तन नहीं दिखाता है।

इलेक्ट्रोकेमिकल बहुलकीकरण और वाष्प चरण बहुलकीकरण को मिलाकर एक तेज प्रक्रिया प्राप्त करने के लिए एक नई प्रक्रिया विकसित की गई। यह नवीन प्रक्रिया, जिसे हम विद्युत सहायता प्राप्त रासायनिक वाष्प बहुलकीकरण (eCVP) नाम दिया गया है, ने पॉलीपाइरोल के निर्माण को बढ़ावा देने के लिए पोलीमराइजेशन के दौरान वोल्टेज (12 V तक) लगाने की लचीलापन प्रदान की। वीपीपी के लिए

उपयोग किए गए ग्लास सेटअप को संशोधित किया गया, और कपड़े के नमूने के साथ श्रृंखला में एक बिजली की आपूर्ति जोड़ी गई। प्रायोगिक डेटा में बढ़ते बहुलकीकरण समय और लागू वोल्टेज के साथ प्रतिरोध में कमी देखी गई। ऑक्सीडेंट (FeCl_3) सांद्रता ने भी समान रूप से महत्वपूर्ण भूमिका निभाई। इस नवीन प्रक्रिया के परिणामस्वरूप 3 मिनट के भीतर वीपीपी विधि की तुलना में उच्च पॉलीपाइरोल ऐड-ऑन और सतह प्रतिरोध में 50 % से अधिक की कमी आई। इसने इलेक्ट्रोक्रोमिक कपड़े के बड़े पैमाने पर निरंतर उत्पादन की संभावना भी दिखाई।

ईसीवीपी का उपयोग करके तैयार किए गए पॉलीपाइरोले लेपित कपड़े का उपयोग इंटरडिजिटैड कैपेसिटिव सेंसर (आईडीएस) के निर्माण के लिए किया गया। चौड़ाई और उंगलियों की संख्या को बदलकर सेंसर का एक कुशल डिज़ाइन प्राप्त करने के लिए विभिन्न डिज़ाइन तैयार किए गए थे। इस प्रकार, अलग-अलग धारिता क्षमता वाले कई डिज़ाइन प्राप्त किए गए। आईडीएस के कैपेसिटिव व्यवहार का मूल्यांकन 20 हर्ट्ज से 2 मेगाहर्ट्ज तक विभिन्न आवृत्तियों पर किया गया, और सबसे स्थिर और लागत प्रभावी डिज़ाइन का चयन किया गया। तैयार आईडीएस का उपयोग आरएच सेंसिंग के लिए किया गया और इसकी तुलना व्यावसायिक रूप से उपलब्ध सेंसर से की गई। एसीटोन और अमोनिया वाष्प के संपर्क में आने पर पॉलीपाइरोले लेपित कपड़े के प्रतिरोध में भी बदलाव देखा गया। चूंकि कपड़ों का व्यवहार अक्सर पर्यावरण पर निर्भर करता है, इसलिए इसे पर्यावरणीय परिवर्तनों से बचाने के लिए पॉलीथीन परतबंदी के साथ एक सेंसर तैयार किया गया। परतबंदित (लैमिनेटेड) और अनपरतबंदित लैमिनेटेड सेंसरों के कैपेसिटेंस बनाम आवृत्ति व्यवहार ने दिखाया कि परतबंदी (लेमिनेशन) ने आर्द्रता सेंसिंग के लिए आईडीएस के कामकाज को प्रभावित नहीं किया।

अंत में, इलेक्ट्रोक्रोमिक कपड़े की निरंतर तैयारी के लिए एक प्रोटोटाइप मशीन डिज़ाइन और विकसित की गई। मशीन का उपयोग नायलॉन, कॉटन और पॉलिएस्टर कपड़े पर अलग-अलग गति से पॉलीपाइरोल का बहुलकीकरण करने के लिए किया गया। पहले से उपचारित कपड़े को ऑक्सीडेंट घोल

में डुबोया गया, उसके बाद निचोड़ा गया। ऑक्सीडेंट से भरपूर इस कपड़े को प्रतिक्रिया कक्ष (रिएक्शन चैंबर) में पाइरोल वाष्प के संपर्क में लाया गया। पाइरोल वाष्प के संपर्क में आने के दौरान, कपड़े पर एक साथ विद्युत वोल्टेज लगाया गया। प्रोटोटाइप मशीन का उपयोग करके इलेक्ट्रोकंडक्टिव कपड़े की सफल तैयारी ने इलेक्ट्रोकंडक्टिव टेक्सटाइल के बड़े पैमाने पर उत्पादन के लिए eCVP प्रक्रिया को बढ़ाने की संभावना को प्रदर्शित किया।

TABLE OF CONTENT

CERTIFICATE.....	III
ACKNOWLEDGEMENT.....	V
ABSTRACT	VII
LIST OF FIGURES	XXIII
LIST OF TABLES	XXXI
CHAPTER 1: INTRODUCTION AND OBJECTIVES	1
1.1 INTRODUCTION	3
1.2 LITERATURE REVIEW	5
1.2.1 Electrically conducting polymers	5
1.2.2 Comparison of different polymerisation methods	7
1.2.3 Vapour phase polymerisation method	10
1.2.4 Electrochemical polymerisation over textile fabrics.....	16
1.2.5 Characterisation of electro-conductive polymers and textiles	18
1.2.5.1 Surface resistivity measurement	18
1.2.5.2 Voltage-current characteristics	19
1.2.5.3 Surface and microstructure analysis	19
1.2.6 Flexible sensors.....	21
1.2.7 Sensors based on electrically conducting fabric	23
1.2.8 Characterisation of textile based sensors	31
1.2.8.1 V-I characteristics	31
1.2.8.2 Sensor sensitivity	32
1.2.8.3 Linearisation	33
1.2.8.4 Response time	33

1.2.8.5 Bandwidth.....	34
1.3 APPLICATIONS	35
1.4 PROBLEM STATEMENT	36
1.5 OBJECTIVES	38
CHAPTER 2: MATERIALS AND METHODS	39
2.1 CHEMICALS USED.....	41
2.2 PREPARATION OF ELECTRODE	42
2.3 PREPARATION OF FABRIC	42
2.4 CYCLIC VOLTAMMETRY	43
2.5 CHRONOAMPEROMETRY	44
2.6 CHRONOPOTENTIOMETRY	45
2.7 POLYMERISATION METHODS	45
2.7.1 Electrochemical polymerisation.....	45
2.7.2 Vapour phase polymerisation (VPP)	46
2.7.3 Electrically assisted chemical vapour polymerisation (ecvp).....	48
2.8 CHARACTERISATIONS	49
2.8.1 Measurement of surface resistance	49
2.8.2 FTIR spectroscopy	50
2.8.3 X-ray diffraction	51
2.8.4 V-I characteristics	52
2.8.5 SEM/EDX	52
2.8.6 Air permeability.....	53
2.8.7 Bending rigidity	54
2.8.8 Effect of bending and turning on conductivity	54
2.8.9 Effect of sonication	55

2.9	SENSOR FABRICATION	55
2.10	SENSING BEHAVIOUR	56
2.10.1	Capacitance measurement.....	56
CHAPTER 3: ELECTROCHEMICAL POLYMERISATION OF PYRROLE		59
3.1	INTRODUCTION	61
3.2	EXPERIMENTAL	63
3.3	RESULTS AND DISCUSSION	63
3.3.1	Cyclic voltammetry (CV)	63
3.3.2	Electrolytic behaviour of different additives during electrochemical polymerisation.....	69
3.3.3	Doping behaviour of different chemicals	73
3.3.4	Behaviour of oxalic acid	76
3.3.5	Effect of combination of electrolyte and dopant on surface resistance of prepared film.....	77
3.3.6	Electrochemical polymerisation over conductive polyester fabric	79
3.4	CHARACTERISATIONS	82
3.4.1	Surface morphology of conductive polyester fabric.....	82
3.4.2	Elemental analysis of polypyrrole	84
3.4.3	FTIR analysis	84
3.4.4	Wide angle XRD analysis.....	86
3.5	SUMMARY.....	88
3.6	SIGNIFICANT OUTCOMES FROM THIS CHAPTER	88
CHAPTER 4: VAPOUR PHASE POLYMERISATION OF PYRROLE.....		91
4.1	INTRODUCTION	93
4.2	EXPERIMENTAL.....	95

4.2.1	Proof of concept	95
4.2.2	Design of vapour phase polymerisation setup	95
4.2.3	VPP process design.....	98
4.3	RESULTS AND DISCUSSION	99
4.3.1	VPP over PET film	99
4.3.2	VPP over polyester fabric	101
4.3.3	Effect of oxidant concentration on fabric surface resistance	103
4.3.4	Effect of dopant concentration on polymerisation of pyrrole	106
4.3.5	Effect of reaction time	107
4.3.6	Effect of monomer vapourisation rate	109
4.4	CHARACTERISATIONS	112
4.4.1	FTIR spectrometry	112
4.4.2	V-I characteristics	113
4.4.3	Bending and turning of the conductive fabric.....	114
4.4.4	Durability	117
4.4.5	Effect of polypyrrole deposition on air permeability.....	119
4.5	SUMMARY.....	120
4.6	SIGNIFICANT OUTCOMES FROM THIS CHAPTER	120

CHAPTER 5: ELECTRICALLY-ASSISTED CHEMICAL VAPOUR

	POLYMERISATION.....	123
5.1	INTRODUCTION	125
5.2	EXPERIMENTAL.....	127
5.2.1	Step-by-step electrochemical polymerisation over VPP.....	127
5.2.2	In situ electrically assisted chemical vapour polymerisation (ecvp)	127
5.2.3	Setup for ecvp	128

5.2.4	The ecvp process.....	130
5.3	RESULTS AND DISCUSSION	132
5.3.1	Effect of electrochemical polymerisation over VPP coated fabric	132
5.3.2	Effect of process parameters on surface resistance and polymer add-on in ecvp	136
5.3.2.1	Applied potential.....	136
5.3.2.2	Polymerisation time	140
5.3.2.3	Rate of monomer vapourisation.....	142
5.3.2.4	Oxidant concentration	143
5.3.2.5	Dopant (ptsa) concentration.....	145
5.4	CHARACTERISATIONS	146
5.4.1	FTIR analysis.....	146
5.4.2	X-ray diffraction analysis	147
5.4.3	V-I characteristics of the electro-conductive fabric.....	148
5.4.4	Effect of ultrasonication.....	149
5.4.5	Bending modulus	150
5.5	SUMMARY.....	151
5.6	SIGNIFICANT OUTCOMES FROM THIS CHAPTER	152
 CHAPTER 6: DEVELOPMENT, CHARACTERISATION AND PERFORMANCE		
ASSESSMENT OF ELECTROCONDUCTIVE FABRICS FOR		
SENSOR APPLICATION.....153		
6.1	INTRODUCTION	155
6.2	EXPERIMENTAL.....	156
6.2.1	Preparation of electroconductive fabric	156
6.2.2	Characterisation	157

6.2.3	Fabrication of interdigitated sensor	159
6.3	RESULTS AND DISCUSSION	160
6.3.1	Effect of sensor design on capacitance	160
6.3.2	Calculated capacitance	163
6.3.3	Humidity sensing using interdigitated sensor	168
6.3.4	Resistive sensing	170
6.3.4.1	Acetone sensing	170
6.3.4.2	Ammonia sensing	172
6.4	SUMMARY	173
6.5	SIGNIFICANT OUTCOME FROM THIS CHAPTER	174

CHAPTER 7: DESIGN AND DEVELOPMENT OF A PROTOTYPE MACHINE

FOR IN SITU CONTINUOUS ELECTRICALLY-ASSISTED

CHEMICAL VAPOUR POLYMERISATION ONTO FABRICS....175

7.1	INTRODUCTION	177
7.2	EXPERIMENTAL	179
7.2.1	Machine design	179
7.2.2	Fabric roll	179
7.2.3	Oxidant trough	180
7.2.4	Pressure rollers	180
7.2.5	Boiler	181
7.2.6	Reaction chamber	182
7.2.7	Winding roller	184
7.3	CONTINUOUS IN SITU ECVP BASED POLYMERISATION PROCESS	184
7.4	RESULTS AND DISCUSSION	186
7.4.1	Effect of voltage	186

7.4.2	Effect of polymerisation time	189
7.5	OUTCOMES OF THE PROTOTYPE MACHINE	190
7.6	SUGGESTED IMPROVEMENTS IN THE PROTOTYPE MACHINE	190
7.7	SUMMARY.....	190
7.8	SIGNIFICANT OUTCOMES FROM THIS CHAPTER	191
CHAPTER 8: SUMMARY, CONCLUSIONS AND FUTURE SCOPE.....		193
8.1	SUMMARY.....	195
8.2	OVERALL CONCLUSIONS.....	197
8.3	FUTURE SCOPE.....	199

REFERENCES

LIST OF FIGURES

Figure 1.1 Different methods for the preparation of electroconductive fabrics.....	4
Figure 1.2 Formation of positive polaron and positive bipolaron in polypyrrole.....	7
Figure 1.3 Setup used for vapour phase polymerisation [46]	11
Figure 1.4 Setup used for vapour phase polymerisation over textile sample [49].....	13
Figure 1.5 Setup for vapour phase polymerisation over textile sample [50]	14
Figure 1.6 Vapour phase polymerisation in vacuum [53].....	15
Figure 1.7 SEM micrographs of polyester fabric coated with polypyrrole using chemical polymerisation done with (a) ferric tosylate without PVA at 0 °C, (b) ferric tosylate with PVA at 0 °C, (c) ferric tosylate with PVA at 20 °C, and (d) APS with PVA at 0 °C [33].....	20
Figure 1.8 The sensing process	21
Figure 1.9 Electrode arrangement in capacitive sensor	26
Figure 1.10 Hysteresis in the pressure-capacitance diagram of a single sensing element with the textile spacer of 6 mm thickness [98]	27
Figure 1.11 Sensitivity at different temperatures.....	28
Figure 1.12 Comparison of the sensing response of the fabricated NH ₃ and humidity sensors before and after bending for 1000 times with the bending radius less than 5 mm [101]	29
Figure 1.13 Plot of temperature and humidity dependence of the sensors [87].....	30
Figure 1.14 Determination of sensitivity from linear sensor response [111].....	33
Figure 1.15 The real time response of sensor to stepwise increase in the concentration of trichloromethane vapour [82]	34
Figure 1.16 SEM images of PCF stretched to 0 %, 5 %, 20 %, and 40 % strains at (a) low and (b) high magnifications. (c) Illustration scheme of electron transfer path	

during stretching [116].....	35
Figure 2.1 Stainless steel electrode	42
Figure 2.2 Schematic for electrode cleaning.....	42
Figure 2.3 Fabric treatment with NaOH before polymerisation	43
Figure 2.4 Schematic of 3-electrode cell	44
Figure 2.5 Julabo F25 water circulator connected to polymerisation setup.....	46
Figure 2.6 Schematic for electrochemical polymerisation.....	46
Figure 2.7 Schematic of the VPP process	47
Figure 2.8 Glass setup for VPP process	47
Figure 2.9 Schematic of eCVP process.....	48
Figure 2.10 Setup for eCVP	49
Figure 2.11 Concentric ring electrode attached with an acrylic sheet for resistance measurement	50
Figure 2.12 Connection of multimeter and electrode for resistance measurement.....	50
Figure 2.13 IRAffinity-1S FTIR	51
Figure 2.14 X'Pert PRO X-ray diffraction instrument	51
Figure 2.15 Schematic arrangement for V-I characteristics measurement	52
Figure 2.16 Zeiss EVO 18 SEM instrument	53
Figure 2.17 APT/AUTO APPLE air permeability tester	53
Figure 2.18 Paramount bending stiffness tester	54
Figure 2.19 Process for fabrication of capacitive sensor	55
Figure 2.20 Capacitance vs frequency measurement using LCR meter	57
Figure 3.1 Cyclic voltammetry potentiostatic.....	65
Figure 3.2 Cyclic voltammetry galvanostatic	65
Figure 3.3 Potentiostatic cyclic voltammogram of additive chemicals (a) without pyrrole,	

and (b) with pyrrole	67
Figure 3.4 Galvanostatic cyclic voltammogram of additives chemical (a) without pyrrole and (b) with pyrrole	68
Figure 3.5 Charge transfer profile of different compounds during polymerisation at (a) 1 V, (b) 3 V, and (c) 5 V	70
Figure 3.6 Current profile of different compounds during polymerisation at (a1) 1 V, (b1) 3 V, and (c1) 5 V.....	71
Figure 3.7 Chronoamperometry of 0.15 mM solution of compounds in the absence of pyrrole at 5V	73
Figure 3.8 Effect of voltage on surface resistance of polypyrrole film	74
Figure 3.9 Effect of voltage on weight add-on % of the polymer	74
Figure 3.10 Cyclic voltammetry without pyrrole at 50 mV/s scan rate for (a) only 0.15 mM oxalic acid up to 1.5 V and (b) 0.15 mM oxalic acid compared to other compounds up to 5 V	77
Figure 3.11 Variation in system current with time using (a) 0.075 mM pTSA and 0.075 mM sodium nitrate, (b) 0.075 mM sodium nitrate and 0.075 mM AQSA-Na, and (c) 0.075 mM pTSA and 0.075 mM AQSA-Na with 0.2 M pyrrole at 3 V for 30 min at 27 °C	78
Figure 3.12 Surface resistance of polypyrrole films prepared using individual compounds and their combinations with 0.2 M pyrrole at 3 V for 30 min at 27 °C.....	79
Figure 3.13 Schematic representation of electrochemical cell with cathode and anode...	80
Figure 3.14 Arrangement of textile fabric with metal anode during electrochemical polymerisation.....	80
Figure 3.15 (a) Hydrolysed polyester fabric, (b) VPP coated fabric electrochemically polymerised with pyrrole without dopant and electrolyte, and (c) VPP coated	

fabric electrochemically polymerised (at 27 °C for 20 min in a solution of 0.015 M sodium nitrate and 0.015 M pTSA in 0.2 M pyrrole).....	82
Figure 3.16 Surface morphology at X500 magnification (a) pTSA + SN doped polypyrrole film, and (b) pTSA + SN doped polypyrrole on fabric	83
Figure 3.17 FTIR spectrogram for neat polypyrrole and polypyrrole polymerised in the presence of different compounds	85
Figure 3.18 X-ray diffraction pattern of polypyrrole polymerised at 3 V using 0.15 mM concentration of different compounds	87
Figure 4.1 Setup for VPP	96
Figure 4.2 Sample holder without sample (left) and without sample (right)	97
Figure 4.3 Modified setup for VPP	98
Figure 4.4 Process schematic for VPP	99
Figure 4.5 Proof of vapour phase polymerisation performed over polyester film.....	100
Figure 4.6 Change in colour of the fabric at different stages of polymerisation	102
Figure 4.7 Effect of oxidant concentration on fabric surface resistance and polymer add on (%).....	104
Figure 4.8 Mechanism of polymerisation of pyrrole using ferric chloride	105
Figure 4.9 Effect of dopant concentration on fabric surface resistance and add-on (%)	107
Figure 4.10 Effect of polymerisation time on fabric surface resistance and polymer add on (%).....	108
Figure 4.11 Effect of monomer temperature on fabric surface resistance and polymer add-on (%)	110
Figure 4.12 FTIR spectra for untreated polyester fabric and polypyrrole-coated polyester fabric	113
Figure 4.13 V-I characteristics of polypyrrole deposited fabric	114

Figure 4.14 Arrangement for testing fabric resistance change with bending (left) and schematic of the arrangement (right)	115
Figure 4.15 Arrangement for measuring fabric resistance change with turning angle ...	116
Figure 4.16 Change in resistance of conductive fabric with turning	116
Figure 4.17 Change in resistance of conductive fabric with bending	117
Figure 4.18 Schematic for sonication of polypyrrole-coated fabric	118
Figure 5.1 Electrochemical polymerisation over VPP	127
Figure 5.2 Schematic of the glass setup for eCVP	128
Figure 5.3 Glass setup for eCVP process	129
Figure 5.4 Schematic of the eCVP process	130
Figure 5.5 Image of polyester fabric at different stages with microscopic images (inset)	131
Figure 5.6 Effect of electrochemical polymerisation time on polymer deposition	133
Figure 5.7 Effect of electrochemical polymerisation time on resistance	134
Figure 5.8 Formation of polypyrrole rods over polyester fibre surface	135
Figure 5.9 Effect of applied potential on fabric resistance and polymer weight add-on using 0.25 M pTSA, 0.75 M FeCl ₃ with 180 sec of exposure to vapours of pyrrole heated at 130 °C	137
Figure 5.10 Change in system current with exposure to vapours of pyrrole heated at 130 °C during eCVP method using 0.25 M p-toluene sulfonic acid (pTSA) and 0.75 M ferric chloride (FeCl ₃)	138
Figure 5.11 Increase in polypyrrole add-on with increase in supplied energy	139
Figure 5.12 Decrease in resistance with increase in energy	139
Figure 5.13 Effect of polymerisation time on fabric surface resistance and polymer weight add-on (%) at 12 V using 0.25 M pTSA, 0.25 M FeCl ₃ for reaction	

time of 180 sec at a reaction temperature of 130 °C.....	141
Figure 5.14 Effect of pyrrole temperature on fabric surface resistance and polymer weight add-on at 12 V using 0.25 M pTSA, 0.25 M FeCl ₃ for 60 sec of exposure to vapours of pyrrole heated at 130 °C.....	143
Figure 5.15 Effect of FeCl ₃ concentration on fabric surface resistance and polymer weight add-on at 12 V using 0.25 M pTSA for 60 sec of exposure to vapours of pyrrole heated at 130 °C	144
Figure 5.16 Effect of pTSA concentration on fabric surface resistance and polymer weight add-on at 12 V using 0.25 M FeCl ₃ for 60 sec of exposure to vapours of pyrrole heated at 130 °C	145
Figure 5.17 FTIR spectrum of uncoated and polypyrrole-coated polyester fabric	147
Figure 5.18 X-ray diffraction pattern.....	148
Figure 5.19 V-I characteristics of the polypyrrole-coated fabric.....	149
Figure 5.20 Decrease in fabric weight and surface resistance with sonication time	150
Figure 6.1 Preparation of fabric for laser cutting.....	159
Figure 6.2 Designs for different sensors	159
Figure 6.3 (a) CAD design of interdigitated sensor as used for laser cutting, (b) 3D visualisation of laser cut fabric, and (c) actual fabric laser cut to interdigitated pattern	160
Figure 6.4 Designs laser cut over polypyrrole-coated fabric	161
Figure 6.5 Interdigitated capacitive sensors obtained after cutting	161
Figure 6.6 Measurement of capacitance using Agilent E4980A LCR meter.....	162
Figure 6.7 Effect of different design parameters on capacitance with increasing frequency	162
Figure 6.8 Schematic of (a) top view of the interdigitated sensor, and (b) cross section	

view of the interdigitated sensor placed over polyethylene substrate.....	163
Figure 6.9 Micrographs (X50) of sensor prepared using polypyrrole-coated fabric	166
Figure 6.10 Laminated fabric sensor with unlaminated contact points	166
Figure 6.11 Laser cutting over laminated fabric	167
Figure 6.12 Comparison of capacitance of laminated and unlaminated sensors	168
Figure 6.13 (a) Setup used for humidity sensing and fabric sensor calibration, and (b) calibration curve for the fabric sensor	169
Figure 6.14 Change in sensor capacitance with relative humidity	170
Figure 6.15 (a) Schematic setup for measurement of V-I characteristics in presence of acetone vapour, and (b) change in V-I characteristics in presence of acetone vapour	171
Figure 6.16 (a) Setup for testing sensor response to ammonia, and (b) change in resistance with increasing ammonia concentration.....	172
Figure 7.1 A schematic diagram of continuous vapour phase polymerisation method. (A) Yarn bobbin; (B) a flask with FeCl_3 solution; (C) heat gun; (D) a filtering flask with pyrrole solution; (E) reaction chamber; (F) an Erlenmeyer flask with normal water; (G) winding bobbin [207].....	177
Figure 7.2 Schematic for continuous eCVP prototype machine	179
Figure 7.3 Fabric roll with handle for easy winding of fabric	179
Figure 7.4 Schematic of the oxidant trough (left) and oxidant trough on machine (right)	180
Figure 7.5 Schematic of fabric squeezing assembly (top) and actual pressure roll for fabric squeezing (bottom)	181
Figure 7.6 Schematic of specifications of boiler (left) and boiler on the machine (right)	182

Figure 7.7 Schematic of reaction chamber (left) and actual image of reaction chamber and the electrode (right)	183
Figure 7.8 Schematic of the fabric winding assembly (left) and fabric roller assembly on the machine (right)	184
Figure 7.9 Continuous polypyrrole-coated fabric production using eCVP method	185
Figure 7.10 (a) Effect of voltage on surface resistance of coated polyester fabric, and (b) weight add-on.....	187
Figure 7.11 (a) Resistance and (b) polypyrrole add-on over cotton and nylon fabrics...	188
Figure 7.12 (a) Decrease in resistance with increase in dwell time and (b) increase in polypyrrole add-on with increase in dwell time	189
Figure 8.1 Suggested machine design with modifications.....	199

LIST OF TABLES

Table 1.1 Different techniques for fabrication of sensors over textiles	22
Table 1.2 Previous studies on different types of sensors based on conducting polymers.	24
Table 2.1 Supporting chemicals used during polymerisation	41
Table 3.1 Pyrrole solutions for CV and electrochemical polymerisation	64
Table 3.2 Charge utilisation factor and surface resistance for various parameters.....	76
Table 3.3 Reduction of surface resistance of polyester fabric on the addition of dopant and electrolyte	81
Table 3.4 Confirmation of doping in polypyrrole film in the presence of different compounds	84
Table 3.5 X-ray diffraction analysis of polypyrrole film polymerised in the presence of different chemicals.....	87
Table 4.1 Resistance and add-on data for different oxidant concentration.....	103
Table 4.2 Resistance and add-on data for different dopant concentration	106
Table 4.3 Resistance and add-on data for different polymerisation time.....	108
Table 4.4 Resistance and add-on data for different monomer temperatures.....	109
Table 4.5 Functional groups and their corresponding wavenumbers.....	112
Table 4.6 Weight change of polypyrrole-coated fabric after rinsing and sonication.....	118
Table 4.7 Change in L, a, b and K/S values after rinse and sonication.....	119
Table 4.8 Air permeability of polyester fabric	119
Table 5.1 Resistance and add-on data for different applied voltages.....	136
Table 5.2 Resistance and add-on data for different polymerisation time.....	141
Table 5.3 Resistance and add-on data for different polymerisation temperature.....	142
Table 5.4 Resistance and add-on data for different oxidant concentration.....	143
Table 5.5 Resistance and add-on data for different dopant concentration	146

Table 5.6 Comparison of bending length of different fabrics	151
Table 6.1 Parameters used for eCVP of pyrrole.....	157
Table 6.2 Technical specifications of Fluke 1620A thermo-hygrometer.....	158
Table 6.3 Capacitance as obtained on multimeter with different design parameters.....	161
Table 6.4 Effect of sensing polymer and sensor parameters on capacitance	165