

University of Wollongong - Research Online

Thesis Collection

Title: Synthesis, characterisation and applications of conducting polymer coated textiles

Author: Jian Wu

Year: 2004

Repository DOI:

Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

Research Online is the open access repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

University of Wollongong Thesis Collections

University of Wollongong Thesis Collection

University of Wollongong

Year 2004

Synthesis, characterisation and
applications of conducting polymer
coated textiles

Jian Wu
University of Wollongong

Wu, Jian, Synthesis, characterisation and applications of conducting polymer coated textiles, Doctor of Philosophy thesis, Department of Chemistry - Faculty of Science, University of Wollongong, 2004. <http://ro.uow.edu.au/theses/1191>

This paper is posted at Research Online.

NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

**SYNTHESIS, CHARACTERISATION AND
APPLICATIONS OF CONDUCTING POLYMER
COATED TEXTILES**

**A thesis submitted in fulfillment of the requirements
for the award of the degree**

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

JIAN WU, B.Sc.

Department of Chemistry

May 2004

*To my parents for their encouragement,
especially in memory of my father*

*To my husband Xifa Yang and my daughter Wenxin Yang
for their support and patience*

THESIS CERTIFICATION

I, Jian WU, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Department of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Jian WU

May 2004

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my supervisors Professor Gordon G. Wallace and Dr. Dezhi Zhou for their enthusiastic supervision and encouragement through this work.

I also deeply appreciate helpful assistance of the staff and students at the Intelligent Polymer Research Institute, especially Professor Leon Kane-Maguire, Associate Professor Geoff Spinks, Dr. Chee Too, Dr. Peter Innis, Dr. Toni Campbell, Dr. Syed Ashraf, Dr. Jie Ding, Dr. Jun Chen, Dr. Simon Moulton, Dr. Norman Barisci and Dr. Benny Kim. Also, I would like to thank Dr. Violeta Misoska and Dr. Jiazhao Wang for their help in running samples on the SEM. Thanks also to Miss Jenny Causley and Dr. K. Konstantinov for their help on HPLC and TGA analysis. I would like to address the help and support of Binbin Xi, Yanzhe Wu, Chunming Yang and Phil Smugreski. I would like to acknowledge the technical assistances of S. Butler and P. Sarakinotis.

I am grateful to the Intelligent Polymer Research Institute and CSIRO for the award of a postgraduate scholarship. Finally, I would like to acknowledge Dr. Mark Loony and Peter Waters from CSIRO TFT for their technical advice and assistance.

PUBLICATIONS

- 1 J. Wu, D. Zhou, C. Too and G. G. Wallace, “Conducting Polymers Coated Textile” ICSM 2004 and *Synthetic Metals* (Submitted).
- 2 “Electromechanical actuators based on fibre and fabrics” G. G. Wallace, J. Wu, V. Aboutanos, G. M. Spinks and D. Zhou, SPIE (2001) [4329-55].
- 3 G.G. Wallace, G. M. Spinks, J. Wu and D. Zhou, “Electrofunctional materials: strain gauges and actuators in fabric structures (Invited paper), SPIE, Smart Materials and MEMS (2000) [4234-4235].

ABSTRACT

This thesis describes preparation and characterisation of a range of novel conducting polymer coated textiles, which have potential in applications such as static dissipation, EMI shielding, heating elements, composite structures and many military applications.

Conducting polypyrrole coated textiles such as nylon Lycra and polyester fabrics have been synthesised using different approaches (Chapter 3). The present study concentrates on preparation of conducting polypyrrole coated textile using an *in-situ* polymerisation method. A range of characterisation techniques for the inherently conducting polymer (ICP) coated fabrics were used: the stability of the surface resistivity, cyclic voltammetry, Scanning Electron Microscopy (SEM), UV-Vis spectroscopy and Thermogravimetric analysis (TGA). It was found that the PPy-coated nylon Lycra fabric could be used as a wearable strain gauge. The strain gauge characteristics have been investigated using both an Instron machine and a “SmartMotor”.

The use of molecular templates to facilitate the polymerisation and the integration of inherently conducting polymers (ICPs) into textiles has been investigated (Chapter 4). Poly(2-methoxyaniline-5 sulfonic acid) or [PMAS] is a water-soluble, fully sulfonated polyaniline that has been used as molecular template. In the first step – “dyeing” of PMAS into the textile, the effect of fabric pre-treatment, solution pH as well as solution temperature have been investigated. In the second step the effects of the ratio of PMAS to aniline, the ratio of aniline to ammonium persulfate and the polymerisation temperature on the polymerisation reaction have also been studied. Characterisation of the templated polyaniline coated fabric prepared using the above “Two step” process

has been undertaken (Chapter 4). The stability of the conductivity, cyclic voltammetry, UV-Vis spectra, SEM studies, TGA analysis and strain gauge characteristics have been determined. Results indicate that templated PAn-coated wool nylon Lycra can be used as the strain gauge as tested with either the Instron machine or “SmartMotor”.

Conducting polymer coated textile fabrics are easily prepared and integrated into truly wearable clothing and garments to create strain sensors with a wide dynamic range. Functional wearable textile sensing systems can monitor human motion, provide immediate bio-feedback to the wearer without changing the properties and functions of the fabric material and with no interference to normal human body motion. This innovative technique can be widely used for injury prevention, rehabilitation, sport technique modification and medical treatment. It will have a number of further potential applications to be used for daily living, work and recreation in the future.

ABBREVIATIONS

μ	micro
$^{\circ}\text{C}$	degree Celsius
A^{-}	anion
ABS	absorbance
Ag/AgCl	silver/silver chloride reference electrode
CEP	conducting electroactive polymer
cm	centimeter
CV	cyclic voltammetry
ΔE	potential difference
E	potential
$\text{E}_{\text{p(a)}}$	anodic peak potential
$\text{E}_{\text{p(c)}}$	cathodic peak potential
EB	emeraldine base
ES	emeraldine salt
g	gram
HPLC	high performance liquid chromatography
I	current
ITO	Indium-tin oxide
K	Kelvin
LB	leucoemeraldine base
M	molar
mA	milliampere(s)
mV	millivolt

n	number of electron
NDSA	1,5-naphthalenedisulfonic acid tetrahydrate
PAn	polyaniline
PB	pernigraniline base
PMAS	poly(2-methoxyaniline-5-sulfonic acid)
PPy	polypyrrole
PS	pernigraniline salt
Pt	platinum
R	resistance
RVC	reticulated vitreous carbon
sec	second
SPAN	sulfonated polyaniline
SEM	scanning electron microscopy
TGA	Thermogravimetry analysis
UV-Vis	ultraviolet-visible

LIST OF FIGURES AND TABLES

1. Figures

Figure 1.1. Schematic of conducting polymers

Figure 1.2. Polypyrrole polymerisation initiation and polymer growth

Figure 1.3. Interconversions between different forms of polyaniline

Figure 1.4. Chemical polymerisation of aniline

Figure 1.5. Structures of some fully sulfonated polyanilines

Figure 1.6. Assignment of electronic absorption bands of emeraldine salt

Figure 1.7. UV-Vis spectra of (a) initial emeraldine salt PAn.(+)-HCSA film and (b) leucoemeraldine base film derived by reduction with PhNHNH₂

Figure 1.8. UV-Vis spectra of (a) initial emeraldine salt PAn.(+)-HCSA film and (b) pernigraniline base film derived by oxidation with ceric ammonium sulfate [93].

Figure 1.9. UV-Vis spectra of PMAS solution during oxidation in 0.1 M (NH₂)S₂O₈, pH 1

Figure 1.10. UV-Vis spectra of PMAS solution during reduction in 0.08 M hydrazine, pH 9

Figure 1.11. Classification of fibres

Figure 1.12. The morphological diagram of a wool fibre

Figure 1.13. The general formula of amino acid

Figure 1.14. Poly (ethylene terephthalate) polymerisation

Figure 1.15. Polymerisation steps used to produce Nylon 66 and Nylon 6 fibres

Figure 1.16. Photomicrograph of Lycra Spandex fibre in a cross-section

Figure 1.17. Photomicrograph of Lycra Spandex fibre in a longitudinal view

Figure 1.18. The repeat unit of a polyether based Spandex used in Lycra fabric

Figure 1.19. (a) The unstretched or amorphous state of the polymer system of an elastomeric fibre; (b) The stretched or more crystalline state of the polymer system of an elastomeric fibre

Figure 1.20. Woven fabrics: plain weave

Figure 1.21. 1/1 rib weft knitted fabric

Figure 1.22. Simple warp knit

Figure 1.23. Face side of the locknit fabric

Figure 1.24. Surface resistivity of various textile products

Figure 2.1. *In-situ* (chemical oxidation) polymerisation method used to coat fabrics

Figure 2.2. (a) Dyeing process of fabric (b) Top view of the fabric secured onto the spindle

Figure 2.3. Template polymerisation of conducting polyaniline on the PMAS-treated fabric.

Figure 2.4. Vapour-phase polymerisation method

Figure 2.5. Cyclic voltammetry cell for conducting polymer coated fabric

Figure 2.6. Cyclic voltammogram of PPy/NDSA coated nylon Lycra in 1.0 M NaNO_3 at a scan rate of 100 mVs^{-1}

Figure 2.7. Top view of the ASTM four-point probe method for the measurement of the electrical conductivity of a piece of conductive fabric. The distance between the two inner electrodes is 0.2 cm. The sample is sandwiched with another connector. A constant current is applied between the two outer electrodes

Figure 2.8. Top view of the AATCC-76 two-point probe method for the measurement of the electrical conductivity of a piece of conductive fabric. The distance between the two parallel electrodes is 1.5 cm. The sample is measured with a standard ohmmeter

Figure 2.9. UV-Visible spectra of PMAS solution before and after dyeing the wool nylon Lycra fabric

Figure 2.10. SEM image of a polypyrrole-NDSA coated nylon Lycra

Figure 2.11. Wheatstone bridge electrical resistance vs. strain testing circuit

Figure 2.12. Resistance vs Strain of polypyrrole coated nylon Lycra fabric when stretched to 50%

Figure 2.13. Force vs Strain of polypyrrole coated nylon Lycra fabric when stretched to 50%

Figure 2.14. Dynamic calibration apparatus

Figure 3.1. Both sides of PPy-coated nylon Lycra prepared at a current density of 2.0 mAcm^{-2} for 4 hours using electrochemical polymerisation

Figure 3.2. SEM of PPy-coated nylon Lycra prepared at a current density of 2.0 mAcm^{-2} for 4 hours using electrochemical polymerisation

Figure 3.3. SEM of PPy-coated nylon Lycra using the vapour polymerisation

Figure 3.4. Typical strain-resistance responses of PPy-coated nylon Lycra fabric under different cycles when stretched to 50%

Figure 3.5. PPy-coated Taffeta polyester after different polymerisation times

Figure 3.6. Resistance change of PPy-coated polyester versus strain

Figure 3.7. The surface resistivity (Ω/\square) of PPy-coated nylon Lycra at different areas of the A4 fabric

Figure 3.8. The surface resistivity (Ω/\square) of PPy-coated nylon Lycra at different areas of coated fabric (7.4 cm x 10.5 cm).

Figure 3.9. The changes of surface resistivity vs storage time of PPy-coated nylon Lycra. Broken line: stored in the open air, bold line: stored in a desiccator

Figure 3.10. Cyclic voltammogram of PPy/NDSA film (ca. 0.1 μm thickness) in 1.0 M NaNO_3 at a scan rate of 100 mV s^{-1}

Figure 3.11. Cyclic voltammogram of PPy/NDSA coated nylon Lycra in 1.0 M NaNO_3 at a scan rate of 100 mVs^{-1}

Figure 3.12. Scanning electron micrograph of uncoated nylon Lycra fibre

Figure 3.13. Scanning electron micrograph of PPy-coated nylon Lycra fibre

Figure 3.14. UV-Vis spectra of uncoated and PPy-coated nylon Lycra fabrics

Figure 3.15. TGA (60-600 $^{\circ}\text{C}$) of PPy/NDSA powder under nitrogen gas

Figure 3.16. TGA (60-600 $^{\circ}\text{C}$) of dopant NDSA under nitrogen gas

Figure 3.17. TGA (50-500 $^{\circ}\text{C}$) of uncoated and PPy-coated nylon Lycra fabrics under nitrogen gas

Figure 4.1. Branched structures of the traditional ortho-para directed enzymatic polymerisation of aniline that results in an electrically inactive form of aniline vs enzymatic polymerization in the presence of SPS

Figure 4.2. Poly (2-methoxyaniline-5 sulfonic acid) (PMAS) structure

Figure 4.3. Thermobath with temperature control used in the dyeing process

Figure 4.4. The spindle with wool fabric before (a) and after (b) dyeing with PMAS

Figure 4.5. Beer's Law plot for aqueous PMAS solution

Figure 4.6. Surface resistivity vs. storage time for PMAS-treated wool nylon Lycra

Broken line: stored in the open air, bold line: stored in a sealed plastic bag.

Figure 4.7. Changes in surface resistivity vs. time for wool nylon Lycra coated with PMAS then coated with PAn prepared at room temperature. Broken line: stored in the open air, bold line: stored in a sealed plastic bag.

Figure 4.8. Changes in surface resistivity vs. time. PMAS templated polyaniline wool nylon Lycra prepared at lower temperature (2-3 °C). Broken line: stored in the open air, bold line: stored in a sealed plastic bag.

Figure 4.9. Cyclic voltammogram of polyaniline (HCl) on a glassy carbon electrode in 1 M HCl at a scan rate of 50 mV/s

Figure 4.10. Cyclic voltammogram (CV) obtained using PMAS-treated wool nylon Lycra as the working electrode in 1 M HCl at a scan rate of 10 mV/s

Figure 4.11. Cyclic voltammogram (CV) obtained using PMAS templated polyaniline coated wool nylon Lycra as working electrode in 1 M HCl at a scan rate of 10 mV/s

Figure 4.12. Cyclic voltammograms (CV) obtained using PMAS templated polyaniline coated wool nylon Lycra as working electrode in 1 M HCl at a scan rate of 10 mV/s. Pink line: stored in the open air for 55 days, blue line: stored in a sealed plastic bag for 55 days.

Figure 4.13. UV-Visible spectra of uncoated, PMAS & *in-situ* templating coated wool nylon Lycra using *ortho*-dichlorobenzene as a solvent

Figure 4.14. UV-Visible spectra of PMAS templated PAn coated wool nylon Lycra under different storage conditions for 55 days

Figure 4.15. UV-Visible spectra of oxidised / reduced forms of PMAS templated PAn-coated wool nylon Lycra

Figure 4.16. UV-Visible spectra of coated wool nylon Lycra before and after heating at 100 °C and 210 °C for 2 hours

Figure 4.17. Scanning electron micrograph of uncoated wool nylon Lycra fibre.

Figure 4.18. Scanning electron micrograph of PMAS-treated wool nylon Lycra fibre.

Figure 4.19. Scanning electron micrograph PMAS templated PAn-coated wool nylon

Figure 4.20. TGA (60-500 °C) PMAS powder

Figure 4.21. TGA (60-600 °C) of templated PAn powder (PMAS+PAn copolymer)

Figure 4.22. TGA (60-600 °C) of uncoated, PMAS-treated and templated PAn coated wool nylon Lycra fabrics

Figure. 5.1. Stress-strain responses of uncoated nylon Lycra fabric for the first two cycles when stretched to 50%

Figure 5.2. Stress-strain responses of uncoated nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%

Figure 5.3. Stress-strain responses of PPy-coated nylon Lycra fabric for the first two cycles when stretched to 50%

Figure 5.4. Stress-strain responses of PPy-coated nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%

Figure 5.5. Stress-strain of uncoated and PPy-coated nylon Lycra fabrics in the wale direction at different strains

Figure 5.6. Stress-strain responses of uncoated wool nylon Lycra fabric for the first two cycles when stretched to 50%

Figure 5.7. Stress-strain responses of uncoated wool nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%

Figure 5.8. Stress-strain responses of PMAS-treated wool nylon Lycra fabric for the first two cycles when stretched to 50%

Figure 5.9. Stress-strain responses of PMAS-treated wool nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%

Figure 5.10. Stress-strain responses of PMAS templated PAn-coated wool nylon Lycra fabric for the first two cycles when stretched to 50%

Figure 5.11. Stress-strain responses of PMAS templated PAn-coated wool nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%

Figure 5.12. Stress-strain of uncoated, PMAS-treated and PMAS templated PAn-coated wool nylon Lycra fabrics in the wale direction at different strains

Figure 5.13. Resistance/Strain relationship for nylon Lycra in the wale and course direction

Figure 5.14. Resistance-strain of PPy-coated nylon Lycra fabric for the first two cycles when stretched to 50%

Figure 5.15. Resistance-strain of PPy-coated nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%

Figure 5.16. Resistance-strain on PPy-coated nylon Lycra fabric in the wale direction at different strains

Figure 5.17. Resistance-strain of PMAS templated PAn-coated wool nylon Lycra fabric for the first two cycles when stretched to 50%

Figure 5.18. Resistance-strain responses of PMAS templated PAn-coated wool nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%

Figure 5.19. Resistance-strain responses for PMAS templated PAn-coated wool nylon Lycra 7010 fabric in the wale direction at different strain

Figure 5.20. Ratio of change in resistance to initial resistance ($\Delta R/R_i$) of PPy-coated nylon Lycra when stretched to 50%

Figure 5.21. Ratio of change in resistance to initial resistance ($\Delta R/R_i$) of PMAS templated PAn-coated wool nylon Lycra when stretched to 70%

Figure 5.22. Electronic signal of resistance response on PPy-coated nylon Lycra at 1 Hz when stretched to 50%

Figure 5.23. Changes in resistance of PPy-coated nylon Lycra fabric in the wale direction at 1 Hz under different strains

Figure 5.24. Changes in resistance of PPy-coated nylon Lycra fabric in the wale direction at different frequencies under different strains

Figure 5.25. Electronic signal of resistance responses on PMAS templated PAn-coated wool nylon Lycra at strain=50%

Figure 5.26. Changes of resistance on PMAS templated PAn-coated wool nylon Lycra fabric in the wale direction at different strain

Figure 5.27. Ratio of change in resistance to initial resistance ($\Delta R/R_i$) of PPy-coated nylon Lycra when stretched from 10% to 50%

Figure 5.28. Ratio of change in resistance to initial resistance ($\Delta R/R_i$) of PMAS templated PAn-coated wool nylon Lycra when stretched from 10% to 70%

Figure 6.1. The joint angle, ϕ for the knee

Figure 6.2. “Intelligent Elbow Strain Gauge”

Figure 6.3. Changes in resistance of PPy-coated nylon Lycra strip on the “Intelligent Elbow Strain Gauge” under different strain ranges

Figure 6.4. Knee sleeve system

Figure 6.5. Intelligent Knee Sleeve

Figure 6.6. Football player wearing the “intelligent knee sleeve” and training to land correctly to protect his knee from potential ligament damage

Figure 6.7. The rehabilitation glove with PPy-coated fabric sensor strips on each finger

2. Tables

Table 1.1. Techniques used for characterisation of conducting polymers.

Table 3.1. Optimisation of molar concentrations of pyrrole/ FeCl_3 /NDSA

Table 3.2. Optimisation of molar concentrations of pyrrole/ FeCl_3 /NDSA

Table 3.3. Optimisation of molar concentrations of pyrrole/ FeCl_3 /NDSA

Table 3.4. Summary of electrochemical polymerisation for PPy-coated nylon Lycra at different current densities

Table 3.5. Summary of electrochemical polymerisation for PPy-coated nylon Lycra at different polymerisation times

Table 3.6. The surface resistivity of PPy-coated nylon Lycra using different concentrations of FeCl_3 in ethanol for soaking the fabric prior to monomer exposure

Table 3.7. The surface resistivity of PPy-coated nylon Lycra using different solvents for oxidant uptake into the textile

Table 3.8. The surface resistivity of PPy-coated nylon Lycra using different temperature for vapour generation

Table 3.9. The surface resistivity and strain gauge factors for PPy-coated nylon Lycra – effect of pyrrole monomer concentrations

Table 3.10. The surface resistivity and gauge factors of PPy-coated nylon Lycra produced under different oxidant FeCl_3 concentrations

Table 3.11. The surface resistivity and gauge factors of PPy-coated nylon Lycra obtained using different dopant concentrations

Table 3.12. The surface resistivity and gauge factor of PPy-coated nylon Lycra obtained by using different reaction times

Table 3.13. The surface resistivity and gauge factors of PPy-coated nylon Lycra produced at different polymerisation temperatures

Table 3.14. The surface resistivity of PPy-coated Taffeta polyester after different polymerisation times

Table 4.1. Summary of wool nylon Lycra washed with and without Sandoclean PC Liquid

Table 4.2. Effect of variation of pH on the application of PMAS

Table 4.3. The effect of variation of temperatures on the application of PMAS

Table 4.4. The surface resistivity of the PMAS templated PAn-coated wool nylon Lycra produced under different PMAS:Aniline ratios

Table 4.5. The surface resistivity of the PMAS templated PAn-coated wool nylon Lycra fabrics produced using different Aniline:APS ratios

Table 4.6. Surface resistivity of the PMAS templated PAn - coated wool nylon Lycra prepared using different temperatures for aniline oxidation

Table 4.7. Consumption of aniline monomer during polymerisation in the presence of PMAS templated wool nylon Lycra using different reaction temperatures

CONTENTS

DEDICATION	I
CERTIFICATION	II
ACKNOWLEDGMENTS	III
PUBLICATIONS	IV
ABSTRACT	V
ABBREVIATIONS	VII
LIST OF FIGURES AND TABLES	IX
 CHAPTER 1	 1
GENERAL INTRODUCTION	1
1.1 CONDUCTING POLYMERS	2
1.1.1. The Development of Conducting Polymer	2
1.1.2. Polypyrrole	3
1.1.3. Polyaniline	6
1.1.3.1. Unsubstituted Polyaniline (PAn)	7
1.1.3.2. Sulfonated Polyaniline	11
1.1.4. Characterisation of Conducting Polymers	15
1.2 FIBRE STRUCTURE & TEXTILE SUBSTRATE	16
1.2.1. Fibre Structure	18
1.2.1.1. Wool Fibre	18
1.2.1.2. Polyester Fibre	21
1.2.1.3. Nylon Fibre	24
1.2.1.4. Spandex Fibre – Lycra Fibre	26

1.2.2.	Fabric Textile Structure	30
1.2.2.1.	Woven Fabrics	31
1.2.2.2.	Knitted Fabrics	33
1.3.	ELECTRICALLY CONDUCTING TEXTILES	37
1.3.1.	Carbon Fibres and Carbon-filled Materials	38
1.3.2.	Metallic Fibres	38
1.3.3.	Metal Coated Materials	39
1.3.4.	Conducting Polymer Coated Textiles	40
1.3.4.1.	Polypyrrole Coated Textiles	42
1.3.4.2.	Polyaniline Coated Textiles	44
1.3.4.3.	Properties of Conductive Textiles	45
1.4.	AIMS OF THE PROJECT	46
1.5.	REFERENCES	49
CHAPTER 2		59
GENERAL EXPERIMENTAL TECHNIQUES		59
2.1.	INTRODUCTION	60
2.2.	PREPARATION OF CONDUCTIVE POLYMER COATED TEXTILES	61
2.2.1.	Chemical Polymerisation	61
2.2.1.1.	<i>In-situ</i> Polymerisation (Chemical Oxidation) Process	61
2.2.1.2.	Template Polymerisation Process	62
2.2.1.3.	Chemical oxidation Using Vapour Phase Monomer	65
2.2.2.	Electrochemical Polymerisation	66

2.3.	CHARACTERISATION METHODS FOR	
	CONDUCTIVE POLYMER COATED TEXTILE	67
2.3.1.	Cyclic Voltammetry (CV)	67
2.3.2.	Electrical Conductivity	69
2.3.3.	UV-Vis Spectroscopy	72
2.3.4.	Scanning Electron Microscopy (SEM)	73
2.3.5.	Thermogravimetric Analysis	74
2.3.6.	High Performance Liquid Chromatography (HPLC)	75
2.3.7.	Instron Testing to Determine Stress/strain Curves	76
2.3.8.	Use of SmartMotor to Determine Strain Gauge	
	Characteristics at Different Frequencies	79
2.4.	REFERENCES	81

CHAPTER 3 **82**

PREPARATION AND CHARACTERISATION OF POLYPYRROLE COATED FABRICS **82**

3.1.	INTRODUCTION	83
3.2.	EXPERIMENTAL	85
3.2.1.	Reagents and Materials	85
3.2.2.	Instrumentation	86
3.2.3.	Preparation of PPy-coated Fabrics Using Different Techniques	86
3.2.3.1.	Electrochemical Polymerisation	86
3.2.3.2.	Chemical Oxidation Using Vapour-phase Monomer	87
3.2.3.3.	<i>In-situ</i> Chemical Oxidation	88
3.2.3.3.1.	Preparation of PPy-coated Nylon Lycra Fabric	89

3.2.3.3.2. Preparation of PPy-coated Polyester Taffeta Fabric	91
3.2.4. Characterisation of PPy-coated Nylon Lycra Fabric	91
3.2.4.1. Surface Resistivity	92
3.2.4.2. Cyclic Voltammetry	92
3.2.4.3. Morphology Analysis	92
3.2.4.4. UV-Vis Spectra	93
3.2.4.5. Thermogravimetric Analysis	93
3.2.4.6. Strain & Stress Testing by Instron 4302 Tensile Tester	93
3.3. RESULTS AND DISCUSSION	94
3.3.1. Effect of Reaction Conditions on Surface Resistivity of PPy-coated Nylon Lycra Coated Using Electrochemical Polymerisation	94
3.3.2. Effect of Reaction Conditions on Surface Resistivity of PPy-coated Nylon Lycra Coated Using Chemical Oxidation of Monomer from Vapour Phase	98
3.3.3. Effect of Reaction Conditions on Surface Resistivity and Gauge Factor of PPy-coated Nylon Lycra Coated Using Chemical Oxidation	101
3.3.3.1. Effect of Pyrrole Monomer Concentration	101
3.3.3.2. Effect of Oxidant Concentration	104
3.3.3.3. Effect of Dopant Concentration	105
3.3.3.4. Effect of Reaction Time	106
3.3.3.5. Effect of Reaction Temperature	108
3.3.4. Effect of Reaction Conditions on Surface Resistivity and Gauge Factor of PPy-coated Polyester Taffeta	109

3.3.5. Characterisation of PPy-coated Nylon Lycra Fabric	113
3.3.5.1. Uniformity of Coated Fabric	113
3.3.5.2. Stability (Surface Resistivity Change vs Time) of PPy-coated Fabric	115
3.3.5.3. Cyclic Voltammetry of PPy-coated Fabric	116
3.3.5.4. Morphology of PPy-coated Fabric	119
3.3.5.5. UV-Vis Spectra of PPy-coated Fabric	121
3.3.5.6. Thermogravimetric Analysis	122
3.4. CONCLUSION	125
3.5. REFERENCES	129

CHAPTER 4 **131**

PREPARATION AND CHARACTERISATION OF POLYANILINE COATED FABRICS **131**

4.1. INTRODUCTION	132
4.2. EXPERIMENTAL	135
4.2.1. Reagents and Materials	135
4.2.2. Instrumentation	136
4.2.3. Preparation of PMAS Templated PAn-coated Fabric	137
4.2.3.1. Integration of the Molecular Template-PMAS (Step One)	137
4.2.3.2. Integration of Cationic Inherently Conducting Polymers (Step Two)	140
4.2.4. Characterisation of PMAS Templated PAn-coated Wool Fabric	141
4.2.4.1. Surface Resistivity	141
4.2.4.2. Cyclic Voltammetry	142

4.2.4.3.	UV-Vis Spectral Analysis	142
4.2.4.4.	SEM	142
4.2.4.5.	Thermogravimetric Analysis	143
4.3.	RESULTS AND DISCUSSION	143
4.3.1.	Effect of Reaction Conditions on Integration of the Molecular Template- PMAS	143
4.3.2.	Effect of Reaction Conditions on Coating of Templated Textile with Polyaniline	148
4.3.2.1.	Effect of Aniline to PMAS Ratio	148
4.3.2.2.	Effect of Oxidant Concentration	149
4.3.2.3.	Polymerisation Temperature	151
4.3.2.4.	Aniline Monomer Consumption at Different Temperatures	152
4.3.3.	Characterisation of PMAS Templated PAn-coated Fabrics	153
4.3.3.1.	Surface Resistivity Change vs Time of PMAS-treated Wool Fabrics	153
4.3.3.2.	Surface Resistivity Change vs Time of PMAS Templated PAn-coated Wool Fabrics	154
4.3.3.3.	Cyclic Voltammetry	156
4.3.3.4.	UV-Vis Spectra	160
4.3.3.5.	SEM	164
4.3.3.6.	Thermogravimetry	167
4.4.	CONCLUSION	171
4.5.	REFERENCES	174

CHAPTER 5	176
CONDUCTIVE POLYMER COATED TEXTILES AND	
THEIR STRAIN GAUGE CHARACTERISTICS	176
5.1. INTRODUCTION	177
5.2. EXPERIMENTAL	178
5.2.1. Materials	178
5.2.2. Instrumentation	179
5.3. RESULTS AND DISCUSSION	180
5.3.1. Mechanical Properties of Uncoated and Polymer-coated Fabrics	
by Instron 4320 Tensile Tester	180
5.3.1.1. PPy-coated Nylon Lycra	180
5.3.1.2. Templated PAn-coated Wool Nylon Lycra	185
5.3.2. Strain Gauge Response of Polymer-coated Fabrics	191
5.3.2.1. PPy-coated Nylon Lycra	192
5.3.2.2. Templated PAn-coated Wool Nylon Lycra	195
5.3.3. Strain Gauge Response of Polymer-coated Fabrics	
at Different Frequencies	200
5.3.3.1. PPy-coated Nylon Lycra	201
5.3.3.2. Templated PAn-coated Wool Nylon Lycra	204
5.4. CONCLUSION	208
5.5. REFERENCES	211
 CHAPTER 6	 212
APPLICATION OF CONDUCTING POLYMER COATED FABRICS	212
6.1. INTRODUCTION	213

6.2.	DEVELOPMENT OF STRETCHABLE CONDUCTIVE TEXTILES	217
6.2.1.	Strain Gauge Performance in Sport Training	217
6.2.2.	Conductive Stretchable Textiles for Sensors and Actuators	223
6.2.3.	Further Potential Applications	225
6.3.	CONCLUSIONS	226
6.4.	REFERENCES	228
 CHAPTER 7		 230
GENERAL CONCLUSIONS		230

CHAPTER 1

GENERAL INTRODUCTION

1.1. CONDUCTING POLYMERS

1.1.1. The Development of Conducting Polymers

The discovery of the electrically conducting properties of doped polyacetylenes by Shirakawa, MacDiarmid and Heeger [1,2] in the 1970s heralded a new era in materials science. The use of a large excess of the polymerisation catalyst produced, a shiny, brittle metal-like material that conducted electricity instead of the previously prepared amorphous polyacetylene. Subsequent doping of the metal-like material with iodine produced a material with a conductivity approaching that of copper (up to 10^5 S cm^{-1}) [3]. This discovery led to the new field of conducting organic polymers, recognised by the award of the 2000 Nobel Prize in Chemistry to the co-discoverers [4,5].

Conducting polymers are materials capable of being doped or dedoped resulting in changes to their electrical properties. In recent years conducting polymers with conjugated double bonds have attracted much attention as advanced materials. A large variety of CEPs have now been made, some of the most common ones are polypyrrole (PPy), polythiophene (PTh), and polyaniline (PAn) (Figure 1.1) [5]. Another type of conducting polymer, frequently used in photovoltaic devices, is poly (*p*-phenylenevinylene) (PPV).

PPy

PTh

PAn

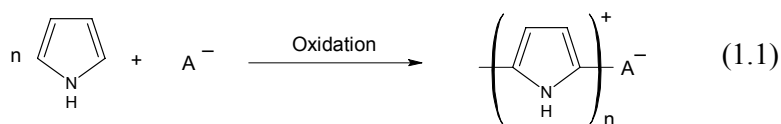
PPV

Figure 1.1. Schematic of conducting polymers [5].

Numerous conducting polymers have been prepared and studied due to their potential use in a wide range of applications. Conducting polymers have been applied in areas such as sensors [6-9,], ion-selective membranes [10-20], polymeric batteries [21-25], corrosion inhibitors [26-28], microactuators [29], electronic wires [30], electrochromic devices [31,32], electromagnetic shielding [33,34] and electronic textiles [35-37]. Most of these applications make use of the electroactivity and conductivity of conducting polymers, as well as their physical and chemical properties.

1.1.2. Polypyrrole

Polypyrrole (PPy) is the most intensively investigated conducting polymer owing to its high stability [38,39] and ease of tailoring [40] to prepare functionalised polypyrrole. Polypyrrole can be prepared using either chemical [41,42] or electrochemical polymerisation methods [43,44]. In both cases, the important step is to incorporate certain charged species into the polymer by a process called “doping”. The polymerisation process is usually expressed as:



Where A^- represents the counterion or so called doping anion being incorporated into the polypyrrole during synthesis, and n is the number of pyrrole repeat unit for each A^- incorporated.

Polymerisation of polypyrrole is initiated by the oxidation of monomer to a radical cation. Polymerisation then proceeds via a radical-radical coupling mechanism rather than radical-monomer mechanism (Figure 1.2).

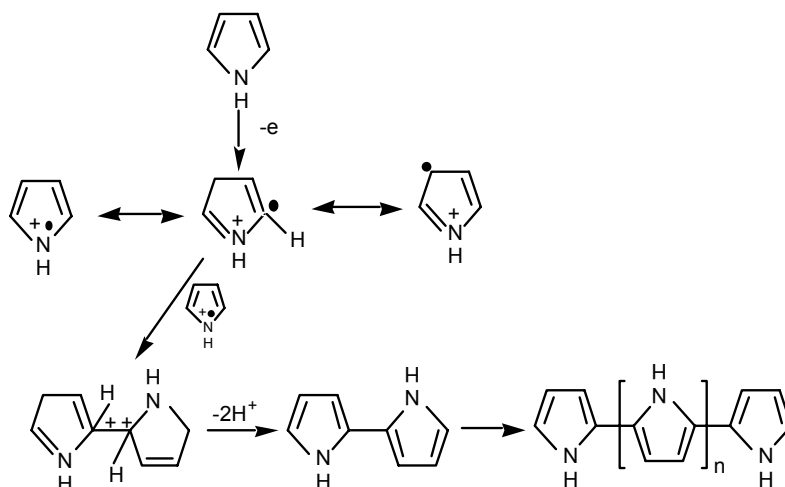


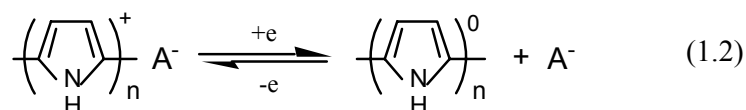
Figure 1.2. Polypyrrole polymerisation initiation and polymer growth.

The chemical polymerisation of pyrrole is a general and useful route to the formation of conductive composites in aqueous media [45-48]. It involves reacting pyrrole monomer with an oxidant and in a suitable solvent. Ferric chloride has been found to be the most commonly used oxidant and water is the main solvent for chemical polymerisation [45]. If ferric chloride is used as an oxidising agent, the counterion is most likely to be Cl^- . Because of the relative mobility of the chloride ion, the resulting polymer is not very stable. However, a separate dopant anion is often added to the reaction solution in order to improve the environmental stability and electrical properties of the polymer. It is well known that the type of doping agent can have a considerable effect on the conductivity and morphology of polypyrrole [49]. For *in-situ* chemical polymerisation, using ferric chloride as an oxidant, the addition of separate dopants leads to a mixture of counterions

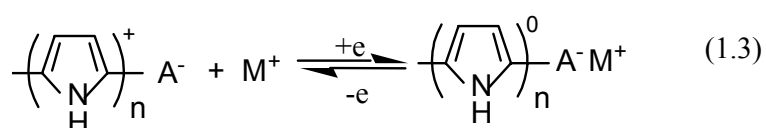
in the polymer. For example, the sodium salts of arylsulfonates are introduced to form more conducting and more stable polypyrrole films [50,51]. This will be discussed in the section on polypyrrole coated fabrics later.

Pyrrole can also be oxidised by electrochemical (galvanostatic, potentiostatic and potentiodynamic) techniques in aqueous or organic solution [52,53]. The potentiodynamic method is usually employed for the investigation of the mechanism of polymerisation or polypyrrole formation. The potentiostatic technique can be used for the preparation of polypyrrole thin films. Due to the variation of the current during the film growth, the rate of polypyrrole deposition is not constant. So this method is not very convenient for synthesis of thin films of desired thickness. Galvanostatic polymerisation is carried out by controlling current so that the polypyrrole deposition occurs at a fixed rate. Hence, the galvanostatic method is commonly used for the preparation of polypyrrole films.

Polypyrrole is electrically conductive and electroactive. The latter term refers to their ability to be electrochemically switched between their reduced and oxidised states. An electrochemical redox switching process [54-57] is illustrated by equations 1.2 and 1.3. When polypyrrole in the conducting state is reduced, the incorporated anion can be released into the surrounding medium to maintain charge neutrality (1.2). On the other hand, the oxidation of the reduced form of the polypyrrole can also be accompanied by the re-insertion of anions back into the polymer.



However, if large anionic molecules such as polyelectrolytes are present as dopants in the conducting polymer, the dopant is relatively immobile and cannot be readily released upon reduction of the polymer. In this situation the electroneutrality of the polymer is maintained by incorporation of cations from the surrounding electrolyte into the polypyrrole matrix (1.3). Thus, this increases the stability and mechanical strength of the polypyrrole film.



Polypyrrole are stable to repetitive oxidation and reduction only below certain anodic/cathodic potential limits, (± 1.0 V vs. Ag/AgCl) [58]. When the potential is taken positive of this value, oxidation results in rapid degradation of the polymer and loss of electroactivity, which is known as overoxidation, because the counterions are expelled irreversibly and the polymer conjugation is destroyed during the overoxidation [59-61].

1.1.3. Polyaniline

The polyaniline family includes the unsubstituted “parent” polyaniline (PAn) and a variety of substituted polymers with substituents either on the aniline rings or on the nitrogen atoms. The “parent” polyaniline and sulfonated polyaniline as well as their coated fabrics will be discussed in this thesis.

1.1.3.1. Unsubstituted Polyaniline (PAn)

Unsubstituted polyaniline exists in different forms with various colours depending on the degree of oxidation and protonation [62]. The oxidation state in the base (unprotonated) form can vary from the fully oxidised polymer (pernigraniline) to the half oxidised polymer (emeraldine) to that of the fully reduced polymer (leucoemeraldine) as shown in Figure 1.3. Colour changes during transition between the different forms of PAn indicate the oxidation or protonation state of the polyaniline.

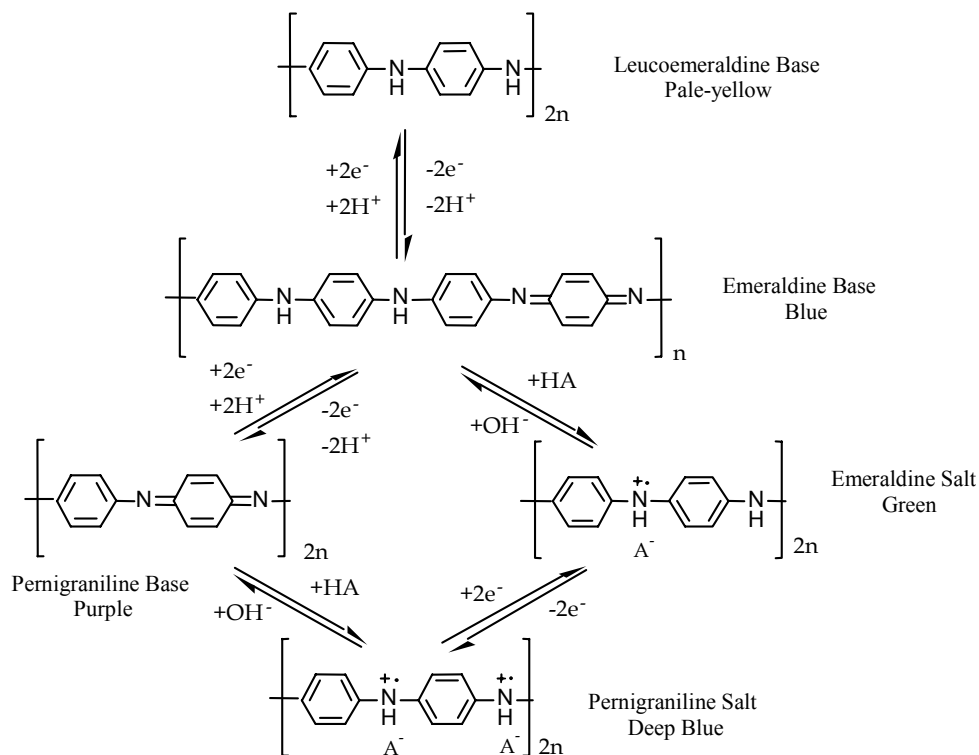


Figure 1.3. Interconversions between different forms of polyaniline.

The only conducting form of PAn, protonated emeraldine salt (PAn.HA), is produced by the oxidative polymerisation of aniline in aqueous acid (HA) with the presence of

radical cations in the structure. The positive charge on the aniline unit is balanced by negatively charged counterions. With the high environmental stability, facile redox and pH switching between the different forms of the polyaniline, relatively high conductivity and low cost, polyaniline is recognised as one of the most promising organic conducting polymers for future commercialisation.

Polyaniline can be synthesised by the oxidation of aniline with an appropriate chemical oxidant or by electrochemical polymerisation on an inert electrode substrate. The conformation of PAn prepared by these two different polymerisation methods indicated that two routes give rise to materials [63-65]. The mechanism of electrochemical oxidation would be related to radicals adsorbed on the electrode surface; which might allow different coupling reactions between the monomer, the intermediate products, and the resulting aniline oligomers and polymers. The chemical oxidation of aniline will be discussed below in detail due to its extensive use in this research.

Chemical polymerisation is usually carried out in an acidic aqueous solution (e.g. HCl) [66,67] of aniline monomer and oxidant. The properties of polyaniline, such as electrical conductivity, morphology and molecular weight, are sensitive to the polymerisation conditions employed. Low temperature (e.g. 0-4 °C) yields higher molecular weight products of polyaniline [68-74]. Oxidants including potassium dichromate [75,76], hydrogen peroxide, ceric nitrate and ceric sulfate [77,78] and ammonium persulfate [75,76,79,80] have been used in chemical polymerisation. The most widely employed chemical oxidant is aqueous ammonium persulfate, which leads to the incorporation of $\text{HSO}_4^-/\text{SO}_4^{2-}$ as the dopant anion (A^-) in the PAn.HA product.

The mechanism of chemical oxidation was proposed by Genies *et al.* [64] and was later confirmed by other researchers [62, 81-83]. The reaction is believed to proceed in four steps (Figure 1.4). The first step is the formation of the radical cation of aniline. The aniline cation radicals with the radical on the *N*- and *para*-positions participate in a subsequent re-aromatisation of the dication of *p*-aminodiphenylamine (*p*ADPA). It is then oxidised to the radical dication (step 2). Although head-to-tail (i.e. *N-para*) coupling is predominant, some coupling in the *ortho*-position also occurs, leading to defects in conjugation in the product [79,84]. In the third step the radical dication couples with the monomeric radical cation of aniline, forming a trimer. The chain then propagates further via coupling of shorter polymer fragment-radicals with the aniline radical cation. The resultant polymer is a deep blue pernigraniline salt. When all oxidant is consumed, the remaining aniline reduces the pernigraniline to form the final product, the green PAn.HA emeraldine salt which precipitates (step 4). In the chemical oxidation polymerisation process the different steps are related in the colour changes. The solution is pink due to *p*ADPA in the second step and becomes deep blue with the formation of the protonated pernigraniline in the third step. Finally, it changes to green due to the emeraldine salt precipitate.

Please see print copy

Step 1. Oxidation of monomer

Please see print copy

Step 2. Radical coupling and oxidation to the diradical dication

Please see print copy

Step 3. Propagation of chain

Please see print copy

Step 4. Reduction of Pernigraniline Salt to Emeraldine Salt

Please see print copy

Figure 1.4 Chemical polymerization of aniline [62]

1.1.3.2. Sulfonated Polyaniline

Sulfonated polyanilines (SPANs), shown in Figure 1.5 (a), are a subclass of the polyaniline family. Characterised by the presence of sulfonic acid groups on the rings that results in self-doping of the polymers and high solubility in water. The introduction of an electron-donating methoxy group in 2-methoxyaniline-5-sulfonic acid (MAS) gives sulfonated aniline an excellent reactivity towards oxidation. One such sulfonated polymer is poly (2-methoxyaniline-5-sulfonic acid) or PMAS (Figure 1.5 b), which has been used for preparation of templated polyaniline coated fabrics in this thesis.

PMAS has been prepared using chemical polymerisation by Shimizu *et al* [85-87] and can also be synthesised electrochemically [88,89] with a higher yield (> 90%), purity and similar conductivity.

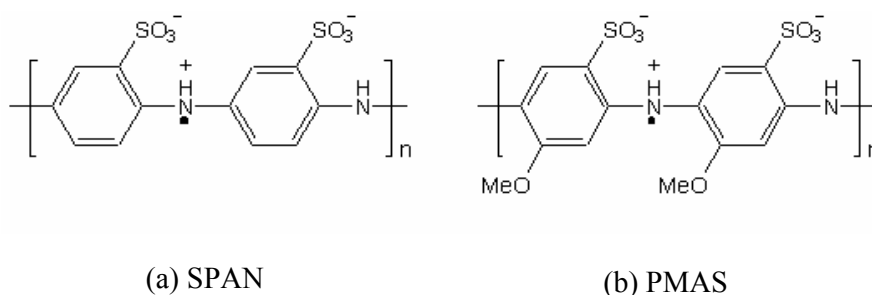


Figure 1.5. Structures of some fully sulfonated polyanilines.

Polyanilines show a strong coupling between their electronic structure and geometric conformation of polymer chains. The position and intensity of the UV-Vis absorption bands for different forms of polyaniline is sensitive to the conformation adopted by the polymer chains, as well as the conjugation length [90]. Leucoemeraldine base (LB)

shows only one absorption band in its UV-Vis spectrum at ca. 320 nm (Figure 1.7 b). This may be assigned to a $\pi - \pi^*$ electronic transition. For emeraldine base (EB), due to a similar low wavelength $\pi - \pi^*$ electronic band corresponding to the benzenoid rings, a strong band at ca. 600 nm is observed that has been attributed to an intermolecular charge transfer exciton associated with the quinoid rings [91]. Pernigraniline base (Figure 1.8 b) shows two absorption peaks at ca. 320 and 530 nm, which may be assigned to a $\pi - \pi^*$ band and a Peierls gap transition [91], respectively.

The UV-Vis spectra of emeraldine salts (ES), formed by protonating EB, exhibit three peaks: a $\pi - \pi^*$ band at ca. 330 nm and two visible region bands at ca. 430 and 800 nm (Figure 1.6) that may be assigned as $\pi \rightarrow$ polaron band and polaron $\rightarrow \pi^*$ band transitions, respectively [5]. Emeraldine salts with a distinct high wavelength polaron peak around 800 nm are thought to have a “compact coil” conformation, which exhibit a broad strong free carrier tail (Figure 1.7a) in the NIR (with λ_{max} red shifted to 1500-2500 nm), when the PAn chain changes conformations from a “compact coil” to an “extended coil” conformation. The delocalization of the polaron along the PAn chains in this “extended coil” conformation results in much enhanced electrical conductivity [90].

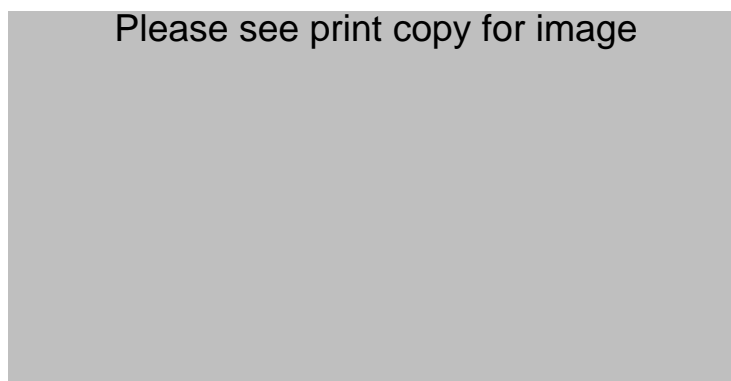


Figure 1.6. Assignment of electronic absorption bands of emeraldine salt [5].

The UV-Vis absorption spectra of the PMAS solution exhibit an intense, sharp peak at 474 nm and a broad peak at ca. 290 nm, attributed to a $\pi - \pi^*$ transition band and a short wavelength polaron transition, respectively, characteristic of poly (2-methoxyaniline-5-sulfonic acid). Oxidation of PMAS in strongly acidic media (pH 1) was investigated by E. Strounina [92]. The initial 475 nm peak of PMAS decreased with time, and was broadened and blue-shifted (Figure 1.9). Chemical reduction of PMAS by hydrazine was also studied [92]. Within 1 min the initial PMAS peak at 475 nm had disappeared and was replaced with a strong peak at 408 nm (Figure 1.10). Over the following 2 hours this 408 nm peak decreased in intensity, while a strong band grew at ca. 330 nm. These latter changes are consistent with conversion to the leucoemeraldine base form of PMAS [92].

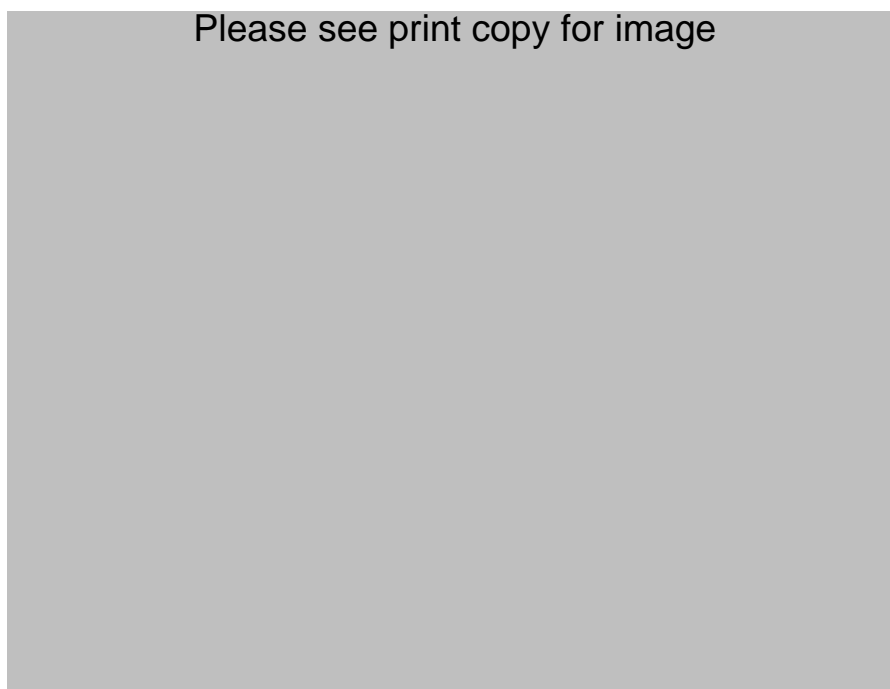


Figure 1.7. UV-Vis spectra of (a) initial emeraldine salt PAn.(+)-HCSA film and (b) leucoemeraldine base film derived by reduction with PhNHNH₂ [93].

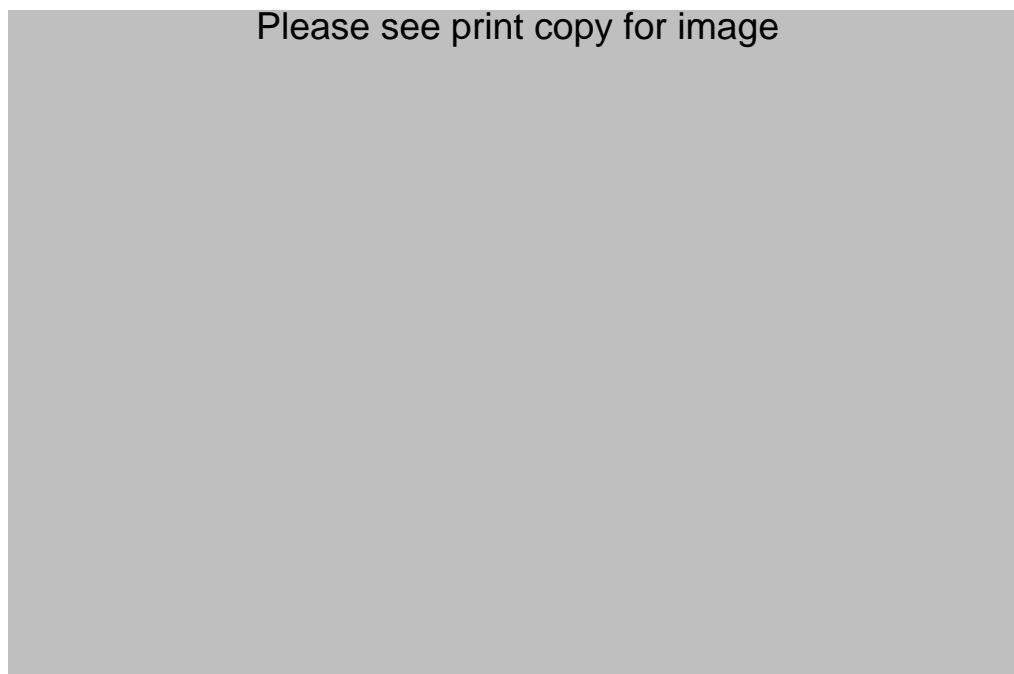


Figure 1.8. UV-Vis spectra of (a) initial emeraldine salt PAn.(+)-HCSA film and (b) pernigraniline base film derived by oxidation with ceric ammonium sulfate [93].

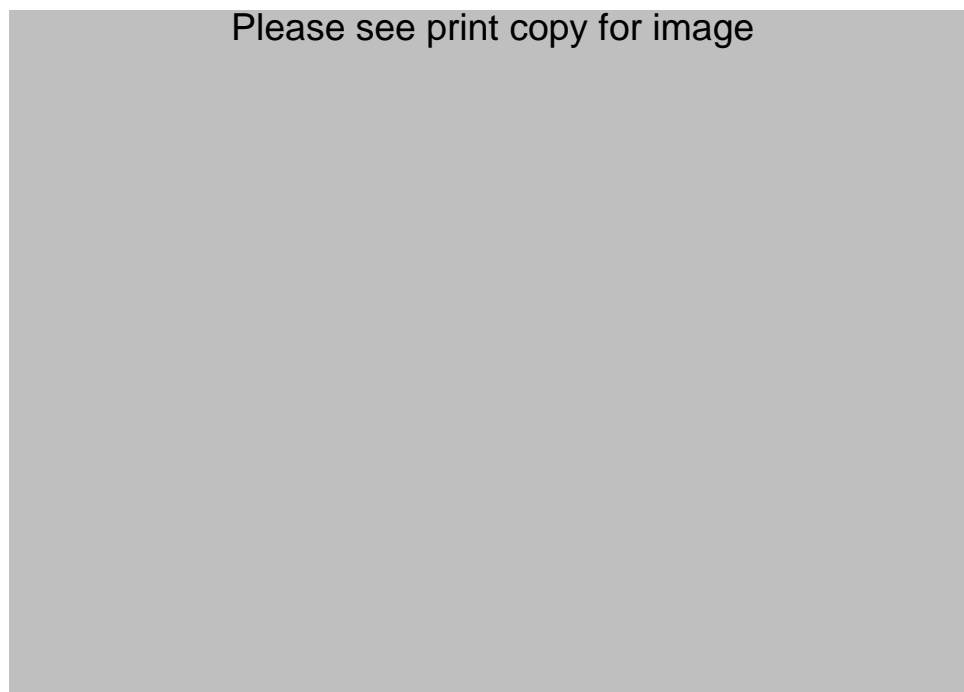


Figure 1.9. UV-Vis spectra of PMAS solution during oxidation in 0.1 M (NH₂)S₂O₈, pH 1 [92].



Figure 1.10. UV-Vis spectra of PMAS solution during reduction in 0.08 M hydrazine, pH 9 [92].

1.1.4. Characterisation of Conducting Polymers

The characterisation of conducting electroactive polymers such as the examination of electrochemical, chemical and physical properties have been carried out by various techniques. Table 1.1 shows the variety of characterisation techniques that can be used.

Table 1.1. Techniques used for characterisation of conducting polymers.

Type	Characterisation techniques	Information obtained
Electrochemical methods	Cyclic Voltammetry Chronoamperometry Chronocoulometry Chronopotentiometry Pulse Voltammetry Quartz Crystal Microbalance (QCM) Impedance Analysis	Polymerisation mechanism, electrochemical properties
Chemical composition and structure	Elemental Analysis Nuclear Magnetic Resonance (NMR) X-ray Photoelectron Spectroscopy (XPS) Raman Spectroscopy IR Spectroelectrochemistry Laser Spectroelectrochemistry UV-Vis Spectroscopy	Polymer composition, electronic structure and counterion effect
Physical properties	Scanning Electronic Microscopy (SEM) Atomic Force Microscopy (AFM) Two & Four probe Conductivity Tensile Strength Analysis Permeability Porosity Analysis Thermogravimetric Analysis (TGA)	Morphology and porous structure, conductivity, mechanical properties and thermal studies

1.2. FIBRE STRUCTURE & TEXTILE SUBSTRATE

Textile fabrics are planar structures produced by interlacing or by entangling yarns or fibres in some manner. A wide range of textile materials is used as substrates for coated fabrics. These textiles may be woven, knitted, or non-woven materials.

The fibre is the basic physical structure or element that makes up a textile product. There are two main types of fibres: natural fibres and synthetic fibres. Natural fibres include protein fibres such as wool and silk, cellulose fibres such as cotton and linen, and mineral fibre asbestos. Man-made fibres are made by chemical synthesis, so they are often called synthetic fibres. Dissolving the polymer from natural sources and then forming the fibre results in the regenerated fibres. Synthetic fibres include polyamides (nylon), polyester, acrylics, vinyls and polyolefins. Regenerated fibres include materials such as rayon, cellulose acetate, regenerated proteins and glasses. Figure 1.11 shows a classification chart of the major fibres.

Woven fabrics such as polyester, knitted fabrics including nylon Lycra and wool nylon Lycra have been used to prepare conducting polymer coated fabrics. An understanding of both the fibre and fabric structures is needed in order to understand fabric coating procedures and their response to an applied stress as will be addressed in this thesis. This section will provide an overall description of woven, knitted fabric structure, and some important fibre structure such as polyester, nylon, wool and elastic Lycra. Details of fabrics used as substrates will also be discussed in each chapter.

Fibre

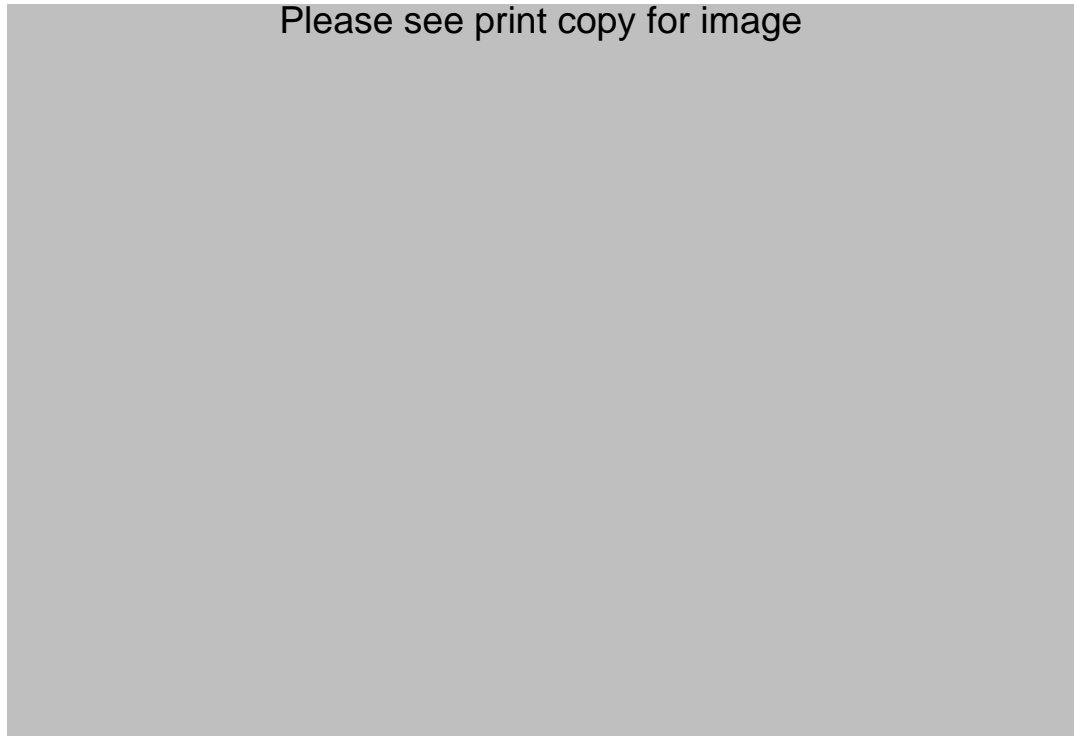


Figure 1.11. Classification of fibres [94].

1.2.1. Fibre Structure

1.2.1.1. Wool Fibre

Wool is a crimped fibre from the fleece of domesticated sheep that is a natural, protein, multicellular, staple fibre. Wool fibres are extremely complex, highly cross-linked keratin protein made up of over 17 different amino acids. The length of wool fibres ranges from about 5 cm for the finest wool to 35 cm for the longest and coarsest wools. Wool fibres vary greatly in their diameter, ranging from about 14 μm for the finest wools to more than 45 μm for the coarsest wools. The colour of the wool fibres vary from off-white to light cream [95].

The complex wool fibre consists of three main components: cuticle, cortex and fibrils [Figure 1.12]. The cuticle is the layer of overlapping epithelial cells that surrounds the wool fibre and consists of the epicuticle, exocuticle, and endocuticle. The cortex of the wool fibre is composed of two distinct sections known as the *ortho*-cortex and *para*-cortex. If the cross-section of the wool fibre is examined after application of a selected dye, the *ortho*-cortex absorbs more dye than *para*-cortex due to the different composition between the *ortho*- and *para*-cortex. The chemical composition of the *para*-cortical cells shows a higher cystine content than the *ortho*-cortical cells. In the *para*-cortical cells, di-sulphide cross-links are formed due to the cystine that is a sulphur containing amino acid. The more the cross-linking, the greater the chemical stability of the *para*-cortical cells. This results in less dye absorption [95].

The cortical cells of the wool fibre consist of a number of macrofibrils that are held together by a protein matrix. Each macrofibril consists of hundreds of microfibrils and each microfibril consists of eleven protofibrils, which spiral about each other. Finally, each protofibril consists of three wool polymers that also spiral around each other. The wool polymer is a linear, keratin polymer including some very short side groups, which usually has a helical configuration. The repeating unit is the amino acids [Figure 1.13] that are linked to each other by the peptide bond ($-\text{CO}-\text{NH}-$) to form the wool polymer. A wool polymer is about 140 nm long and about 1 nm thick. The wool polymer has a helical or spiral configuration known as alpha-keratin in its normal relaxed state. Stretching the wool fibre will tend to also stretch, straighten or unfold its polymers. The unfolded configuration of the wool polymer is called beta-keratin, which will always attempt to return to its relaxed state [95].

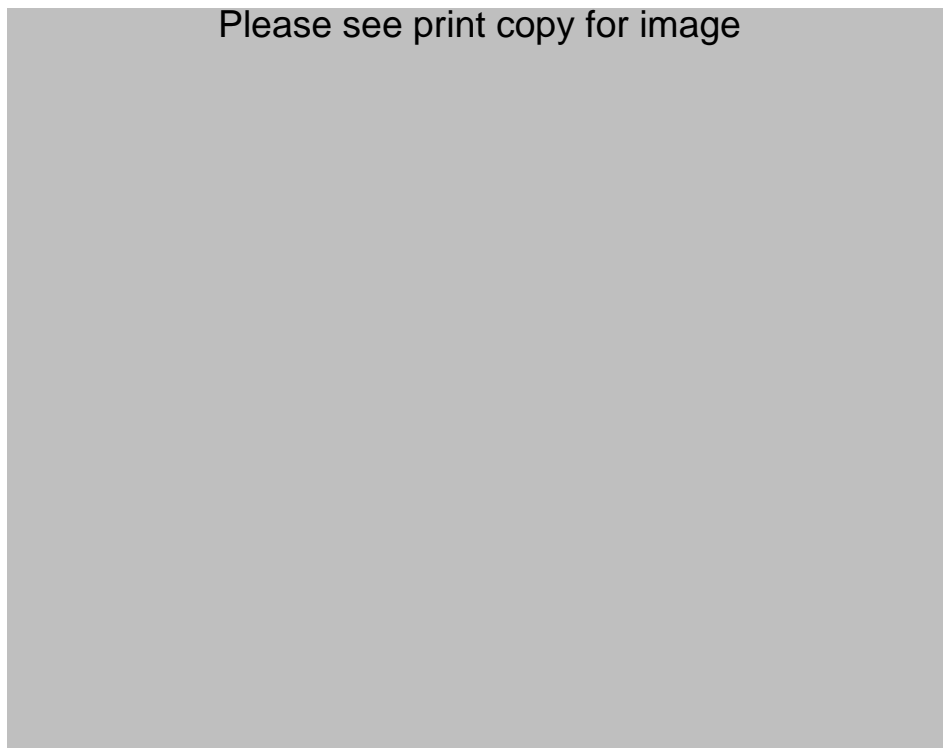


Figure 1.12. The morphological diagram of a wool fibre [95].

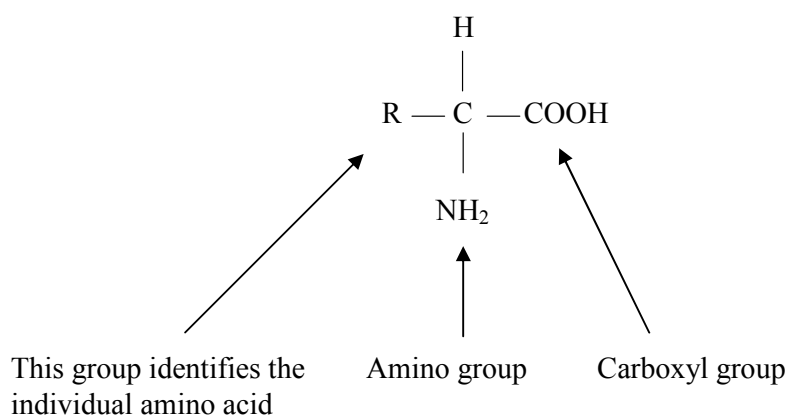


Figure 1.13. The general formula of amino acid.

Wool fibre consists of 50.8% Carbon, 7.2% Hydrogen, 18.5% Nitrogen, 21.2% Oxygen and 2.3% Sulfur [96]. Wool is more resistant to acid than to alkalis. Diluted acids even at boiling point do not damage wool. Wool also has a good affinity for dyes due to the

polarity of its polymers and its amorphous nature [95]. Its chemical structure enables the fibre to unite chemically with a wide variety of dyestuffs such as acid dyes, chrome or mordant dyes, pre-metallised dyes and reactive dyes.

Wool has very good elastic recovery and excellent resiliency. In its crimped configuration, a single fibre when dry can be extended by approximately 30% and when wet by between 60% to 70%. If released immediately after stretching it will eventually return to its original length although it would be irreversibly weakened if extended more than 30% [97].

Wool fabrics are quite likely to shrink after weaving or knitting as a result of yarn and fabric relaxation. The application of a number of polymers to wool fabrics prevents shrinkage. For example, Hercosett 57 [98] is a polyaminoamide with reactive azetidinium side-chains that form cross-links between the polymer chains. They also form covalent links with amino and thiol groups in the wool protein. Hercosett 57 gives the wool a mild chlorination treatment to modify the surface of the fibres and allows the polymer to spread evenly on the surface.

1.2.1.2. Polyester Fibre

Polyester refers to a class of polymers containing a number of repeat ester groups in the polymeric chain. It is the most widely used synthetic fibre. Although polyester fibres have several different chemical structures with different commercial products, it is very important that those are made from poly (ethylene terephthalate). The polymer is made by condensing ethylene glycol with either terephthalic acid or its dimethyl ester. The

first step involves reaction of an excess of glycol with acid or ester. Elimination of water or methanol forms a mixture of glycol esters of terephthalic acid. Then elimination of glycol from the hydroxyethyl ester results in formation of a high molecular weight polymer (Figure 1.14). Poly (ethylene terephthalate), the repeating unit of the polyester polymer, has a degree of polymerisation of 115 to 140 units; that is, $n = 115$ to 140 [94]. Compared with nylon, polyesters are rather heavy fibres with a density of 1.39 g/cm^3 . For this reason polyester textiles are manufactured as light weight thin fabrics; as thick polyester fabrics are too heavy [95].



Please see print copy for image

Figure 1.14. Poly (ethylene terephthalate) polymerisation [99].

Polyester from poly (ethylene terephthalate) is a strong fibre due to the extremely crystalline polymer system. The fibre is stiffer and completely hydrophobic because of

its chemical groups, such as the methylene, the slightly polar carbonyl groups and the ester groups. The stiffness makes it suitable for blending in staple forms with other fibres such as cotton to make the fabric comfortable. The elongation at break of the polyester fibre varies from 15% to 50% depending on the degree of orientation and nature of crystalline structure within the fibre. The fibre shows moderate (80%-97%) recovery from low elongations (2% - 10%) [94].

Polyester fibres can be regarded as being completely hydrophobic due to the lack of polarity and the extremely crystalline nature. The extremely hydrophobic nature of the polyester fibres means that dye molecules are difficult to integrate into the polyester fibres. The reason is that the inter-polymer spaces in the crystalline regions of the fibre's polymer system are too small for the relatively large dye molecules. Dye molecules can be described as having the shape of slips of paper with length, breadth and thickness. Only relatively small molecules of dispersed dyes, with 0.80 nm length, 0.40 nm breadth and 0.40 nm thickness, can be used to dye polyester fibres [94].

Poly (ethylene terephthalate) polyester is highly resistant to chemical attack by acid, bases, or oxidising or reducing agents except hot concentrated acids and bases. Polyester fibres are available in a variety of types with special characteristic that alters its behaviour in some way. These new fibres are created by altering the cross section shape from round to multi-lobal, by a change in fibre formulae or by varying the physical process. Polyester fibres melt at temperatures from 238 to 290 °C depending upon type [100].

1.2.1.3. Nylon Fibre

Nylon is the generic name given to linear synthetic polyamides of different chemical structures made by many different manufacturers. The most important fibres are Nylon 66 and Nylon 6. Nylon 66 is polyhexamethylene adipamide, a condensation polymer of hexamethylene diamine and adipic acid. The suffix 66 stands for the number of carbon atoms in the monomers. Nylon 6 is polycaprolactamide, prepared from the monomer ϵ -caprolactam. The reaction sequences are given below (Figure 1.15) [101]. For Nylon 66 and Nylon 6 fibres, the degrees of polymerisation (n) are from 50 to 80 and 200, respectively [94].

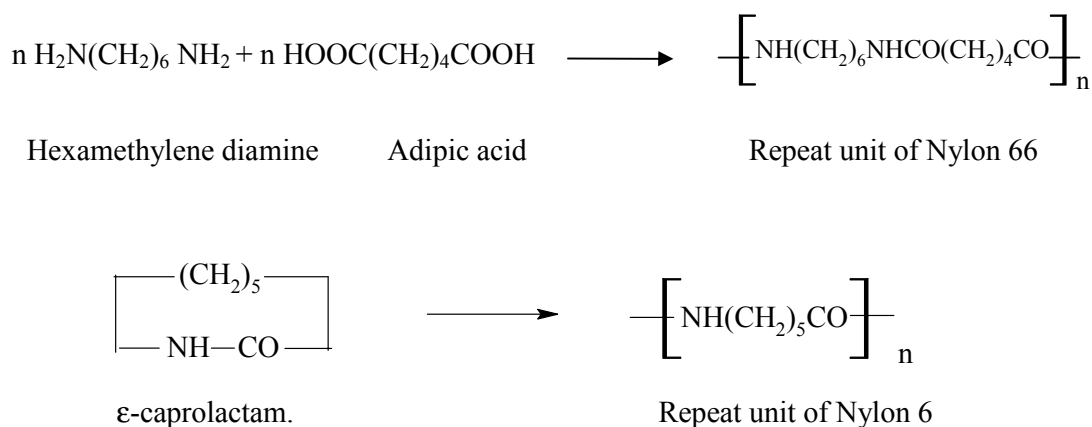


Figure 1.15. Polymerisation steps used to produce Nylon 66 and Nylon 6 fibres.

The most important chemical group in the nylon polymer is the polar amide groups (---NH---CO---). This owes its polarity to the slightly negative charge on the oxygen atom, that is the carbonyl oxygen, and the slightly positive charge on its hydrogen atom, that is the imino hydrogen. The other important groups are the amino groups, ---NH_2 , found at the end of the nylon polymers. The polymer system of nylon is estimated to be about 65% to

85% crystalline that enables the nylon polymer to form strong, uniform and optimum number of hydrogen bonds [95].

Nylon fibres have a good elastic property due to the very regular grid of strong hydrogen bonds in their polymer systems. When these hydrogen bonds operate over very short distances, they are able to exert their optimum strength, preventing polymer slippage and causing the polymers return to their original position in the polymer system. It has been estimated that the elasticity of nylon fibres is about 22% when a load is applied. Other factors such as moisture will affect the elasticity of nylon fibres. When nylon fibres are wet the water molecules will hydrolyse a significant number of hydrogen bonds in the amorphous regions of the polymer system, which results in the loss of elasticity and increase in extensibility of nylon filaments or staple fibres [95].

The nylon fibres are fairly resistant to chemical attack. They are less resistant to acid than to alkalis. The amide groups in the nylon polymers are hydrolysed under acidic conditions. As a result the nylon fibres are weakened. Alkali hydrolysis occurs when the nylon fibres are exposed to alkalis for a long time. This also results in a weakening of the nylon textile materials.

The nylon fibres contain both acid carboxylic and basic amino end groups which become positively and negatively charged respectively. These fibres can be readily dyed with acid, pre-metallised or disperse dyes. Acid dyes molecules are sodium salts and can dissociate in aqueous dye liquor to form the acid dye anion that is negatively charged and is attracted to the cationic or positively charged groups in the nylon polymer. Pre-metallised dyes molecules contain a metal atom such as chromium. Pre-

metallised dye molecules dissociate to produce a dye anion in aqueous dye liquor, which is attracted to the cationic groups in the nylon polymers. Disperse dyes molecules are non-polar and hydrophobic which impart nylon fabric good wash-fastness. This is due to the insolubility in water of disperse dyes, making it difficult to be washed out of the nylon polymers [94,95].

1.2.1.4. Spandex Fibre - Lycra Fibre

Spandex fibres are elastomeric fibres which possess extremely high elongation (400%-800%) at break. The first spandex was introduced by the DuPont Corporation as Fibre K in 1958. Spandex is a generic term given to synthetic fibres that comprise at least 85% of segmented polyurethane.

One of the most popular spandex fibres is Lycra, a trade name given to a spandex elastomer made by DuPont. But the trade name is often used incorrectly to refer to all materials that incorporate spandex fibres [102,103]. This spandex fibre, Lycra, is produced as delustred, very white multifilament, each with a somewhat dog-bone cross-section. These multi-filaments are fused together at points of contact in an irregular pattern to give the appearance of a monofilament fibre [104]. Figure 1.16 and Figure 1.17 show the photomicrographs of Lycra spandex fibre in a cross-section and a longitudinal view (Courtesy of E. I. DuPont de Nemours & Company) [103].

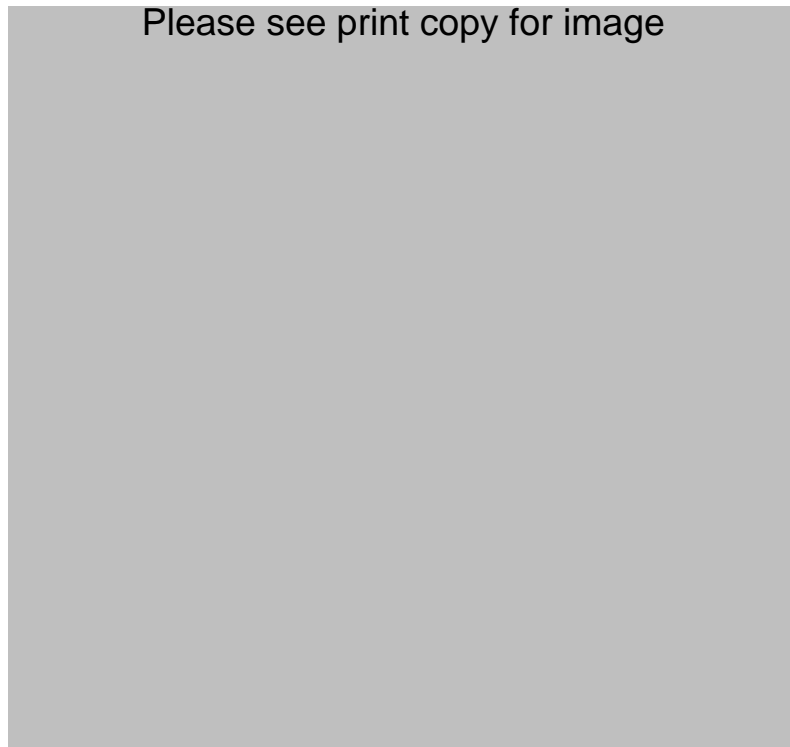


Figure 1.16. Photomicrograph of Lycra Spandex fibre in a cross-section [103].

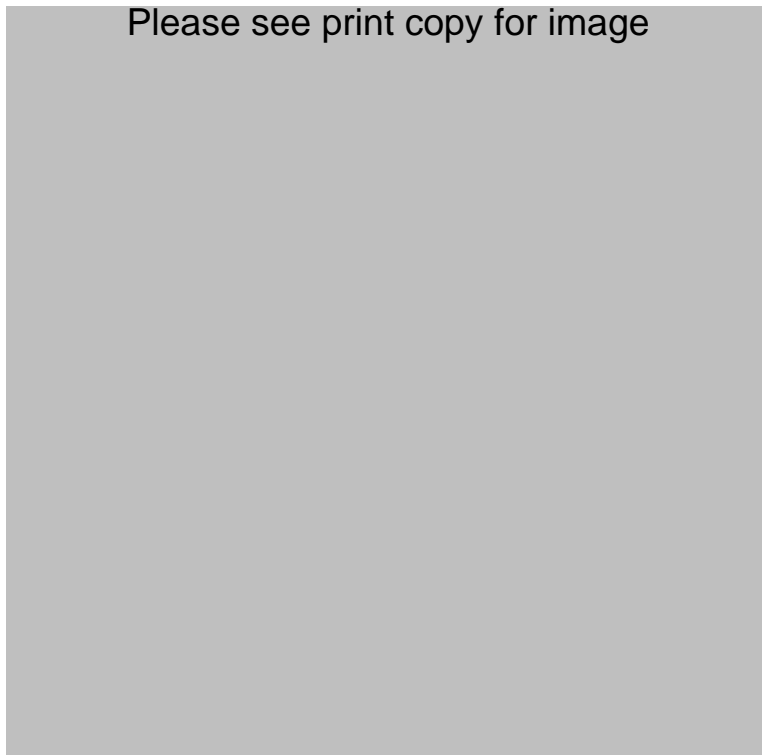


Figure 1.17. Photomicrograph of Lycra Spandex fibre in a longitudinal view [103].

Spandex consists of two types of elastomeric polymers, such as polyether type for Lycra and polyester type for Vyrene. Each is extruded into filaments with excellent elastic properties but different in their resistance to alkalis. The polyether type of polymer (for example Lycra) is depicted in Figure 1.18 and the degree of polymerisation (n) is unknown.

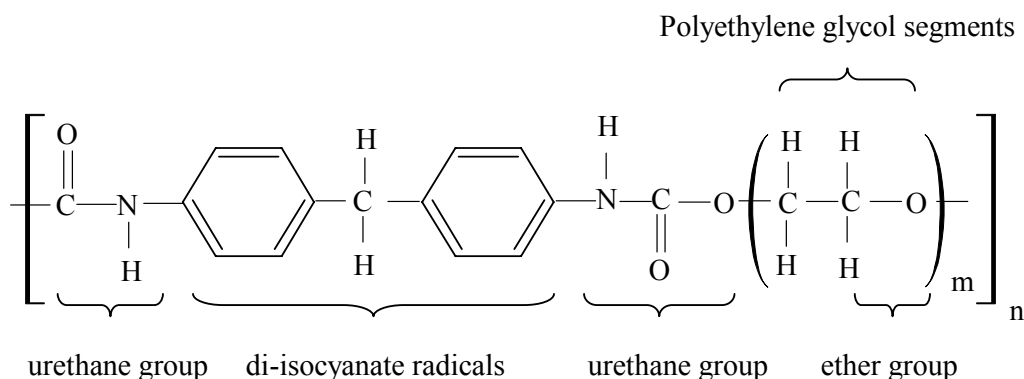


Figure 1.18. The repeat unit of a polyether based Spandex used in Lycra fabric.

Polyether type of elastomeric polymer is linear and composed of alternatively hard and soft segments. The hard segments are consisted of short urethane radicals and short di-isocyanate radicals. The aromatic or benzene structure of the di-isocyanate radicals imparts a certain degree of rigidity to the spandex fibre, which will also form hydrogen bonds with other di-isocyanate radicals of adjacent polymers. The hard segments are chemically more inert and therefore generally make the elastomeric polymer stable [95].

The soft segments in the spandex fibres consist of long polyethylene glycol radicals that are linear as well as multidirectional. They cause polymers to fold and coil upon themselves and result in a predominantly amorphous polymer system with excellent extensibility when the filament is stretched. The polymer contains both crystalline and

amorphous regions of the polymer system of an elastomeric filament prior to being stretched (Figure 1.19 a) and when stretched (Figure 1.19 b).

The elastomeric polymer system is held together by a significant number of covalent cross-links. When the filament is not stretched, there is hydrogen bonding between the di-isocyanate radicals of the adjacent polymers that enhance the rigidity imparted by the di-isocyanate radicals. These hydrogen bonds are continually broken and reformed between the stretched and relaxed filament.

The presence of soft segments allows the fibres to be stretched over large extensions. In the relaxed state they pull the elastomeric polymers back to their original configuration in the polymer system. When the elastomeric polymer is stretched, the polymers unfold their soft segments and the hard segments provide the rigidity to allow this to happen repeatedly. If spandex fibre is fully extended, any excessive stretching will result in crystalline filament break down and degradation. There are no significant polar groups on the elastomeric polymer which means that the polymer system is not attacked by the water molecules. So the elastic properties are unaffected by moisture.

Spandex fibres are very stable to chemical attack. They can be attacked by acid and bases only at higher concentrations and under more extreme reaction conditions [94]. Due to the hydrophobic and very crystalline nature of the polymer system elastomeric textiles tend to be difficult to dye with dyes. Only disperse dyes, acid dyes and metal complex dyes are used for these materials. Lycra blending with nylon and dyeing with disperse dyes is the most suitable [105].

Please see print copy for image



Figure 1.19. (a) The unstretched or amorphous state of the polymer system of an elastomeric fibre; (b) The stretched or more crystalline state of the polymer system of an elastomeric fibre [95].

1.2.2. Fabric Textile Structure

A fabric is a structure made from yarns, fibres or non-fibrous substances such as plastics, rubber or metal. The fabrics made from yarns are more complex than the others. The major fabric construction methods are used including weaving, knitting, braiding and lacing. Weaving and knitting methods and their products such as woven and knitted fabrics will be described below.

1.2.2.1. Woven Fabrics

The process of converting a set of yarns into a fabric, on a loom, is called weaving. The mechanism consists of interlacing two sets of yarns at right angles to each other in many different designs depending on the type of loom used [101]. By varying the interlacing, a wide variety of different fabric constructions can be made. A fabric can be identified as woven fabric if yarns can be unravelled from adjacent sides.

Fabric such as Taffeta polyester is woven in a plain weave form because of its simplicity. The plain weave interlace of two series of threads, warp and weft. The warp threads run the length of the fabric and the weft threads run across the width. Figure 1.20 shows the plain weave. The section drawings at the side and the bottom of the plan show that warp and weft interlace with each other in a similar manner. This form of interlacing results in a very tight structure in the fabric because the alternate interlacing gives no room for sideways movement of the threads.

The elasticity of the materials varies according to the tightness of the structure and the elasticity of the fibre and yarn. The elongation only shows a slight increase both in the warp and weft directions because of the interlacings, which resist an attempt to pull the warp or weft straight. The diagonal direction known as bias is obtained because the force is not directly along a yarn direction but is pulling across both series of threads. True bias is an angle 45° between warp and weft [102].

About 40% of all fabrics produced are in plain weave. Some examples of plain weaves are voile, muslin, poplin, cambric, sheeting, lawn, organdy, shantung, taffeta or canvas [106]. The smooth surface of plain weave fabrics is ideal for printed designs and surface manipulations. A polyester taffeta fabric made in plain weave has been used to prepare conducting polymer-coated fabric using chemical polymerisation in this thesis.

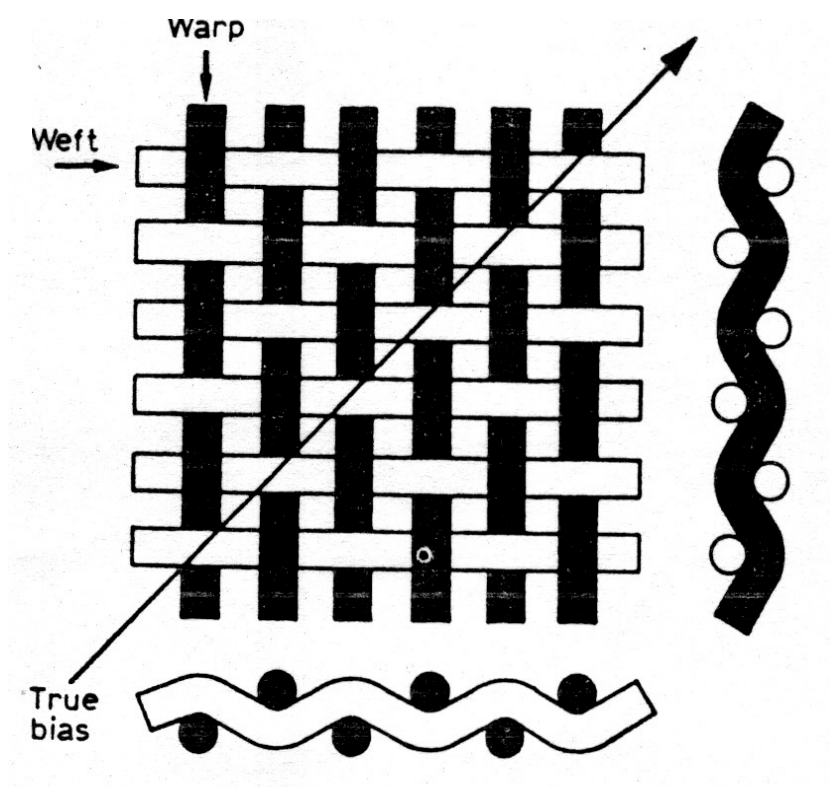


Figure 1.20. Woven fabrics: plain weave.

1.2.2.2. Knitted Fabrics

Knitting is a process whereby fabrics are formed by the interlacing of neighboring yarn loops. These are of two basic types: weft-knitted and warp-knitted. In the construction and analysis of knits, two terms are used frequently: wale and course. Wale refers to a column of loops that are parallel to the loop axis. A course is a series of successive loops lying crosswise of a knit fabric that is at right angles to a line passing through the open throat to the close end of the loops [100].

The weft knitting process is the method of creating a fabric via the interlocking of loops in a weft-wise or crosswise direction. Three most popular and fundamental structures of weft-knitted structures are jersey (plain), rib, and purl. In jersey knit fabrics, the vertical component of the loops appears on the face side, and the horizontal component is seen on the reverse side of the fabric. Purl fabrics are produced on machines with needles that have hooks at both ends [101].

Rib structure differs from the jersey fabric in that it has identical appearance in both directions. In this structure the loops in some wales knit to the face of the fabric and others knit to the back. Figure 1.21 shows 1/1 rib knitted fabric, wales 1 and 3 show the loop sides on the face as normal jersey knit whilst 2 and 4 are the opposite. This fabric creates a double fabric effect because wales 1 and 3 tend to draw together on the face of the fabric and wales 2 and 4 draw together on the back. The width of a 1/1 rib fabric would be about half that of a similar plain knit fabric but it would have great elasticity widthways [102].

The knitted fabrics such as various wool nylon Lycra fabrics from CSIRO Textile and Fibre Technology (TFT) have been prepared using a ' Moorgate' 10 gauge rib knitting machine by knitting a core-spun nylon/Lycra yarn together with the wool yarn. Core spinning is the technique of spinning a sheath of roving staple fibre around an elastomer core while the core is stretched. The core is completely hidden and does not change the fabric surface. The sheath gives aesthetic properties to the yarn and the core gives just enough stretch for comfort [106].

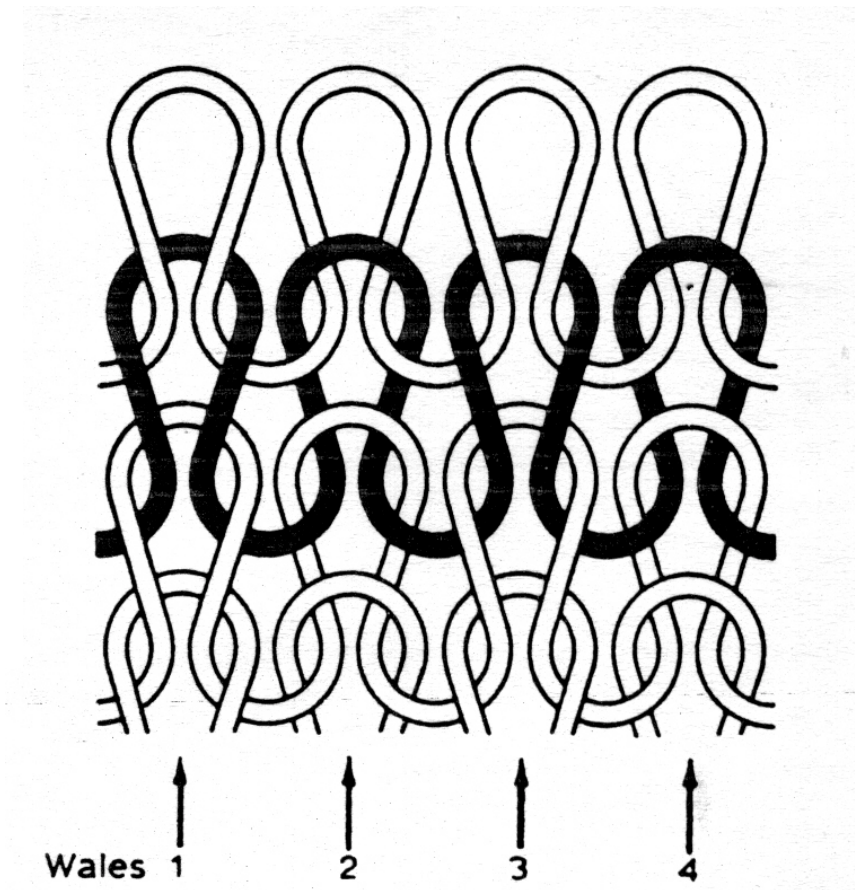


Figure 1.21. 1/1 rib weft knitted fabric.

In warp knitting, the loops are formed in a vertical or warp-wise direction. Warp knit construction has the advantage of being stable in both directions where the amount of

stretch is controlled by the type of warp knit used. The simplest form of the warp knit is shown in Figure 1.22. For all warp knitted fabrics the elasticity is greater in the crosswise direction [102].

Polypyrrole coated fabrics have been prepared by using nylon Lycra fabric. The most common type of nylon Lycra consists of a knitted fabric formed by the warp knit method. The style of warp knit used for nylon Lycra is referred to as locknit. Figure 1.23 shows the face side of the fabric using the locknit. It will be seen that the wales consists of vertical double loops, but only one loop is seen in an actual fabric because the other is hidden behind it [102].

Production of locknit fabrics require two guide bars, one of them moves only the needle space whilst the other moves needle spaces in the opposite direction. These crossing laps form the back of the fabric and the straight wales form the face [102]. Nylon Lycra is formed by extending the elastic Lycra fibre to a predetermined length and combining it side by side with the inelastic nylon fibre in the knitting operation. The spandex fibre is usually inserted and buried in the fabric construction under tension. It can be seen that each fibre in the fabric represents a group of nylon fibres in which the elastic Lycra fibre is laid in the middle.

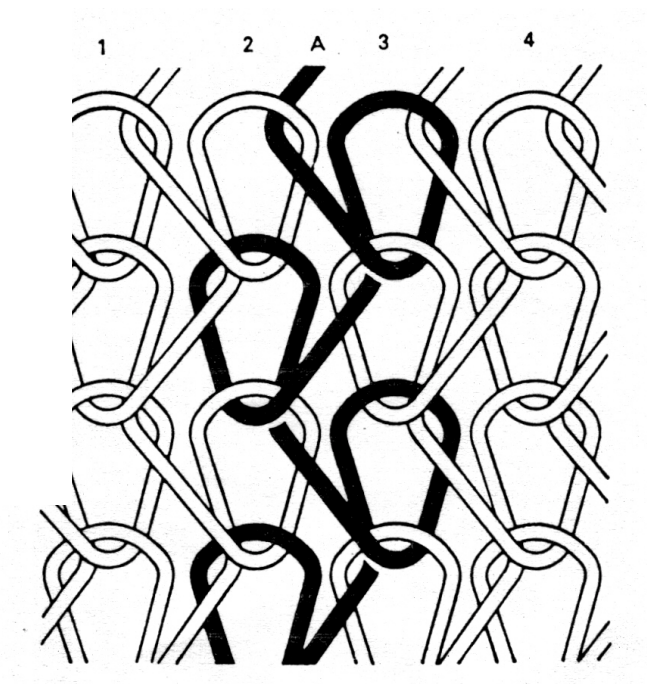


Figure 1.22. Simple warp knit.

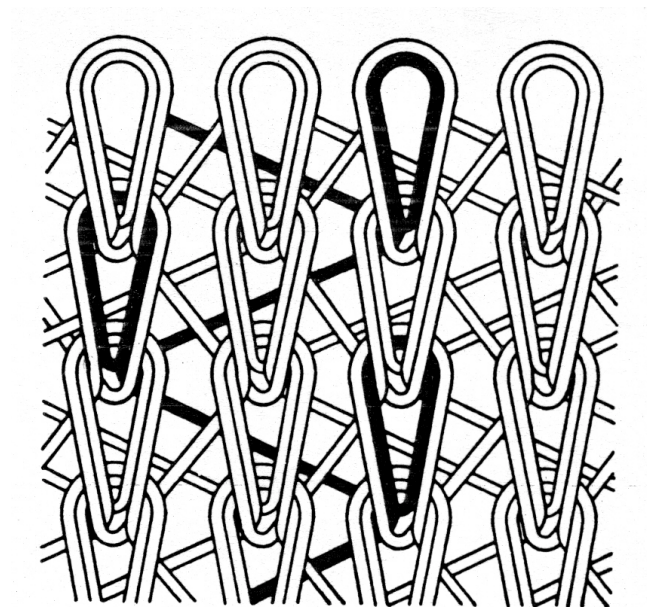


Figure 1.23. Face side of the locknit fabric.

1.3. ELECTRICALLY CONDUCTING TEXTILES

Electrically conducting textiles contain an electronic component such as carbon, metal or conducting polymer integrated into a conventional fabric structure. With the rapid development of the electrical and particularly the electronics industry, flexible, highly conducting and semi-conducting materials have been prepared by using different techniques that will be described in the following sections. Surface resistivity of various textile products is shown in Figure 1.24. The electrical properties of fabrics are measured by the surface resistivity and expressed in ohm/square (Ω/\square).

Surface resistivity

Please see print copy for image

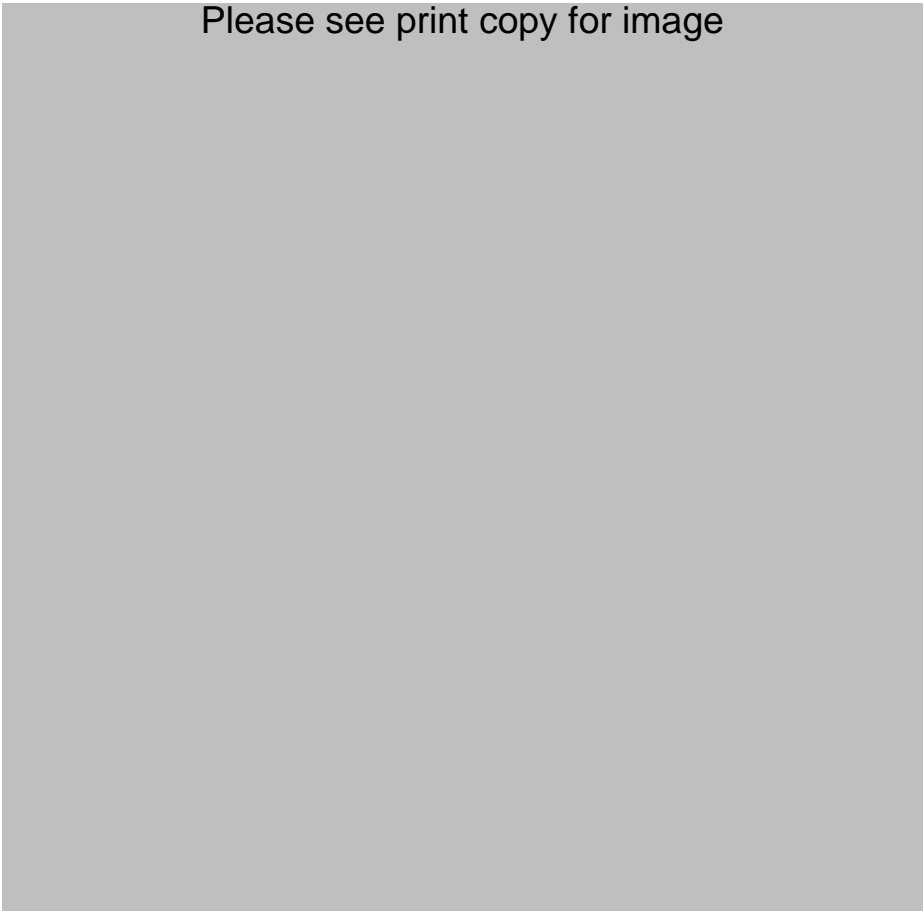


Figure 1.24. Surface resistivity of various textile products [50].

1.3.1. Carbon Fibres and Carbon-Filled Materials

Carbon fibres are very important in industry because they are widely used in aerospace products, the construction industry and medicine. Graphite is a special type of carbon fibre that is made by converting filament fibre such as rayon or acrylic into pure carbon. Carbon fibre is also blended with other fibres to create epitropic fibres that conduct electricity, which are used in static-resistant carpeting [103,107].

Carbon-blended polymers, such as nitrile rubber and chlorobutyl rubber or Neoprene and natural rubber can be produced under certain mixing conditions [108]. Another product, conducting plastics, can be made by incorporating conductive carbon fillers in the plastic. In carbon-filled polymers, the major use of carbon-plastic composites has been in cables, belts, automobile tyres, and hospital equipment, for the purpose of dissipating static charges [108,50]. Carbon fibres and whiskers have also been incorporated by blending into textiles [109].

1.3.2. Metallic Fibres

Metallic fibres are the first man-made fibres, defined as fibres composed of metal, plastic-coated metal, or metal-coated plastic. Gold, silver and aluminium are the metals most often used in textile products. Since ancient times, gold and silver have been used as yarns for fabric decoration. Recently, aluminium yarns, aluminised plastic yarns aluminised nylon yarns, and other metals and their alloys are also used [107]. Two processes are now used to make aluminium yarns. One is a laminating process that seals a layer of aluminium between two layers of acetate or polyester film, which is then cut

into strips for yarns. The other is a metallising process that deposits vaporised aluminium under high pressure on the polyester film [94,106].

Stainless-steel fibres were developed in 1960. They are produced as both filament and staple. Superfine filament of stainless-steel (3-15 μm) is made and added to fabrics in a number of ways. They can be woven or knitted and can be used as either the wrap or core of core yarns. If 1 to 3% stainless-steel staple fibre is blended with other textile fibre, it will be enough to reduce static permanently [106].

Metallic fibres are used to cut down on static electricity build-up and have a side effect of decreasing flammability. They also can be used to create tyre cord, wiring, and cabling and to assist heart surgery. Other applications for metallic fibres include upholstery, blankets, and work clothing. The limitation on the use of metallic fibres is that metals do not have many of the properties usually attributed to textile fibres. Metals are much heavier than the other textile fibres. They cannot be folded and make the fabrics too stiff to drape well [103,106,107].

1.3.3. Metal Coated Materials

Various methods have been developed to coat textile materials by metals such as coating metal powder with binders, vacuum deposition, sputter coating and electroless coating. In the process of metal coating with a binder, about 65-70% of high leafing aluminium pastes are incorporated into a polymeric carrier, which are synthetic rubber, PVC, polyurethanes, silicones, acrylic emulsions and others, and spread coated on the fabric. Vacuum deposition is carried out by placing the substrate into a vacuum chamber

over a set of crucibles, which contain the metals to be coated in the form of a powder or wire. The crucible is heated to melt the metal and then evaporate it. The metal atoms coming out of the molten metal hit the surface of the substrate and condense in the form of solid metal [101].

Sputtering is a momentum transfer process. In sputtering, the incident particles are usually ions due to the fact that they can be accelerated by an applied electrical potential. When the kinetic energy exceeds the surface atom binding energy, the surface will be damaged as atoms are forced into new lattice positions. Atoms may be dislodged or sputtered from the surface. These sputtered atoms and ions can be condensed on a substrate to form a thin film coating [110]. This method is applicable to a wide range of materials and gives more uniform coating with better adhesion [101].

Electroless plating is a process used to deposit metal film on a surface without the use of electrical energy. In electroless plating, a metallic coating is formed as a result of a chemical reaction between the reducing agent present in the solution and metal ions. Electroless plating methods have some advantages; such as non-conducting materials can be metallised, the coating is uniform; the process is simple and does not require electrical energy [101,110]. Electroless plating of textiles is being adopted for different functional applications.

1.3.4. Conducting Polymer Coated Textile

Polypyrrole and polyaniline can be coated on the textile to form conducting polymer textile. There are various methods that can be used for this purpose. The most

commonly used methods are chemical polymerisation (*in-situ* polymerisation, “Two-step” process), or electrochemical polymerisation.

In an *in-situ* polymerisation process, pyrrole or aniline monomer is chemically polymerised usually from aqueous solution and subsequently deposited onto the surface of the textile. To obtain uniform coating on the textile, the oxidation of the monomer must be maintained slow. This is achieved by controlling the concentration of both monomer and oxidant. The *in-situ* polymerisation of pyrrole was first used on paper by Bjorklund and Lundström [108] and later was developed for textiles by Milliken Research Corporation [112-115]. It has been found that either pyrrole or aniline monomers could be polymerised onto the textile under certain conditions to form a smooth, coherent coating on the surface of the textile materials [35]. At present there are some research groups focusing on the *in-situ* polymerisation of pyrrole on textiles. They are Achilles Corporation in Japan, Milliken Research Corporation in the US and the Centre d’Etudes et de Recherches sur les Matériaux (CEREM) in France.

In the “two-step” process, coating is achieved by deposition of an oxidising agent onto the textile fibres, followed by exposure to either liquid or vapour pyrrole monomer [111,116]. Compared with the *in-situ* polymerisation process normally carried out in aqueous solution, a two-step process can be accomplished using different organic solvents. Some methods used in the two-step process are described: either the monomer can be applied from the vapour phase resulting in the coating with a layer of polypyrrole or polyaniline on the cotton threads [106,117], or pyrrole monomer impregnates first on the porous substrate such as fibreglass fabric and then the substrate is exposed to an oxidant to form the polymer composite [118].

Some fibres and textiles can be coated with conducting polymers using an electrochemical polymerisation process. The insulating nature of fibres such as cotton, silk and wool fibres become electrically conducting when they are subjected to electrical treatment in the solution containing pyrrole or aniline monomer [119-121]. Electrically conductive polymer single-phase and composite fibres have been synthesised by using electrochemical flow cells. The hydrodynamic force has been used to control the direction of polymer deposition to form these conductive fibres [122].

Another simple approach to producing conductive textiles is to spread the conducting polymer solution onto the surface of the materials, followed by the evaporation of the solvent. Modification of conducting polymers to get more soluble polymer derivatives has been achieved. For example, sulfonation of polyaniline enhances the solubility of the resulting polymer in water [86]. Other methods for preparing conductive textiles include diffusion [123,124] and emulsion deposition [125,126].

1.3.4.1. Polypyrrole Coated Textiles

Polypyrrole is widely used to prepare conducting textiles due to the unique ability of the polymerising species to absorb onto a hydrophobic surface and form uniform coherent films using *in-situ* chemical polymerisation. Numerous investigators have produced conducting polypyrrole coating on textiles and other substrates [51,127-140]. Ideal pyrrole monomer concentration ranges from 1g/L to 2g/L. Under these conditions the polymerisation occurs on the surface of the fabrics and no excessive polymer is formed in the liquid phase. In order to oxidise pyrrole to fully oxidised polypyrrole, at least 2.33 moles of ferric chloride is needed for each mole of pyrrole monomer [50]. Various

oxidising agents such as ferric chloride [37,130], potassium persulfate [128], and ferric perchlorate [129] have been used. The physical properties, morphology and electrochemical characteristics of polypyrrole are influenced by the oxidising agents [141]. The influence of the acid concentration on the Fe^{3+} equilibria has been studied during the synthesis of a polypyrrole film on a non-conducting substrate [142].

The optimal degree of doping for polypyrrole has been found to be 0.25-0.33 with the best electrical properties of the polymer. This means that every three or four repeat units carry a positive charge neutralised with a counterion [143,144]. Various doping agents including p-toluenesulfonic acid [145], anthraquinone-2-sulfonic acid, 2-naphthalenesulfonic acid, and trichlorobenzenesulfonic acid [146-148] have also been used. If ferric chloride is used as an oxidant, the counterion is most likely Cl^- , the polymer is not very stable due to the relatively high mobility of the chloride ion [50]. Investigators at Milliken Research Corporation found a significant dependence of electrical properties of the polypyrrole on the dopant used. Aromatic sulfonic acids such as benzenesulfonic acid, 4-toluenesulfonic acid, naphthalenesulfonic acid and anthraquinone-2-sulfonic acid can be added to lead to a mixture of counterions in the polymer. A more planar dopant ion leads to the formation of more conductive polypyrrole films [50,51]. Meantime, investigation of substrate surface effect indicates that conductivity and adhesion can be optimised by tuning the hydrophobicity of the substrate surface [144].

1.3.4.2. Polyaniline Coated Textiles

The technique of impregnating cellulose fibres with aniline black has been known for a long time as a dyeing process, although not for conductive purposes [149]. The first *in-situ* polymerisation of aniline on a textile was reported by Milliken Research Corporation [35] and then has been used by other researchers [36,150,151]. In order to obtain polymerisation on the textile surface, the polymerisation process must be carefully controlled due to the highly toxic benzidine moiety formed during the oxidative polymerisation reaction under acidic conditions. Usually the polymerisation is initiated by using a persulfate catalyst like potassium or ammonium persulfate in aqueous media under acidic conditions, in which very dilute monomer solution is used ($\sim 0.03 \text{ molL}^{-1}$) [50].

Several variations on preparation of conductive polyaniline coated fabrics have been reported. Poly (vinyl alcohol) fibres were coated with polyaniline by *in-situ* polymerisation at the Huazhong University in China [152]. A continuous process to treat textiles with polyaniline was carried out by the Atomic Energy Commission in France [153,154]. Another similar process was patented by researchers at the E.I. DuPont de nemous Co. [155]. The textile substrates and fibres were first soaked with a solution containing aniline monomer and hydrochloric acid and then exposed to the oxidising agent. Compared with polypyrrole-coated textiles, it is necessary to wash with water containing sufficient amounts of the counterions after polymerisation. The polyaniline-coated fabric has been washed in 2 M hydrochloric acid solution and then dried. This process results in a uniform, coherent layer of chloride-doped polyaniline after washing three times with hydrochloric acid solution [153,154].

Recently, a series of experiments on various textile fibres in yarns treated with aniline at different oxidative polymerisation conditions have been carried out by Mehdi Nouri *et al* [149]. Coating of polyaniline on nylon, cotton, and acrylics has been found to be more effective in increasing conductivity than polyaniline on polyester and wool yarns [149]. Surface treatment such as plasma treatment has been applied to the fabrics in order to improve surface adhesion and increase polyaniline deposition. With oxygen plasma treatment, polar groups such as -OH and -OOH are introduced onto the surface of nylon 6 fibre. These polar groups increase surface activity, promote polymerisation and result in higher electrical conductivity [156].

1.3.4.3. Properties of Conductive Textiles

With few exceptions, the mechanical properties of conductive polymers are rather poor due to the cross-linked nature and aromatic character of the backbone [50]. Polypyrrole with a rigid chain is brittle [157] and fractures at low strain [158]. By introducing conducting polymers into suitable materials, mechanical properties of the coated textiles remain the same as the textile substrate, with minor variations depending on process conditions. Nylon Lycra is one such fabric, being highly elastic to large strain and readily coated with polypyrrole. The strain gauge characteristics of polypyrrole-coated nylon Lycra have been recently investigated [159,160].

The electrical properties of conducting textiles depend on the mass of the substrate, the individual textile fibre, the thickness of polymer coating and the conductivity of the coated polymers. Volume conductivities of polyaniline-coated textiles have been reported to be as high as 20 Scm^{-1} , whereas polypyrrole-coated fabrics have been

measured in the 100 Scm^{-1} range [50]. The resistance of conducting textiles can be measured using four point-probe or two point-probe techniques and normally expressed as a sheet resistance in ohms per square rather than a volume conductivity.

Conducting polymer coated textiles are much less stable in air due to the reaction with oxygen. It has been proposed that the reaction of oxygen with the polymer backbone results in loss of conjugation [161]. These defects inhibit charge carrier mobility, effectively decreasing the conductivity. The polymerisation of pyrrole with ferric chloride on the textiles results in a significant amount of chloride doping in the polypyrrole. Investigators at Milliken Research Corporation have shown that polypyrrole powders with higher chlorine contents display lower stabilities [50]. The chloride-free conducting textiles show no measurable decrease in conductivity after 30 days at 100°C in an argon atmosphere [162]. The thermal stability of polyaniline-nylon 6 composite fabrics has been studied by Kyung Wha Oh *et al* [163]. A series of inorganic and organic dopants have been used in the *in-situ* polymerisation. Generally, stability of the electrical conductivity of organic aryl sulfonic acid doped polyaniline-nylon 6 fabrics is better than that of HCl doped materials. The thermal stability of the conductivity increases as the molecular weight of the dopant increase, since dopants of higher molecular weight cannot be liberated during heat treatment [163].

1.4. AIMS OF THE PROJECT

The general aim of the project is to study the preparation and characterisation of conducting polymer coated textiles, especially to explore the feasibility of their

application as wearable strain-gauge sensors. Polypyrrole and polyaniline coated textiles have been chosen for this study.

Due to the ease of synthesis, high conductivity and low cost, one of the most useful methods is to coat textiles with a thin layer of conducting polymers using *in-situ* chemical polymerisation. Other techniques used to grow a thin polymer film on the fabric surface have also been investigated. The work can be divided into three sections.

1. Preparation and characterisation of polypyrrole coated textiles

In this section various processing methods for the synthesis of conductive fabrics based on polypyrrole and using different reaction conditions have been studied. The mechanical and electrical properties have been investigated. A particular goal is to optimise strain gauge characteristics on the polypyrrole coated textiles. This part includes Chapters 3 and 5.

2. Preparation and characterisation of templated polyaniline coated textiles

In-situ templated polymerisation has been used to prepare conductive polyaniline coated textiles. Fabrics have been made conductive by techniques such as dyeing textiles with template molecules followed by coating them with conductive polyaniline. The water-soluble conductive poly (2-methoxyaniline-5-sulfonic acid) (PMAS) has recently been employed as a template for polyaniline in preparing conductive textiles. The possibility of developing templated fabrics as a strain sensor has also been studied. This section is described in Chapter 4 and 5.

3. Applications of conducting polymer coated textiles

It is well known that conducting polymers coated substrates have currently been used in many applications. Chapter 6 describes a preliminary study to assess the feasibility of a strain gauge produced from conducting polymers coated fabrics. In addition, the study investigates the possibilities and potential for further study in this field.

1.5. REFERENCES

1. H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, (1977) 578.
2. E. M. Conwell, L. J. Rothberg, *Sci. Spectra.*, 5 (1996) 64.
3. A. G. MacDiarmid, J. C. Chiang, A. E. Richter, N. L. D. Somasiri, A. J. Epstein, *Conducting Polymers* ed.; Reidel: Dordrecht, Holland, 1975.
4. R. F. Service, *Science*, 290 (2000) 425.
5. J. Causley, *BSc (Honours) Thesis*, University of Wollongong, Australia, 2002.
6. D. Kincal, A. Kamer, A. D. Child, J. R. Reynold, *Synth. Met.*, 92 (1998) 53.
7. N. T. Kemp, G. U. Flanagan, A. B. Kaiser, H. J. Trodahl, B. Chapman, A. C. Partridge, R. G. Buckley, *Synth. Met.*, 101 (1999) 3.
8. H. L. Ge, Y. C. Lin, *Sensors and Actuators B Chemical*, 21 (1994) 57.
9. T. C. Pearce, J. W. Gardener, S. Friel, P. N. Bartlett and N. Blair, *Analyst*, 118 (1993) 371.
10. P. Burgmayer, R. W. Murray, *J. Am. Chem. Soc.*, 104 (1982) 6139.
11. P. Burgmayer, R. W. Murray, *J. Electroanal. Chem.*, 147 (1983) 339.
12. P. Burgmayer, R. W. Murray, *J. Phys. Chem.*, 88 (1984) 2515.
13. H. Zhao, W. E. Price, G. G. Wallace, *J. Electroanal. Chem.*, 334 (1992).
14. A. Mirmohseni, W. E. Price, G. G. Wallace, H. Zhao, *J. Intell. Mat. Sys. Struct.*, 4 (1993) 43.
15. H. Zhao, W. E. Price, G. G. Wallace, *J. Membr. Sci.*, 87 (1994) 47.
16. H. Zhao, W. E. Price, P. R. Teasdale, G. G. Wallace, *React. Polym.*, 23 (1994) 213.
17. D. Zhou, H. Zhao, W. E. Price, G. G. Wallace, *J. Membr. Sci.*, 98 (1995) 173.

18. A. Mirmohseni, W. E. Price, G. G. Wallace, *J. Membr. Sci.*, 100 (1995) 239.
19. H. Zhao, W. E. Price, C. O. Too, D. Zhou, G. G. Wallace, *J. Membr. Sci.*, 119 (1996) 199.
20. G. G. Wallace, G. Spinks, P. R. Teasdale, *Conducting Electroactive Polymers*, Technomic, New York, 1998.
21. P. Novak, W. Vielstich, *J. Electrochem. Soc.*, 137 (1990) 1973.
22. R. C. D. Peres, M. A. De Paoli, S. Panero, B. Scrosati, *J. Power Source*, 40 (1992) 299.
23. W. Wernet, M. Monkenbusch, G. Wegner, *Mol. Liq. Cryst.*, 118 (1985) 193.
24. K. Nishio, M. Fujimoyo, T. Suzuki, *J. Power Sources*, 34 (1991) 153.
25. T. Matsunaga, H. Daifuku, T. Nakajima, T. Dwagoe, *Polym. Adv. Tech.*, 1 (1990) 33.
26. A. Akelah, *J. Mater. Sci.*, 21 (1986) 2978.
27. P. May, *Physical World*, 8 (1995) 52.
28. A. Ivaska, *Electroanalysis*, 3 (1991) 247.
29. E. Smela, *J. Micromec. Microeng.*, 9 (1999) 1.
30. C. Jerome, D. Labaye, I. Bodart, R. Jerome, *Synth. Met.*, 101 (1993) 3.
31. J. M. Kim, S. M. Chang, H. W. Lee, Y. S. Kwon, Y. H. Oh, *Synth. Met.*, 85 (1997) 1371.
32. B. P. Belle, G. Hagen, S. Sunde, R. Odegard, *Synth. Met.*, 54 (1993) 315.
33. F. Jonas, L. Schrader, *Synth. Met.*, 41 (1991) 831.
34. A. J. Epstein, J. Yue, *U.S. Patent* 5, 237, 991, 1991.
35. R. V. Gregory, W. C. Kimbrell, and H. H. Kuhn, *Synth. Met.*, 28 (1989) 823.
36. E. M. Genies, C. Petrescu, and L. Olmedo, *Synth. Met.*, 41, (1991) 655.

37. H. H. Kuhn, and W. C. Kimbrell, *U.S. Patents*, 4,803,096 (1989) and 4,975,317 (1990).
38. H. Shirakawa, and S. Ikeda, *Polym. J.*, 2 (1971) 231.
39. I. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Sci, Polym. Chem. Ed.*, 12 (1974) 11.
40. S. P. Armes, *Synth. Met.*, 20 (1987) 365.
41. A. F. Diaz and K. K. Kanazawa, *J. C. S. Chem. Comm.*, (1979), 635.
42. K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Wwak, J. A. Logan, J. F. Rabolt, and G. B. Street, *J. C. S. Chem. Comm.*, (1979) 854.
43. K. J. Kim, P. V. Chen, D. E. Wiley and A. G. Fane, *J. Membr. Sci.*, 80 (1993) 241.
44. W. R. Bowen, R. S. Kingdon, and H. A. M. Sabuni, *J. Membr. Sci.*, 40 (1989) 219.
45. V. Bocchi, G. P. Gardini, *J. Chem. Soc., Chem., Commun.*, (1986) 148.
46. S. P. Armes and B. Vincent, *J. Chem. Soc., Chem. Commun.*, (1987) 287.
47. H. Eisazadeh, G. Spinks, and G. G. Wallace, *Material Forum*, 16 (1992) 341.
48. V. Bocchi and G. P. Gardini, S. Rapi, *J. Mat. Sci. Lett.*, 6 (1987) 1283.
49. L. F. Warren, J. A. Walker, D. P. Anderson, and C. G. Rhodes, *J. Electrochem. Soc.*, 136 (1989) 2286.
50. H. H. Kuhn and A. D. Child, "Electrically Conducting Textile", *Handbook of Conducting Polymers, Second Edition*, Marcel Dekker, Inc. New York, 1998. pp 994.
51. N. V. Bhat and Y. B. Shaikh, *J. Appl. Polym. Sci.*, 53 (1994) 187.
52. J. Prejza, I. Lundström and T. Skotheim, *J. Electrochem. Soc.*, 129 (1982) 1685.
53. G. B. Street, T. C. Clarke, M. Krounbi, K. K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, and G. Weiser, *Mol. Cryst. Liq. Cryst.*, 83 (1982) 253.

54. L. L. Miller, B. Zinger, Q. X. Zhou, *J. Am. Chem. Soc.*, 109 (1987) 2267.
55. T. Matencio, M. A. D. Paoli, R. C. D. Peres, R. M. Torresi, S. I. Torresi, *Synth. Met.*, 72 (1995) 59.
56. C. Zhong, K. Doblhofer, *Electrochimical Acta.*, 35 (1990) 1971.
57. P. Pickup, *J. Electroanal. Chem.*, 225 (1987) 273.
58. A. Michalska, A. Lewenstam, and A. Ivaski, A. Hulanicki, *Electroanalysis*, 5 (1993) 261.
59. P. Novak, and W. Vielstich, *J. Electrochem. Soc.*, 137 (1990) 1036.
60. P. Novak, and W. Vielstich, *J. Electrochem. Soc.*, 137 (1990) 1681.
61. F. Berk, U. Sarsch and R. Michaelis, *J. Electroanal. Chem.*, 169 (1993) 3510.
62. J. Stejskal, P. Kratochvil and A. D. Jenkins, *Collect. Czech. Chem. Commun.*, 60 (1995) 1747.
63. I. D. Norris, L. A. P. Kane-Maguire and G. G. Wallace, *Macromolecules*, 31 (1998) 19.
64. E. M. Genies, A. Boyle, M. Lapkowski and C. Tsintavis, *Synth. Met.*, 36 (1990) 139.
65. F. Lux, *Polymer*, 35 (1994) 2915.
66. A. G. MacDiarmid, J. C. Chiang, M. Halpern, W. S. Huang, S. L. Mu, N. L. D. Somasiri, W. Wu and S. I. Yaniger, *Mol. Cryst.*, 121 (1985) 173.
67. A. G. MacDiarmid, N. L. D. Somasiri, W. R. Salaneck, I. Lundstrom, B. Liedberg, M. A. Hasan, R. Erlandsson and P. Konrasson, *Springer Series in Solid State Science*, Vol. 63, Springer, Berlin, 1985, pp 218.
68. P. N. Adams, P. J. Laughlin and A. P. Monkman, *Synth. Met.*, 76 (1996) 157.
69. P. N. Adams and A. P. Monkman, *Synth. Met.*, 87 (1997) 165.

70. J. Stejskal, A. Riede, D. Hlavata, J. Prokes, M. Helmstedt and P. Holler, *Synth. Met.*, 96 (1998) 55.
71. J. Stejskal, I. Sapurina, J. Prokes and J. Zemek, *Synth. Met.*, 105 (3) (1999) 195.
72. M. Vilcnik, M. Zigon, M. Zupan and A. Sebenik, *Acta Chimica Slovenica*, 45 (2) (1998) 172.
73. P. M. Beadle, Y. F. Nicolau, E. Banka, P. Rannou and D. Djurado, *Synth. Met.*, 95 (1) (1998) 29.
74. P. N. Adams, L. Abell, A. Middleton and A. P. Monkman, *Synth. Met.*, 84 (1) (1997) 61.
75. E. M. Genies, C. Tsintavis and A. A. Syed, *Mol Cryst., Liq. Cryst.*, 121 (1985) 181.
76. H. Kuzmani, E. M. Genies and A. A. Syed, *Springer Series in Solid State Science, Vol. 63*, Springer, Berlin, 1985, PP 223; H. Kuzmani, N. S. Sariciftci, *Synth. Met.*, 18 (1987) 353.
77. R. L. Hand and R. F. Nelson, *J. Electrochem. Soc.*, 125 (1978) 1059.
78. R. L. Hand and R. F. Nelson, *J. Am. Chem. Soc.*, 96 (1974) 850.
79. L. T. Yu, M. S. Borrdon, M. Josefowicz, G. Belogrey, F. H. Cristofini and R. Buvet, *J. Polym. Sci.*, 10 (1987) 2931.
80. H. A. Pohl and E. H. Engelhardt, *J. Phys. Chem.*, 66 (1962) 2085.
81. D. E. Stilwell and S. M. Park, *J. Electrochem. Soc.*, 135 (1998) 2254.
82. F. L. Klavetter and Y. Cao, *Synth. Met.*, 55 (1993) 989.
83. K. Tzou and R. V. Gregory, *Synth. Met.*, 47 (1992) 267.
84. M. Doriomedoff, F. H. Cristofini, R. De Surville, M. Jozefowicz, L. T. Yu and R. Buvet, *J. Chem. Phys.*, 68 (1971) 1055.

85. S. Shimizu, T. Saitoh, M. Uzawa, M. Yuasa, T. Maruyama, K. Watanabe, *Abstracts, International Conference on Science and Technology of Synthetic Metals*, Snow Bird, Utah 1996, pp 328.
86. S. Shimizu, T. Saitoh, M. Uzawa, M. Yuasa, K. Yano, T. Maruyama, K. Watanabe, *Synth. Met.*, 85 (1997) 1337.
87. W. Lee, G. Du, S. M. Long, A. J. Epstein, S. Shimizu, T. Saitoh, M. Uzawa, *Synth. Met.*, 84 (1997) 807.
88. R. Guo, J. N. Barisci, P. C. Innis, C. O. Too, G. G. Wallace, D. Zhou, *Synth. Met.*, 114 (2000) 267.
89. D. Zhou, P. C. Innis, G. G. Wallace, S. Shimizu, S.-I. Maeda, *Synth. Met.*, 114 (2000) 287.
90. G. G. Wallace, G. M. Spinks, L. A. P. Kane-Maguire, P. R. Treasdale, *Conductive Electroactive Polymers, Intelligent Materials Systems, Second Edition*, CRC Press LLC, 2003.
91. R. P. McCall, J. M. Ginder, J. M. Leng, H. J. Ye, S. K. Manohar, J. G. Masters, G. E. Asturias, A. G. MacDiarmid and A. J. Epstein, *Phsy. Rev.*, 41 (1990) 5202.
92. E. V. Strounina, *PhD Thesis*, University of Wollongong, Australia, 2002.
93. I. Norris, *PhD Thesis*, University of Wollongong, Australia, 1999.
94. H. L. Needles, *Handbook of TEXTILE FIBERS, DYES, and FINISHES*. Garland STPM Press, New York & London. 1981, pp 1-3, 107, 110, 146
95. E. P. G. Gohl, L. D. Vilensky, *Textile Science*, Longman Cheshire Pty Limited, Melbourne, 1980, pp 4-5, 40-54, 65-71, 71-79, 89.
96. I. B. Wingate, *Textile Fabrics and Their Selection, Fourth Edition*, Prentice-Hall, Inc., 1955, pp 309-311.
97. A. E. Henderson, *Wool and Woolclassing*, A. H. & A. W. REED, 1965, pp 20.

98. M. Lewin, E. M. Pearce, ed., *Handbook of Fiber Chemistry, Second Edition*, Marcel Dekker, Inc., 1998, pp 390-391.
99. J. E. McIntyre, *The Chemistry of Fibres*, Edward Arnold (Publisher) Limited, London, 1971, pp 41.
100. M. L. Joseph, *Essentials of Textiles*, Holt, Rinehart and Winston, 1976, pp 100, 168-180.
101. A. K. Sen, *Coated Textiles*, Technomic Publishing Company, Inc., 2001, pp 55-56, 63, 67-69, 193-197.
102. E. Miller, *Textiles Properties and Behaviour in Clothing Use*, Redwood Books, London, Great Britain, 1995, pp 10-11, 81-83, 95-102.
103. P. G. Tortora, *Understanding Textiles*, Macmillan Publishing Co., Inc., New York, USA, 2nd Edition, 1982, pp 116-117, 152-157.
104. R. E. Griffith, M. D. Potter, B. P. Corbman, *Fibre to Fabric, Australian Edition*, McGraw-Hill Book Company, Australia, 1970, pp 331-336.
105. R. W. Moncrieff, *Man-Made Fibres*, Heywood & Company Ltd. London, 1963, pp 402.
106. N. Hollen, J. Saddler, *Textile, Fourth Edition*, The Macmillan Company, New York, 1973, pp 98-99, 101-102, 113.
107. V. H. Elsasser, *Textiles: Concepts and Principles*, Delmar Publishers, 1972, pp 138, 142.
108. E. K. Sichel (ed.) *Carbon Black Polymer Composites*, Marcel Dekker, New York, 1982.
109. W. Löbel, *Mater. Sci.*, 16 (1990) 73.
110. D. Satas (ed.), *Coating Technology Handbook*, Marcel Deckker, New York, 1981, pp 187, 217, 691.

111. R. B. Bjorklund and I. Lundström, *J. Electron. Mater.*, 13 (1984) 211.
112. H. H. Kuhn and W. C. Kimbrell, *U. S. Patent* 4,975,317 (1990).
113. H. H. Kuhn and W. C. Kimbrell, *U. S. Patent* 4,981,718 (1991).
114. H. H. Kuhn and W. C. Kimbrell, *U. S. Patent* 5,030,508 (1991).
115. H. H. Kuhn, *U. S. Patent* 5,108,829 (1992).
116. S. Tan, H. Ge, *Polymer*, 37 (1996) 965.
117. S. Tan, H. Ge, *New Polym Mater.*, 5 (1998) 169.
118. P. R. Newman, *U. S. Patent* 4,617,228 (1986).
119. S. N. Bhadani, S. K. Sen Gupta, G. C. Sahu, and M. Kurmari, *J. Polym. Mater.*, 13 (1996) 61.
120. S. N. Bhadani, S. K. Sen Gupta, G. C. Sahu, and M. Kurmari, *J. Appl. Polym. Sci.*, 61 (1996) 207.
121. S. N. Bhadani, M. Kurmari S. K. Sen Gupta, and G. C. Sahu, *J. Appl. Polym. Sci.*, 64 (1997) 1073.
122. S. Li, C. W. Macosko, and H. S. White, *Adv. Mater.*, 5 (1993) 575.
123. X. Jin, K. Gong, *J. Coated Fabrics*, 26 (1996) 37.
124. M. Selim, M. Dawy, and A. Sawaby, *Polym. Plast. Technol. Engng.*, 38 (1999) 713.
125. S. P. Armes and M. Aldissi, *Polymer*, 31 (1990) 569.
126. P. Tadros, S. P. Armes, and S. Y. Luk, *J. Mater. Chem.*, 2 (1992) 125.
127. H. Naarmann, *Eur. Patent* 0.133,939 B1 (1985).
128. M. Ito, Y. Katagawa, H. Tajima, Y. Sawachika, M. Kimura, and I. Mizoguchi, *Jpn. Patent* 62,275,137 A2 (1987).
129. H. Naarmann and W. Heckmann, *Eur. Patent* 206,133 A1 (1986).
130. T. Mitsutake, S. Narisawa, and Y. Yoshii, *Jpn. Patent* 63,213,518 A2 (1988).

131. S. Hishida, Electrically conductive synthetic fibers, *Jpn. Patent* 61,282,479 A2 (1986).
132. R. Qian, Y. Chen, J. He, M. Wu and J. Qiu, *Chinese Patent*, 86,101,389 A (1987).
133. K. Yasuba and M. Matsunaga, *Jpn. Patent*, 63,042,972 A2 (1988).
134. S. Miyata, and T. Ozio, *U.S. Patent*, 4,699,804 (1987).
135. T. Mizuki and K. Watanabe, *Jpn. Patent*, 01,266,280 (1989).
136. G. W. Bartholomew, K. Jongchul, R. A. Volpe, and D. J. Wenzel, *U. S. Patent*, 5,211,810 (1993),
137. M. Nakata, Y. Shiraishi, M. Taga, and H. Kise, *Makromol. Chem.*, 193 (1992) 765.
138. J. H. Han, T. Motobe, Y. E. Whang, and S. Miyata, *Synth. Met.*, 45 (1991) 261.
139. D. R. Rueda, C. Arribas, F. J. Balta-Calleja, and J. M. Palacios, *Synth. Met.*, 52 (1992) 101.
140. A. Bhattacharya, A. De, and S. N. Bhattacharya, *Synth. Met.*, 65 (1994) 35.
141. K. Nishio, M. Fujimoto, O. Ando, H. ONO, T. Murayama, *J. Appl. Electrochem.*, 26 (1996) 425.
142. R. C. G. M. van den Schoor, R. H. M. van de Leur, J. H. W. de Wit, *Synth. Met.*, 102 (1999) 1404.
143. J. K. Avlyanov, H. H. Kuhn, J. Y. Josefowicz and A. G. MacDiarmid, *Synth. Met.*, 84 (1997) 153.
144. M. Aldissi (ed), *Intrinsically Conducting Polymers: An Emerging Technology*, Kluwer Academic publishers, 1993, pp 25-34.
145. J. A. Walker, L. F. Warren, and E. F. Witucki, *J. Polym. Sci., Part A: Polym. Chem.*, 26 (1988) 1285.

146. J. C. Thieblemont, M. F. Planche, C. Petrescu, J. M. Bouvier, and G. Bidan, *Synth. Met.*, 59 (1993) 81.
147. H. H. Kuhn, *Sen-i Gakkai Symp. Prepr.*, A (1993)103.
148. H. H. Kuhn, Characterization and application of polypyrrole-coated textiles, in *Intrinsically Conducting Polymers* (M. Aldissi, ed.), Kluwer, Dordrecht, 1993, pp 25.
149. M. Nouri, M. H. Kish, A. A. Entezam and M. Edrisi, *Iranian Polymer Journal*, 9 (2000) 49.
150. D. C. Trivedi and S. K. Dhawan, *Synth. Met.*, 59 (1993) 267.
151. M. Ikuo, *Jpn. Patent*, 03,119,612 (1991).
152. H. Liu, X. Li, X. Gou, and H. Xie, *Gaofenzi Cailiao Kexue Yu Gangcheng*, 10 (1994) 22.
153. J. L. Forveille and L. Olmedo, *Synth. Met.*, 65 (1994) 5.
154. F. Jousse, L. Delnaud, and L. Olmedo, Processing of conductive fabrics in composite application, *40th Int. SAMPE Symp. Exhib.*, 1995, pp 360.
155. C. H. Hsu, *Eur. Patent*, 0 355 518 A2 (1990).
156. K. W. Oh, S. H. Kim, E. A. Kim, *J. Appl. Polym. Sci.*, 81 (2001) 684.
157. Y. Chen, R. Qian, G. Li, and Y. Li, *Polym. Commun.*, 32 (1991) 189.
158. D. Kelkar, N. Bhat, *Polymer*, 34 (1983) 986.
159. P. Whitten, *BEng Thesis*, University of Wollongong, Australia, 1998.
160. A. Mazzoldi, D. De Rossi, F. Lorussi, E. P. Scilingo, R. Paradiso, *AUTEX Research Journal*, 2 (2002) 4.
161. B. Ennis, V. Truong, *Synth. Met.*, 59 (1993) 387.
162. J. Moreland, *Master Thesis*, Clemson University, 1992.
163. K. W. Oh and K. H. Hong, *Textile Res. J.*, 71 (2001) 726.

CHAPTER 2

GENERAL EXPERIMENTAL TECHNIQUES

2.1. INTRODUCTION

This chapter describes the major preparation and characterisation methods employed in this thesis. The various preparation techniques used for polymer coating of textiles include:

- (1) *In-situ* (chemical oxidation) polymerisation.
- (2) Template polymerisation.
- (3) Chemical oxidation using vapour phase monomer.
- (4) Electrochemical polymerisation.

The various techniques used to characterise the coated fabrics prepared in this work include:

- (1) Electrochemical characterisation techniques, [cyclic voltammetry (CV)].
- (2) Determination of electrical conductivity by both two-probe and four-probe method.
- (3) UV-Vis spectroscopy.
- (4) Scanning Electron Microscopy (SEM).
- (5) Thermogravimetric analysis (TGA).
- (6) Monomer consumption determined by High Performance Liquid Chromatography (HPLC).
- (7) Instron testing to determine stress/strain curves.
- (8) Use of a SmartMotor to determine strain gauge characteristics at different frequencies.

All these methods will be discussed with a brief explanation of their theoretical aspects in this chapter. Detailed experimental procedures for these processes will be given elsewhere in each relevant chapter.

2.2. PREPARATION OF CONDUCTIVE POLYMER COATED TEXTILES

2.2.1. Chemical Polymerisation

Chemical polymerisation is carried out by mixing monomer, dopant and oxidant in a suitable solvent. The chemical method enables the preparation of these polymers on a large scale without requiring special equipment. Since it is desirable to utilise aqueous solutions, most of the research involving chemical oxidative polymerisation on substrates has employed the water-soluble monomers aniline and pyrrole as starting materials.

The polymerisation of pyrrole and aniline proceeds through the formation of radical cations that couple to form oligomers, which are further oxidised to form additional radical cations; as previously described in Chapter 1 (1.1.2 and 1.1.3). The polymerisation rate is controlled by the concentration of monomer and oxidant as well as temperature.

2.2.1.1. *In-situ* Polymerisation (Chemical Oxidation) Process

The *in-situ* polymerisation process is a process where the monomer such as pyrrole is polymerised from an aqueous solution of oxidant and deposits onto the surface of the

textile fabrics. At first a piece of fabric is soaked in an aqueous solution containing both monomer and dopant for about 20 minutes. Then an oxidant solution is added into the container to initialise the polymerisation on the fabric surface. At the end of the *in-situ* polymerisation, each fabric is covered with a thin layer of polymer. The coated fabric is then washed with excessive amounts of distilled water to remove starting materials. Figure 2.1 below shows the five steps used in an *in-situ* polymerisation process. M, OX and NDSA represent monomer, oxidant, and dopant used for *in-situ* polymerisation.

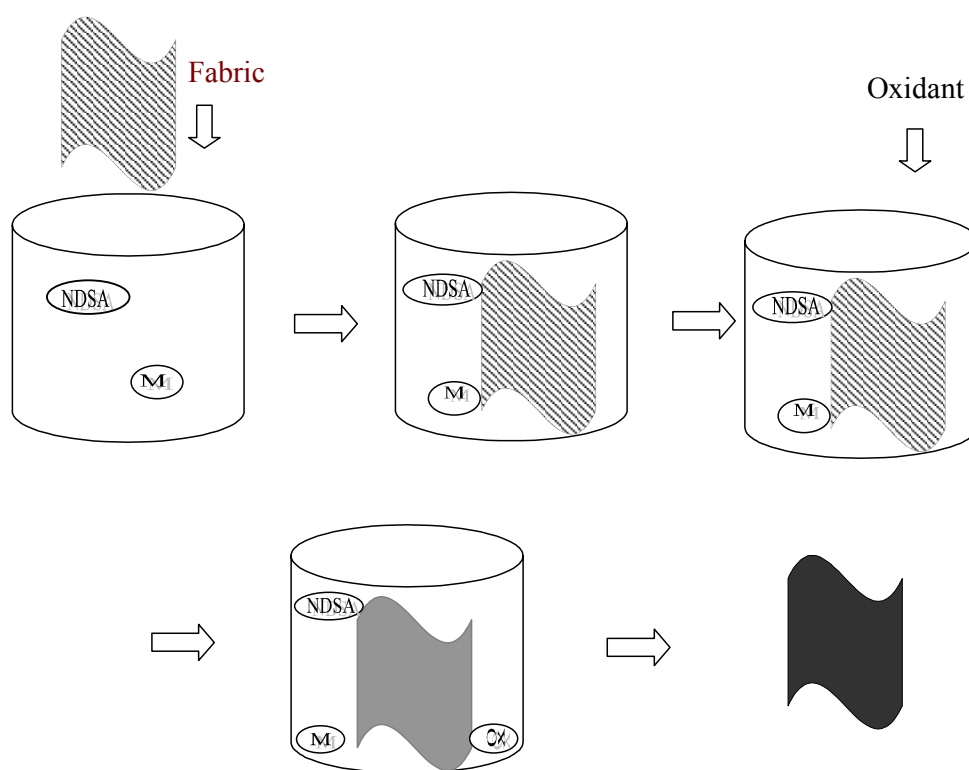


Figure 2.1. *In-situ* (chemical oxidation) polymerisation method used to coat fabrics.

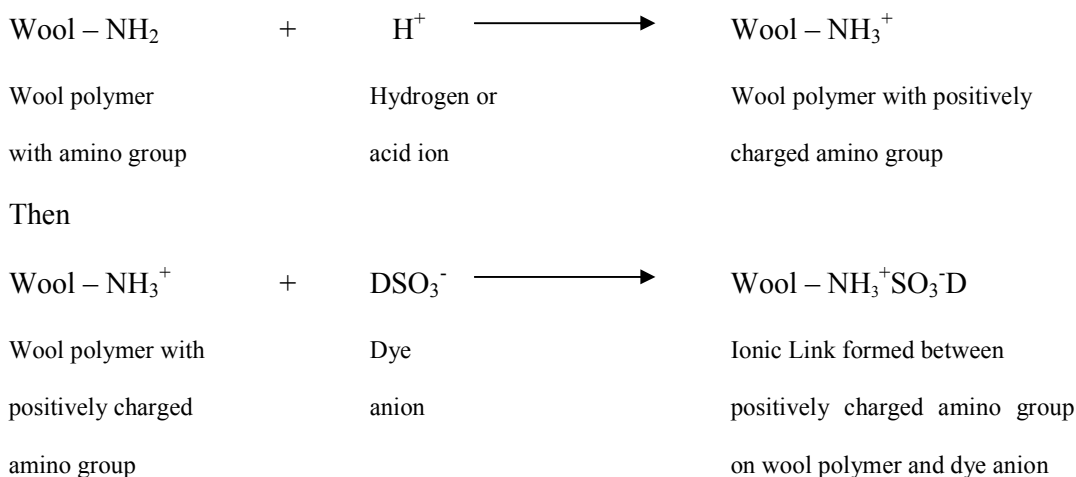
2.2.1.2. Template Polymerisation

Fabrics can be made electrically conductive by introducing a molecular template such as dyeing textile with template molecules followed by coating with conducting polymers.

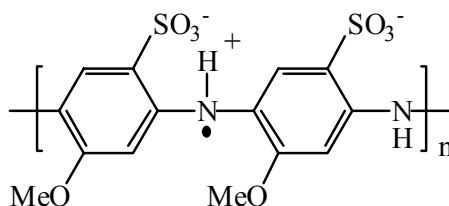
We have used a water-soluble poly (2-methoxyaniline-5 sulfonic acid) (PMAS) to facilitate the integration of conducting electroactive polymers (CEPs) into a range of conductive textiles. The template polymerisation method is composed of a “Two-Step” process as described below.

Step One: Integration of Molecular Template

Acid dyes are so called because they are usually used under acidic conditions. The application of acid dyes to textile fibres results in an ionic or salt link between the dye molecules and the fibres. Under this condition, the amino groups in wools become positively charged and will interact with the negatively charged dye-anion. This can be represented as follow [1]:



Water-soluble poly (2-methoxyaniline-5 sulfonic acid), structure shown below, has been used as a molecular template (details in Chapter 4). Figure 2.2 shows the dyeing process.



Poly (2-methoxyaniline-5 sulfonic acid (PMAS))

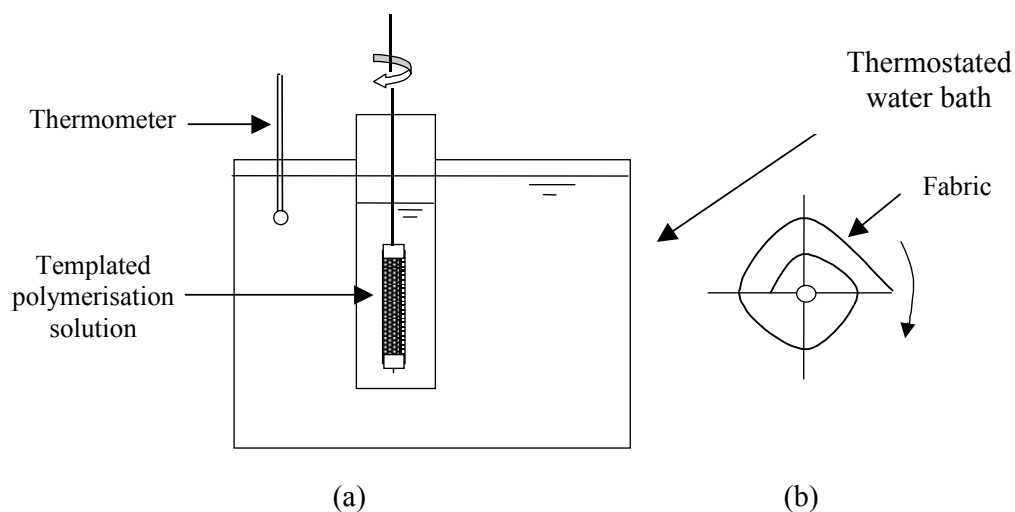


Figure 2.2. (a) Dyeing process of fabric (b) Top view of the fabric secured onto the spindle.

Step Two: Integration of Cationic Inherently Conducting Polymers (ICPs)

After uptake of PMAS the modified fabrics was exposed to aniline or pyrrole containing solutions and a chemical oxidant introduced. The sulfonate groups on the PMAS are negatively charge and aniline is primarily positively charge. PMAS served as a large molecular counterion that was integrated and essentially locked into the polyaniline chains (Figure 2.3). This approach is based on preferential electrostatic alignment of aniline monomer onto an anionic template to form templated polyaniline coated fabrics.

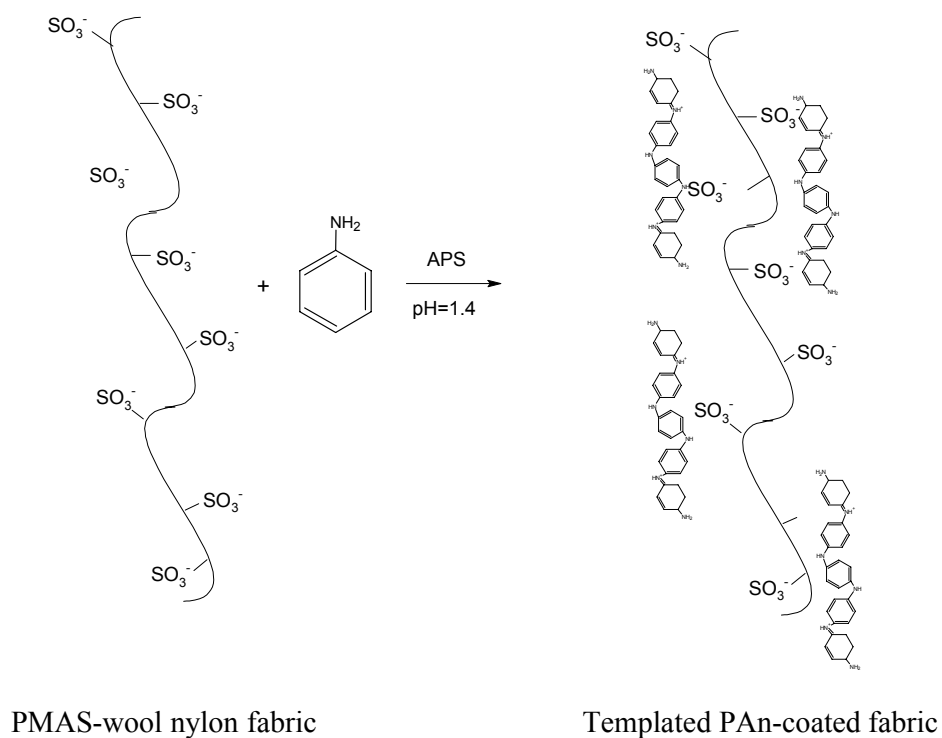


Figure 2.3. Template polymerisation of conducting polyaniline on the PMAS-treated fabric.

2.2.1.3. Chemical Oxidation Using Vapour Phase Monomer

Preparation of conducting polymer textiles can also be carried out in “two steps” instead of “one step” *in-situ* polymerisation. In a “two-step process”, coating is achieved by deposition of an oxidising agent on to the textile fabrics, followed by exposure to pyrrole monomer vapour. For example, Ge and Tan [2] used vapour-phase polymerisation to prepare polypyrrole-coated cotton fibres.

In vapour-phase polymerisation, the different fabrics are pre-wetted with an oxidizing agent in ethanol or methanol and then exposed to pyrrole vapour. Polypyrrole will subsequently deposit on the fabrics as the solvent vaporises (Figure 2.4).

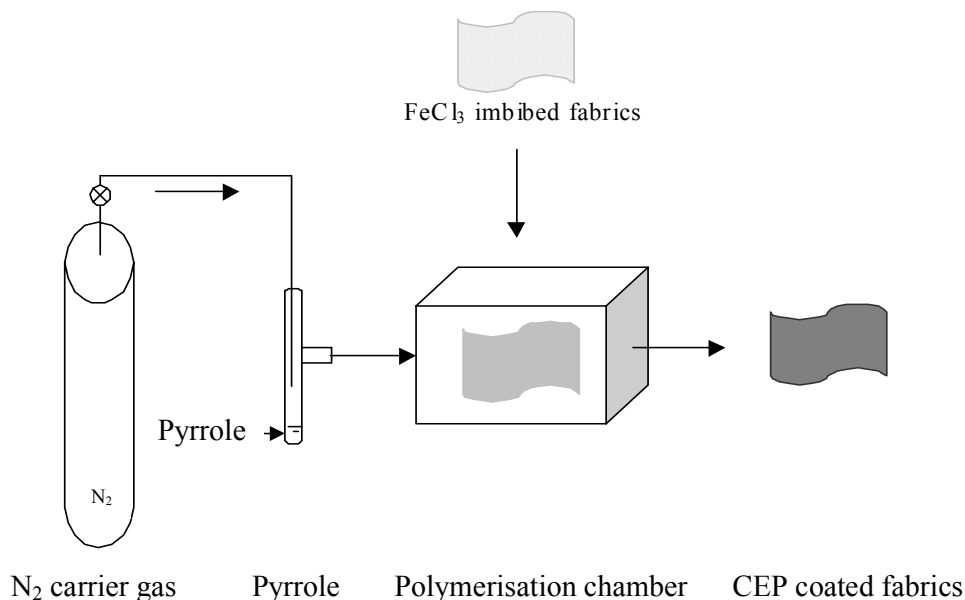


Figure 2.4. Vapour-phase polymerisation method.

2.2.2. Electrochemical Polymerisation

For electrochemical polymerisation, conducting polymer-coated textile can be prepared using a three-electrode voltammetric cell comprising a working electrode, a reference electrode and an auxiliary electrode. Usually, the working electrode is made of platinum [3], gold [4], glassy carbon [5], indium-tin oxide (ITO) coated glass [6], stainless steel, or reticulated vitreous carbon (RVC). The auxiliary electrode should have a large surface area so that it does not limit the passage of current. Auxiliary electrodes are usually made of platinum gauze or RVC. Galvanostatic polymerisation (current density of from 0.5 mAcm^{-2} to 2.0 mAcm^{-2}) was commonly used in this study.

Galvanostatic polymerisation is the most commonly used method for electrochemical polymerisation of conducting polymers [7,8]. During galvanostatic polymerisation, a constant current density is applied between the working and auxiliary electrodes. The thickness of the deposited polymer layer can be controlled by controlling current density and deposition time. In order to maintain current flow, monomer is oxidised at the anode and eventually forms a polymer coating. The potential of the working electrode vs a reference electrode is recorded as a function of time during the polymerisation process.

2.3. CHARACTERISATION METHODS FOR CONDUCTIVE POLYMER COATED TEXTILE

2.3.1. Cyclic Voltammetry (CV)

Cyclic voltammetry is one of the most common electrochemical techniques, and is extensively used for electrochemical characterisation of conducting polymers. In general, CV involves the measurement of current at the working electrode as a function of applied potential. The resulting current-potential plot is the cyclic voltammogram. CV is the most effective and versatile electrochemical technique available for the study of redox systems. In this work, CV was used for characterisation of the conductive polymer coated fabrics. Samples of conductive polymer coated fabrics measuring 2 cm x 1 cm were wrapped around reticulated vitreous carbon (RVC) as working electrode. An Ag/AgCl (3 M NaCl) reference electrode was used (Figure 2.5). Experiments were carried out using a Princeton Applied Research Model 363 potentiostat/galvanostat coupled to an ADInstruments PowerLab 4/20.

A typical cyclic voltammogram of polypyrrole-coated nylon Lycra doped with naphthalenedisulfonic acid in 1.0 M NaNO_3 is given in Figure 2.6. This shows the redox process of PPy/NDSA coated fabric with peak potentials $E_{p(c)}$ and $E_{p(a)}$ appearing at -0.53 and +0.35 V respectively when scanned between -1.0 V to +1.0 V at 100 mVs^{-1} . The oxidation and reduction of PPy/NDSA are accompanied by cation (Na^+) expulsion and insertion respectively, so that the overall charge neutrality of the polymer is maintained.

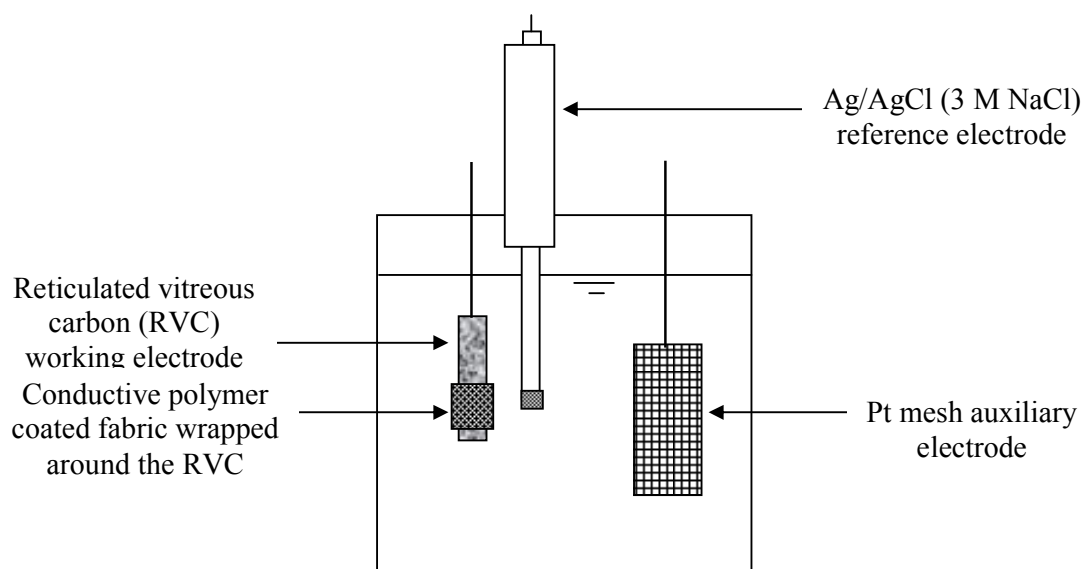


Figure. 2.5. Cyclic voltammetry cell for conducting polymer coated fabric.

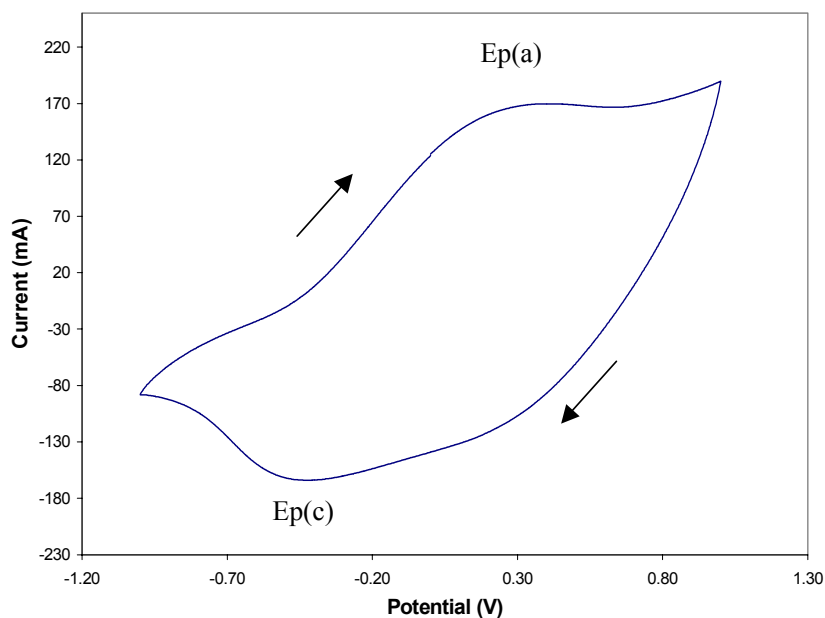


Figure 2.6. Cyclic voltammogram of PPy/NDSA coated nylon Lycra in 1.0 M NaNO_3 at a scan rate of 100 mVs^{-1} . The polypyrrole coated nylon Lycra was prepared using the *in-situ* method for 2 hours in an aqueous solution containing 0.015 M pyrrole, 0.04 M FeCl_3 and 0.005 M NDSA.

2.3.2. Electrical Conductivity

One of the most striking properties of conductive polymer coated fabrics is their ability to conduct electric current. The accurate measurement of electrical conductivity is a major step in understanding electronic fabrics. The conductivity of the conductive textile was measured in two different ways – i.e. the ASTM four point-probe technique [9] and the AATCC 76 two point-probe technique [10].

The ASTM method is a standard method applied to all kinds of materials that exhibit surface or volume resistivity within the range of $1\sim 10^{-7} \text{ (S cm}^{-1}\text{)}$. It is required that the

sample to be tested should have a uniform polymer layer and can be cut into a regular shape (such as a small strip 1.0 cm x 0.5 cm).

Another standard test method of conductivity measurement, AATCC-76, is available and has been used for the purpose of measuring the resistivity of textile fabrics in the textile industry. Resistivity can be measured with a standard ohmmeter capable of measuring values between 1 and 100 Mega ohms (4.0 cm x 4.0 cm).

In the ASTM method, two identical electrical connectors are used. The four electrodes on each connector are arranged in a pattern as shown in Figure 2.7. This method is widely used for the measurement of the electrical conductivity of conductive polymers and coated fabrics. The polymer-coated fabric to be tested is placed in contact with the four electrodes and tightly sandwiched with the other connector. A constant DC current is then applied between the two outer electrodes, which will generate a potential gradient along the current flow direction. According to Ohm's Law, the resistance of the material is proportional to the potential drop across the two inner electrodes. The resistivity of the polymer-coated fabric can then be calculated according to the cross-sectional area of the coated fabric, DC current applied and the potential drop across the two inner electrodes.

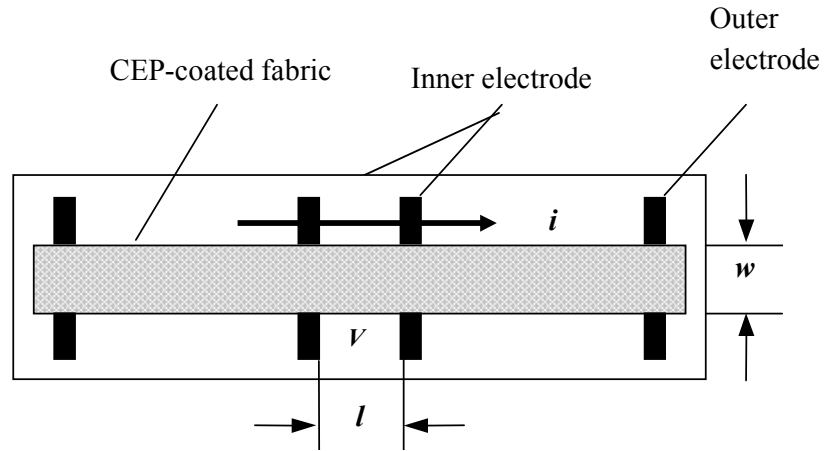


Figure 2.7. Top view of the ASTM four-point probe method for the measurement of the electrical conductivity of a piece of conductive fabric. The distance between the two inner electrodes is 0.2 cm. The sample is sandwiched with another connector. A constant current is applied between the two outer electrodes.

According to this method, the surface resistivity can be calculated as follows:

$$\rho_s = \frac{wv}{il} \quad (2.1)$$

Where ρ_s is the surface resistivity (Ω/Square), l is the distance between the two inner electrodes (cm), v is the potential drop across the inner electrodes (V), w is the sample width (cm) and i is the current applied (A).

A modified version of AATCC-76 method is used, with two parallel electrodes 12 cm long and 1.5 cm apart placed in contact with the fabric (Figure 2.8). The size of the test specimen should be such as to accommodate the width of the electrodes. After proper conditioning of the textile specimen, the electrodes of the ohmmeter are firmly placed on it ensuring good contact. The resistance is measured in both length and width directions after steady state is reached. The lower reading in each direction is recorded. The resistivity ρ_s in ohms per square is calculated according to:

$$\rho_s = \frac{Rw}{l} \quad (2.2)$$

Where ρ_s is the surface resistivity (Ω/\square), l is the distance between the two parallel electrodes (cm), R is the resistance of the fabrics measured in the ohmmeter and w is the sample width (cm).

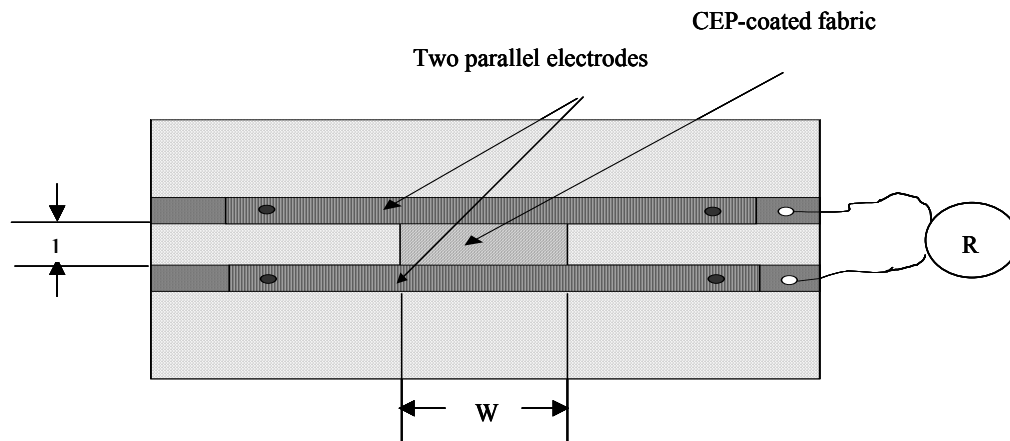


Figure 2.8. Top view of the AATCC-76 two-point probe method for the measurement of the electrical conductivity of a piece of conductive fabric. The distance between the two parallel electrodes is 1.5 cm. The sample is measured with a standard ohmmeter.

2.3.3. UV-Vis Spectroscopy

The UV-Vis spectra of conducting polymer solution and their coated fabrics were recorded between 190 nm and 1100 nm using a Shimadzu UV 1601 spectrophotometer [11]. Figure 2.9 shows the UV-Visible spectra of PMAS solution before and after dyeing the wool nylon Lycra fabric. The UV-Vis absorption spectra of the PMAS solution exhibit an intense, sharp peak at 474 nm and a broad peak at ca. 290 nm,

attributed to a $\pi - \pi^*$ transition band and a short wavelength polaron transition, respectively, characteristic of poly (2-methoxyaniline-5-sulfonic acid).

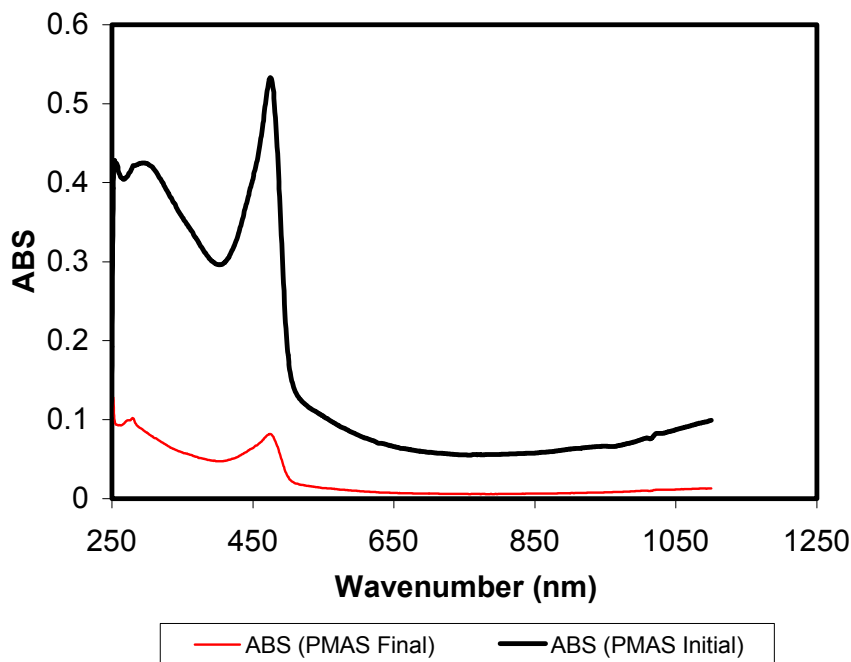


Figure 2.9. UV-Visible spectra of PMAS solution before and after dyeing the wool nylon Lycra fabric.

2.3.4. Scanning Electron Microscopy (SEM)

The morphology and microstructure of the conducting polymer-coated fabrics prepared in this work have been investigated using SEM. The images obtained were recorded using the Leica Model Stereoscan 440 scanning electron microscope at the Department of Materials Engineering, University of Wollongong. SEM samples, such as untreated fabrics, PPy-coated nylon Lycra, PMAS templated polyaniline coated fabrics, were sputter coated with a thin layer of gold to make them sufficiently conductive and were then cut into $0.5 \times 0.5 \text{ cm}^2$ pieces. Up to eight samples were placed on one sample holder. The SEM images were taken at different magnifications, varying between 500

and 30,000, in order to obtain detailed information on the samples. A typical SEM image of polypyrrole-NDSA coated nylon Lycra is given in Figure 2.10.

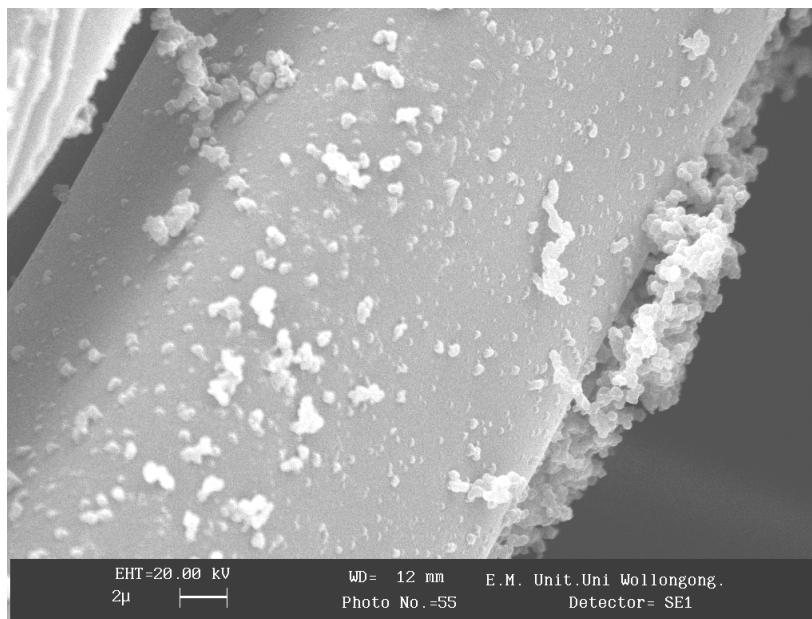


Figure 2.10. SEM image of a polypyrrole-NDSA coated nylon Lycra. The polypyrrole coated nylon Lycra was prepared by the *in-situ* method for 2 hours in an aqueous solution containing 0.015 M pyrrole, 0.04 M FeCl_3 and 0.005 M NDSA.

2.3.5. Thermogravimetric Analysis

Thermal gravimetry was carried out using a TGA 92 Thermoanalyzer, which is made up of the thermobalance in the strict sense including balance, furnace, gas circuit and power. A temperature programmer was used to increase temperature from room temperature to the required temperature at 10 °C per minute heating rate.

Thermal properties of different fabrics coated with different conducting polymers have been studied and results will be discussed in Chapter 3 and Chapter 4.

2.3.6. High Performance Liquid Chromatogram (HPLC)

High Performance Liquid Chromatogram (HPLC) is rapidly becoming the method of choice for separations and analysis in many fields. Almost anything that can be dissolved can be separated by HPLC with proper selection of HPLC column. An HPLC system offers a combination of speed, reproducibility and sensitivity.

The HPLC separation is achieved by injecting sample dissolved in a solvent into a stream of solvent (mobile phase) being pumped into a column packed with solid separating material (stationary phase). The interaction is a liquid-solid separation. It occurs when a mixture of compounds dissolved in a solvent either remain in the solvent or adsorb to the solid packing material in the column. Separation occurs on a reverse phase column due to each compound having a different partition rate between the solvent and the packing material. As a result, components with the highest affinity for the column packing are retarded and eluted last. These separated compounds are detected as they pass through a detector which sends signals to a recorder or computer thus detaining a chromatogram. The peak data of the chromatogram can be used to quantitate the amount of each material present with standard calibration [12, 13].

An LC-10AT Shimadzu Liquid Chromatograph with 5 μm spherical C18 column has been used for the determination of monomer concentration in this work. The consumption of aniline monomer in the polymerisation process has been determined by measuring aniline monomer concentrations before and after polymerisation-. The mobile phase composed of 10% methanol, 90% water with added (5 ml/L) ion pairing reagent tetrabutylammonium dihydrogen phosphate. The flow rate of 0.8 mlmin^{-1} was

maintained by a HPLC pump. Results will be discussed in the following chapters respectively.

2.3.7. Instron Testing to Determine Stress/strain Curves

All strain tests were performed using an Instron 4302 Universal Material Tensile Tester equipped with a computer interface for data collection. A 10 N and a 100 N load cell were used during the stain testing.

Rectangular samples, with dimensions 70 x 20 mm, were cut from the coated fabrics. They were mounted in the jaws of the Instron tensile machine. After being mounted in the Instron machine, approximately 50 mm of the sample remained free to be strained. The coated fabric was then stretched/released at a controlled speed. A typical speed of 100 mmmin⁻¹ was used. An illustration of the sample setup required for the force and resistance measurement is shown in Figure 2.11. The resistance of conductive polymer coated fabrics is calculated from the measured potential, using a Wheatstone bridge circuit, according to the equation:

$$R_I = R_2 / (V_{in}/E_0 + 0.5) - R_2 \quad (2.3)$$

Where R_I is the resistance measured, R_2 is the resistance of the known three resistors in the Wheatstone bridge circuit, V_{in} is the measured potential and E_0 is the applied potential of the battery.

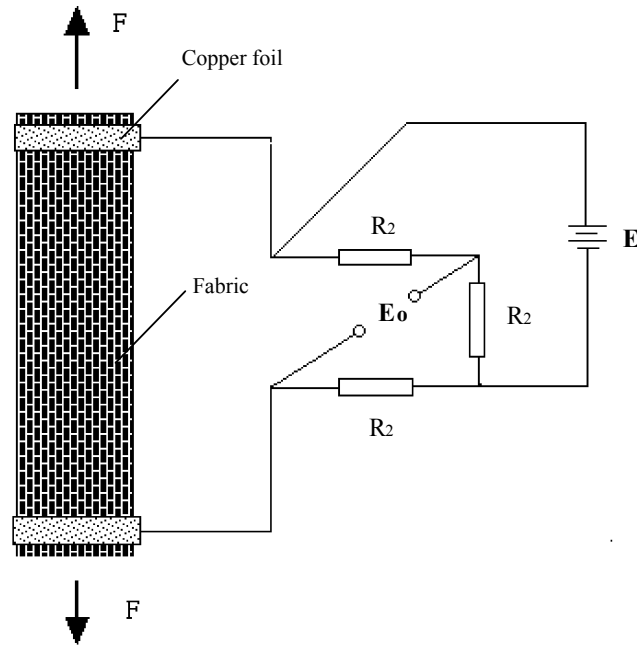


Figure 2.11. Wheatstone bridge electrical resistance vs. strain testing circuit.

Typical Resistance vs Strain and Force vs Strain responses of polypyrrole coated nylon Lycra fabric when stretched to 50% are given in Figure 2.12 and Figure 2.13 respectively. The resistance of polypyrrole coated nylon Lycra fabric decreased from $1630\ \Omega$ to $530\ \Omega$ when stretched from 0 to 50%. The drawing force increased 2.22 N when coated fabric was stretched to 50%.

Gauge factor (GF) is defined as the ratio of the fractional change in resistance to the fractional change in length:

$$GF = (\Delta R/R_0) / (\Delta l/l_0) \quad (2.4)$$

Where R_0 is the resistance of non-stretched fabric and l_0 is the length of non-stretched fabric sample.

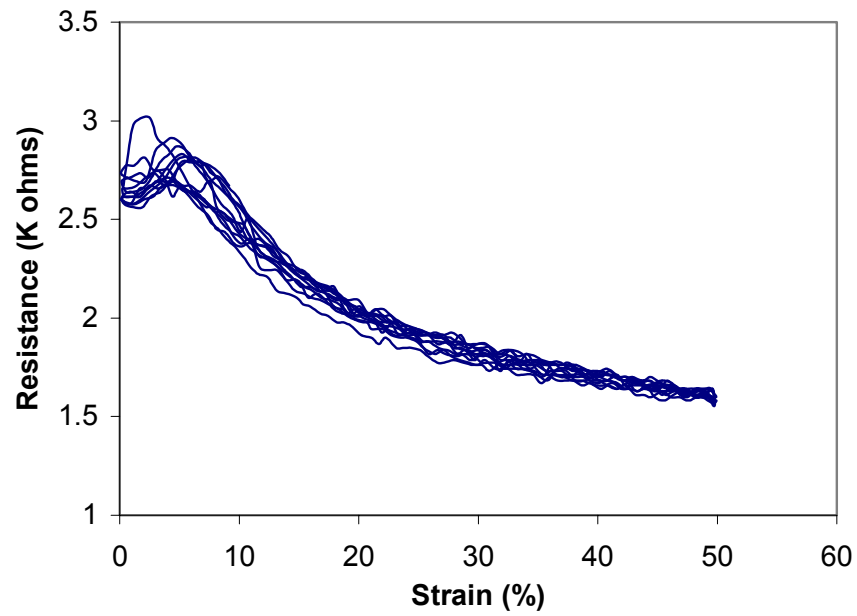


Figure 2.12. Resistance vs Strain of polypyrrole coated nylon Lycra fabric when stretched to 50%.

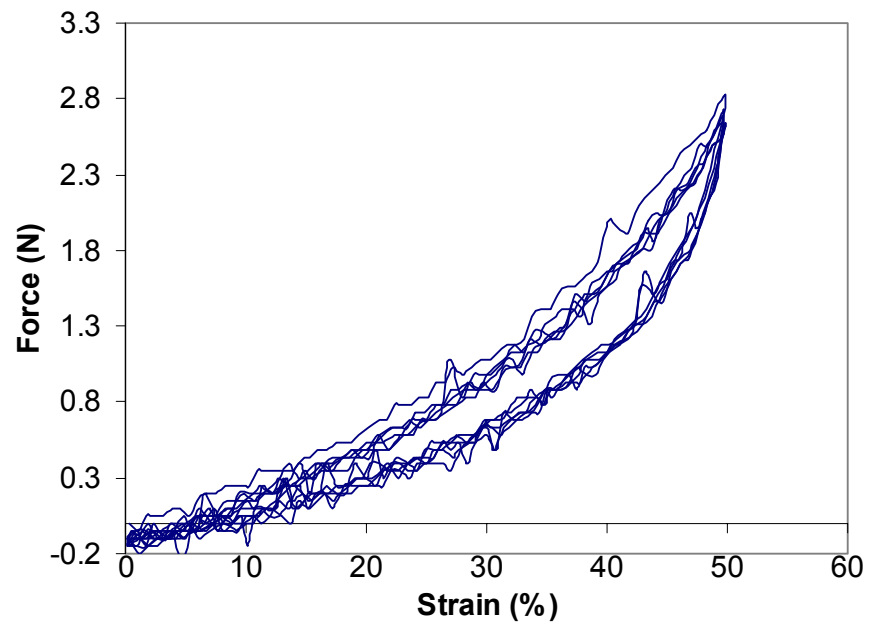


Figure 2.13. Force vs Strain of polypyrrole coated nylon Lycra fabric when stretched to 50%.

2.3.8. Use of “SmartMotor” to Determine Strain Gauge Characteristics at Different Frequencies

The dynamic strain gauge calibration system consisted of an Animatics Corp. SmartMotor™, a displacement transducer (Linear Variable Differential Transformer, or LVDT), and a 5 N load cell (Figure 2.14). Displacement and data collection were controlled by custom-written software (LabView 6i; National Instruments). The dynamic calibration system was capable of moving at velocities of up to 10 cm s^{-1} with displacements of up to 200 mm in 0.0016 mm steps. Fabric sensor samples were tested at frequencies up to 1 Hz and amplitudes up to 24 mm. Data were collected at 50 Hz and signals averaged to eliminate extraneous noise.

SmartMotor together with a load cell and LVDT have been fitted according to Figure 2.14. The load cell is capable of measuring forces up to 5 N while the LVDT provides more accurate position information than merely relying on the controller position signal which may have a time lag due to acceleration.

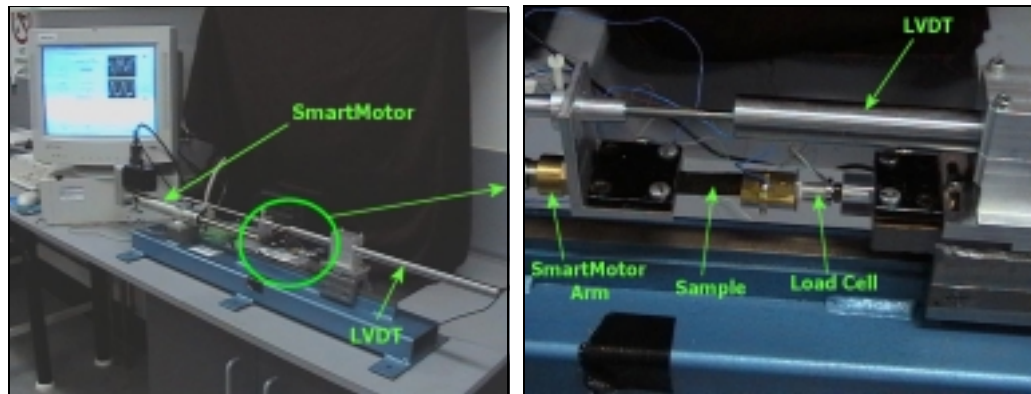


Figure 2.14. Dynamic calibration apparatus.

A voltage divider has been connected to the SmartMotor in order to measure the resistance of the coated fabric strips during the dynamic calibration process.

The system uses a voltage divider such that resistance can be calculated according to:

$$R_p = R_r (V_{ex} - V_m) / V_m \quad (2.5)$$

Where R_p is the resistance on the coated fabric and R_r is the resistance of the reference resistor, V_{ex} is the excitation voltage and V_m is the measured voltage during the dynamic calibration process.

The conductive fabrics strips were subjected to sinusoidal linear elongations, equating to strain amplitudes between 0% and 70%, at frequencies spanning 1 Hz to 3 Hz. The strains were applied in the direction of the fabric strip's highest compliance. The linear relationship between the applied strain and resistance was determined by plotting the average of the peak resistance values against the average of each strain interval. The linear range and gauge factor will be discussed in Chapter 5.

2.4. REFERENCES

1. E. P. G. Gohl, L. D. Vilensky, *Textile Science*, Longman Cheshire Pty Limited, Melbourne 1980, pp 90-98.
2. S. W. Tan, H. Ge, *Polymer*, 37 (1996) 965.
3. S. Asavapiriyant, G. K. Chandler, G. A. Gunawardena, D. Pletcher, J. *Electroanal. Chem.*, 177 (1984) 229.
4. G. Tourillon, F. Garnier, *J. Polymer. Sci.*, 22 (1984) 33.
5. C. O. Too, S. A. Ashraf, H. Ge, K. J. Gilmore, S. G. Pyne, G. G. Wallace, *Polymer*, 34 (1993) 2684.
6. M. Salmon, G. Bidan, *J. Electrochem. Soc.*, 132 (1985) 1897.
7. E. M. Genies, J. M. Pernaut, *J. Electroanal. Chem.*, 191 (1985) 111.
8. M. Yamaura, T. Hagiwara, M. Hirasaka, T. Demura, K. Iwata, *Synth. Met.*, 28 (1989) 157.
9. ASTM, Designation, D 4496, pp 453-457.
10. AATCC 76 –1995, Electrical resistivity of fabrics, *AATCC Technical Manual*, pp 100-101 (1996).
11. Shimadzu Corporation, *Instruction Manual UV-1601 Operation Guide*, 1994.
12. M. C. McMaster, *HPLC, A Practical User's Guide*, VCH Publishers, Inc., 1994.
13. T. Hanai, *HPLC, A Practical Guide*, Published by The Royal Society of Chemistry, Cambridge CB4 0WF, UK, 1999.

CHAPTER 3

PREPARATION AND CHARACTERISATION OF POLYPYRROLE COATED FABRICS

3.1. INTRODUCTION

Conducting polypyrrole can be coated onto textile surfaces using either electrochemical or chemical oxidation of pyrrole in the presence of the fabric. It has been shown that non-conducting fibres such as cotton, silk and wool fibres become conductive when they are coated with polypyrrole or polyaniline [1-3]. For chemical oxidation, two major approaches have been used:

- (1) Chemical oxidation using vapour phase monomer
- (2) *In-situ* chemical oxidation (*In-situ* polymerisation)

Preparation of conductive polypyrrole coated textiles using these two approaches has been described in Chapter 2. However only the “*in-situ* polymerisation process” has been developed commercially. Some research groups focusing on the *in-situ* polymerisation of pyrrole on textiles are Achilles Corporation in Japan, Milliken Research Corporation in US and the Centre d’Etudes et de Recherches sur les Matériaux (CEREM) in France.

Preliminary investigations into the synthesis of conductive fabrics using either electrochemical or chemical oxidation have been investigated in this chapter. The present study concentrates on the preparation of conducting polypyrrole coated textile with a particular emphasis on strain gauge characteristics. It has been found that the *in-situ* polymerisation method is able to produce conductive polypyrrole coated textiles, such as nylon Lycra and Taffeta polyester fabrics suitable for such a purpose. The reaction conditions of the *in-situ* polymerisation process have been optimised.

The measurement of conductivity or surface resistivity of these fabrics has been carried out in two different ways – i.e. the ASTM four point-probe technique and the AATCC 76 two point-probe technique (Refer to Chapter 2). The stability of the coated fabrics has been investigated by measuring the change in surface resistivity versus aging time.

Cyclic voltammetry (CV), a commonly used electrochemical method for the determination of electroactivity, was employed for the characterisation of inherently conducting polymers (ICPs) coated textiles. The oxidation and reduction potentials for ICPs can be conveniently determined using cyclic voltammetry. The peak position and current flow during oxidation and reduction provide an assessment of the reversibility of these redox reactions [4].

The morphology and microstructure of conductive polymer coated materials can be investigated using scanning electron microscopy (SEM).

In recent years, spectroscopic techniques have become invaluable tools for probing the electronic and molecular structure of conducting polymers. One of the most useful techniques is UV-Visible spectroscopy. Light absorption causes electronic transition between valence and conduction bands, and specific absorption peaks in the UV-Visible spectrum are indicative of the nature of the charge carriers and the number of charge carriers present [4].

Thermal gravimetric analysis (TGA) has been widely applied to study and characterise polymeric materials. It is a dynamic method in which the weight loss of a sample is measured continuously as the temperature is changed at a constant rate. A plot of mass

vs. temperature (a thermogram) provides both qualitative and quantitative information including kinetic information on the degradation, oxidation, evaporation or sublimation of samples in any condensed form [5].

In this chapter, the characterisation of the polypyrrole coated nylon Lycra especially those prepared using *in-situ* chemical polymerisation have been investigated with respect to:

- (1) Uniformity of the PPy-coated nylon Lycra
- (2) Stability of the surface resistivity of PPy-coated fabric
- (3) Cyclic Voltammetry
- (4) SEM microstructural analysis
- (5) UV-Vis spectroscopic studies
- (6) Thermogravimetric analysis

Details of general experimental methods have been given in Chapter 2. Synthesis and properties of conductive polypyrrole coated fabrics will be discussed in each section of this chapter.

3.2. EXPERIMENTAL

3.2.1. Reagents and Materials

Pyrrole monomer from Merck was redistilled and stored below $-18\text{ }^{\circ}\text{C}$ before use. Ferric chloride (FeCl_3) was of analytical reagent grade purity and obtained from BDH Chemicals. 1,5-naphthalenedisulfonic acid tetrahydrate (NDSA) (97% purity) from

Aldrich Chemicals was used as a doping agent during the polymerisation of pyrrole. Polypyrrole/NDSA powder was prepared in the chemical oxidation at IPRI. All other chemicals used were of analytical reagent (AR) grade unless otherwise stated. All aqueous solutions were prepared with Milli-Q water ($\sim 18 \text{ M}\Omega$). White nylon Lycra and Taffeta polyester fabrics were obtained from Spotlight Pty.

3.2.2. Instrumentation

A Perkin-Elmer Lambda 900 UV-VIS-NIR spectrophotometer, a Princeton Applied Research Model 363 potentiostat/galvanostat coupled to an ADInstruments PowerLab 4/20 for cyclic voltammetry, a Leica Cambridge 440 camera for SEM, and a TGA 92 Thermoanalyzer were used in this work. An Instron 4302 Universal Material Tensile Tester equipped with a computer interface for data collection was used for strain test.

3.2.3. Preparation of PPy-coated Fabrics Using Different Techniques

3.2.3.1. Electrochemical Polymerisation

Conducting polypyrrole coated textiles were prepared using a two-electrode voltammetric cell including a stainless steel plate working electrode and a RVC auxiliary electrode. All electrocoatings were performed using an EG&G Princeton Applied Research potentiostat/galvanostat Model 363.

Effect of Current Density: The polymerisation solution consisted of 0.05 M pyrrole monomer and 0.015 M dopant NDSA in a total volume of 100 ml. Nylon Lycra fabric of 4 cm x 4 cm dimensions was stretched tightly onto the surface of the stainless

steel working electrode. Current densities, varied between 1.0 mAcm^{-2} and 2.0 mAcm^{-2} , were used to prepare conductive PPy-coated nylon Lycra fabrics.

Effect of Polymerisation Time: The electrochemical polymerisation time was varied between 1 hour and 4 hours for preparation of PPy-coated nylon Lycra fabrics. The polymerisation solution consisted of 0.05 M pyrrole monomer and 0.015 M dopant NDSA in a total volume of 100 ml. Nylon Lycra fabric (4 cm x 4 cm) was stretched tightly onto the surface of the stainless steel plate working electrode. A current density of 2.0 mAcm^{-2} was used in this case.

3.2.3.2. Chemical Oxidation Using Vapour-phase Monomer

Preparation of conducting polypyrrole coated textiles was also carried out using chemical oxidation with vapour-phase monomer. The coating was achieved by imbibing an oxidising agent into the textile fabric, followed by exposure of the fabric to vaporised pyrrole monomer in an enclosed chamber or reactor. The effect of oxidant concentration, reaction temperature and solvent has been investigated.

Effect of Oxidising Agent (FeCl_3) Concentration: Ferric chloride (FeCl_3) was used as an oxidant and dissolved in ethanol (EtOH) solvent. The molar concentrations of FeCl_3 in ethanol used were 0.1 M, 0.2 M and 0.3 M, respectively. Three pieces of nylon Lycra fabrics of 1/4 A4 size (10.5 cm x 14.9 cm) were pre-wetted with different concentrations of oxidant (FeCl_3) in ethanol and exposed to pyrrole monomer vapour carried by nitrogen (Refer to Figure 2.4). Polypyrrole was subsequently deposited onto

the fabric surface as the solvent evaporated. The polymerisation was carried out at room temperature ($\sim 25\text{ }^{\circ}\text{C}$) for one and a half hours.

Effect of Solvents: Two different organic solvents, methanol and ethanol, were used and compared. Ferric chloride (FeCl_3) was dissolved either in methanol (MeOH) or ethanol (EtOH) respectively. The FeCl_3 molar concentration in both methanol and ethanol was 0.3 M. In a vapour-phase polymerisation, a piece of nylon Lycra (10.5 cm x 14.9 cm) was pre-wetted with an oxidising agent (FeCl_3) in either ethanol or methanol, and then was exposed to pyrrole monomer vapour. Polypyrrole subsequently deposited on the fabrics as the solvent evaporated. The vapour-phase polymerisation occurred at room temperature ($\sim 25\text{ }^{\circ}\text{C}$) for one and a half hours.

Effect of Temperature: Pyrrole monomer was heated at $50\text{ }^{\circ}\text{C}$ in an oil bath. A piece of nylon Lycra (10.5 cm x 14.9 cm) was immersed in 0.3 M $\text{FeCl}_3/\text{EtOH}$ solution and then exposed to pyrrole monomer vapour generated from pyrrole exposed to $50\text{ }^{\circ}\text{C}$ in an oil bath for one and a half hours.

3.2.3.3. *In-situ* Chemical Oxidation

Preparation of conductive polypyrrole coated textiles using an *in-situ* oxidation process has been described by Kuhn and others [6-8]. According to their work, polymerisation can be carried out in an aqueous solution containing pyrrole monomer, oxidant and a doping agent such as 1,5-naphthalenedisulfonic acid tetrahydrate (NDSA).

3.2.3.3.1. Preparation of PPy-coated Nylon Lycra Fabric

Factors such as concentration of pyrrole monomer, oxidant (FeCl_3) and dopant [1,5-naphthalenedisulfonic acid tetrahydrate (NDSA)] have been investigated. The reaction temperature and time were also investigated.

Effect of Pyrrole Monomer Concentration: Pyrrole monomer was dissolved in 500 ml Milli-Q water and then the dopant NDSA was added into the pyrrole monomer solution. In order to investigate the effect of pyrrole monomer concentration on the surface resistivity and gauge factor of PPy-coated fabrics, three different concentrations of pyrrole were used (Table 3.1). Three pieces of A4 size (29.7 cm x 21 cm) nylon Lycra fabrics were immersed, one in each of the three solutions for 20 minutes before adding the solution containing the oxidant (FeCl_3). Oxidant solution was prepared by dissolving FeCl_3 in 500 ml Milli-Q water.

Polypyrrole deposited onto the surface of the nylon Lycra fabric after addition of the oxidant solution. The reaction was generally carried out at room temperature (22 °C –25 °C) for 2 hours.

Table 3.1. Optimisation of molar concentrations of pyrrole/ FeCl_3 /NDSA

	Pyrrole (M)	FeCl_3 (M)	NDSA (M)
(a)	0.0075	0.04	0.005
(b)	0.015	0.04	0.005
(c)	0.030	0.04	0.005

Effect of Oxidant Concentration: Three different oxidant solutions (Table 3.2) were also prepared by dissolving FeCl_3 in 500 ml Milli-Q water. Polypyrrole was then deposited on the surface of nylon Lycra fabrics for 2 hours at room temperature (22 °C –25 °C).

Table 3.2. Optimisation of molar concentrations of pyrrole/ FeCl_3 /NDSA

	Pyrrole(M)	FeCl_3 (M)	NDSA (M)
(a)	0.015	0.02	0.005
(b)	0.015	0.04	0.005
(c)	0.015	0.08	0.005

Effect of Dopant Concentration: Three different NDSA solutions (Table 3.3) were used for the preparation of PPy-coated nylon Lycra fabric.

Table 3.3. Optimisation of molar concentrations of pyrrole/ FeCl_3 /NDSA

	Pyrrole (M)	FeCl_3 (M)	NDSA (M)
(a)	0.015	0.04	0.0025
(b)	0.015	0.04	0.005
(c)	0.015	0.04	0.010

Reaction Time: The reaction time is an important factor in determining the final properties of the conductive textile obtained. Different reaction times varied from 1 hour to 6 hours were used to prepare PPy-coated nylon Lycra fabric in an aqueous solution containing 0.015 M pyrrole concentration, 0.04 M FeCl_3 concentration and 0.005 M NDSA at room temperature.

Reaction Temperature: Three solution temperatures were investigated: (1) sub-room temperature (4 °C), (2) room temperature (22 °C) and elevated temperature (50 °C). The polymerisation was carried out in an aqueous solution containing 0.015 M pyrrole monomer, 0.04 M FeCl₃ and 0.005 M NDSA for 2 hours.

3.2.3.3.2. Preparation of PPy-coated Polyester Taffeta Fabric

Taffeta polyester fabric was also coated with polypyrrole by the oxidation process at room temperature. Polymerisation was carried out using the conditions optimised for coating nylon Lycra (0.015 M pyrrole, 0.04 M FeCl₃ and 0.005 M NDSA).

Six pieces of Taffeta polyester fabrics (21 cm x 29.8 cm) were immersed in 500 ml of pyrrole/NDSA solution and soaked for 20 minutes. Then oxidant FeCl₃ solution (500 ml) was added into the pyrrole/NDSA solution. Polypyrrole deposited on the fabric surface. The reaction time was varied from 1 hour to 24 hours at room temperature.

3.2.4. Characterisation of PPy-coated Nylon Lycra Fabric

Characterisation of polypyrrole-coated nylon Lycra fabrics was carried out to determine electrical conductivity, uniformity of the polymer coating, cyclic voltammetry (CV), scanning electron microscopy (SEM), UV-Vis spectra and thermogravimetry (TGA). All PPy-coated fabric samples used were prepared in an aqueous solution containing 0.015 M pyrrole monomer, 0.04 M oxidant FeCl₃ and 0.005 M dopant NDSA at room temperature for 2 hours.

3.2.4.1. Surface Resistivity

The conductivity of the PPy-coated nylon Lycra fabric was measured in two different ways – i.e. the ASTM four point-probe technique and the AATCC 76 two point-probe technique that have been described in Chapter 2.

3.2.4.2. Cyclic Voltammetry

Cyclic voltammetry was conducted in a three-electrode electrochemical cell (Refer to Schematic 2.5) using a reticulated vitreous carbon (RVC) onto which the PPy-coated nylon Lycra measuring 2 cm x 1 cm was wrapped as working electrode. An Ag/AgCl (3 M NaCl) reference electrode and platinum mesh auxiliary electrode were used for the study conducted in 1 M sodium nitrate solution. Experiments were carried out using a Princeton Applied Research Model 363 potentiostat/galvanostat coupled to an ADInstruments PowerLab 4/20.

3.2.4.3. Morphology Analysis

The morphology and microstructure of the conducting polypyrrole-coated fabrics have been investigated using SEM. The images, were obtained using the Leica Cambridge 440 camera at the Department of Materials Engineering, University of Wollongong. SEM samples, such untreated fabrics, PPy-coated nylon Lycra, were sputter coated with a thin layer of gold to make them sufficiently conductive and then cut into 0.5 cm x 0.5 cm pieces. The SEM images were taken at different magnifications, varying between 500 and 30,000, in order to obtain detailed information on the samples.

3.2.4.4. UV-Vis Spectra

The UV-Vis spectra of uncoated and PPy-coated fabrics were recorded between the wavelength of 300 nm and 1100 nm using a Perkin-Elmer Lambda 900 UV-VIS-NIR spectrophotometer. All the fabrics were cut into 1.5 cm x 1.5 cm pieces.

3.2.4.5. Thermogravimetric Analysis

Thermal gravimetry was carried out using a TGA 92 Thermoanalyzer. A temperature profile was programmed to increase from 60 °C to 500 °C at a heating rate of 10 °C per minute. Thermogravimetric analysis was studied by measuring the weight loss of uncoated, PPy/NDSA-coated nylon Lycra fabrics, dopant NDSA and polypyrrole/NDSA powder during heating.

3.2.4.6. Strain & Stress Testing by Instron 4302 Tensile Tester

Strain test on PPy-coated fabrics was performed using an Instron 4302 Universal Material Tensile Tester equipped with a computer interface for data collection. A 10 N load cell was used during the strain testing. Rectangular samples, with dimensions 7.0 cm x 2.0 cm, were cut from the coated fabrics. They were mounted in the jaws of the Instron tensile machine. After being mounted in the Instron machine, approximately 5.0 cm of the sample remained free to be strained. The coated fabric was then stretched/released at a typical speed 100 mm/min for cycling test.

3.3. RESULTS AND DISCUSSION

3.3.1. Effect of Reaction Conditions on Surface Resistivity of PPy-coated Nylon Lycra Coated Using Electrochemical Polymerisation

Galvanostatic control was used to oxidise the monomer to prepare PPy-coated nylon Lycra using electrochemical polymerisation. During the galvanostatic polymerisation a constant current density was applied between the working and auxiliary electrodes. The thickness of the deposited polypyrrole layer can be controlled by controlling current density and deposition time. In order to maintain current flow, pyrrole monomer was oxidised at the anode and eventually formed a polypyrrole coating. Table 3.4 and Table 3.5 summarise the results of electrochemical polymerisation for PPy-coated nylon Lycra prepared using different current densities and time.

Table 3.4 Summary of electrochemical polymerisation for PPy-coated nylon Lycra at different current densities (All other conditions as detailed in the Experimental Section).

Current Density (mAcm ⁻²)	Polymerisation Time (Hrs)	Observation
1.0	4	Only surface of the fabric close to the electrode was coated with PPy
1.5	4	Incomplete coverage and non uniform PPy coating
2.0	4	Uniform homogenous PPy coating

When galvanostatic methods were used for growing polypyrrole onto the textiles, it was found that no polymer was observed in the solution. The pyrrole monomer oxidised and deposited on the fabric surface (working electrode). Increasing the current densities in the polymerisation results in a uniform homogenous polypyrrole coating on both sides of the textile.

Table 3.5 Summary of electrochemical polymerisation for PPy-coated nylon Lycra at different polymerisation times.

Current Density (mAcm ⁻²)	Polymerisation Time (Hrs)	Observation of Conducting Polymer Coating
2.0	1	No PPy coating on the fabric surface
2.0	2	Only surface of the fabric close to the electrode was coated with PPy
2.0	3	Incomplete coverage and non uniform PPy coating
2.0	4	Uniform homogenous PPy coating

Results indicate that with the increase of polymerisation time up to 4 hours, a smooth polypyrrole coating can be observed using a current density of 2.0 mAcm⁻². The surface resistivity was measured to be 0.34 KΩ/□. Figure 3.1 shows both sides of the PPy-coated nylon Lycra fabric coated using electrochemical polymerisation.

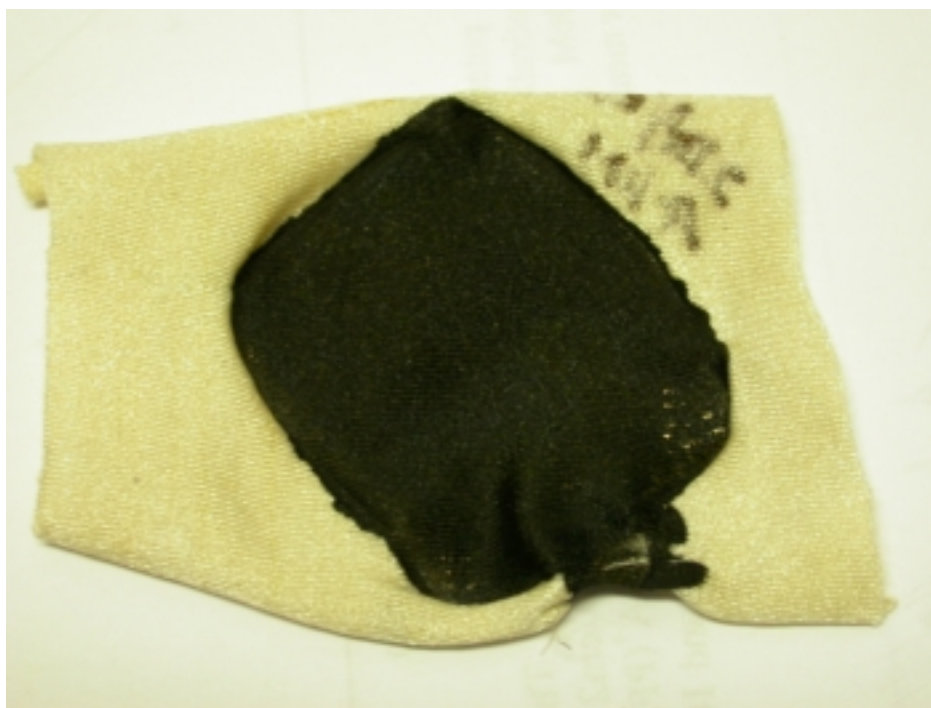


Figure 3.1. Both sides of PPy-coated nylon Lycra prepared at a current density of 2.0 mAcm^{-2} for 4 hours using electrochemical polymerisation.

A scanning electron micrograph (SEM) of the PPy-coated nylon after electrodeposition of PPy is shown in Figure 3.2. A thick layer of polypyrrole was coated onto the individual fibres of the textile after 4 hours reaction time. The SEM analysis shows that each individual fibre coated with polypyrrole displayed the “cauliflower” morphology [9-12]. The morphology of the deposit with nodules between ca. 4 to 6 μm was similar to PPy electrodeposited onto other substrates [13-15]. A polymer layer thickness of ca. 17 μm was estimated from the SEM images. As a result, the polymer coating was easily detached from the substrate fibre when the fabric was stretched. Another limitation of the electrochemical method is the maximum size which can be coated; only a small size (4 cm x 4 cm) of fabric can be prepared using this approach.

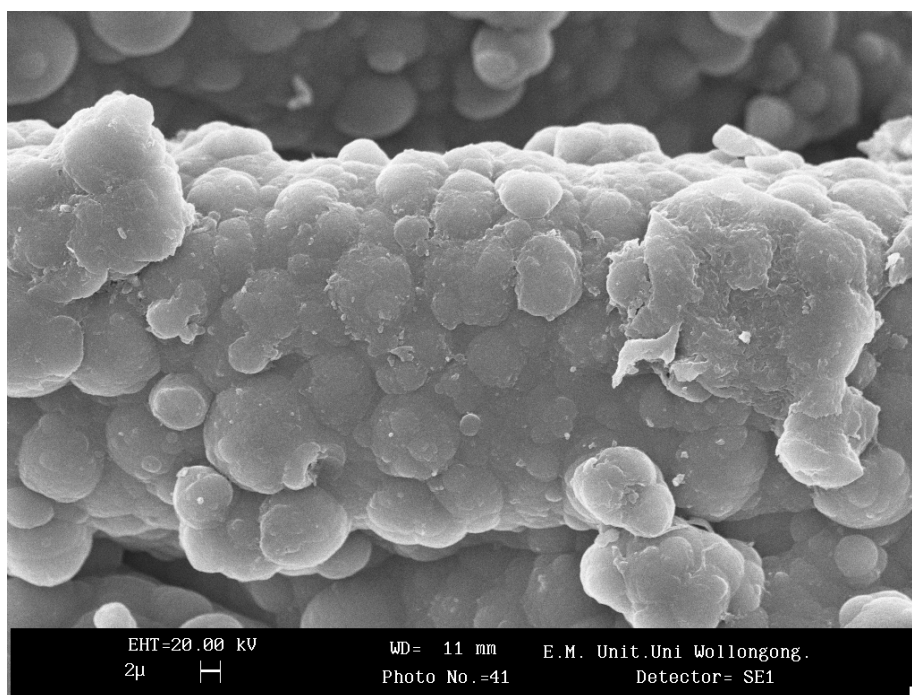


Figure 3.2. SEM of PPy-coated nylon Lycra prepared at a current density of 2.0 mAcm^{-2} for 4 hours using electrochemical polymerisation.

3.3.2. Effect of Reaction Conditions on Surface Resistivity of PPy-coated Nylon Lycra Coated Using Chemical Oxidation of Monomer from Vapour Phase

Using nylon Lycra, the effects of oxidant concentration, solvent, reaction time and temperature on the polymerisation process have been investigated (Table 3.6 to Table 3.8).

The effect of using different oxidant concentrations (FeCl_3 in ethanol) is summarised in Table 3.6. Initially, the fabric was yellow (colour of FeCl_3) and then was quickly covered with black polypyrrole during the polymerisation process. It was found that the thickness of the polypyrrole formed increased with increasing concentration of FeCl_3 , as depicted by the change of the colour from greyish to a totally dark PPy-coated nylon Lycra. The more conductive PPy-coated fabric ($3.53 \text{ K}\Omega/\square$) was obtained using higher oxidant concentration (0.3 M). The surface resistivity of the coated fabric decreases with increasing oxidant concentration.

Polypyrrole has been prepared by chemical polymerisation in FeCl_3 solution with various solvents. The conductivity of polypyrrole shows its highest value when polymerisation takes place in solvents possessing an OH group, which are protic solvent. Some solvents such as acetone and acetonitrile, react with FeCl_3 and thus cannot be used as a reaction medium [16]. In this work solvents such as ethanol and methanol were used to prepare the oxidant FeCl_3 solution. Results from Table 3.7 indicate that more conductive PPy-coated nylon Lycra can be obtained using ethanol instead of methanol as a solvent.

Table 3.6 The surface resistivity of PPy-coated nylon Lycra using different concentrations of FeCl_3 in ethanol for soaking the fabric prior to monomer exposure (All other conditions as detailed in the Experimental Section).

Oxidant Concentration ($\text{FeCl}_3/\text{EtOH}$) (M)	Surface Resistivity ($\text{K}\Omega/\square$)
0.1	64.5
0.2	15.4
0.3	3.53

Table 3.7 The surface resistivity of PPy-coated nylon Lycra using different solvents for oxidant uptake into the textile.

Solvent	Surface Resistivity ($\text{K}\Omega/\square$)
FeCl_3 in EtOH (0.3 M)	3.53
FeCl_3 in MeOH (0.3 M)	9.57

The use of higher temperature can generate more pyrrole vapour and result in a fast polymerisation process. A lower surface resistivity ($2.33 \text{ K}\Omega/\square$) on the PPy-coated fabric can be obtained by heating pyrrole so as to generate more pyrrole vapour in vapour-phase polymerisation (Table 3.8). This is in contrast to the general trend of chemical polymerisation occurring in solution, in which the conductivity of polypyrrole is enhanced at lower temperature [17]. The vapour pressure of pyrrole was low at low temperature that resulted in less pyrrole monomer in the vapour, so that less polypyrrole was produced. The lower the reaction temperature, the slower the diffusion of the

pyrrole monomer to the FeCl_3 . The slow diffusion rate could lead to the formation of polypyrrole with a structure of high resistance [18].

Table 3.8 The surface resistivity of PPy-coated nylon Lycra using different temperature for vapour generation.

Temperature (°C)	Surface Resistivity ($\text{K}\Omega/\square$)
25	3.53
50	2.33

After coating the fabric became stiff and lost the original “handle” of the textile. Scanning electron micrograph (SEM) of the PPy-coated nylon Lycra is shown in Figure 3.3. The SEM analysis shows that the polypyrrole layer is not uniform and smooth. The polymer surface layer is full of cracks [See arrows in Figure 3.3].

In summary, polypyrrole coated fabric can be prepared using the chemical oxidation of monomer from vapour phase. The lowest surface resistivity ($2.33 \text{ K}\Omega/\square$) has been obtained using 50°C for vapour generated using ethanol as a solvent to imbibe the oxidant into the textile. The coated nylon Lycra fabric lost its elastic property after coating due to damage of the fibres by pyrrole vapour.

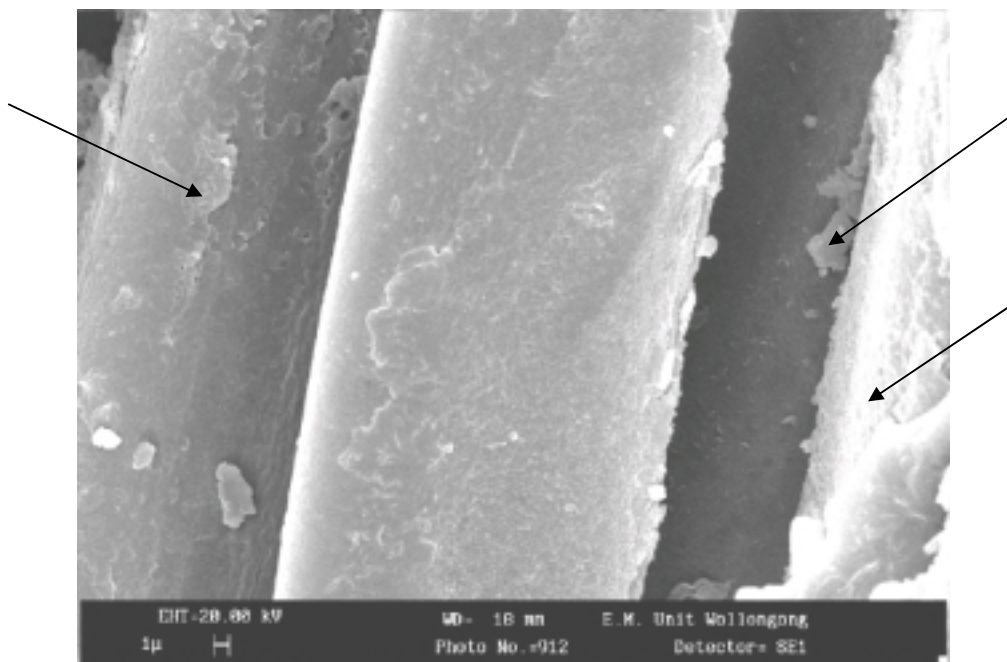


Figure 3.3. SEM of PPy-coated nylon Lycra using the vapour polymerisation.

3.3.3. Effect of Reaction Conditions on Surface Resistivity and the Gauge Factor of PPy-coated Nylon Lycra Coated Using Chemical Oxidation

3.3.3.1. Effect of Pyrrole Monomer Concentration

The electrical properties of conductive textiles have been investigated and surface resistivity as low as $5 \Omega/\square$ has been reported using multiple coatings [7]. In this thesis, PPy-coated nylon Lycra fabric produced by chemical oxidation using different monomer concentrations was studied with respect to surface resistivity and sensitivity as a strain gauge. It was found that the thickness of the PPy coating increased with increase in the pyrrole monomer concentration, as depicted by the changes of the colour from brown to dark brown, then totally to dark blue. It indicated that a higher concentration of pyrrole monomer led to a fast oxidation process. It was also found that

polypyrrole precipitation occurred in the aqueous solution when using a pyrrole monomer concentration of 0.030 M. The surface resistivity of PPy-coated nylon Lycra obtained under different pyrrole monomer concentrations are shown in Table 3.9.

Table 3.9 The surface resistivity and strain gauge factors for PPy-coated nylon Lycra – effect of pyrrole monomer concentrations (All other reaction conditions are in the Experimental Section).

Concentration of Pyrrole (M)	Surface Resistivity (Ω/\square)	Gauge Factor (absolute value) $(\Delta R/R)/(\Delta l/l)$ (Strain Ranges 0~50%)
0.0075	774	0.68
0.015	244	0.74
0.030	101	0.15

Note: $\text{FeCl}_3 = 0.04 \text{ M}$, NDSA = 0.005 M

The sensitivity of the coated fabric for use as a strain gauge (gauge factor) has also been investigated. These coated fabrics were stretched to 50% and the gauge factor then calculated (Table 3.9). The typical strain-resistance responses of PPy-coated nylon Lycra fabric under different cycles are given in Figure 3.4.

Investigation of polypyrrole coated nylon Lycra has shown that its resistance changed when the coated fabric is stretched (Figure 3.4). The strain gauge characteristics of polypyrrole coated nylon Lycra will be discussed in detail in Chapter 5. Increasing pyrrole monomer concentration from 0.015 M to 0.030 M led to an increase in the polymerisation rate (the colour of the solution became dark in only a couple of minutes)

and improved conductivity of the fabric (from 244 to 101 Ω/\square). However, the resistance of the coated textiles did not change linearly with the polymer add on as expected. This effect may be due to the formation of percolating networks, as multiple monolayers are deposited and hopping between conducting islands is facilitated [7]. It was also found that the sensitivity of the strain gauge decreased, i.e. only a small change in conductivity occurred for fabrics with higher conductivity (gauge factor is 0.15). Decreasing the pyrrole monomer concentration from 0.015 M to 0.0075 M resulted in an increase in the surface resistivity on the fabric (From 244 to 774 Ω/\square). Results in Table 3.9 show that fabrics with moderate conductivity had the largest gauge factor 0.74 (absolute value).

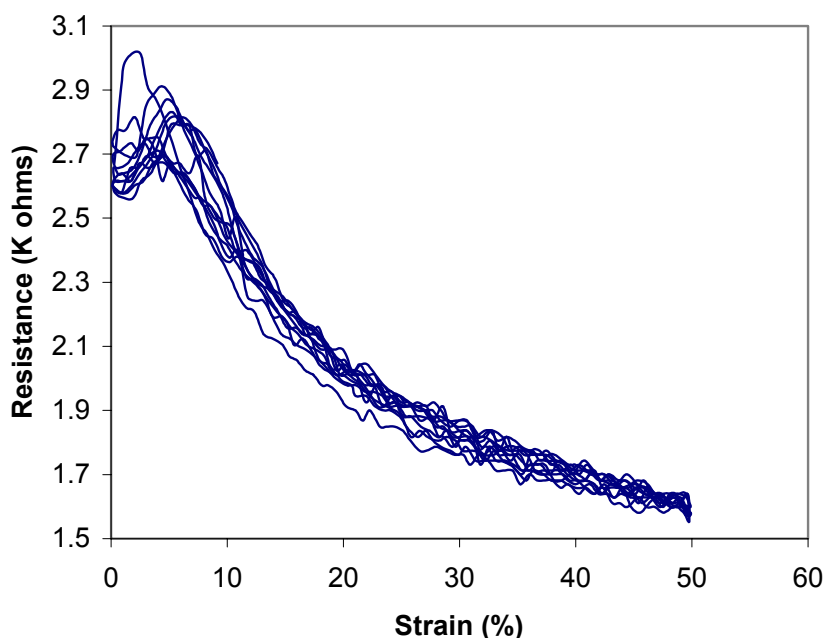


Figure 3.4. Typical strain-resistance responses of PPy-coated nylon Lycra fabric under different cycles when stretched to 50%. The PPy-coated nylon Lycra was prepared by *in-situ* chemical oxidation for 2 hours in an aqueous solution containing 0.015 M pyrrole, 0.04 M FeCl_3 and 0.005 M NDSA.

3.3.3.2. Effect of Oxidant Concentration

Three different oxidant concentrations were used to prepare PPy-coated nylon Lycra fabrics. It was found that the thickness of the PPy coating increased with the FeCl_3 concentrations, as depicted by the changes of the colour from brown to dark brown. No polymer was found in the solution during the chemical oxidation process. The surface resistivity of PPy-coated nylon Lycra fabrics prepared under different oxidant concentrations was measured using the four point-probe method. Gauge factors of these coated fabrics were then calculated when stretched up to 50%. All results are given in Table 3.10.

According to Gregory, Kimbrell and Kuhn [6], the *in-situ* chemical oxidation should be carried out using pyrrole monomer, ferric chloride hexahydrate and a doping agent separately dissolved in water. The final solution contains 0.02 M pyrrole, 0.042 M ferric chloride hexahydrate and 3 g L^{-1} doping agent. A modification of this process has been reported by Boutrois and co-workers [19]. They suggested that the molar ratio of the reactants is more important than the concentrations. The molar ratio of pyrrole and FeCl_3 of 2.3:1 was recommended.

Increasing oxidant concentration from 0.04 M to 0.08 M, the molar ratio of pyrrole to FeCl_3 increased from 2.66:1 to 5.3:1. This means that excess FeCl_3 was added into the solution, so no significant effect was found on surface resistivity (from $244 \Omega/\square$ to $212 \Omega/\square$) with increasing FeCl_3 concentration from 0.04 M to 0.08 M. Decreasing the oxidant FeCl_3 concentration from 0.04 M to 0.02 M leads to the increase of surface resistivity on the coated nylon Lycra fabric (from $244 \Omega/\square$ to $429 \Omega/\square$). Results in

Table 3.10 show that the lower surface resistivity ($244 \Omega/\square$) and larger gauge factor (0.74) have been obtained by using oxidant concentration of 0.04 M FeCl_3 .

Table 3.10 The surface resistivity and gauge factors of PPy-coated nylon Lycra produced under different oxidant FeCl_3 concentrations (All other reaction conditions are in the Experimental Section).

Concentration of FeCl_3 (M)	Surface Resistivity (Ω/\square)	Gauge Factor (absolute value) $(\Delta R/R)/(\Delta l/l)$ (Strain Ranges 0~50%)
0.02	429	0.84
0.04	244	0.74
0.08	212	0.62

Note: Pyrrole = 0.015 M, NDSA = 0.005 M

3.3.3.3. Effect of Dopant Concentration

Three different dopant concentrations were used in the chemical oxidation to prepare PPy-coated textiles. It was found that the thickness of the PPy coating increased with the NDSA (doping agent) concentrations, as depicted by the changes of the colour from brown to dark brown. No polypyrrole precipitate was found in the solution during the chemical oxidation process. The surface resistivity and gauge factors of PPy-coated nylon Lycra fabrics using different dopant concentrations were measured and given in Table 3.11.

Table 3.11 The surface resistivity and gauge factors of PPy-coated nylon Lycra obtained using different dopant concentrations (All other reaction conditions are in the Experimental Section).

Concentration of NDSA (M)	Surface Resistivity (Ω/\square)	Gauge Factor (absolute value) $(\Delta R/R)/(\Delta l/l)$ (Strain Ranges 0~50%)
0.0025	330	0.22
0.005	244	0.74
0.010	319	0.51

Note: Pyrrole = 0.015 M, FeCl_3 = 0.04 M,

The optimal degree of doping for polypyrrole has been found to be 0.25-0.33 with the best electrical properties of the polymer. This means that every three or four repeat units carry a positive charge neutralised with a counterion [8,20]. Increasing the dopant concentration from 0.0025 M to 0.005 M led to a decrease in surface resistivity of the fabric due to the changes of the molar ratio of pyrrole and dopant from 0.03 to 0.06. However, further increase in the dopant concentration to 0.010 M resulted in an increase in the surface resistivity. Results in Table 3.11 show that the lowest surface resistivity ($244 \Omega/\square$) and the largest gauge factor (0.74) can be obtained by using a dopant concentration of 0.005 M.

3.3.3.4. Effect of Reaction Time

The above work (effects of pyrrole, FeCl_3 and NDSA concentrations) indicated that the higher conductivity and the more sensitive strain performance of PPy-coated nylon

Lycra had been obtained using the following conditions: pyrrole concentration 0.015 M, FeCl_3 concentration 0.04 M and NDSA concentration 0.005 M. The reaction time used to prepare PPy-coated nylon Lycra fabric using the *in-situ* chemical oxidation process was investigated using these conditions. It was found that the thickness of the PPy coating increased with the reaction time, as depicted by the changes of the colour from grey, brown, to dark blue. No polymer was found in the solution. After washing with water, examination of the sample showed that an even and smooth PPy coating was formed on the fabric surface.

The surface resistivity of all coated fabrics prepared under different reaction times was measured using the four point-probe method. Gauge factors of these coated fabrics were also calculated from 0 to 50% strain. All results are given in Table 3.12.

Table 3.12 The surface resistivity and gauge factor of PPy-coated nylon Lycra obtained by using different reaction times (All other reaction conditions are in the Experimental Section).

Reaction Time (Hours)	Surface Resistivity (Ω/\square)	Gauge Factor (absolute value) $(\Delta R/R)/(\Delta l/l)$ (Strain Ranges 0~50%)
1	400	0.62
2	244	0.74
3	267	0.71
4	338	0.60
6	393	0.49

Note: Pyrrole = 0.015 M, FeCl_3 = 0.04 M, NDSA = 0.005 M

Bulk quantities of polypyrrole can be obtained as fine powders using oxidative polymerisation. In many experiments the early stages of the oxidative polymerisation were monitored at short reaction times [21]. The polypyrrole-coated textiles were prepared and the polymerisation was conducted at the desired temperature for various times, usually from 2 to 6 hours [6]. Results from Table 3.12 show that surface resistivity and gauge factor vary with reaction time. The surface resistivity of the PPy-coated nylon Lycra varies from $400 \Omega/\square$ (after 1 hour) to a minimum of $224 \Omega/\square$ (after 2 hours) and rising to $393 \Omega/\square$ (after 6 hours). This means polymerisation is nearly completed at about 2 hours. This suggests that the reaction time can be chosen to be 2 hours because of the low surface resistivity ($224 \Omega/\square$) and large gauge factor (0.74).

3.3.3.5. Effect of Reaction Temperature

Three solution temperatures were investigated: (1) sub-room temperature (4°C), (2) room temperature (22°C) and (3) higher temperature (50°C). It was found that the thickness of the PPy coating increased with reaction temperatures, as depicted by the changes of the colour from grey to dark brown. It indicated that a higher reaction temperature led to a fast oxidation process. It was also found that polypyrrole precipitate occurred in the aqueous solution at higher temperature (50°C). The surface resistivity of coated fabrics prepared at different reaction temperatures were measured (Table 3.13). Gauge factors of these coated fabrics were also measured when coated fabrics were stretched between 0 and 50%.

Table 3.13 The surface resistivity and gauge factors of PPy-coated nylon Lycra produced at different polymerisation temperatures (All other reaction conditions are in the Experimental Section).

Polymerisation Temperature (°C)	Surface Resistivity (Ω/\square)	Gauge Factor (absolute value) $(\Delta R/R)/(\Delta l/l)$ (Strain Ranges 0~50%)
4	654	1.03
22	255	1.00
50	230-400	0.85-1.90

Note: Pyrrole = 0.015 M, FeCl_3 = 0.04 M, NDSA = 0.005 M

As the temperature was increased from room temperature to 50 °C, the surface resistivity and the gauge factor of the coated fabric were different in the different area on the fabric. The reason is that the higher temperature resulted in a fast polymerisation reaction, which led to a darkening of the solution after only a couple of minutes (the colour change at room temperature was observed after 10 minutes), and the formation of an uneven polypyrrole coating on the fabric surface. In addition to the polypyrrole deposited on the surface of the fabric, there was also excessive precipitate formed in the solution. In contrast, an even smooth polypyrrole layer can be obtained on the surface of the fabric at lower temperature (4 °C), but the polymerisation process tended to take longer, requiring more than 2 hours. Room temperature is recommended for medium to fast preparation of conductive polypyrrole coated textile.

3.3.4. Effect of Reaction Conditions on Surface Resistivity and Gauge Factor of PPy-coated Polyester Taffeta

PPy-coated polyester fabric (Taffeta) was also prepared using the conditions optimised above for nylon Lycra. It was found that the thickness of the PPy coating increased with the reaction time, as depicted by the changes of the colour from silver, grey, brown, blue to dark green (Figure 3.5). No polymer was found in the solution. After washing with water, a uniform and smooth PPy coating was found to have formed on the fabric surface. The surface resistivity was measured by using the four point-probe method and the results are summarised in Table 3.14. Results indicated that the longer the polymerisation time, the more conductive the PPy-coated Taffeta polyester fabrics.

It was also found that the PPy-coated polyester Taffeta experiences resistance change when stretched. Figure 3.6 shows the change in resistance of PPy-coated polyester during the strain. At the beginning, the resistance decreased upon applying drawing force along the fibre direction. This is due to the drawing process initially causing the realignment/rearrangement of the fibres on the fabric. The inter-connections between individual fibres are increased and better contacts are made. As shown in Figure 3.4 and Figure 3.6, different fabrics show different response to strain. The resistance of nylon Lycra fabric can change up 50% due to its mechanical property of elastic Lycra fibre. The non-elastic polyester fabric can be stretched around 5% without detachment of the polypyrrole layer from the fibre and loss of physical contacts between fibres. Thus the resistance of PPy-coated polyester fabric decreased down to a certain point (e.g. at strain between 4-6%) at which the resistance of the fabrics started to increase.

Compared with the nylon Lycra fabric, the polyester Taffeta can be used as a strain gauge for the measurement of a small strain (4-6 %) and a large gauge factor up to 3.95 (absolute value). Gauge factors of PPy-coated polyester prepared using different

polymerisation times are given in Table 3.14. The gauge factor of the coated polyester prepared using 24 hours reaction time cannot be measured due to the small change in the resistance on this more conductive fabric during strain.

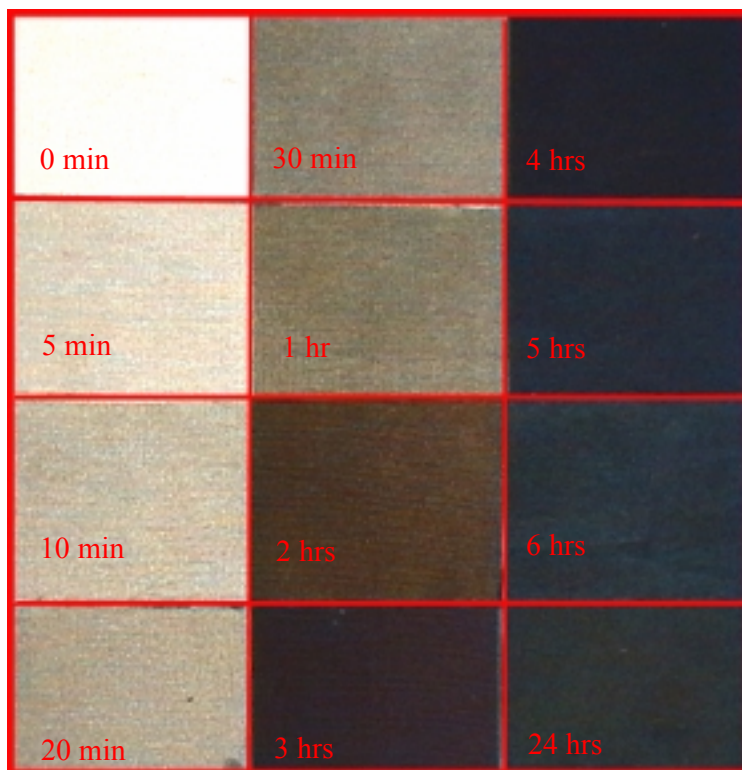


Figure 3.5. PPy-coated Taffeta polyester after different polymerisation times.

Table 3.14 The surface resistivity of PPy-coated Taffeta polyester after different polymerisation times.

Polymerisation Time (Hours)	Surface Resistivity (Ω/\square)	Gauge Factor (absolute value) $(\Delta R/R)/(\Delta l/l)$ (Strain Ranges 4~6)
1	5960	2.80
2	3920	3.95
3	1130	1.36
4	872	1.44
6	816	0.74
24	564	N/A

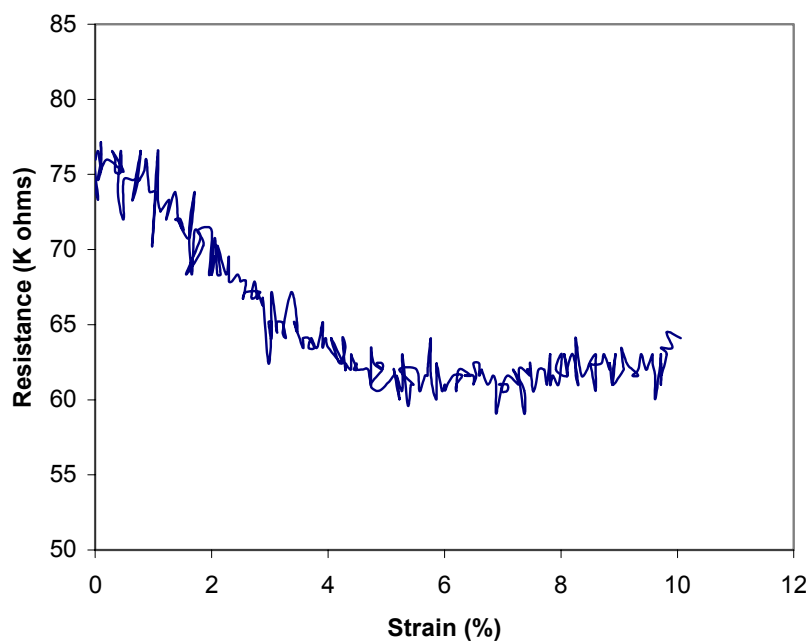


Figure 3.6. Resistance change of PPy-coated polyester versus strain. The PPy-coated polyester was prepared by *in-situ* chemical oxidation for 2 hours in an aqueous solution containing 0.015 M pyrrole, 0.04 M FeCl_3 and 0.005 M NDSA.

3.3.5. Characterisation of PPy-coated Nylon Lycra Fabric

3.3.5.1. Uniformity of Coated Fabric

Using the optimal reaction conditions discussed above, the uniformity of the polypyrrole layer on the nylon Lycra fabric was investigated. Nylon Lycra fabrics of A4 size (29.7 cm x 21 cm) were coated with polypyrrole in the *in-situ* chemical oxidation process previously described.

One piece of PPy-coated nylon Lycra was cut into 9 strips from different areas of the whole A4 size fabric (Figure 3.7). The surface resistivity was measured using the four point-probe method. The surface resistivity varied from 85.5 to 100.3 Ω/\square . The biggest variation in surface resistivity across the whole surface was 4.9 Ω/\square and the standard deviation of surface resistivity was 5.6 Ω/\square . This represents only 1.2% of variation across the whole surface in a single piece of coated fabric.

Another piece of PPy-coated nylon Lycra of A4 size was cut into 8 small pieces of 7.4 cm x 10.5 cm each. Five small strips were cut from the 1/8 A4 size coated fabric at different areas (Figure 3.8). The surface resistivity of different areas of 1/8 A4 fabric was measured by using the same method. The surface resistivity ranged from 110.1 to 129.5 Ω/\square . The biggest variation across the whole surface was 7.5 Ω/\square . The standard deviation of surface resistivity on 1/8 A4 size was 9.1 Ω/\square . This represents about 7.8% of variation in surface resistivity observed in this coated fabric.

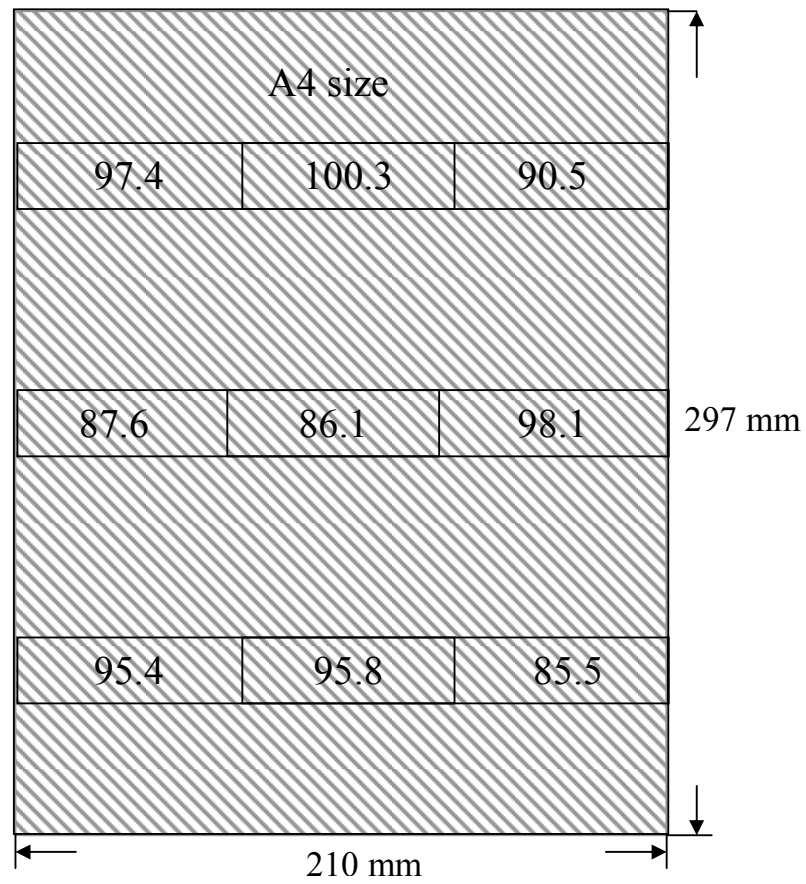


Figure 3.7. The surface resistivity (Ω/\square) of PPy-coated nylon Lycra at different areas of the A4 fabric.

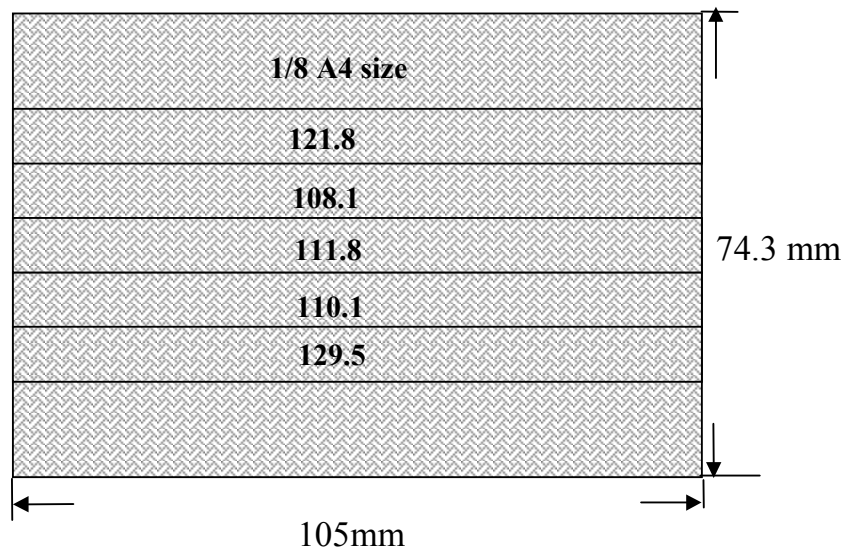


Figure 3.8. The surface resistivity (Ω/\square) of PPy-coated nylon Lycra at different areas of the 1/8 A4 fabric.

Results from Figure 3.7 and Figure 3.8 show that there are minor variations (1.2% in A4 size and 7.8% in 1/8 A4 size) in surface resistivity at different areas of PPy-coated nylon Lycra fabric. Considering the edge effect, it appears that more uniform PPy-coated nylon Lycra can be prepared in large sizes using the *in-situ* chemical oxidation process.

3.3.5.2. Stability (Surface Resistivity Change vs Time) of PPy-coated Fabric

Polypyrrole coated nylon Lycra fabric was cut into two small pieces 4 cm long by 4 cm wide each. One of them was exposed to ambient air whilst the other was stored in a desiccator. Changes in the surface resistivity vs storage time of PPy-coated fabric were measured using the two point-probe method. The effect of storage condition has a significant impact on the electrical resistivity of the fabrics. Changes in resistivity vs time are shown in Figure 3.9. Broken and bold lines represent changes of the surface resistivity of PPy-coated nylon Lycra fabrics stored in air and in a desiccator respectively.

In general, the conductive PPy-coated nylon Lycra fabric was less stable in air due to the high reactivity with a variety of atmospheric chemicals, especially oxygen [7]. The surface resistivity of the coated fabric increased 1103% when stored in air for 54 days. In comparison, the surface resistivity of the PPy-coated nylon Lycra was more stable in a desiccator; the surface resistivity increased 194% when stored in a desiccator for 54 days. The degradation of polypyrrole on the coated fabrics can be reduced by storing coated fabrics in the desiccator in order to avoid oxidative reaction in the air.

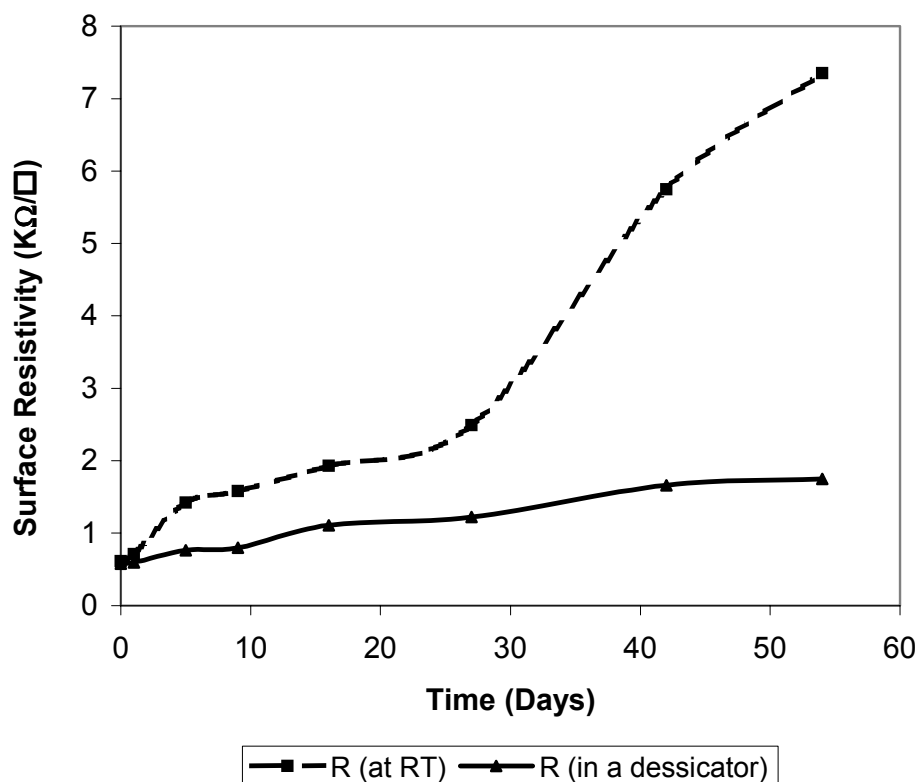


Figure 3. 9. The changes of surface resistivity vs storage time of PPy-coated nylon Lycra. Broken line: stored in the open air, bold line: stored in a dessicator.

3.3.5.3. Cyclic Voltammetry of PPy-coated Fabric

Polypyrroles are electrically conductive and electroactive. The latter term refers to their ability to be electrochemically switched between their reduced and oxidised states. The electrochemical behaviour of PPy-coated nylon Lycra fabric was studied by cyclic voltammetry over the potential range from -1.0 V to +1.0 V (vs Ag/AgCl) in 1.0 M NaNO₃ solution.

In order to compare the electroactivity of polypyrrole film and PPy-coated fabric, cyclic voltammetry (CV) of the polypyrrole film was also performed using a three-electrode

electrochemical cell. PPy/NDSA film was grown galvanostatically on a glassy carbon electrode ($d = 3.0$ mm) at a current density of 0.1 mA cm^{-2} for 5 minutes from a polymerisation solution containing 0.05 M pyrrole and 0.015 M NDSA.

Typical cyclic voltammograms of polypyrrole film and polypyrrole coated nylon Lycra, doped with 1,5-naphthalenedisulfonic acid, in 1.0 M NaNO_3 are given in Figure 3.10 and Figure 3.11 respectively.

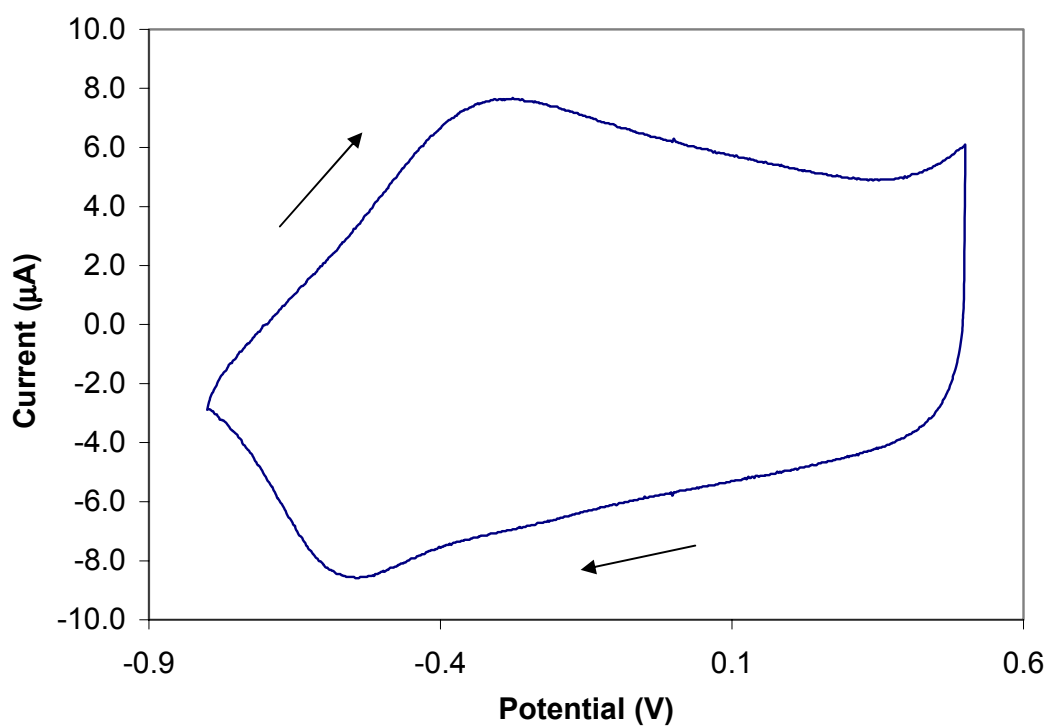


Figure 3.10. Cyclic voltammogram of PPy/NDSA film (ca. $0.1 \mu\text{m}$ thickness) in 1.0 M NaNO_3 at a scan rate of 100 mV s^{-1} . PPy/NDSA was grown galvanostatically on a glassy carbon electrode ($d = 3.0 \text{ mm}$) at a current density of 0.1 mA cm^{-2} for 5 minutes from a polymerisation solution containing 0.05 M pyrrole and 0.015 M NDSA.

The CV of PPy/NDSA film indicates that polypyrrole is electroactive with only one pair of broad redox peaks appearing at $E_{p(c)} = -0.60$ V and $E_{p(a)} = -0.30$ V respectively when scanned between -0.8 V to $+0.5$ V at 100 mVs^{-1} (Figure 3.10). The separation of peak potentials $\Delta E = E_{p(a)} - E_{p(c)} = +0.30$ V. The oxidation and reduction of PPy/NDSA are accompanied by cation (Na^+) expulsion and insertion respectively, so that the overall charge neutrality of the polymer is maintained, because NDSA is a medium to large anion trapped within the polymer matrix [4].

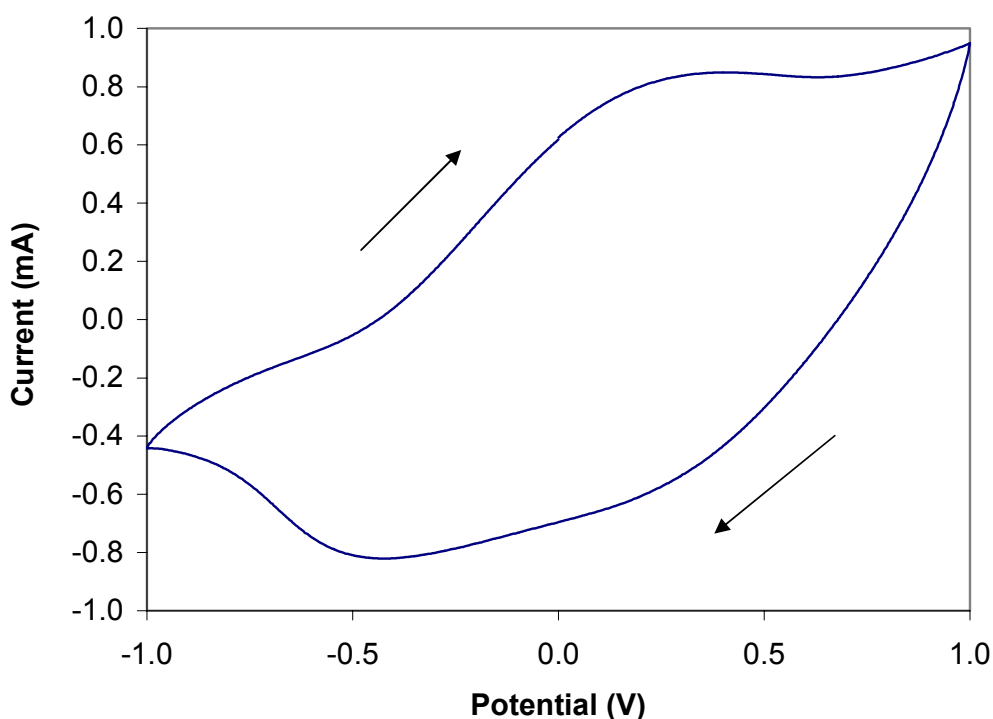


Figure 3.11. Cyclic voltammogram of PPy/NDSA coated nylon Lycra in 1.0 M NaNO_3 at a scan rate of 100 mVs^{-1} . The polypyrrole coated nylon Lycra was prepared using the *in-situ* method for 2 hours in an aqueous solution containing 0.015 M pyrrole, 0.04 M FeCl_3 and 0.005 M NDSA .

The redox process of PPy/NDSA coated nylon Lycra fabric with peak potentials $E_{p(c)}$ and $E_{p(a)}$ appear at -0.55 and +0.35 V respectively (Figure 3.11) when scanned between -1.0 V to +1.0 V at 100 mVs^{-1} . The separation of peak potentials $\Delta E = E_{p(a)} - E_{p(c)} = 0.90 \text{ V}$. This shows that the polypyrrole coated nylon Lycra is electroactive with only one pair of broad redox peaks. But cathodic and anodic peak potentials $E_{p(c)}$ and $E_{p(a)}$ of PPy-coated nylon Lycra fabric were shifted from -0.60 to -0.55 V and -0.30 to +0.35 V respectively compared with PPy/NDSA film. This might be due to the high surface area (200 mm^2) of the fabric that is about 28 times larger than the surface area (7.07 mm^2) of the PPy/NDSA film. Charging current may play a significant role during cycling. Another reason might be due to the different thickness and density of the polypyrrole layer between the film and fabric surface.

3.3.5.4. Morphology of PPy-coated Fabric

Scanning electron microscopy (SEM) studies of polypyrrole coated nylon Lycra prepared using the conditions optimised revealed the morphology of polypyrrole particles and its thin layer coating on the single fibre. Two pieces of nylon Lycra fabrics including uncoated and coated were prepared for SEM. Scanning electron micrographs of uncoated and PPy-coated nylon Lycra were obtained and given in Figure 3.12 and Figure 3.13.

Evidence for the formation of polypyrrole layer on the nylon Lycra fabric surface was provided by closely examining the change in the fibres' morphology observed after *in-situ* polymerisation of pyrrole on the fabric. Prior to pyrrole polymerisation on the nylon Lycra fabric, the SEM image of the surface of the fibre had a clear and smooth

morphology with a few small spots due to dust or other chemicals used in the weaving process (Figure 3.12). Compared with uncoated nylon Lycra fibre, a thin, uniform and coherent polypyrrole layer was found on the fibres after *in-situ* polymerisation (Figure 3.13). The SEM analysis shows that each individual fibre was deposited with polypyrrole with nodules between ca 200 nm to 500 nm. Some of the polypyrrole particles were loosely attached which will be eventually washed away. But most of the polypyrrole nodules were small in size and coherently attached to the surface of fibres. This layer of polypyrrole remains attached to the surface and cannot be washed away.

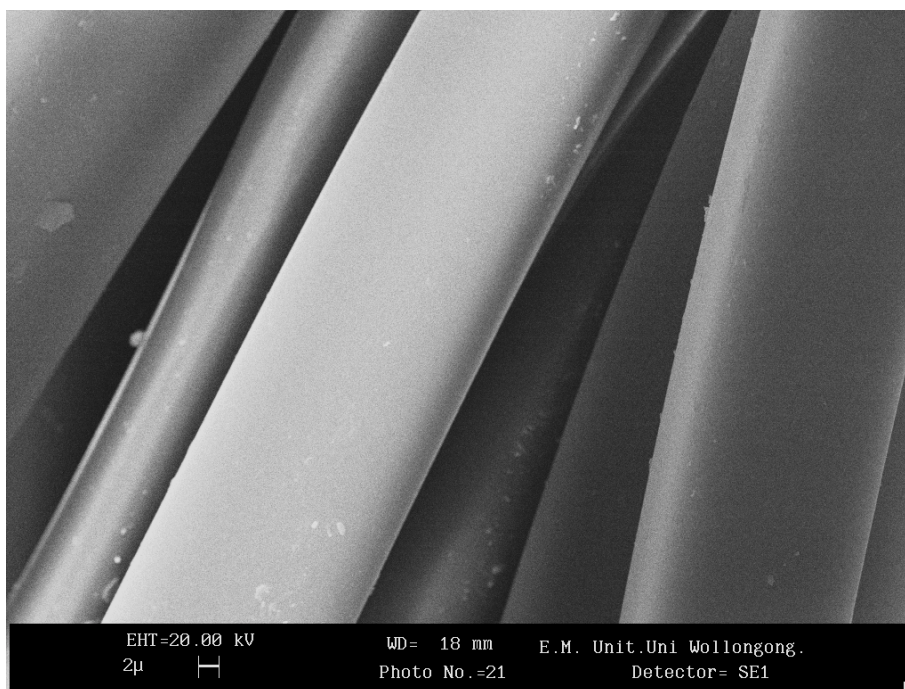


Figure 3.12. Scanning electron micrograph of uncoated nylon Lycra fibre.

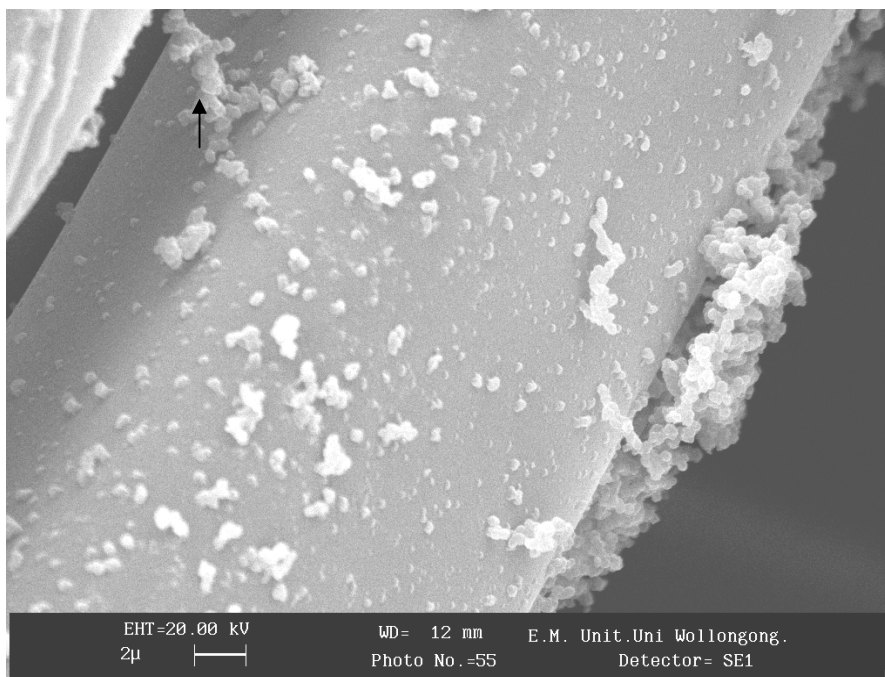


Figure 3.13. Scanning electron micrograph of PPy-coated nylon Lycra fibre.

3.3.5.5. UV-Vis Spectra of PPy-coated Fabric

UV-Vis spectra can be used to elucidate the changes in electronic structure of polypyrrole on the coated textiles. Diaz and Yakushi employed this method to study PPy growth [22,23]. The absorption of UV-Visible radiation by polymers leads to transition among the electronic energy levels of the macromolecules and results a typical electronic absorption spectrum.

UV-Vis absorption spectra of uncoated and the PPy-coated nylon Lycra fabrics produced using the conditions optimised above are shown in Figure 3.14. Compared with the spectrum of uncoated nylon Lycra, the intensities of peaks at 410 nm and 580 nm assigned as $\pi - \pi^*$ transition, polaron and bipolaron bands, respectively [24] were observed, corresponding to conductive polypyrrole deposited on the nylon Lycra fabric.

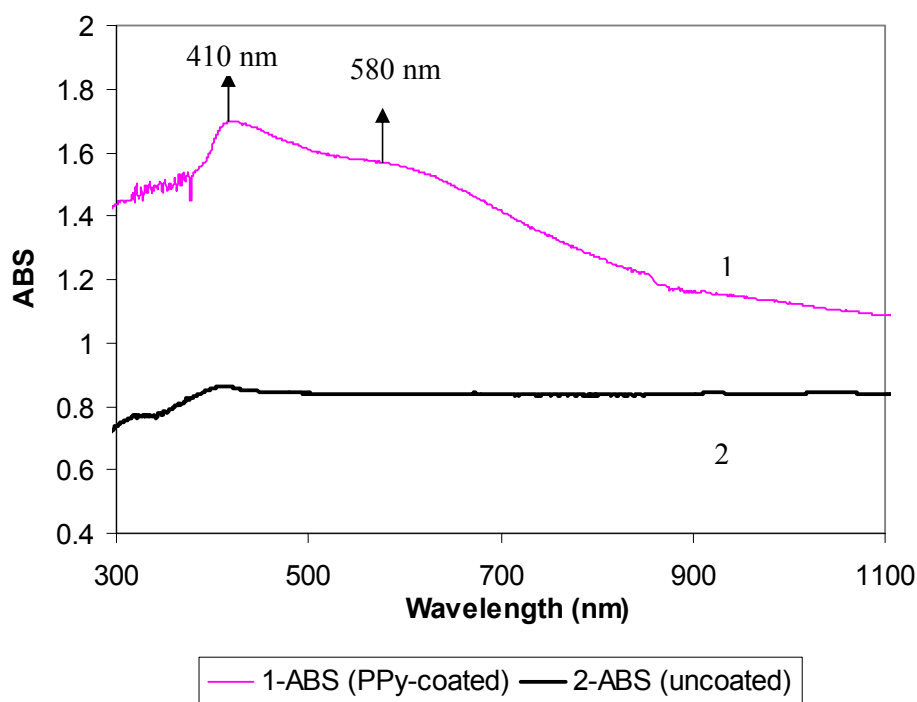


Figure 3.14. UV-Vis spectra of uncoated and PPy-coated nylon Lycra fabrics. The polypyrrole coated nylon Lycra was prepared using the *in-situ* method for 2 hours in an aqueous solution containing 0.015 M pyrrole, 0.04 M FeCl_3 and 0.005 M NDSA.

3.3.5.6. Thermogravimetric Analysis

Thermal gravimetry was carried out using a TGA 92 thermoanalyzer. A temperature programmer was used to increase temperature from around 60 °C to 500 °C at a heating rate of 10 °C per minute under nitrogen atmosphere. For the thermal analysis of polypyrrole coated nylon Lycra fabrics, TGA is used in determining the decomposition by weight loss of the samples including uncoated, PPy/NDSA-coated nylon Lycra fabrics, dopant NDSA and polypyrrole/NDSA powder during an experiment.

Thermogravimetric analysis of PPy/NDSA powder is shown in Figure 3.15. Weight loss occurred in two steps. The first weight loss (4%) observed between 100 and 150 °C represents the weight loss of moisture absorbed by the polymer powder. The major second weight loss (beyond 150 °C) is presumably due to the decomposition of the dopant. The total weight loss observed on PPy/NDSA powder from 250 to 500 °C was 25%. The TGA carried out on the pure NDSA (the doping agent used for fabrics coating) in Figure 3.16 also indicates that the mass loss observed for temperatures up to 190 °C is about 16%; attributed to a decrease in moisture content. The NDSA is not stable at temperatures above 260 °C. The total weight loss observed of dopant NDSA from 250 to 500 °C is 45%. Similar results were found in R. Ansari's work [5].

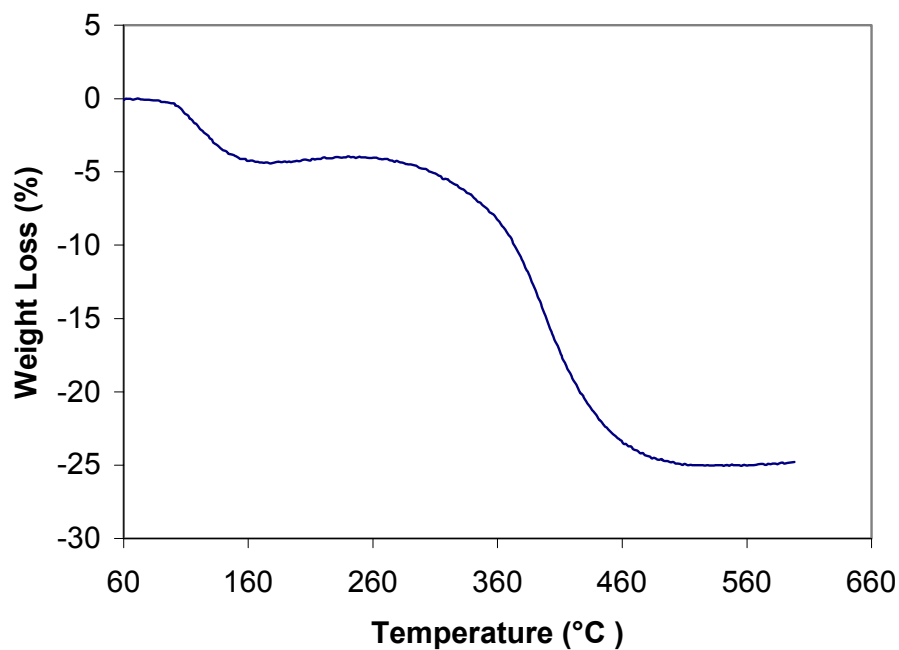


Figure 3.15. TGA (60-600 °C) of PPy/NDSA powder under nitrogen gas.

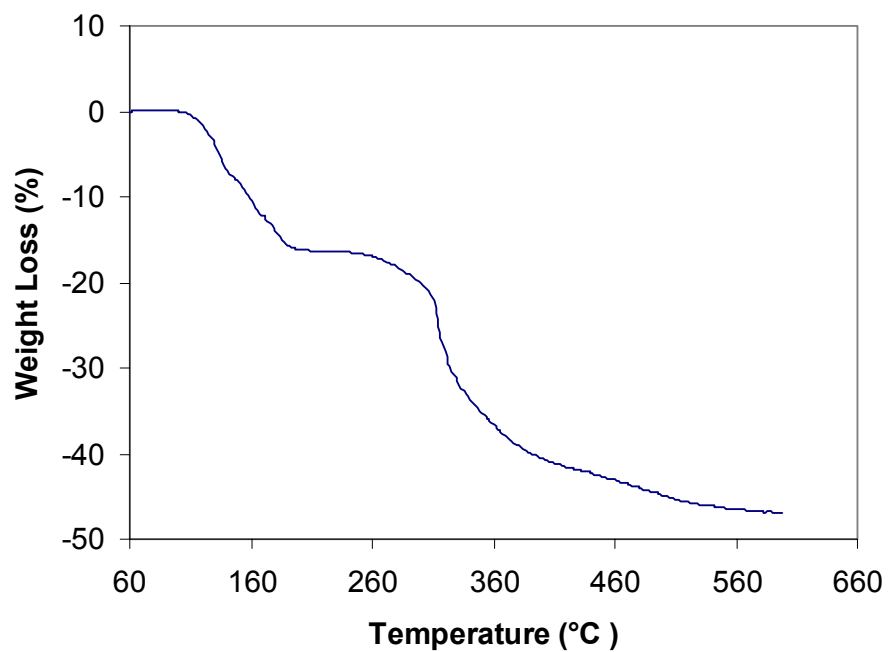


Figure 3.16. TGA (60-600 °C) of dopant NDSA under nitrogen gas.

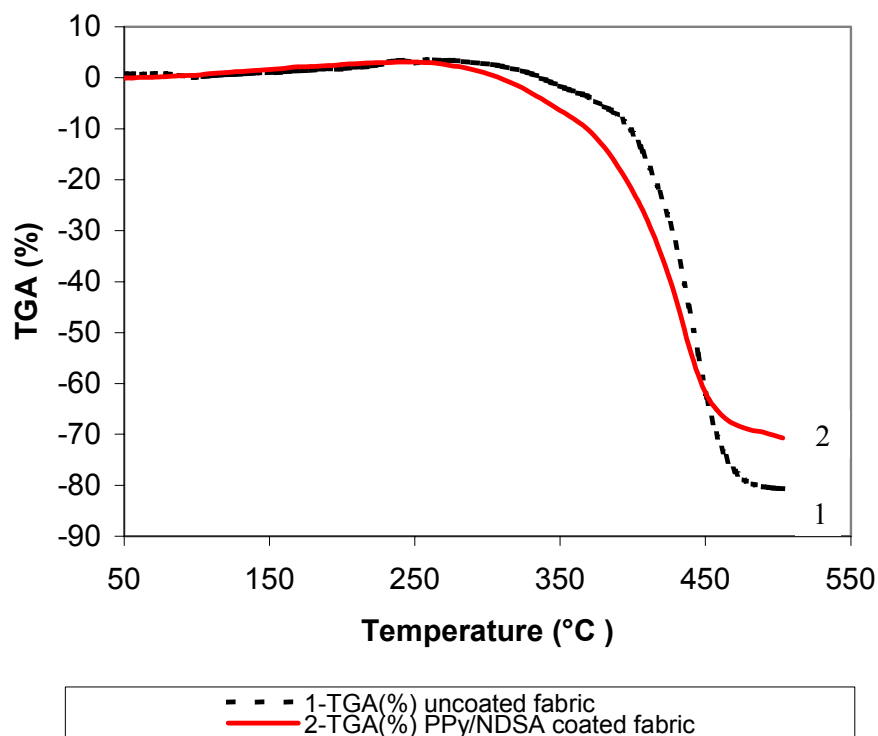


Figure 3.17. TGA (50-500 °C) of uncoated and PPy-coated nylon Lycra fabrics under nitrogen gas.

The TGA curves of uncoated and PPy-coated nylon Lycra fabrics are similar and shown in Figure 3.17. They reveal only one stage of weight loss under nitrogen atmosphere. Since these fabric samples were very dry by storing in a desiccator, there was no significant weight loss of moisture. For uncoated nylon Lycra fabric, a mass loss of only 1.6% was observed until 350 °C. This indicates that the nylon Lycra fabric is thermally stable at high temperature. The weight loss of PPy/NDSA coated fabric starts from around 260 °C because of chemical decomposition of the polypyrrole and the counterion. The PPy/NDSA coated nylon Lycra is less stable than uncoated fabric with a mass loss of 6.3% at 350 °C due to the break down of the polypyrrole backbone and chemical decomposition of the dopant NDSA.

In summary, PPy coated fabric shows less stability at elevated temperature than the fabric itself. As indicated in the thermogram of PPy powder, the PPy itself starts to decompose at around 250 °C and dopant NDSA starts to decompose at around 260 °C. These results agree well with the thermograms of PPy coated fabric. The polypyrrole coating does not improve or enhance the thermal stability of the fabrics.

3.4. CONCLUSION

In this work, a number of approaches including chemical and electrochemical polymerisation processes used to coat fabrics with conducting polypyrrole have been investigated.

Electrodeposition of polypyrrole on nylon Lycra fabric enables a uniform polypyrrole layer to be formed around each fibre. The coating process was carried out under

galvanostatic control for about 4 hours. An optimal current density of 2 mAcm^{-2} has been established. The surface resistivity of nylon Lycra coated with polypyrrole using electrochemical polymerisation is $334 \text{ } \Omega/\square$. The SEM analysis shows that each individual fibre has been coated with polypyrrole of typical cauliflower morphology with nodules of between ca 4 to 6 μm wide. A thicker polymer layer (ca. 17 μm .) is formed around the fibre. This detaches from the fibre when it is stretched.

Using chemical oxidation and vaporised monomer, either methanol or ethanol can be used as the solvents to imbibe FeCl_3 into the textile. The surface resistivity of the fabric decreases with an increase in concentration of the FeCl_3 and polymerisation temperature. The lowest surface resistivity $2330 \text{ } \Omega/\square$ is obtained in the chemical oxidation using vapour phase monomer. The polypyrrole layer is full of cracks as shown by the SEM image. This means PPy-coated fabric cannot be used as a strain gauge due to the changes of mechanical property of the fibre after vapour polymerisation.

In the *in-situ* chemical oxidative polymerisation process, reaction conditions have been optimised. Polypyrrole coated nylon Lycra and Taffeta polyester fabrics have been prepared in an aqueous solution containing 0.015 M pyrrole monomer, 0.04 M oxidant FeCl_3 and 0.005 M dopant NDSA. Effects of polymerisation temperature, polymerisation time and different oxidants and dopants on the surface resistivity and sensitivity of strain gauge have also been studied. The surface resistivity and gauge factor can be tailored by varying polymerisation conditions such as polymerisation time, reaction temperature and concentration of chemicals. After *in-situ* chemical oxidation polymerisation at room temperature for 2 hours, the surface resistivity is the lowest.

This means polymerisation is completed in the earlier reaction stage. Following these results, it is suggested that the *in-situ* polymerisation process can be carried out at room temperature in about 2 hours.

Compared with electrochemical and vapour-phase polymerisation methods, PPy-coated fabric prepared by *in-situ* polymerisation process is the best. Large areas of nylon Lycra fabric have been coated with an ultra thin uniform layer of conducting polymer. The *in-situ* polymerisation method does not change the mechanical property of the fabric, so these coated fabrics can be used as a strain gauge on a large scale to suit applications such as biomechanical monitoring.

Conductive PPy-coated nylon Lycra fabric is less stable in air due to their high reactivity with atmospheric chemicals such as oxygen. The degradation of polypyrrole on the coated fabric can be reduced by storing the coated fabrics in a desiccator in order to avoid oxidative reaction in air. Minor variations in surface resistivity have been found at different areas on different size PPy-coated nylon Lycra fabrics.

The electrochemical switching of PPy-coated nylon Lycra fabric has been investigated by cyclic voltammetry. One pair of redox peaks is obtained on PPy-coated nylon Lycra fabric due to its electroactive behaviour. Scanning electron microscopy (SEM) studies of polypyrrole coated nylon Lycra revealed the morphology of polypyrrole particles and thin layer coating on the single fibres. The SEM analysis shows that each individual fibre has been deposited with polypyrrole with nodules of between ca 200 nm to 500 nm width. UV-Visible studies confirm that nylon Lycra fabric has been coated with a thin layer of polypyrrole.

The thermograms of PPy-coated fabric demonstrate similar characteristics as uncoated nylon Lycra fabric. They reveal only one stage of weight loss under a nitrogen atmosphere. The thermal stability of PPy/NDSA coated nylon Lycra is less than uncoated fabric; presumably due to early breakdown of the polypyrrole coating layer and the chemical decomposition of the doping agent NDSA.

3.5. REFERENCES

1. S. N. Bhadani, S. K. Sen Gupta, G. C. Sahu, and M. Kurmari, *J. Polym. Mater.*, 13 (1996) 61.
2. S. N. Bhadani, S. K. Sen Gupta, G. C. Sahu, and M. Kurmari, *J. Appl. Polym. Sci.*, 61 (1996) 207.
3. S. N. Bhadani, M. Kurmari S. K. Sen Gupta, and G. C. Sahu,, *J. Appl. Polym. Sci.*, 64 (1997) 1073.
4. G. G. Wallace, G. M. Spinks, L. A. P. Kane-Maguire, P. R. Teasdale, *Conductive Electroactive Polymers, Intelligent Materials Systems, Second Edition*, CRC Press LLC, 2003, pp 29.
5. R. Ansari, *PhD Thesis*, University of Wollongong, 1995.
6. R. V. Gregory, W. C. Kimbrell, and H. H. Kuhn, *Synth. Met.*, 28 (1989) 823.
7. H. H. Kuhn and A. D. Child, “Electrically Conducting Textile”, *Handbook of Conducting Polymers, Second Edition*, Marcel Dekker, Inc. New York, 1998. pp 994.
8. H. H. Kuhn, M. Aldissi (ed), *Intrinsically Conducting Polymers: An Emerging Technology*, Kluwer Academic publishers, 1993, pp 25-34.
9. H. Zhao, W. E. Price and G. G. Wallace, *J. Electroanal. Chem*, 334 (1992) 111.
10. H. Zhao, W. E. Proce, and G. G. Wallace, *J. Membrane Sci.*, 87 (1994) 47.
11. A. C. Partridge, C. Milestone, C. O. Too and G. G. Wallace, *J. Membrane Sci.*,132 (1997) 245.
12. K. K. Shiu, S. K. Pang and H. K. Cheung, *J. Electroanal. Chem.*, 367 (1994) 115.
13. J. Ding, *PhD Thesis*, University of Wollongong, 2001.

14. D. Zhou, *PhD Thesis*, University of Wollongong, 1997.
15. J. M. Davey, S. F. Ralph, C. O. Too and G. G. Wallace, *Synth. Met.*, 99 (1999) 199.
16. S. Machida and S. Miyata, *Synth. Met.*, 31 (1989) 311.
17. V. Bocchi, G. P. Gardini and S. J. Rapi, *J. Mater. Sci. Lett.*, 6 (1987) 1283.
18. S. W. Tan, H. Ge, *Polymer*, 37 (1996) 965.
19. J.P. Boutrois, R. Jolly and C. Pétrescu, *Synth. Met.*, 85 (1997) 1405.
20. J. K. Avlyanov, H. H. Kuhn, J. Y. Josefowicz and A. G. MacDiarmid, *Synth. Met.*, 84 (1997) 153.
21. S. Rapi, V. Bocchi and G. P. Gardini, *Synth. Met.*, 24 (1988) 217.
22. A. Diaz, J. Castillo, J. Logan, and W. Lee, *J. Electroanal. Chem.*, 129 (1981) 115.
23. K. Yakushi, L. Lauchlan, T. Clake and G. Street, *J. Chem. Phys.* 79 (1983) 4774.
24. J. Bredas, J. Scott, K. Yakushi and G. Street, *Phys. Rev. B*, 30 (1984) 1023.

CHAPTER 4

PREPARATION AND CHARACTERISATION OF POLYANILINE COATED FABRICS

4.1. INTRODUCTION

The approaches on how to prepare polyaniline-coated textiles have been described in Chapter 1 (Refer to 1.3.4.). The use of polyelectrolyte as a polymerisation template has recently been reported for enzymatic induced polymerisation of aniline [1-3]. A molecular template is often a polyelectrolyte capable of interacting with monomers prior to polymerisation and also functions as a dopant. A major improvement in the synthesis and doping of polyaniline has been achieved using polyelectrolyte (polyanion)-assisted chemical polymerisation to simultaneously form a water-soluble and doped conductive complex of polyaniline [4-7]. As shown in schematic Figure 4.1, polyelectrolyte such as sulfonated polystyrene (SPS) acts as a template upon which the aniline monomers and oligomers preferentially align themselves and form a complex that leads to mostly *para*-directed synthesis and results in the conducting emeraldine salt form of polyaniline [3]. The polyelectrolyte also serves as the dopant, a large counterion integrated and locked to the polyaniline chains. Finally, the polyelectrolyte template serves to provide water solubility of the final template-polyaniline complex for facile and inexpensive processing [3].

Results from CSIRO Textile and Fibre Technology using a one-step polymerisation have shown that the electrical resistance of polyaniline coated wool fabric was very high (greater than $200\text{G}\Omega$) [8, Personal communication]. Therefore, in this work, a two-step process was used to improve the conductivity as described in the following. Formation of the conducting textile can be used as a template to facilitate the polymerisation and integration of inherently conducting polymers (ICPs) into textiles. Compared with one-step polymerisation process, the template used may be chosen to

introduce certain functionalities into the fabric; for example, heat-sensitivity and biocompatibility. The water-soluble conducting poly (2-methoxyaniline-5 sulfonic acid) or PMAS has been employed as a molecular template for polyaniline in preparing conducting wool nylon Lycra fabric. Wool nylon Lycra consisting of 90.5% wool, 8.0% nylon and 1.5% Lycra was used in this work. Amino groups can be found in both wool and nylon fibre structures (Refer to Chapter 1, Figure 1.8). In acidic conditions the amino groups become positively charged and will attract negatively charged anion from polyelectrolytes.

Please see print copy for image



Figure 4.1. Branched structures of the traditional ortho-para directed enzymatic polymerisation of aniline that results in an electrically inactive form of aniline vs enzymatic polymerization in the presence of SPS [3].

Integration of molecular template on textiles is a process similar to dyeing fabrics. Most dyeing processes are carried out from aqueous solutions. Textile fibres swell to a greater

or less extent owing to the presence of hydrophilic groupings in the fibre when immersed in a dyeing solution or bath. Pre-treatment of fabric surface from hydrophobic to hydrophilic can make the pore size of the fibres greater in the water-swollen state than in the dry state. There are several theories used to explain how the dye molecules penetrate the fibres. One of them is that a fibre is a network of pores, similar to a sponge, although the fibre contains channels rather than the chambers of a more absorbent sponge. With soluble dye molecules in solution, the dye is able to penetrate the fibre through such network of channels or pores [9]. Another theory concerns the actual molecular structure within a polymer structure of fibres. When polymers are heated and their energy states increase, the molecules begin more vigorous vibrations and position shifts than when they are cool. As a result, the polymer in the increased energy state produces more “inner volume” for dye molecules to penetrate the fibre surface and then enter deeper into its amorphous regions [9]. When the dye liquor has cooled and the fibre dried, the polymer system will close up again and return to its former dimensions, trapping and entangling the dye molecules which entered it. In such circumstances, van der Waals’ forces may develop to assist the polymer system to retain the dye molecules within the fibres [10].

An enzymatic synthesis of a conducting molecular complex of polyaniline and poly(vinylphosphonic acid) has been carried out by Lynne Samuelson and co-workers [11]. Conducting polyaniline fibres have been spun from a water-soluble form of polyaniline which was enzymatically synthesised [12]. In this process, aniline is enzymatically polymerized in the presence of a polyelectrolyte that serves as a matrix within which the monomers align and preferentially react to form water-soluble, electrically active polyaniline [12]. The application of molecular template to textile fibres results in an

ionic link between the template molecule and the fibres. Poly (2-methoxyaniline-5 sulfonic acid) or PMAS is a water-soluble “polyelectrolyte” and has been used as a molecular template in this work. The effect of fabric pre-treatment, solution pH and temperature on uptake of the molecular template have been investigated.

The effects of the ratio of PMAS to aniline, the ratio of aniline to ammonium persulfate and the polymerisation temperature on the polymerisation reaction in step 2 (Refer to Chapter 2.2.1.2) have also been studied. High Performance Liquid Chromatography (HPLC) was used to determine the consumption of the aniline monomer during the polymerisation process.

Characterisation of PMAS-treated fabric and the templated polyaniline coated fabrics have also been investigated in this chapter using:

- (1) Surface Resistivity,
- (2) Cyclic voltammetry,
- (3) UV-Vis spectra,
- (4) SEM microstructure, and,
- (5) Thermogravimetry.

Details of general experimental methods have been described in Chapter 2.

4.2. EXPERIMENTAL

4.2.1. Reagents and Materials

+Wool nylon Lycra fabric consisting of 90.5% wool, 8.0% nylon and 1.5% Lycra provided by CSIRO Textile and Fibre Technology (TFT) has been investigated. Highly sulfonated polyaniline - poly (2-methoxyaniline-5-sulfonic acid) (PMAS) was prepared using a chemical polymerisation as described before. PMAS (Figure 4.2) has a sulfonate group on each repeat unit which makes it highly soluble in aqueous media (up to 30% w/w). The emeraldine base powder was obtained from Santa Fe Science and Technology, USA. PMAS templated polyaniline powder (or PMAS + PAn copolymer) was prepared chemically at IPRI.

Aniline monomer purchased from Aldrich Chemical Co., was distilled before use and was stored under nitrogen at a temperature below $-18\text{ }^{\circ}\text{C}$ in a freezer. HPLC grade methanol was purchased from Ajax Ltd and used without further purification. Ammonium persulfate (APS) was used as oxidant from Ajax Finechem Company. All other reagents used were purchased from Aldrich and were of analytical reagent (AR) grade. Aqueous solutions were prepared using Milli-Q water ($18\text{ M}\Omega\cdot\text{cm}$).

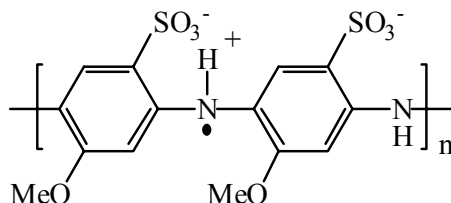


Figure 4.2. Poly (2-methoxyaniline-5 sulfonic acid) (PMAS) structure.

4.2.2. Instrumentation

The template polymerisation reaction temperature was controlled using a thermobath - Julabo F 20 thermostat with temperature variation less than $\pm 1\text{ }^{\circ}\text{C}$. A Heidolph RZR

2020 overhead stirrer (40~2000 rpm), with a custom made dyeing spindle supplied by CSIRO (Figure 4.4).

A Shimadzu UV 1601 spectrophotometer for UV-Vis measurement, a Princeton Applied Research Model 363 potentiostat/galvanostat coupled to an ADInstruments PowerLab 4/20 for cyclic voltammetry, a Leica Cambridge 440 camera for SEM, and a TGA 92 Thermoanalyzer were used in this work. A Shimadzu Liquid Chromatograph (LC-10AT) with a 5 μm C18 column was used for the determination of monomer concentration.

4.2.3. Preparation of PMAS Templated PAn-coated Fabric

4.2.3.1. Integration of the Molecular Template-PMAS (Step One)

Integration of the molecular template into textiles is a process similar to dyeing and requires optimisation of sample pretreatment, dye bath composition and temperature. The effect of pre-treatment of wool nylon Lycra, pH control and dye temperature uptake of PMAS and the conductivity of the resultant fabric was investigated.

In order to remove mineral, silicone oils and other contaminants absorbed on the fabric surface before applying the PMAS template, all fabrics were cleaned with the use of detergent from Clariant (Australia) Pty Ltd, Sandoclean PC Liquid. The scouring agent was prepared by adding 1 ml Sandoclean PC Liquid and 1 gram of sodium bicarbonate in 1 litre of water and then heated to 70 °C. The wool nylon Lycra fabric of 20 grams was immersed into this scouring agent and washed for 20 minutes at 70 °C, using 50ml liquor for every 1g fabric. The fabric was then removed from the scouring agent and

rinsed in hot water for 20 minutes at 70 °C. Finally, the wool nylon Lycra was rinsed under cold tap water.

A piece of wool nylon Lycra was secured onto a dyeing spindle and soaked in a 1.0 gL⁻¹ solution of a non-ionic wetting agent, (Lissadol TN 450, ICI Australia Limited, which is anonyphenol ethoxylate with 8 to 10 molecules of ethoxy groups) and then rinsed thoroughly with tap water.

The “dye solution” containing the molecular template was prepared by dissolving PMAS in Milli-Q water. Typically, 10% (w/w) of PMAS to fabric was used. The solution was stirred for 20 minutes using a magnetic stirrer and solution pH was adjusted by adding concentrated hydrochloric acid (HCl).

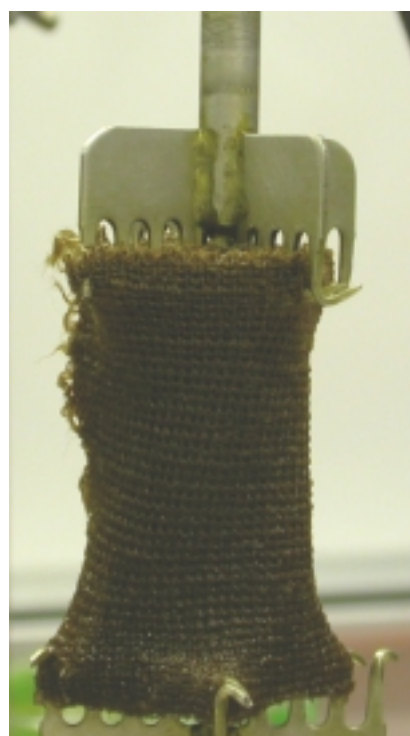
Then the fabric secured on the spindle was placed in a cylinder containing PMAS solution at high temperature for 4 hours and rotated at 300 rpm. UV-Visible spectra of the PMAS solution were obtained before and after dyeing. The PMAS-treated fabric was removed from the solution and washed thoroughly in cold tap water and then left to dry overnight. The conductivity of the PMAS-treated fabric was measured using the two point-probe method. Figure 4.3 shows a photograph of the thermobath with temperature control for the dyeing process. The spindles with wool fabric before and after dyeing with PMAS are shown in Figure 4.4(a) and Figure 4.4(b).



Figure 4.3. Thermobath with temperature control used in the dyeing process.



(a)



(b)

Figure 4.4. The spindle with wool fabric before (a) and after (b) dyeing with PMAS.

4.2.3.2. Integration of Cationic Inherently Conducting Polymers (Step Two)

The PMAS coated fabric was then used as a template to form polyaniline using *in-situ* polymerisation. After polymerisation, the PMAS templated PAn-coated wool nylon Lycra fabrics were washed with cold tap water and then dried at room temperature.

Effect of Aniline to PMAS Ratio

Three pieces of fabric cut from PMAS-treated wool nylon Lycra were immersed in three separate solutions containing different concentrations of aniline monomer. The solutions were adjusted to pH 1.4 by adding concentrated HCl before putting the fabric in the solutions. The PMAS concentration was calculated based on a dimer repeat unit. The ratios of aniline monomer to ammonium persulfate used were 1:0.25, 2:0.50 and 3:0.75. The APS was added dropwise using a burette over a period of about 17 hours at room temperature.

Molar ratio of PMAS/Aniline/APS (the APS used ranged from 0.25 – 0.75)

	PMAS	Aniline	(NH ₄) ₂ S ₂ O ₈
(a)	1	1	0.25
(b)	1	2	0.50
(c)	1	3	0.75

Effect of Oxidant Concentration

Three pieces of fabric were cut from PMAS-treated wool nylon Lycra and immersed in the same concentration of aniline monomer (adjusted to pH 1.4). Then polymerisation was initiated by using different concentration of ammonium persulfate for 17 hours.

Molar ratio of PMAS/aniline/ammonium persulfate (the ratio of PMAS/Aniline=1:2 was maintained)

	PMAS	Aniline	(NH ₄) ₂ S ₂ O ₈
(a)	1	2	0.5
(a)	1	2	1.0
(c)	1	2	2.0

Polymerisation Temperature Using the ratios that gave the most conductive fabrics, three different reaction temperatures including room temperature (25 °C), 15 °C and 2 °C, to prepare the polyaniline were investigated.

Aniline Monomer Consumption The consumption of aniline monomer in the polymerisation process was determined by measuring aniline monomer concentration before and after polymerization using High Performance Liquid Chromatography (HPLC). The mobile phase consisted of 10% methanol: 90% water. 5 ml of ion pairing reagent tetrabutylammonium dihydrogen phosphate was added for every 1 L of solution above. A flow rate of 0.8 ml min⁻¹ was used.

4.2.4. Characterisation of PMAS Templated PAn-coated Wool Fabric

Characterisation of templated PAn-coated wool nylon Lycra fabrics was carried out using surface resistivity, cyclic voltammetry (CV), scanning electron microscopy (SEM), UV-Vis spectra and thermogravimetry (TGA) on coated fabrics.

4.2.4.1. Surface Resistivity

The stability was investigated by measuring the surface resistivity of PAn-coated wool nylon Lycra fabric using the AATCC 76 two point-probe technique.

4.2.4.2. Cyclic Voltammetry

Cyclic voltammetry was conducted in a three-electrode electrochemical cell (Refer to Chapter 2, Schematic 2.5) using a reticulated vitreous carbon (RVC) onto which the PAn-coated wool nylon Lycra measuring 2 cm x 1 cm was wrapped. An Ag/AgCl (3 M NaCl) reference electrode and platinum mesh auxiliary electrode were used. The HCl solution was purged with nitrogen gas for 10 minutes prior to use. The lower and upper potential limits were set at -0.4, -0.6 and 1.0 V, respectively, and the linear sweep scan rate was set to 10 mV/s.

4.2.4.3. UV-Vis Spectra

UV-Vis absorption spectra were obtained after immersing the wool in a liquid of similar refractive index (*ortho*-dichlorobenzene) and using a reference cell containing only *ortho*-dichlorobenzene [13]. This renders the wool fabric transparent.

4.2.4.4. SEM

The morphology and microstructure of the conducting PAn-coated fabrics have been investigated using SEM. The images obtained were recorded using the Leica Cambridge 440 camera at the Department of Materials Engineering, University of Wollongong. SEM samples, such as uncoated fabrics, PMAS-treated and templated PAn-coated wool

nylon Lycra fabrics, were sputter coated with a thin layer of gold to make them sufficiently conductive and then cut into 0.5 cm x 0.5 cm pieces. The SEM images were taken at different magnifications varying between 500 and 30,000 in order to obtain detailed information on the samples.

4.2.4.5. Thermogravimetric Analysis

Thermal gravimetry was carried out using a TGA 92 Thermoanalyzer. A temperature profile was programmed to increase from 60 °C to 500 °C at a heating rate of 10 °C per minute. Thermogravimetric analysis has been performed by measuring the weight loss of pure polymers and uncoated, PMAS-treated, templated PAn-coated wool nylon Lycra fabrics.

4.3. RESULTS AND DISCUSSION

4.3.1. Effect of Reaction Conditions on Integration of the Molecular Template -PMAS

Effect of pre-treatment of fabric surface: A non-ionic wetting agent, (Lissadol TN 450, ICI Australia) has been used to pretreat the wool fabric surface in order to render it hydrophilic. Surface pre-treatment was carried out using a detergent, Sandoclean PC Liquid, from Clariant (Australia) Pty Ltd. 70 °C was used for treatment in order to remove mineral, silicone oils and other contamination [14].

Two pieces of wool nylon Lycra fabrics of approximately the same mass (ca. 2.64 – 2.88 g) were dyed with PMAS. One of them was washed with Sandoclean PC Liquid

before the dyeing process; the other was not washed with Sandoclean PC Liquid. UV-vis spectra of the PMAS solution were obtained before and after dyeing. The amount of PMAS depletion was calculated from the decrease in intensity of the absorbance peak at 475 nm in the UV-Vis spectra. The concentration of aqueous PMAS solution employed in this chapter were estimated from their absorbances at 475 nm, the λ_{\max} of PMAS, by reference to the Beer's Law plots shown in Figure 4.5. These plots were constructed by adding increasing amounts of a 1 gL⁻¹ PMAS solution to 50 ml of water and recording the UV-Vis spectrum. Beer's Law is seen to be obeyed over a PMAS concentration range from 0.02 gL⁻¹ to 0.1 gL⁻¹. Surface resistivity of these two pieces of PMAS-treated wool nylon Lycra fabrics was measured by the two point-probe method. Results are given in Table 4.1.

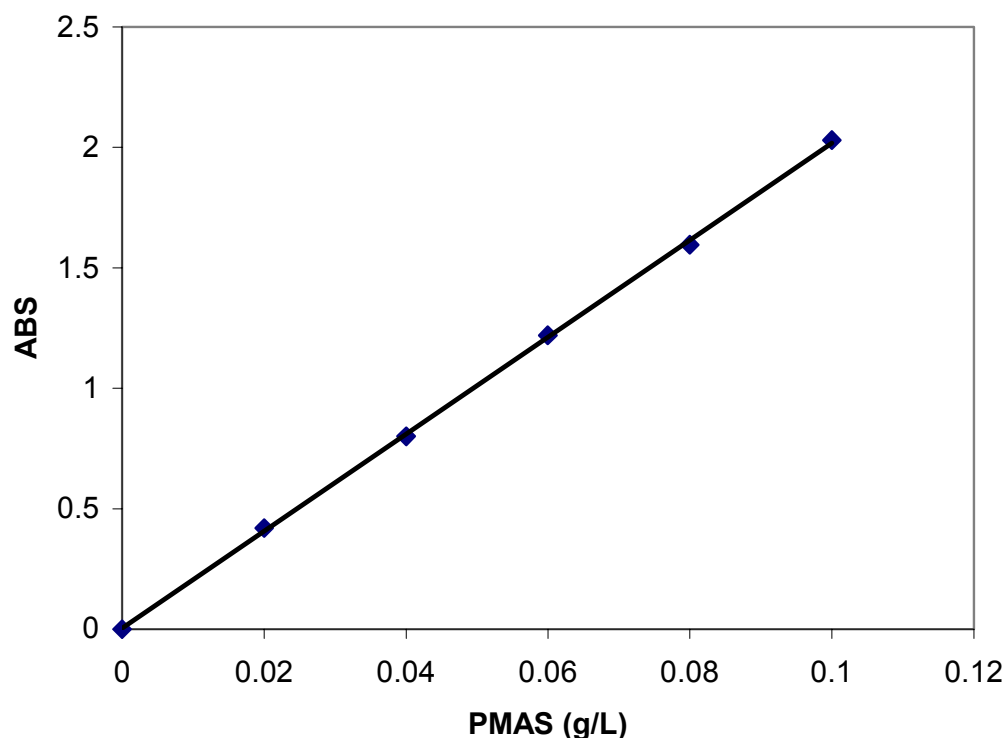


Figure 4.5. Beer's Law plot for aqueous PMAS solution.

Results indicate that pre-treatment with Sandoclean PC Liquid results in an increase in exhaustion of the PMAS on the fabric surface from about 50% to 84%. High exhaustion of PMAS on the fabric results in improved conductivity. The surface resistivity of PMAS-treated wool nylon Lycra (unwashed) was too high to measure accurately. The surface resistivity of PMAS-treated wool nylon Lycra fabric after washing with Sandoclean PC Liquid decreases to $53.3 \text{ M}\Omega/\square$.

Table 4.1 Summary of wool nylon Lycra washed with and without Sandoclean PC Liquid

Fabric Sample (g)	Polymer	PMAS Solution (g)	ABS 475 nm	Exhaustion (%)	PMAS on the fabric (g)	Surface Resistivity ($\text{M}\Omega/\square$)
2.86 (Washed)	PMAS 0.286g	Before dyeing	0.533	84.8	0.243	53.3
		After dyeing	0.081			
2.64 (Unwashed)	PMAS 0.264g	Before dyeing	0.464	50.6	0.134	>>200
		After dyeing	0.229			

Effect of pH control: Protein fibres such as wool fibres are of an amphoteric character, being capable of combining with both acids and bases. When a wool fibre is placed in an acid or alkaline solution the solution pH generally changes due to the adsorption of hydrogen ions from the solution or the liberation of hydrogen ions by the protein. The gain of these hydrogen ions from the acid solution makes the wool positively charged and consequently an equivalent number of negatively charged ions enter the fibres. If wool fibres are placed in a very strong acid solution the protein will adsorb the maximum possible number of hydrogen ions, so that all the carboxyl groups will be unionized and all the amino groups will carry a hydrogen ion and be positively charged. With an increase in the pH of the solution, there will be loss of hydrogen ions

until at about pH 6 when nearly all the carboxyl groups are ionized and be negatively charged [15].

The template molecule PMAS contains sulfonic acid groups. The formation of template PMAS coated wool fabric can be helped by acid-base interactions between the negative sulfonate groups on the PMAS chain and positive amino groups in wool fibres. When an electrolyte such as PMAS is adsorbed by wool fibre, the whole fibre must contain equivalent number of anions and cations. In this case, PMAS becomes closely associated with the wool fibre, being combined with it. Wool is more resistant to acid than to alkalis. Diluted acids even at boiling point do not damage wool. Using a strong acid such as hydrochloric acid in the dyeing process with PMAS, enables amino groups on the wool fibre to adsorb more hydrogen ions and subsequently attach a maximum possible number of sulfonate groups to the PMAS chain.

The effect of pH on the uptake of PMAS and the resistance of the resultant textile were investigated. The lowest resistance 184 M Ω and maximum exhaustion (up to 99.6% of PMAS) were obtained using a pH of 1.4. A pH of 1.4 was used for all subsequent work.

Table 4.2 Effect of variation of pH on the application of PMAS [16].

Initial pH	Resistance	Exhaustion (%) 475nm
Please see print copy for image		

Effect of temperature of the dye bath: The rate of dyeing is greatly dependent on temperature. In general, higher temperatures are to ensure adequate penetration of the polymer structure of the fibre. Below about 40 °C, there is practically no transfer of dye molecules from the dye liquor to the fibre polymer system [17]. When dyeing at elevated temperatures, dye molecule penetration of the fibre polymer system is increased significantly. At a temperature of about 100 °C the heat generates a very large amount of energy in the constituents of the dye liquor, and at the same time swells the fibre thus enabling the dye molecules to penetrate the fibre polymer system more readily [17].

Three different temperatures (40 °C, 60 °C and 90 °C) were used to investigate the optimal uptake of PMAS on the wool nylon Lycra fabric. Table 4.3 shows the effect of variation of temperatures on the application of PMAS.

Table 4.3 The effect of variation of temperatures on the application of PMAS.

Temperature (°C)	Surface Resistivity (MΩ/□)	Exhaustion (%) 475nm
---------------------	-------------------------------	-------------------------

Considering concentrated HCl may damage wool fibres on boiling [18], the dyeing temperature of 90 °C was chosen as a compromise between getting maximum exhaustion of the PMAS, and minimising the fibre damage.

4.3.2. Effect of Reaction Conditions on Coating of Templated Textile with Polyaniline

4.3.2.1. Effect of Aniline to PMAS Ratio

Template polymerisation of aniline was carried out using ammonium persulfate (APS) as oxidant in the presence of PMAS-treated wool nylon Lycra fabric at room temperature. The amount of PMAS uptake on the wool nylon Lycra was calculated from the decrease in intensity of the absorbance peak at 475 nm in the UV-Vis spectra (Figure 4.5). Three different aniline concentrations based on the amount of PMAS uptake on the fabric were used to prepare conductive PMAS templated PAn coated wool fabrics. The molar ratio of PMAS to aniline was chosen and given in Table 4.4. The surface resistivity was measured (Table 4.4).

Table 4.4 The surface resistivity of the PMAS templated PAN-coated wool nylon Lycra produced under different PMAS:Aniline ratios at room temperature.

Wool nylon Lycra	Molar Ratio of PMAS to Aniline (1:1)	Molar Ratio of PMAS to Aniline (1:2)	Molar Ratio of PMAS to Aniline (1:3)
Surface resistivity ($M\Omega/\square$)	9.17	1.85	3.65

Results from Table 4.4 indicate that the surface resistivity on the coated fabrics are affected by initial molar ratio of aniline to PMAS on the fabrics. The best conductivity of the wool nylon Lycra is $1.85 M\Omega/\square$, which is coated with polyaniline using the ratio of PMAS to aniline of 1:2. The PMAS concentration was calculated based on a dimer repeat unit. There is one sulfonate group on each repeat unit of PMAS which is negatively charged and aniline is primarily positively charged. Each repeat unit of PMAS serves as a large molecular counterion that is integrated with 2 units of aniline monomer. This approach is based on preferential electrostatic alignment of aniline monomer onto an anionic template by appropriate control of molar ratio of aniline to PMAS to form more conductive templated polyaniline coated fabrics.

4.3.2.2. Effect of Oxidant Concentration

The mechanism of chemical oxidation was described in Chapter 1. The reaction is believed to proceed in four steps (Refer to Figure 1.4). When all oxidant is consumed, the remaining aniline reduces the pernigraniline to form the final product, the green emeraldine salt with good conductivity. Normally chemical polymerisation of aniline is carried out in an aqueous acid solution of aniline and oxidant with a slight excess of

aniline, because an equivalent or excess amount of oxidant results in fast hydrolysis of the product [19-20]. Polyaniline with high molecular weight synthesised at - 40 °C using a 0.25:1 mole ratio of oxidant to aniline was reported by Adams *et al.* [21].

The effect of the concentration of oxidant (APS) has been investigated here using three different oxidant concentrations to prepare PMAS templated PAn coated wool nylon Lycra fabrics at room temperature. The surface resistivity of the coated fabrics was measured using the two point-probe method (Table 4.5).

Results from Table 4.5 indicate that less resistive wool nylon Lycra fabric can be obtained by using lower concentration of the oxidant ammonium persulfate. The best result was obtained from a ratio of aniline to APS of 1:0.25. Using more concentrated oxidant (APS) results in the over-oxidation of conducting polymer, which is the irreversible chemical oxidative degradation of a conducting polymer on the coated fabric and leads to loss of conductivity.

Table 4.5 The surface resistivity of the PMAS templated PAn-coated wool nylon Lycra fabrics produced using different Aniline:APS ratios at room temperature.

Wool nylon Lycra	Molar Ratio of Aniline to APS (1:0.25)	Molar Ratio of Aniline to APS (1:0.50)	Molar Ratio of Aniline to APS (1:1.0)
Surface resistivity (M Ω /□)	1.85	3.07	297.9

4.3.2.3. Polymerisation Temperature

MacDiarmid and Epstein [22] reported that the molecular weight of polyaniline could be increased by decreasing the polymerisation temperature. In another experiment, they fractionated polyaniline base by preparative gel permeation chromatography (GPC). The conductivity of fractions protonated in 1 M HCl rose with increasing molecular weight from 1.2 S cm^{-1} for $M \approx 20000$ to 17 S cm^{-1} for $M \approx 170000$ after which it was essentially constant up to $M \approx 320000$ [22]. The effect of the polymerisation temperature, room temperature (25°C), 15°C and 2°C , used during aniline oxidation onto the templated textile was investigated here.

It was found that no polymerisation had occurred in the solution using different temperatures. The coatings were uniform and the colour of PMAS templated PAn coated fabric changed from dark brown at room temperature to dark green at lower temperature (2°C). It indicates that more conductive emeraldine salt was formed on the wool fabric surface.

The surface resistivity of PMAS templated PAn coated wool fabric using different temperatures was measured (Table 4.6). As expected from the work of MacDiarmid and Epstein discussed above, the lower the reaction temperature, the lower the resistivity of the coated fabrics.

Table 4.6 Surface resistivity of the PMAS templated PAn - coated wool nylon Lycra prepared using different temperatures for aniline oxidation.

Reaction temperature (°C)	Surface resistivity ($M\Omega/\square$)
25	0.624
15	0.360
2	0.064

4.3.2.4. Aniline Monomer Consumption at Different Temperatures

The consumption of aniline monomer during oxidation on to the PMAS templated wool nylon Lycra fabric using different temperatures was determined by measuring aniline monomer solution before and after the polymerisation process (Table 4.7).

HPLC results indicate that more aniline monomer (30%) was consumed in the polymerisation process at lower temperature. It seems that the lower temperature is likely to increase the degree of polymerisation to form conductive emeraldine salt on the wool nylon Lycra fabric. It also confirms previous results that the surface resistivity of templated PAn coated wool nylon Lycra fabric decreases from $624 K\Omega/\square$ to $64 K\Omega/\square$ when temperature is decreased from 25 °C to 2 °C.

Table 4.7. Consumption of aniline monomer during polymerisation in the presence of PMAS templated wool nylon Lycra using different reaction temperatures.

Type of templated fabric	Aniline consumed (%) (25 °C)	Aniline consumed (%) (15 °C)	Aniline consumed (%) (2 °C)
PMAS templated PAn coated wool nylon Lycra fabric	21.2	23.6	29.9

4.3.3. Characterisation of PMAS Templated PAn-coated Fabrics

4.3.3.1. Surface Resistivity Change vs Time of PMAS-treated Wool Fabrics

The surface resistivity for the PMAS-treated material was found to be $28.8 \text{ M}\Omega/\square$ immediately after coating. The PMAS-treated wool nylon Lycra fabric was cut into two small pieces of dimensions 4 cm long 4 cm wide. One was stored in air and the other was stored in a snap lock resealable bag obtained from Glad Company. The snap lock resealable bags are made from thick safe low density polyethylene with an oxygen permeability coefficient of $2.2 \times 10^{-13} \text{ cm}^3 (273.15 \text{ K}; 1.013 \times 10^5 \text{ Pa}) \times \text{cm} \times / (\text{cm}^2 \times \text{sec} \times \text{Pa})$ [23]. So this plastic bag can be used as an oxygen barrier.

The changes of the surface resistivity vs. time of both PMAS-treated fabrics were measured using the two point-probe method. Results are shown in Figure 4.6. It was found that PMAS-treated wool nylon Lycra was less stable in air. The surface resistivity of this fabric increased by a factor of 16 after exposure in air for 54 days. The degradation in conductivity can be reduced by storing the coated fabric in a sealed plastic bag in order to avoid oxidative reaction in air. The surface resistivity of the PMAS-coated wool nylon Lycra did not change after storing in the plastic bag for 54

days. The reason is that the sealed bag is basically classified as non-permeable, so the attack in the bag is negligible.

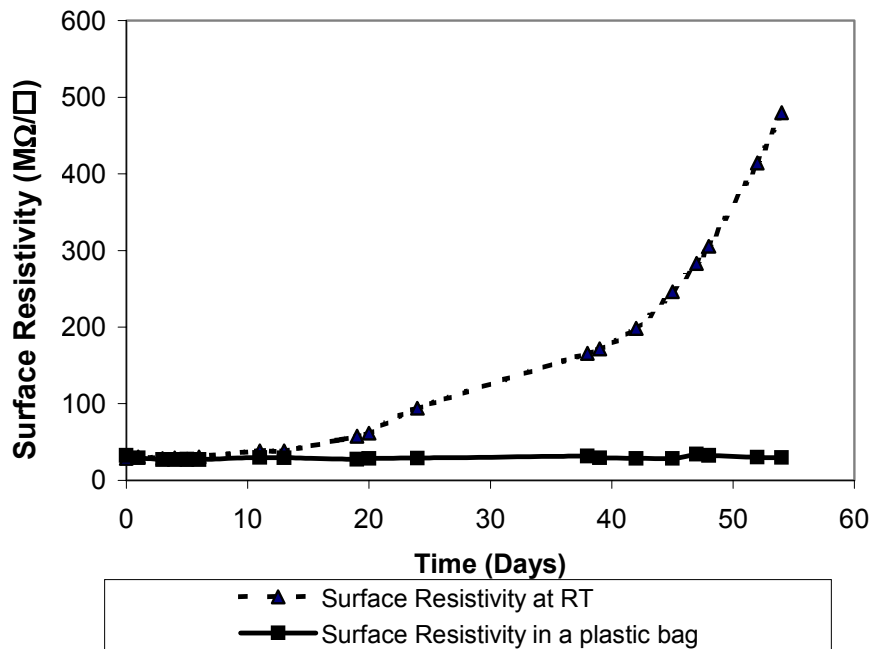


Figure 4.6. Surface resistivity vs. storage time for PMAS-treated wool nylon Lycra. Broken line: stored in the open air, bold line: stored in a sealed plastic bag.

4.3.3.2. Surface Resistivity Change vs Time of PMAS Templated PAn-coated Wool Fabrics

The surface resistivity as a function of time after coating was also measured for samples coated with PAn at two different temperatures. Each coated fabric was cut into two small pieces 4 cm x 4 cm in size. One was stored in the open air; the other was stored in a snap lock resealable bag provided from the Glad Company. Changes of the surface resistivity vs. storage time of both coated fabrics were measured using the two point-probe method (Figure 4.7 and Figure 4.8).

Results again confirm that the conductivity of the polyaniline coated fabric is less stable in air. The surface resistivity of templated PAn-coated wool nylon Lycra fabric prepared either at room temperature or at lower temperature increased by 230 times and 225 times respectively after exposure to air for 55 days. The degradation of polyaniline on the coated fabric can be reduced by storing the fabric in the sealed plastic bag in order to avoid oxidative reaction in air. The surface resistivity of templated PAn-coated wool nylon Lycra fabrics prepared either at room temperature or at a lower temperature increased about 1.9 times for both after storing in a plastic bag for 55 days.

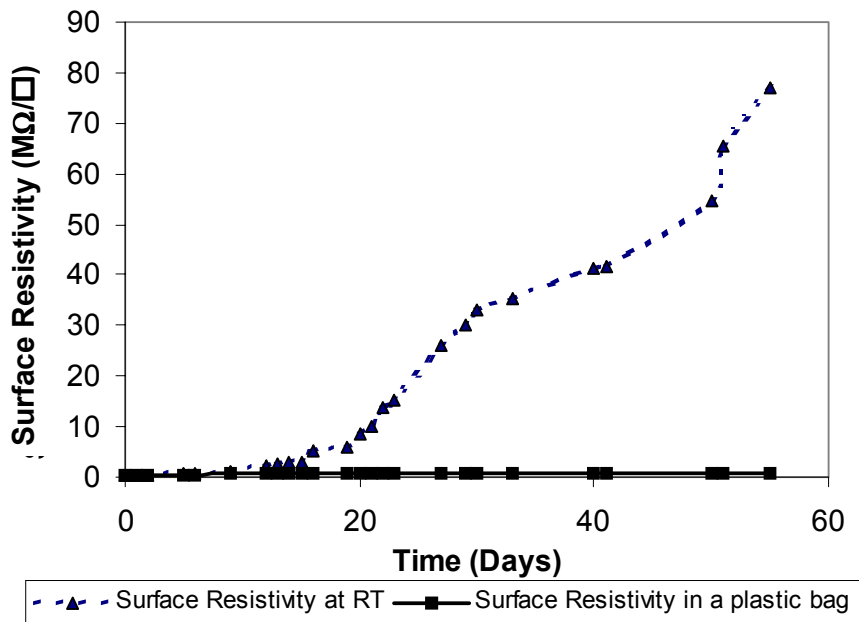


Figure 4.7. Changes in surface resistivity vs. time for wool nylon Lycra coated with PMAS then coated with PAn prepared at room temperature. Broken line: stored in the open air, bold line: stored in a sealed plastic bag.

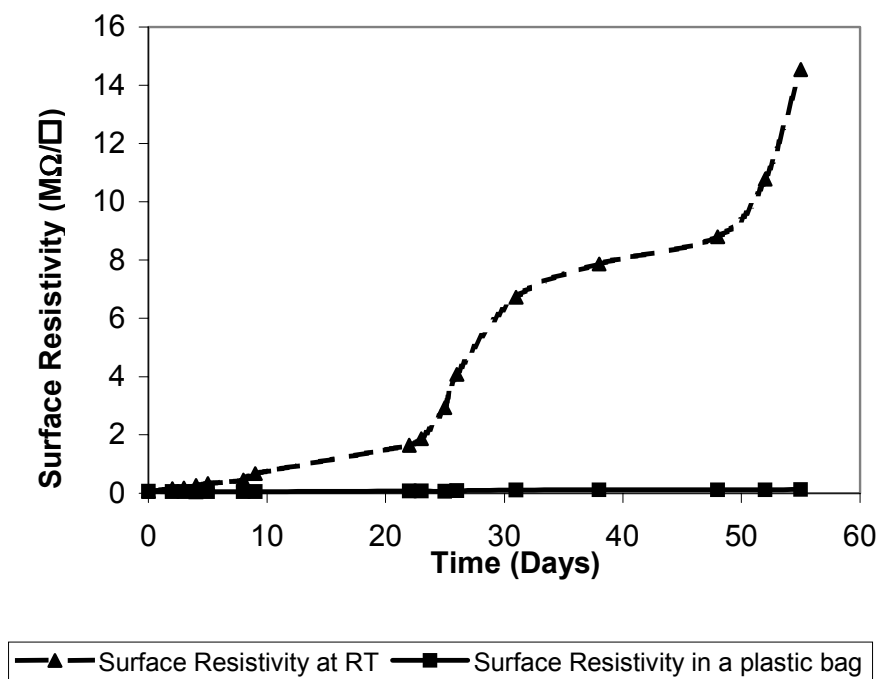


Figure 4.8. Changes in surface resistivity vs. time. PMAS templated polyaniline wool nylon Lycra prepared at lower temperature (2-3 °C). Broken line: stored in the open air, bold line: stored in a sealed plastic bag.

Cyclic voltammetry and UV-Vis spectra of PMAS templated PAn coated wool nylon Lycra before and after storage are investigated later.

4.3.3.3. Cyclic Voltammetry

Polyaniline is the only conducting organic polymer that exists in three easily accessible oxidation states [24]. The chemical properties are varied and can be controlled by application of a potential and/or by change of pH. There are two distinct redox processes as well as pH switching between unprotonated and protonated states. The redox processes are readily observed using cyclic voltammetry [25]. The most

conductive form of polyaniline is the emeraldine salt form that exists between about +0.20 V and +0.60 V vs. Ag/AgCl. At less positive potentials, the fully undoped form (leucoemeraldine) is much less conductive, as is the fully oxidised form (pernigraniline) at higher potentials [25]. Figure 4.9 shows the electrochemical switching property of polyaniline on a glassy carbon electrode in 1 M HCl. The potentials at which colour changes occur and the change in the potential of the second redox reaction with pH are shown [25]. Two anodic peaks and two cathodic peaks are assigned to the oxidations of leucoemeraldine to emeraldine salt and emeraldine salt to pernigraniline, respectively.

In order to investigate the electroactivity of the polyaniline coated wool nylon Lycra fabrics, cyclic voltammetry was carried out in 1 M HCl aqueous solution. Two small pieces of coated wool nylon Lycra fabric were cut from PMAS-treated and PMAS templated PAn coated wool nylon Lycra fabrics respectively. The cyclic voltammograms (CV) of PMAS-treated and polyaniline-PMAS coated textiles are shown in Figure 4.10 and Figure 4.11.

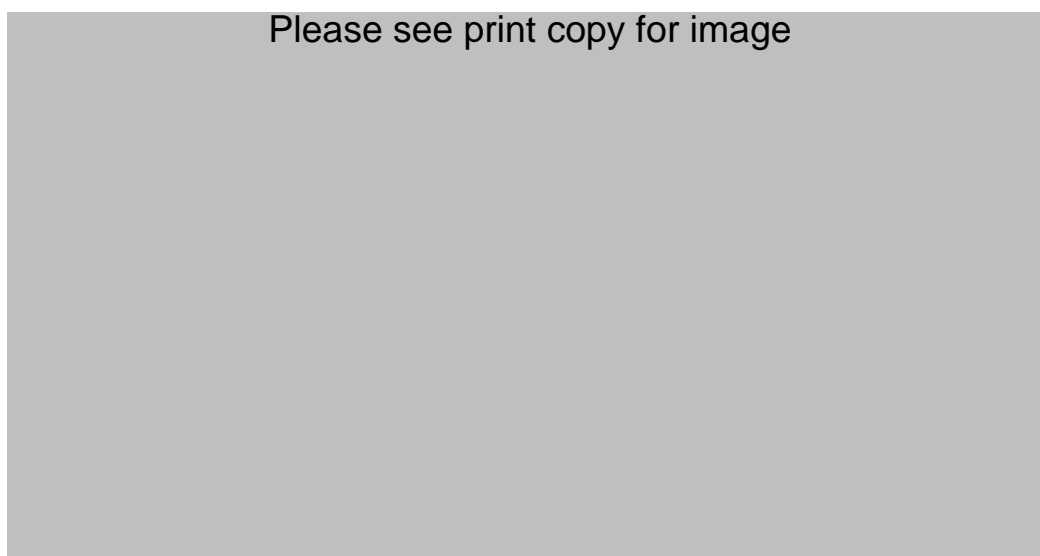


Figure 4.9. Cyclic voltammogram of polyaniline (HCl) on a glassy carbon electrode in 1 M HCl at a scan rate of 50 mV/s [25].

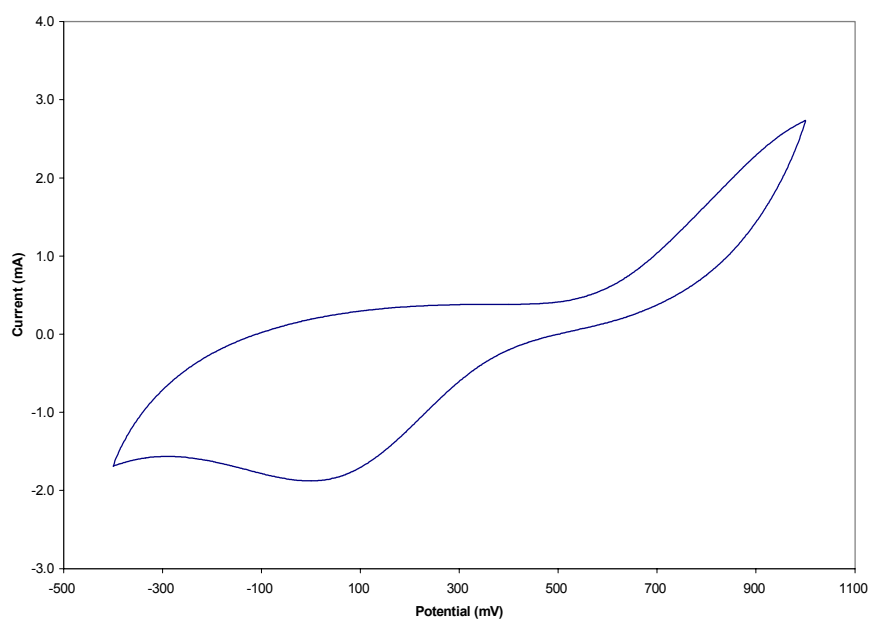


Figure 4.10. Cyclic voltammogram (CV) obtained using PMAS-treated wool nylon Lycra as the working electrode in 1 M HCl at a scan rate of 10 mV/s.

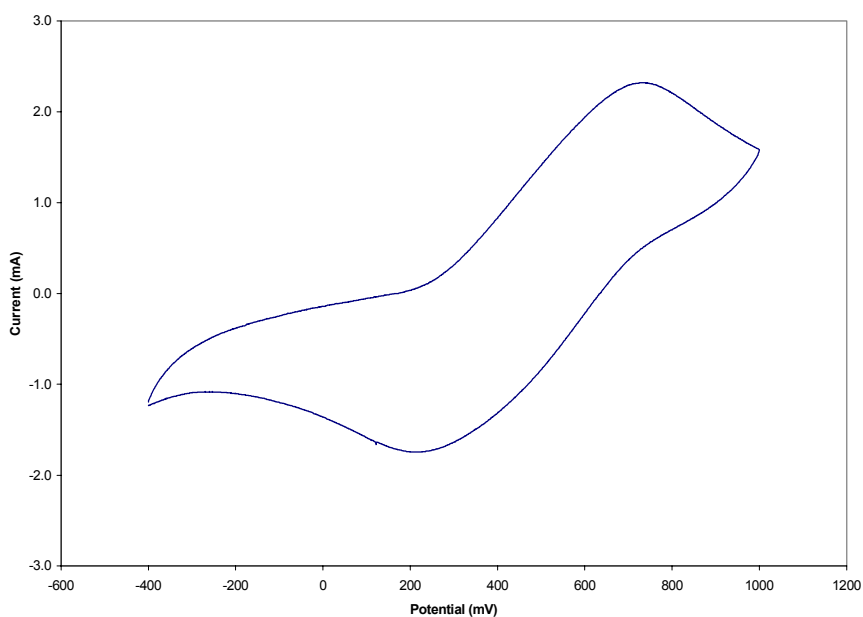


Figure 4.11. Cyclic voltammogram (CV) obtained using PMAS templated polyaniline coated wool nylon Lycra as working electrode in 1 M HCl at a scan rate of 10 mV/s.

Compared with the two sets of redox peaks obtained with PAn (Figure 4.9), The redox peaks are poorly defined for PMAS-treated wool nylon Lycra fabric over the full potential window from -0.4 V to 1.0 V due to the lower conductivity and high surface area of the fabric. However, a set of redox peaks are observed on PMAS templated PAn coated wool nylon Lycra fabric. This shows the redox process of this coated fabric with peak potentials $E_{p(c)}$ and $E_{p(a)}$ appearing at $+0.19$ and $+0.73$ V respectively when scanned between -0.4 V to $+1.0$ V. Similar result was observed by W. Liu and co-workers for polyaniline/sulfonated polystyrene complex [26]. These peaks may be assigned as the first redox wave in the parent PAn. The absence of the second redox process is believed to be due to the exceptional resistance of the PAn to oxidation to the pernigraniline state when complexed to a polyelectrolyte [26].

The cyclic voltammograms (CV) of PMAS templated PAn-coated wool nylon Lycra under different storage conditions are shown in Figure 4.12. The coated textiles were stored in the open air or a sealed plastic bag for 55 days respectively (Refer to 4.3.3.2). The redox peaks were observed on the coated fabrics with peak potentials $E_{p(c)}$ and $E_{p(a)}$ appearing at around $+0.24$ V and $+0.65$ V respectively when scanned between -0.6 V to $+1.0$ V. Results from CV indicate that the redox charge of polyaniline decreases with increasing surface resistivity. It also confirms the increase in surface resistivity on the coated fabric after storing in the open air compared to that stored in a sealed- plastic bag.

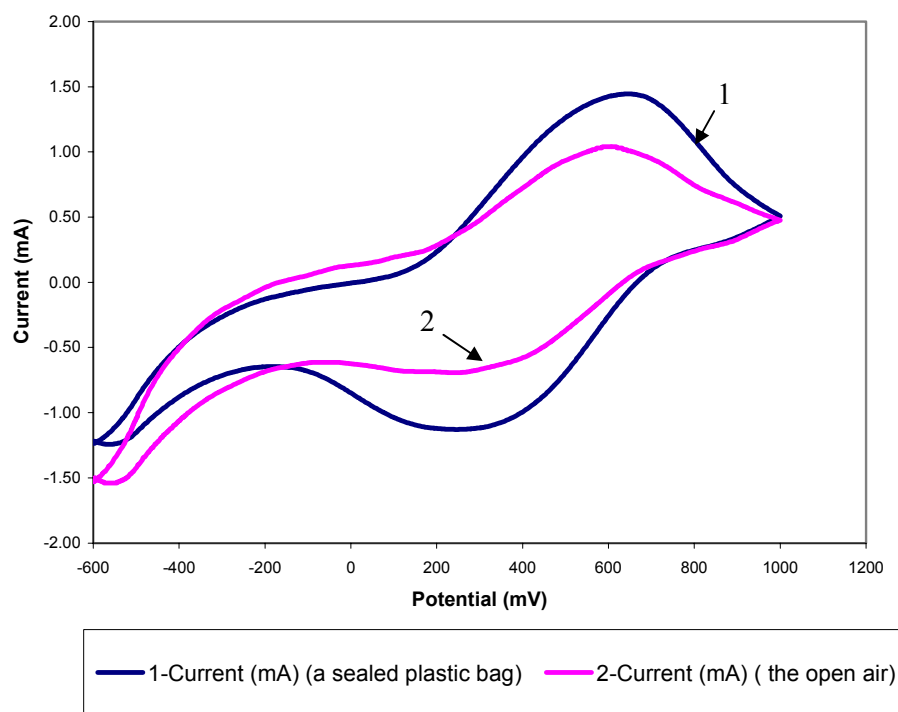


Figure 4.12. Cyclic voltammograms (CV) obtained using PMAS templated polyaniline coated wool nylon Lycra as working electrode in 1 M HCl at a scan rate of 10 mV/s. Pink line: stored in the open air for 55 days, blue line: stored in a sealed plastic bag for 55 days.

4.3.3.4. UV-Vis Spectra

Three small pieces of wool nylon Lycra fabrics were cut from uncoated and polyaniline coated textile respectively. The UV-Visible spectra using *ortho*-dichlorobenzene as a solvent on uncoated, PMAS-treated and PMAS templated PAn coated wool nylon Lycra fabrics are shown in Figure 4.13. Spectrum 1 shows no absorption obtained on uncoated wool nylon Lycra fabric and Spectrum 2 exhibits a band localized at ca. 480 nm, characteristic of PMAS on the wool nylon Lycra after the dyeing process. There are two peaks observed in spectrum 3 at ca. 445 nm and 480 nm, assigned as a low wavelength

polaron $\rightarrow \pi^*$ band transition from PAn emeraldine salt and a $\pi - \pi^*$ transition band from PMAS, respectively. Spectrum 3 also exhibits a broad band around 800 nm and a broad strong free carrier tail, corresponding to conductive PAn emeraldine salt on the wool nylon Lycra fabric.

Spectrum 1 from Figure 4.14 shows 3 bands localized at ca. 330 nm, 440 nm and 800 nm respectively, characteristic of conductive emeraldine salt on the coated wool fabric stored in the sealed plastic bag. Spectrum 2 from Figure 4.14 shows that the absorption intensity of the polaron band is much weaker compared to the intensity absorption at ca. 440 nm. The intensity of absorption at ca. 810 nm decreases, which suggests that the higher conductive emeraldine salt decreased on the coated fabric stored in the open air. Hence the surface resistivity of PAn-coated fabric increases after exposure to the open air.

UV-Vis spectra of oxidized and reduced forms of PMAS templated PAn-coated wool nylon Lycra are shown in Figure 4.15. The oxidised and reduced forms of PAn-coated textile were prepared by immersing the fabric into 0.1 M FeCl_3 or Na_2SO_3 for 2 hours respectively. The absorption intensities at ca. 440 nm and 800 nm disappear in spectrum 1 of Figure 4.15, only one absorption band was obtained in its UV-Vis spectrum at ca. 325 nm. This confirmed that the emeraldine PAn salt has been reduced from the leucoemeraldine base (LB) [27]. Spectrum 2 in Figure 4.15 shows the oxidised form of PAn-coated fabric. It shows a new band at ca. 660 nm that maybe characteristic of pernigraniline salt (PS). Protonation of PB causes a violet-to blue colour change due to the formation of PS. This change is associated with the loss of the PB bond at 530 nm and the appearance of a strong PS peak at ca. 700 nm [25].

The UV-Vis spectrum of PMAS templated PAn-coated fabric before and after heating at 100 °C and 200 °C for 2 hours are shown in Figure 4.16. It is evident that three localised peaks in spectrum 1 and spectrum 2, characteristic of emeraldine salt (ES), which means only water and dopant molecules loss at ca. 100 °C. Results from spectrum 3 in Figure 4.16 shows that emeraldine PAn salt has started to decompose at above 210 °C as indicated by the decrease of the absorption intensity at ca. 430 nm and 800 nm. Thermal stability of PAn-coated textile by TGA will be discussed in detail later.

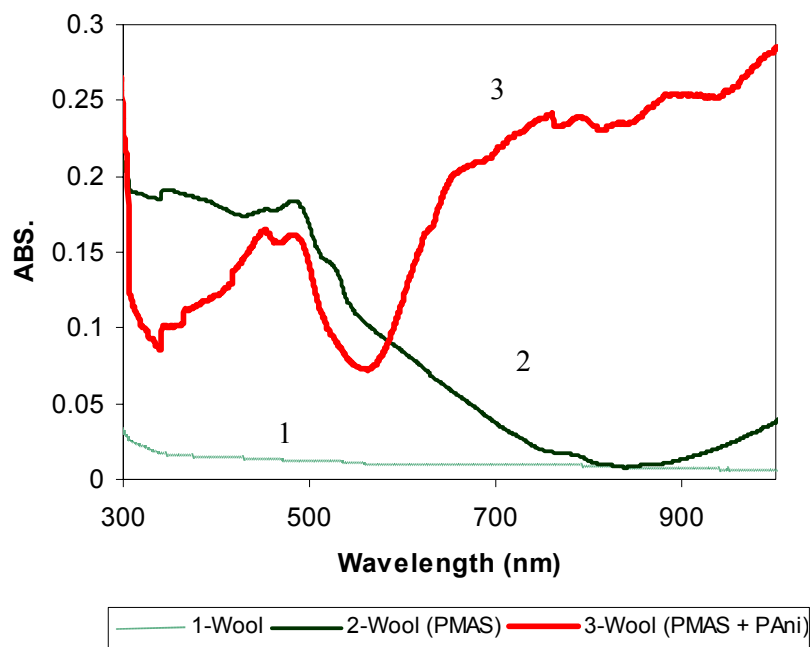


Figure 4.13. UV-Visible spectra of uncoated, PMAS & *in-situ* templating coated wool nylon Lycra using *ortho*-dichlorobenzene as a solvent.

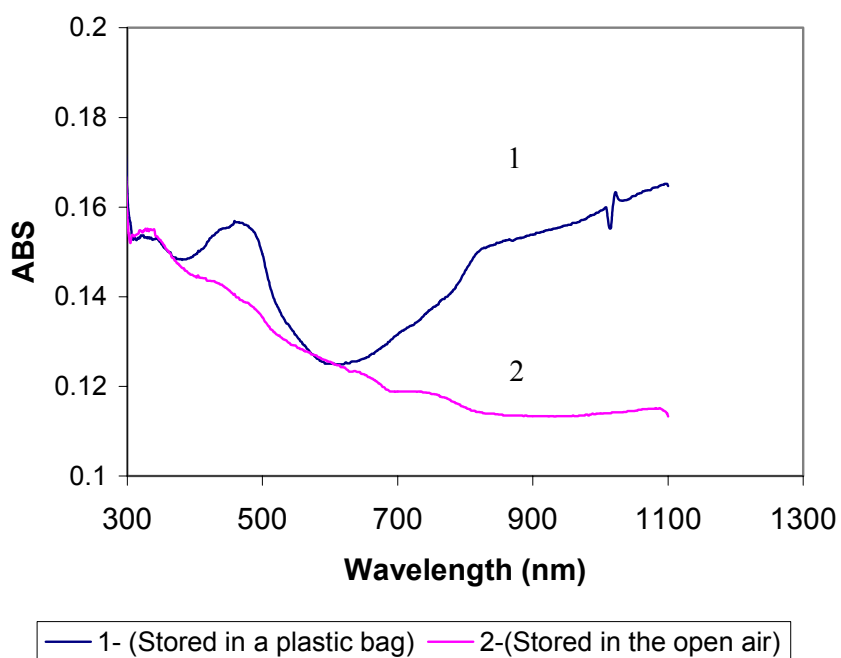


Figure 4.14. UV-Visible spectra of PMAS templated PAN coated wool nylon Lycra under different storage conditions for 55 days.

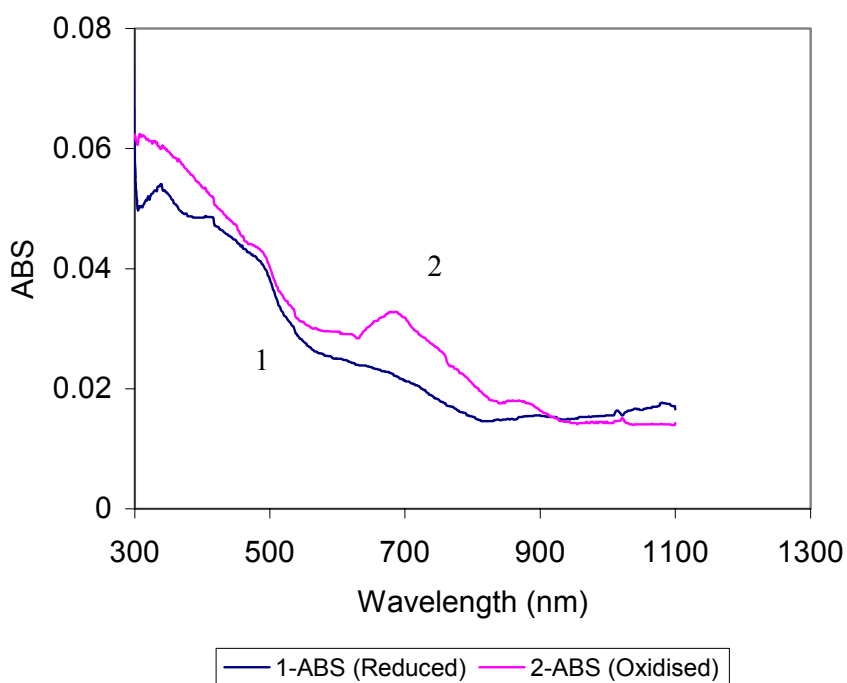


Figure 4.15. UV-Visible spectra of oxidised / reduced forms of PMAS templated PAN-coated wool nylon Lycra.

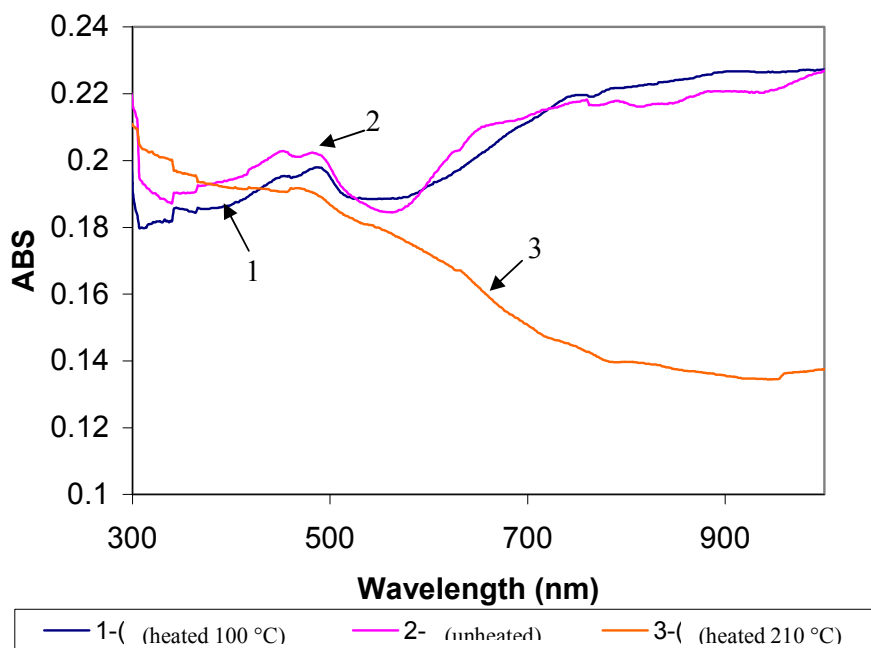


Figure 4.16. UV-Visible spectra of coated wool nylon Lycra before and after heating at 100 °C and 210 °C for 2 hours.

4.3.3.5. SEM

Scanning electron micrographs of uncoated, PMAS-treated and PMAS templated PAn coated wool nylon Lycra fabrics are shown below (Figure 4.17 ~ Figure 4.19).

Evidence for the formation of PMAS and PMAS templated PAn layer on the wool nylon Lycra fabric surface was obtained by closely examining the change in morphology observed after dyeing with PMAS and polymerisation with aniline on the fabric. Prior to application of polyaniline on the wool nylon Lycra fabric, the SEM image of the surface of the fibre has a clear and smooth morphology (Figure 4.17) and indicates that the untreated fibre has a nice, clean and sharp image. Compared with uncoated wool nylon Lycra fibre, the PMAS treated (in application of PMAS template)

fabric shows deposition of PMAS with blurred SEM cuticle's image (Figure 4.18). The diameters of uncoated and PMAS-treated fibre are ca. 20 μ and 21 μ respectively. A thicker polymer layer was formed from the PMAS templated PAn coated fibre and its diameter is ca. 24 μ (Figure 4.19). In some part of the SEM field, there was total coverage of templated PAn on the cuticle, so the cuticle was not visible.

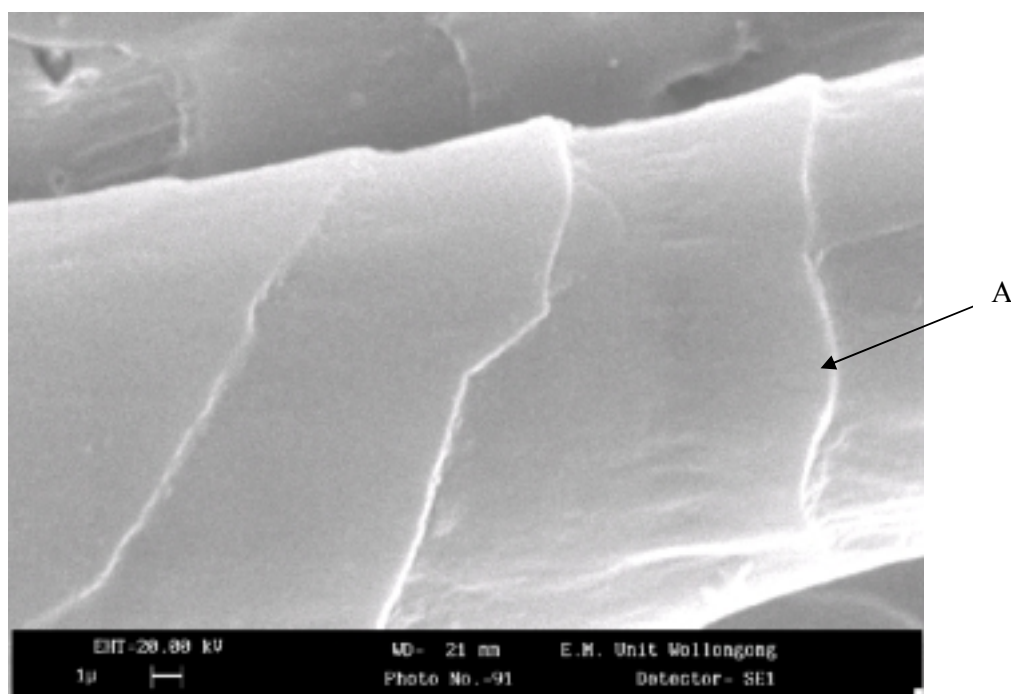


Figure 4.17. Scanning electron micrograph of uncoated wool nylon Lycra fibre.

A: clear and sharp image of cuticle.

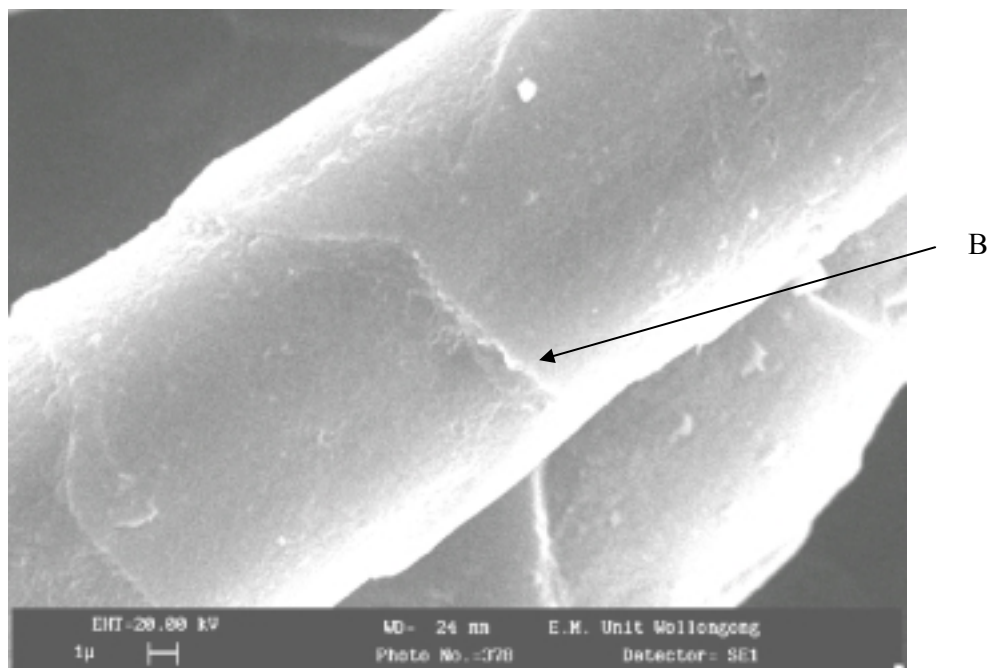


Figure 4.18. Scanning electron micrograph of PMAS-treated wool nylon Lycra fibre.

B: blurred cuticle.

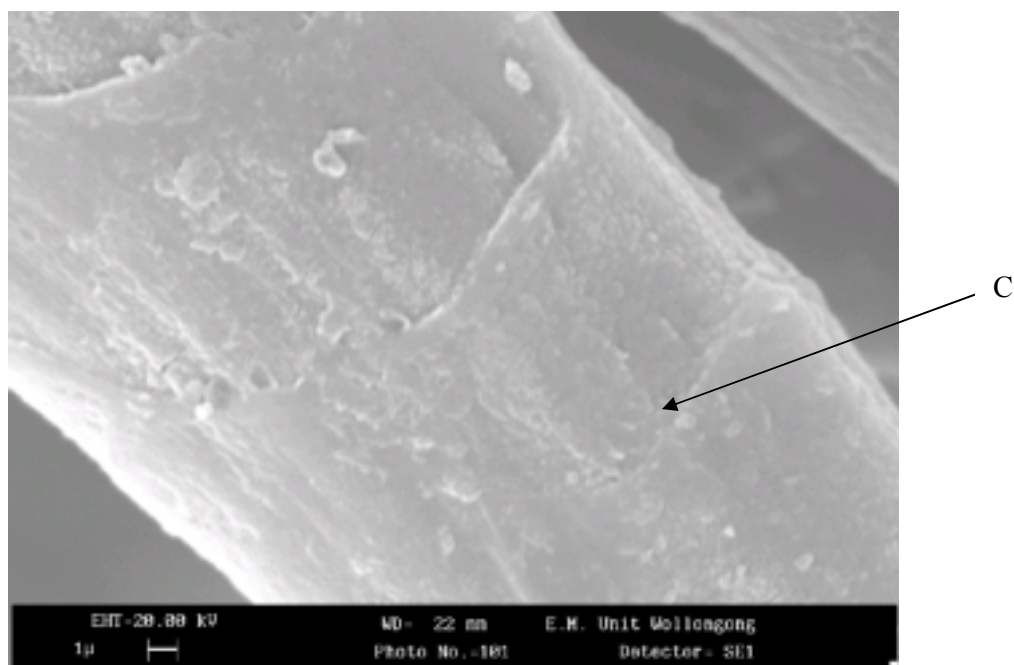


Figure 4.19. Scanning electron micrograph PMAS templated PAN-coated wool nylon

Lycra fibre. C: invisible cuticle.

4.3.3.6. Thermogravimetry

Thermogravimetric analysis is one of the commonly used methods to determine material stability by monitoring weight changes of a sample, resulting from chemical or physical transformations as a function of temperature and heating rate. For the thermal analysis of polyaniline coated nylon Lycra fabrics, TGA is used in determining the decomposition by weight loss of the samples including uncoated, PMAS-treated, PMAS templated PAn-coated wool nylon Lycra fabrics, PMAS powder, templated PMAS powder and emeraldine PAn powder during an experiment.

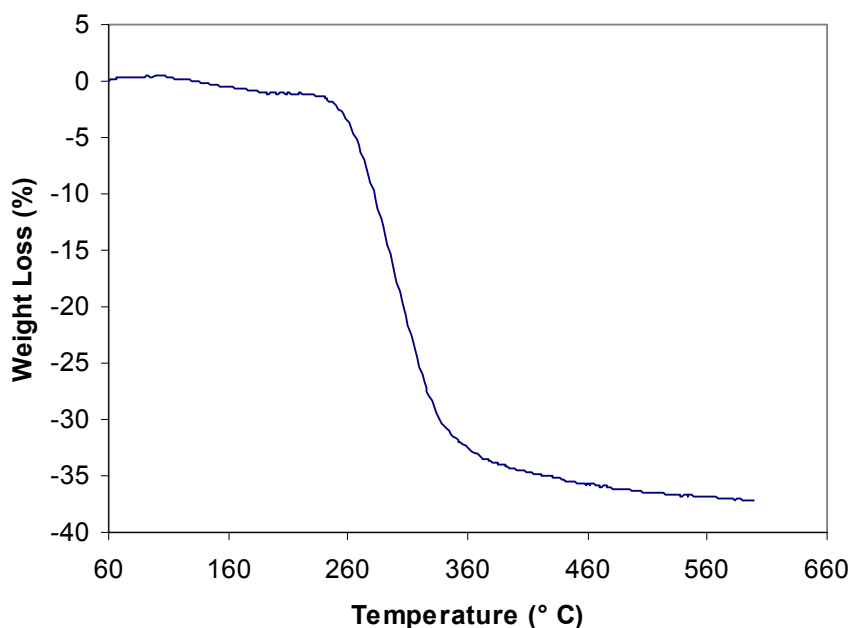


Figure 4.20. TGA (60-500 °C) PMAS powder.

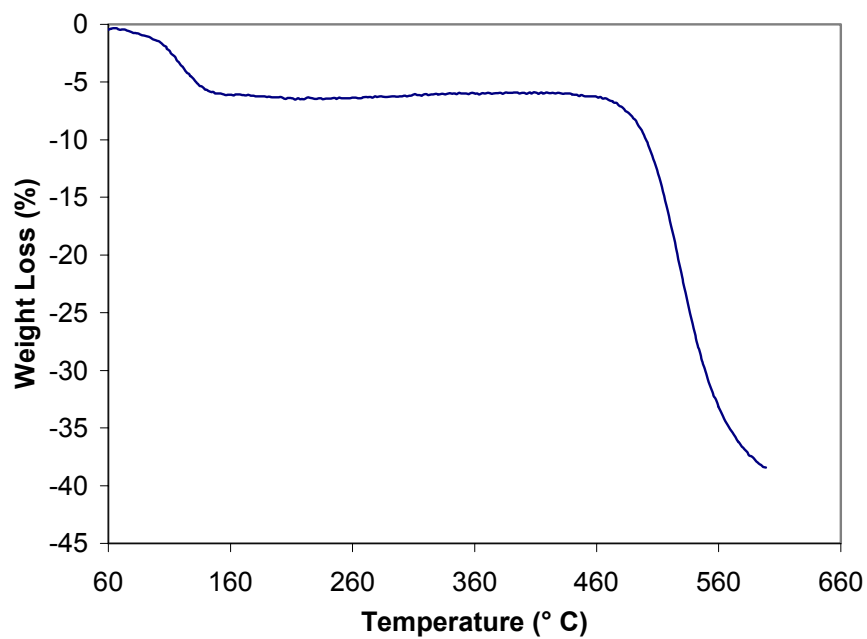


Figure 4.21. TGA (60-600 °C) of emeraldine base powder.

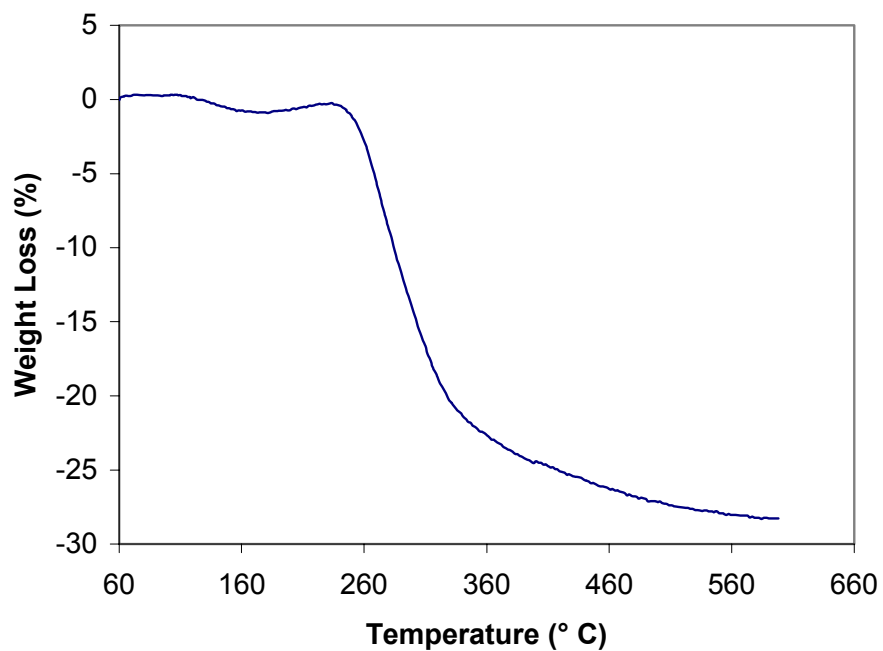


Figure 4.22. TGA (60-600 °C) of templated PAn powder (PMAS+PAn copolymer).

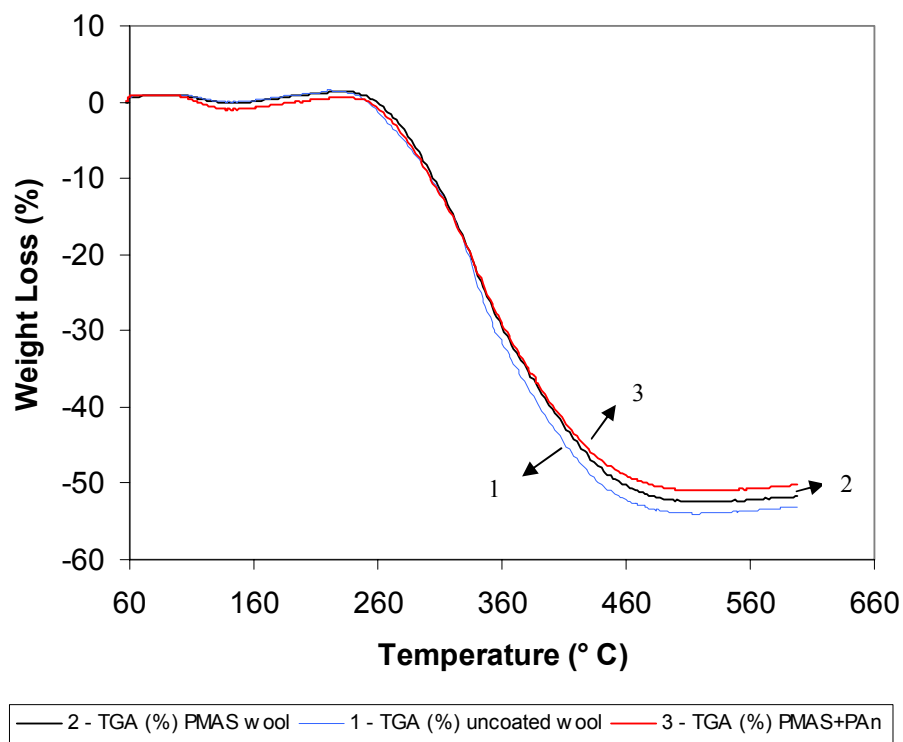


Figure 4.23. TGA (60-600 °C) of uncoated, PMAS-treated and templated PAn coated wool nylon Lycra fabrics.

PMAS powder prepared chemically at IPRI showed poor thermal stability compared with polyanilines (Figure 4.20). About 0.5% weight loss was observed up to a temperature of 150 °C, this may be attributed to evaporation of moisture. The major weight loss of PMAS powder was observed between 250 °C and 360 °C. The total weight loss at 600 °C was 37.2% due to degradation of the polymer backbone.

The emeraldine base powder (Santa Fe Science and Technology, USA) was also found to be the most thermally stable form of polyaniline (Figure 4.21). After the initial weight loss ca. 6% observed at about 150 °C, there was a major weight loss between 470 °C and 600 °C with a total weight loss of 38.4%.

PMAS templated polyaniline powder (or PMAS+PAn copolymer) prepared chemically at IPRI showed similar thermal stability as PMAS powder (Figure 4.22). After the initial weight loss of 0.78% at around 160 °C, representing water loss, the major weight loss started at about 250 °C and total weight loss at 600 °C was 28.3%. This means that PMAS templated polyaniline powder is less stable than the emeraldine PAn powder at higher temperature presumably due to the early break down of PMAS

Comparison of the TGA curves for uncoated, PMAS-treated and PMAS templated PAn coated wool nylon Lycra fabrics was made. It was found that their weight loss followed a similar trend (Figure 4.23). They all had a two-stage weight loss under nitrogen atmosphere. The first weight loss between 60 °C-150 °C is attributed to the loss of water absorbed to suffer by the fabrics. After the initial weight loss, uncoated wool nylon Lycra fabric was observed only minimal mass loss until 240 °C, but no more weight loss on the PMAS-treated and the PMAS templated PAn coated wool nylon Lycra fabrics were observed until 250 °C. The total weight loss of uncoated, PMAS-treated and PMAS templated PAn-coated wool fabrics were 53.0%, 51.7% and 50.2% respectively. In addition, the TGA of PMAS templated PAn coated fabric demonstrates similar characteristics as that of PMAS templated PAn powder. So the PMAS is the major factor in controlling the thermostability of the composite.

On the other hand, the thin layer of conductive PAn emeraldine salt can slightly improve the thermostability of the natural wool nylon Lycra fabric from 240 to 250 °C.

4.4. CONCLUSION

PMAS templated polyaniline-coated wool nylon Lycra fabrics have been prepared in the presence of a polyelectrolyte for the first time. The template molecule has been chosen in order to introduce particular functional groups, for example, the sulfonated groups into the fabrics. Once supported on the fabric surface, the sulfonated groups are expected to complex the aniline monomer during the polymerisation process, so that the addition of oxidant to the solution will cause polyaniline to form on the fabric.

Pre-treatment of fabrics washed with Sandoclean PC Liquid, use of a low reaction pH (1.4) and high dye bath temperature (up to 90 °C) significantly increases the exhaustion of PMAS with a concomitant decrease in the resistivity of the fabric.

The subsequent polymerisation of aniline onto the PMAS template in the textile has then been optimised. Factors in the polymerisation process such as the molar ratio of aniline to PMAS and aniline to APS, polymerisation temperature as well as solution pH have been investigated. The molar ratio of 1:2:0.5 between PMAS, aniline and APS was found to produce a more conductive fabric. Use of a lower polymerisation temperature results in formation of a more conductive polyaniline layer on the fabric surface. This means that the lower reaction temperature leads to production of a more conductive emeraldine salt on the fabric and thus improve its conductivity. Generally, the lower the polymerisation solution temperature, the more conductive the resultant fabrics.

The consumption of aniline monomer during the polymerisation process was measured by HPLC. Results indicate that more aniline monomer (30%) can be consumed in the

polymerisation process at lower temperature. It appears that the lower temperature is likely to increase the degree of polymerisation to form conductive emeraldine salt on the wool nylon Lycra fabric. This result has also confirmed that the surface resistivity of templated PAn coated wool nylon Lycra fabric decreases with reducing polymerisation temperature.

Conductive templated polyaniline coated wool nylon Lycra fabrics are less stable in air, even when prepared at a lower temperature, due to their high reactivity with oxygen. The degradation of polyaniline on the coated fabric can be reduced by storing the coated fabrics in a sealed plastic bag in order to avoid oxidative reaction in air. Scanning electron micrographs of uncoated and PMAS templated PAn coated wool nylon Lycra indicate that a thin, uniform and coherent polyaniline layer has been coated on the single fibre after the templating polymerisation process.

The electrochemical switching of PMAS-treated and PMAS templated PAn coated wool nylon Lycra fabrics have been characterized by cyclic voltammetry. It is hard to find the redox peaks for PMAS-treated wool nylon Lycra fabric due to its low conductivity on the fabric. But a pair of redox peaks is obtained on PMAS templated PAn coated wool nylon Lycra fabric. These peaks may be assigned as the first redox wave in the parent PAn. The absence of the second redox process is believed to be due to the exceptional resistance of the pernigraniline state.

The UV-Visible spectrum using *ortho*-dichlorobenzene as a solvent shows no absorbance on uncoated wool nylon Lycra fabric. A band localized at ca. 480 nm characteristic of PMAS was observed using the PMAS-treated textile. There are two

peaks observed in the UV-Vis spectrum of PMAS templated PAn coated textile. These are assigned as a low wavelength polaron $\rightarrow \pi^*$ band (445 nm) transition from PAn emeraldine salt and a $\pi - \pi^*$ transition band (480 nm) transition from PMAS, respectively. A band around 800 nm and a broad strong free carrier tail, corresponding to conductive PAn emeraldine salt on the wool nylon Lycra fabric was also observed.

The thermograms of all coated fabric samples and related polymers employed on the textile have been studied. Results indicate that the emeraldine base powder is the most thermally stable form (up to 470 °C) of polyaniline. It is also found that the PMAS templated PAn powder is not stable after heating to 250 °C, same as the PMAS powder, possibly due to the early break down of PMAS. PMAS-treated and PMAS templated PAn coated wool nylon Lycra fabrics demonstrate similar characteristics as uncoated wool nylon Lycra fabric. They revealed two separate stages of weight loss under nitrogen atmosphere. The first weight loss may be attributed to the loss of water or solvent on all the fabrics. After the initial weight loss, uncoated fabric showed only minimal mass loss until 240 °C, but no more weight loss on the PMAS-treated and the PMAS templated PAn coated fabrics were observed until 250 °C. This means that the thin layer of conductive PAn emeraldine salt can improve the thermal stability of the natural wool nylon Lycra fabric from 240 to 250 °C. However, templated PAn-coated wool nylon Lycra fabric is less stable than PAn emeraldine powder due to the limitation of the fabric thermal stability and break down of PMAS first on the fabric.

4.5. REFERENCES

1. W. Liu, A. L. Cholli, R. Namaswamy, J. Kumar, S. Tripathy, F. F. Bruno and L. Samuelson, *J. Am. Chem. Soc.*, 121 (1999) 11345.
2. W. Liu, J. Kumar, S. Tripathy, K. J. Senecal and L. Samuelson, *J. Am. Chem. Soc.*, 121 (1999) 71.
3. L. Samuelson, A. Anagnostopoulos, K. Alva, J. Kumar and S. Tripathy, *Macromolecules*, 31 (1998) 4376.
4. J. Liu, L. Sun, J. Hwang and S. Yang, *Mater. Res. Soc. Symp. Proc.*, 247 (1992) 601.
5. L. Sun, S. Yang, J. Liu, *Polym. Prepr.* 33 (1992) 379.
6. M. Angelopoulos, N. Patel, J. Shaw, N. Labianca and S. Rishton, *J. Vac. Sci. Technol.*, B11 (1993) 2794.
7. L. Sun, H. Liu, R. Clark and S. Yang, *Synth. Met.*, 84 (1997) 67.
8. P. Waters, *Process Report* of Effect of H₂SO₄ treated fabrics on aniline *in-situ* polymerisation templating
9. M. Bogle, *TEXTILE DYES, FINISHES, and AUXILIARIES*, Garland Publishing, Inc, New York & London. 1977, Chapter 5, pp 51-56.
10. E. P. G. Gohl, L. D. Vilensky, *Textile Science*, Longman Cheshire Pty Limited, Melbourne, 1980, pp 89-92.
11. R. Nagarajan, S. Tripathy and J. Kumar, *Macromolecules*, 33 (2000) 9542.
12. X. Wang, H. Schreuder-Gibson, M. Downey, S. Tripathy and L. Samuelson, *Synth. Met.*, 107 (1999) 117.
13. Foundation Issue 7, www.frst.govt.nz/publications/foundation/7/11.cfm.
14. Technique information from Clariant.

15. T. Vickerstaff, *The Physical Chemistry of Dyeing*, OLIVER AND BOYD, London, 1954, pp 351, 378.
16. P. Waters, *Process Report* to UOW of outcomes on PMAS applications to textiles- (From 17/4 to 24/5/02)
17. E. P. G. Gohl, L. D. Vilensky, *Textile Science*, Longman Cheshire Pty Limited, Melbourne, 1980, pp 91.
18. I. B. Wingate, *Textile Fabrics and their selection, Fourth Edition*, Prentice-Hall, Inc., 1955, pp 309-311.
19. E. M. Genies, C. Tsintavis and A. A. Syed, *Mol. Cryst., Liq. Cryst.*, 121 (1985) 181.
20. J. P. Travers, J. Croboczek, F. Devreux, F. Genoud, M. Nechtschein, A. A. Syed, E. M. Genies and C. Tsintavis, *Mol. Cryst., Liq. Cryst.*, 121 (1985) 195.
21. P. N. Adams and A. P. Monkman, *Synth. Met.*, 87 (1997) 169.
22. A. G. MacDiarmid, A. J. Epstein, *Mater. Res. Soc. Symp. Proc.*, 247 (1992) 565.
23. J. Brandrup, E. Immergut, and E. Grulke (Editors) *Polymer Handbook, Fourth Edition*, John Wiley & Sons, Inc, 1999, pp 543.
24. W. S. Huang, B. D. Humphrey and A. G. MacDiarmid, *J. Chem. Soc. Faraday Trans.*, 82 (1995) 2385.
25. G. G. Wallace, G. M. Spinks, L. A. P. Kane-Maguire, P. R. Treasdale, *Conductive Electroactive Polymers, Intelligent Materials Systems, Second Edition*, CRC Press LLC, 2003.
26. W. Liu, J. Kumar, S. Tripathy, K. J. Senecal, and L. Samuelson, *J. Am. Chem. Soc.* 121 (1999) 71.
27. I. Norris, *PhD Thesis*, University of Wollongong, Australia, 1999.

CHAPTER 5

CONDUCTIVE POLYMER COATED TEXTILES AND THEIR STRAIN GAUGE CHARACTERISTICS

5.1. INTRODUCTION

A strain gauge produces a signal that corresponds to a change in dimensions. This can be used to monitor flow rates, pressure, motion and displacement. Engineering strain is defined as the change in length, as referenced to the original length ($\Delta l/l$). Most strain gauges convert an applied strain directly into electrical resistance [1]. Strain is calculated by measuring the change in resistance. Strain sensors can be made from wire, foil, deposited metal films, and semiconductor materials. In this chapter we describe the development of flexible high strain devices using conductive polymer-coated textiles.

Flexible strain gauges have been designed previously using graphite [2] and elastomers impregnated with conductive fillers [3]. For example, nitrile-rubber based composites filled with short carbon fibres or carbon black have been used to make flexible strain gauges. The electrical conductivity of the polymer composite depends on the formation of a continuous conductive network in the insulating polymer matrix. With the application of strain, the conductivity shows an appreciable change due to the combined effect of the formation and destruction of conductive networks. By coating textiles with conducting polymer, it is possible to produce flexible strain gauges that can undergo strain without mechanical damage to the polymer coating, nor changing the wearability (handle)/ mechanical properties of the underlying textile.

The strain gauge characteristic of conductive polymer coated fabrics is very important due to a range of applications to monitor human motion. Flexible strain gauges using conducting polymer coated textiles have been investigated by De Rossi and co-workers [4,5]. The presence of conductive elements gives these coated materials piezoresistive

properties and enables the detection of local strain on the fabric [4,5]. As the conductive polymer coated textiles such as nylon Lycra conform to the shape of the human body, such coated fabrics can be applied as wearable biomechanical sensors, whether it is during rehabilitation, training program or even “real game”. Applications of strain gauges of conductive polymer coated textiles will be described in Chapter 6.

Conductive polymer coated textiles have been prepared using the different approaches described in both Chapter 3 and Chapter 4. In this current chapter, strain gauge characteristics of both polypyrrole and polyaniline coated textiles have been investigated using both Instron 4302 Tensile Tester and “Smart-Motor”. Mechanical and electrical properties of all textiles during the strain gauge performance will be discussed in details in this chapter.

5.2. EXPERIMENTAL

5.2.1. Materials

Preparation of PPy-coated nylon Lycra fabric: Polypyrrole coated nylon Lycra fabric used for strain gauge performance evaluation was prepared in an aqueous solution containing 0.015 M pyrrole monomer, 0.04 M oxidant FeCl_3 and 0.005 M dopant NDSA at room temperature for 2 hours. For details see Chapter 3 Section 3.2.3.3.1.

Preparation of PMAS-treated wool nylon Lycra fabric: PMAS-treated wool nylon Lycra was prepared in a dye bath. For experimental details see Chapter 4 Section 4.2.3.1.

Preparation of PMAS templated PAn-coated wool nylon Lycra fabric: The PMAS-treated (or templated) wool nylon Lycra fabrics were immersed in the aniline monomer solution. The solutions were adjusted to pH 1.4 with concentrated HCl before fabric addition. The APS was added drop-wise using a burette over 17 hours at different temperature respectively (Refer to Chapter 4 Section 4.2.3.2.).

5.2.2. Instrumentation

Mechanical properties were determined using an Instron 4302 Universal Material Tensile Tester equipped with a computer interface for data collection. A 10 N load cell was used during the strain testing. Rectangular samples, with dimensions 7.0 cm x 2.0 cm, were cut from untreated and polymer coated fabrics respectively. They were mounted in the jaws of the Instron tensile machine. After being mounted in the Instron machine, approximately 50 mm of the sample remained free to be strained. The coated fabric was then stretched/released at a typical speed of $100 \text{ mm} \cdot \text{min}^{-1}$ for cycling test. Resistance of the polymer coated fabrics was calculated from the measured potential according to the Wheatstone bridge circuit equation.

The dynamic strain gauge test was carried out using a calibration system (Refer to Figure 2.9) consisted of an Animatics Corp. Smart-Motor™, a displacement transducer (Linear Variable Differential Transformer, or LVDT), and a 5 N load cell. Polymer coated fabric sensor samples were tested at different frequencies varying from 0.5 Hz to 1.5 Hz. Data was collected at 50 Hz and signals averaged to eliminate extraneous noise.

Uncoated and polymer coated fabric strips of 1.5 cm x 3.0 cm were subjected to sinusoidal linear elongations, equating to strain amplitudes between 0% and 70%. The linear relationship between the applied strain and resistance was determined by plotting the average of the valley resistance values against the average of each strain interval.

5.3. RESULTS AND DISCUSSION

5.3.1. Mechanical Properties of Uncoated and Polymer-coated Fabrics by Instron 4320 Tensile Tester

Nylon Lycra and wool nylon Lycra consist of nylon, Lycra and wool fibres knitted together respectively, with good elastic properties due to the soft segments consisting of polyether type repeat unit in Lycra fibre (Refer to Chapter 1). In order to investigate the effect of coating these fabrics with conducting polymer, multi-cycled strain stress tests have been performed and the results are discussed below.

5.3.1.1. PPy-coated Nylon Lycra

The typical stress-strain responses of uncoated nylon Lycra fabric under different cycles are given in Figure 5.1 and Figure 5.2. There is a small variation noticed in the mechanical responses between the first and the rest of the cycles, and this is believed to be due to non-reversible structural changes when the fabrics are subjected to external force. It has been found that the system approaches to a steady state equilibrium after a couple of cycles [6]. The changes of force of uncoated nylon Lycra fabrics during the first two cycles also show a small variation when stretched up to 50% (Figure 5.1). Figure 5.2 shows the fifth and the sixth cycles of strain-force response for uncoated

nylon Lycra fabric between 0 and 50% strain in the wale direction. Results indicate a repeatable response can be obtained after about 4 cycles.

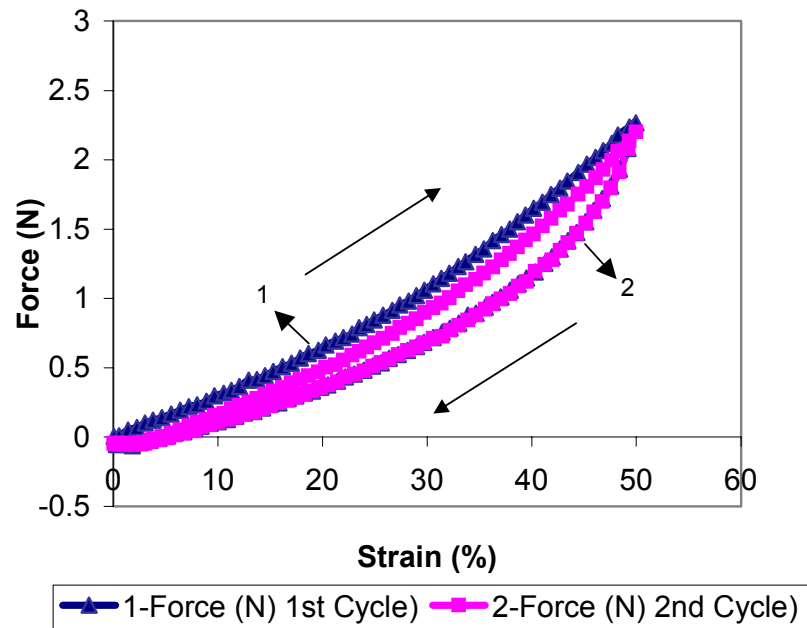


Figure 5.1. Stress-strain responses of uncoated nylon Lycra fabric for the first two cycles when stretched to 50%.

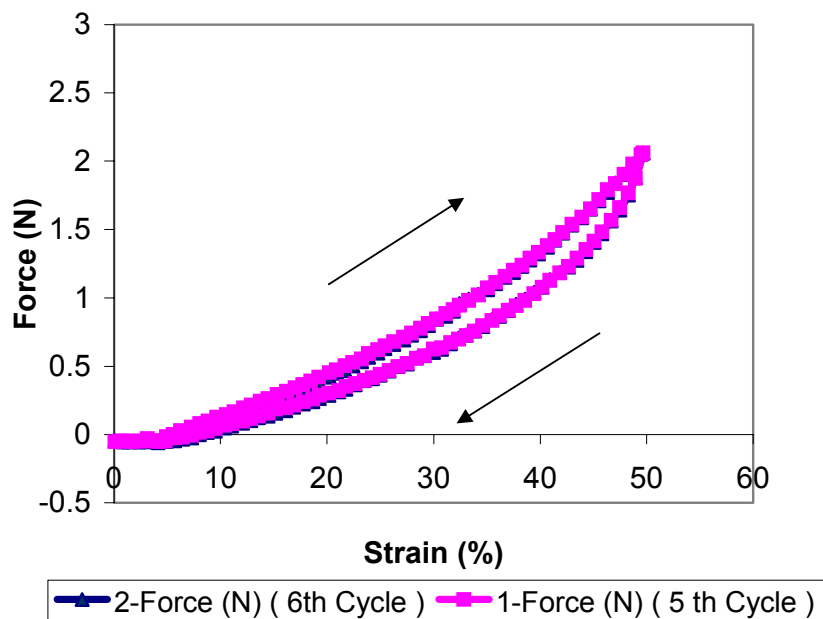


Figure 5.2. Stress-strain responses of uncoated nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%.

In general, conducting polymers are inherently brittle, and as a result cannot be stretched more than a few percent without breaking [7]. Polypyrrole is a rigid chain polymer, which is brittle [8] and fractures at low strain [9] because of its heavily cross-linked nature. Nylon Lycra consists of Lycra and nylon fibres knitted together. The presence of soft segments allows the fibres to be stretched over large extensions. (Refer to Figure 1.14]. After introducing conductive polypyrrole into nylon Lycra fabric, the mechanical property of PPy-coated nylon Lycra was investigated. The typical stress-strain responses of PPy-coated nylon Lycra fabric under different cycles are given in Figure 5.3 and Figure 5.4. The change of force of PPy-coated nylon Lycra fabrics for the first two cycles is shown in Figure 5.3 when stretched up to 50%. Figure 5.4 shows the fifth and the sixth cycles of strain-force response for PPy-coated nylon Lycra fabric between 0 to 50% of strain in the wale direction. To achieve a repeatable response, the

coated nylon Lycra fabric needs to be preconditioned by cycling the fabrics at least three or four cycles over the maximum strains to be tested.

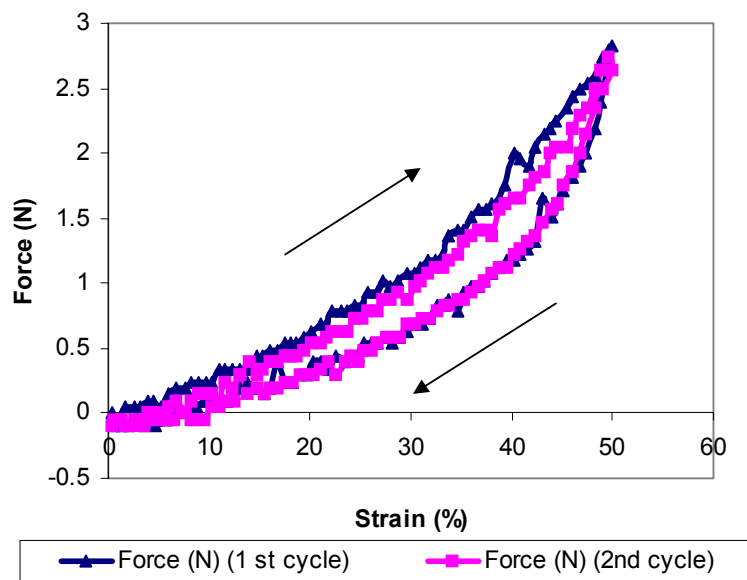


Figure 5.3. Stress-strain responses of PPy-coated nylon Lycra fabric for the first two cycles when stretched to 50%. PPy-coated nylon Lycra was prepared using conditions as described in Chapter 3 Section 3.2.3.3.1.

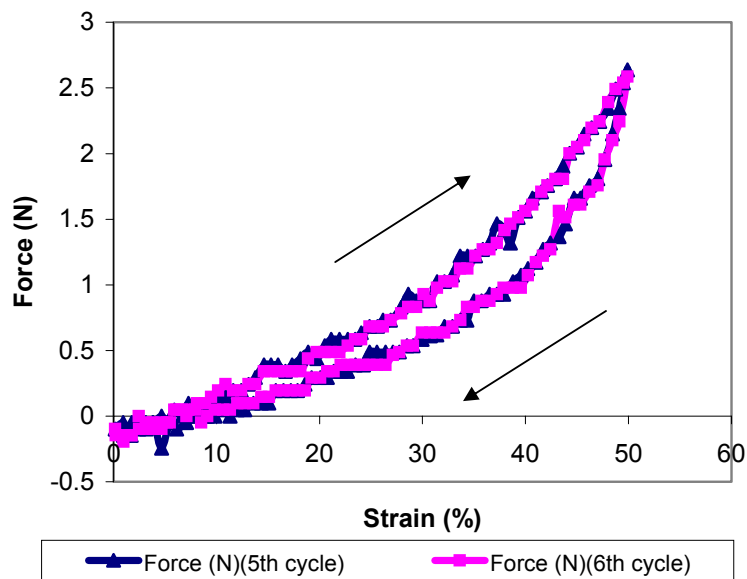


Figure 5.4. Stress-strain responses of PPy-coated nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%. PPy-coated nylon Lycra was prepared using conditions as described in Chapter 3 Section 3.2.3.3.1.

Figure 5.5 compares the changes of average force on uncoated and PPy-coated nylon Lycra fabrics in the wale direction with a strain ranging from 0 to 70%. Results indicate that the mechanical property of PPy-coated nylon Lycra is similar to uncoated fabric when stretched up to 50%. This means the thin layer of polypyrrole coating does not affect the mechanical property of coated fabric at lower strain ranges (0-50%). When stretched to more than 50%, PPy-coated fabrics show increased drawing force, for example, from 4.45 N (uncoated fabric) to 5.67 N (coated fabrics) when stretched to 70%. Minor variations of the mechanical property have been observed when stretching coated fabric to higher strain ranges (eg. more than 60%). A possible explanation is that a thin layer of polypyrrole makes the fabric a little stiff, which can be neglected at low

strain. With increasing strain, more drawing force is needed. The results suggest that the strain ranges should be chosen to be below 50%.

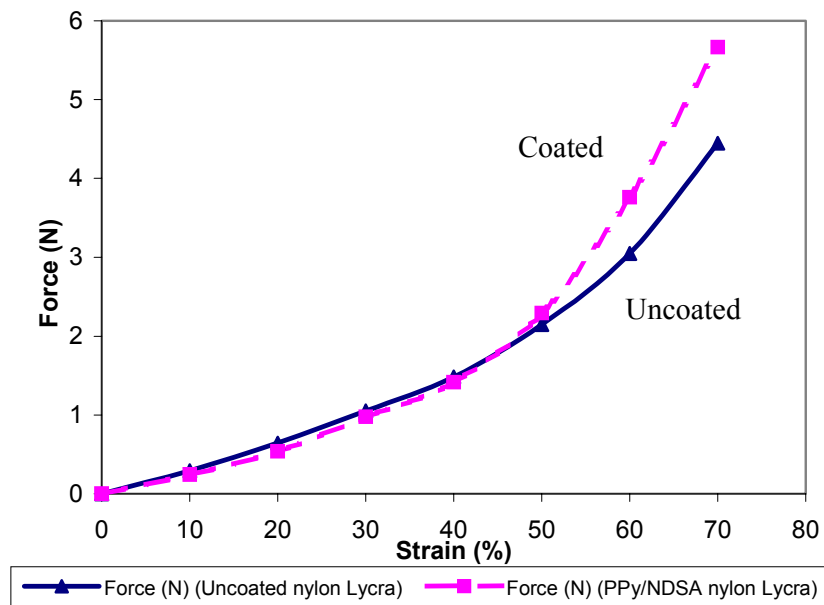


Figure 5.5. Stress-strain of uncoated and PPy-coated nylon Lycra fabrics in the wale direction at different strains.

5.3.1.2. Templated PAn-coated Wool Nylon Lycra

The typical stress-strain responses of uncoated wool nylon Lycra fabric under different cycles are given in Figure 5.6 and Figure 5.7. The changes of force for uncoated wool nylon Lycra fabric during the first two cycles show a small variation when stretched up to 50% (Figure 5.6). Figure 5.7 shows the fifth and the sixth cycles of strain-force response for uncoated wool nylon Lycra fabric between 0 and 50 % strain in the wale direction. A repeatable response of uncoated wool nylon Lycra fabric was obtained by cycling at least three or four cycles over the maximum strains to be tested.

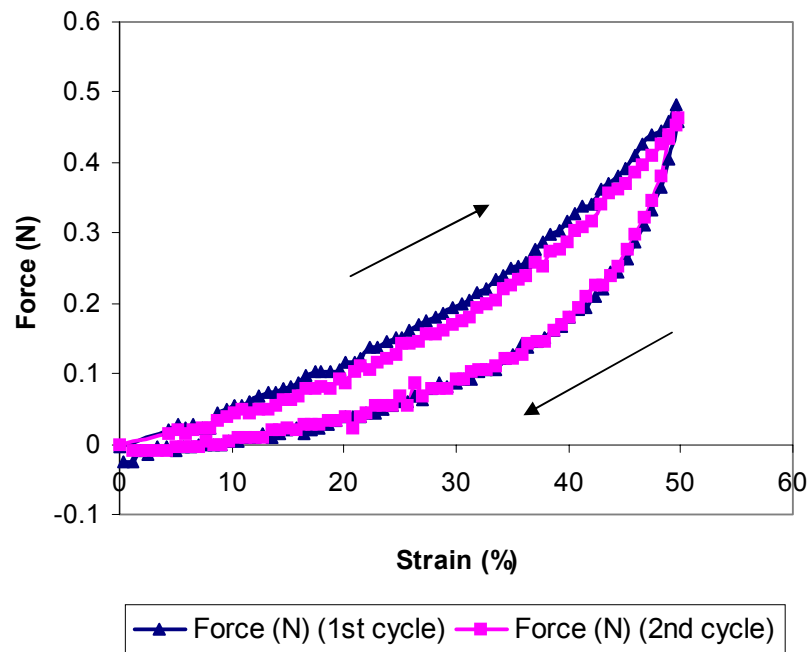


Figure 5.6. Stress-strain responses of uncoated wool nylon Lycra fabric for the first two cycles when stretched to 50%.

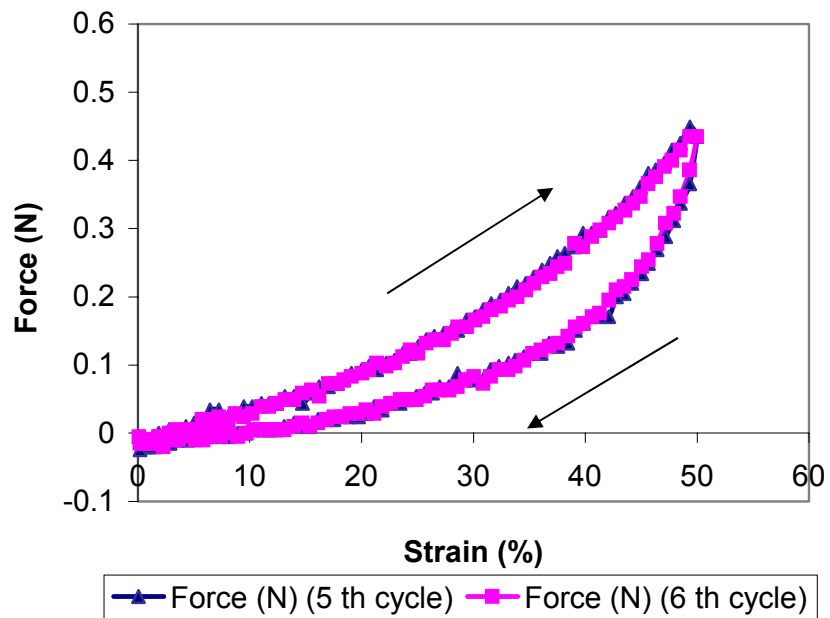


Figure 5.7. Stress-strain responses of uncoated wool nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%.

The typical stress-strain responses of PMAS-treated wool nylon Lycra fabric under different cycles are given in Figure 5.8 and Figure 5.9. The changes of force on PMAS-treated wool nylon Lycra fabric when stretched up to 50% during the first two cycles are shown in Figure 5.8. Figure 5.9 shows the fifth and the sixth cycles of strain-force response for uncoated nylon Lycra fabric between 0 to 50 % strain in the wale direction.

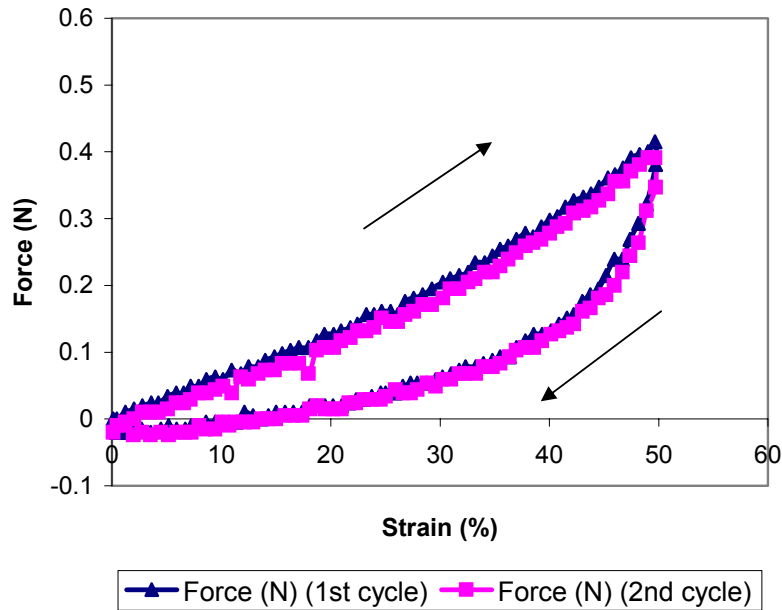


Figure 5.8. Stress-strain responses of PMAS-treated wool nylon Lycra fabric for the first two cycles when stretched to 50%. PMAS-treated wool nylon Lycra was prepared using conditions as described in Chapter 4 Section 4.2.3.1.

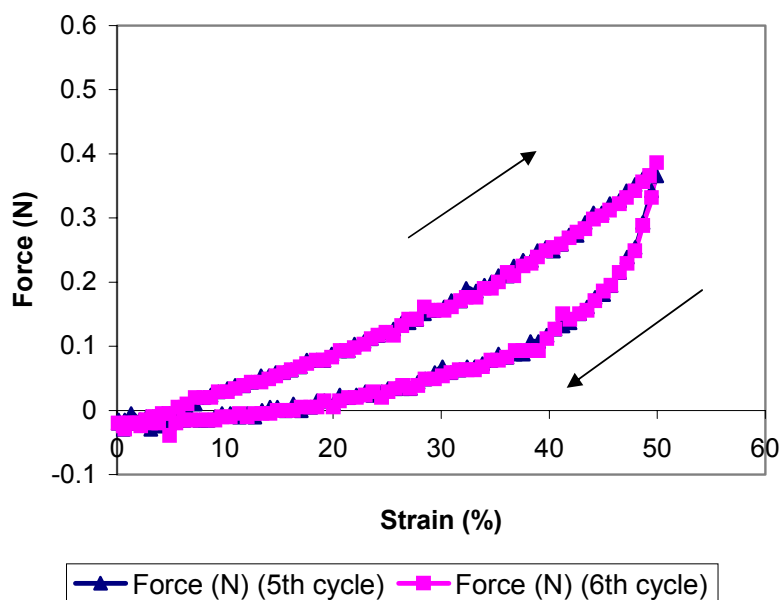


Figure 5.9. Stress-strain responses of PMAS-treated wool nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%. PMAS-treated wool nylon Lycra was prepared using conditions as described in Chapter 4 Section 4.2.3.1.

Figure 5.10 and Figure 5.11 show the typical stress-strain responses of PMAS templated PAn-coated wool nylon Lycra fabric under different cycles. The changes of force on PMAS-treated wool nylon Lycra fabric when stretched up to 50% during the first two cycles are shown in Figure 5.10. Figure 5.11 shows the fifth and the sixth cycles of strain-force response for uncoated nylon Lycra fabric between 0 and 50 % strain in the wale direction. To achieve a repeatable response, the coated wool nylon Lycra fabric needs to be preconditioned by cycling the fabrics at least three or four cycles over the maximum strains to be tested.

Figure 5.12 shows changes of force on uncoated, PMAS-treated and PMAS templated PAn-coated wool nylon Lycra fabrics in the wale direction at different strain ranges from 0 to 70%. The PMAS shows little effect on the elasticity of the wool nylon Lycra

in low strain range, but the elasticity of PMAS templated PAN-coated wool nylon Lycra fabric decreases due to a layer of templated polyaniline on the fabric surface. The drawing force increased from 1.27 N to 2.53 N when fabrics were stretched to 70%. A characteristic linear relation between force and strain can be obtained especially at a strain under 50%.

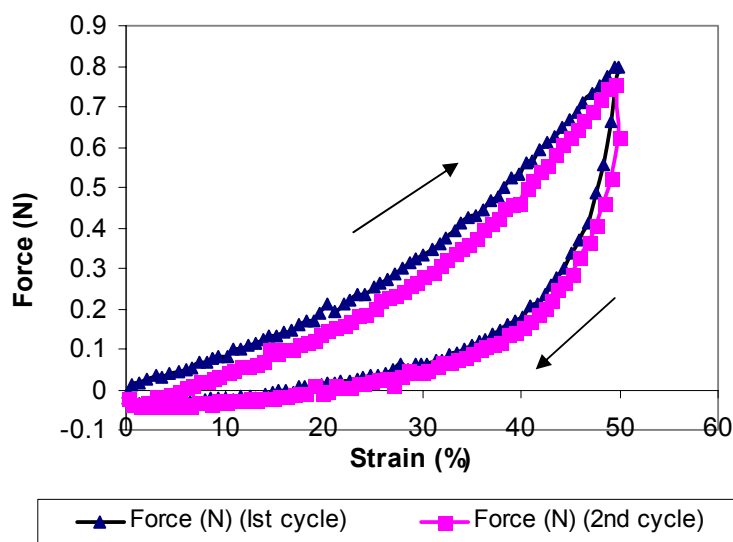


Figure 5.10. Stress-strain responses of PMAS templated PAN-coated wool nylon Lycra fabric for the first two cycles when stretched to 50%. PMAS templated PMAn coated wool nylon Lycra was prepared using conditions as described in Chapter 4 Section 4.2.3.2.

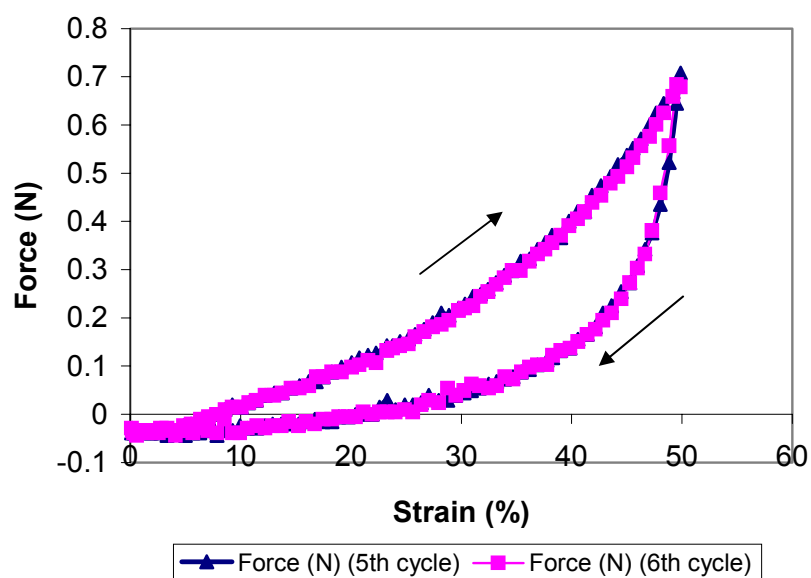


Figure 5.11. Stress-strain responses of PMAS templated PAn-coated wool nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%. PMAS templated PAn coated wool nylon Lycra was prepared using conditions as described in Chapter 4 Section 4.2.3.2.

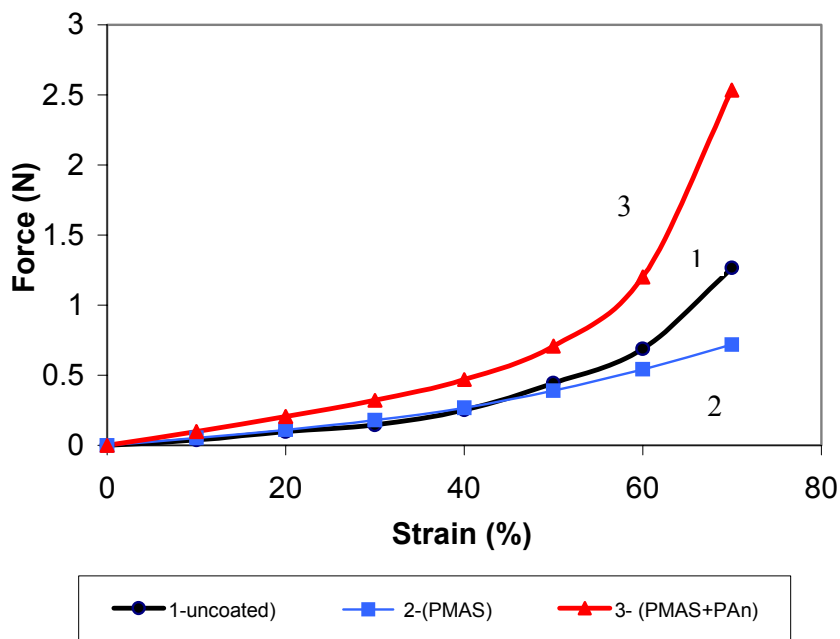


Figure 5.12. Stress-strain of uncoated, PMAS-treated and PMAS templated PAn-coated wool nylon Lycra fabrics in the wale direction at different strains.

5.3.2. Strain Gauge Response of Polymer-coated Fabrics

Strain gauge characteristics of conductive polymer coated textiles have been investigated using the Instron 4302 Tensile tester. The polymer coated fabrics undergo changes in resistance when stretched-released. By comparing the strain testing results for the polymer coated fabrics in two directions (wale direction and cross direction), it has been found that the resistance along the wale direction changed significantly when subject to stretching (Figure 5.13). So the strain gauge characteristic for the fabrics depends on the stretching direction. To simplify the strain gauge characterisation process, only the wale direction has been investigated in order to achieve high sensitivity.

Please see print copy for image

Strain (%)

Figure 5.13. Resistance/Strain relationship for nylon Lycra in the wale and course direction [10].

5.3.2.1. PPy-coated Nylon Lycra

The typical resistance-strain responses of PPy-coated nylon Lycra fabric under different cycles have been given below. The resistance-strain response for the first two cycles with a strain range between 0 and 50% in the wale direction for PPy-coated nylon Lycra fabric are presented in Figure 5.14. Figure 5.15 shows the resistance-strain response of the fifth and the sixth cycles for PPy-coated nylon Lycra fabric. The change in resistance-strain response between the first cycle and subsequent cycles is linked to a change in the mechanical property of the coated fabric, as shown in Figure 5.3. It is found that the nylon Lycra has a little stiffness during the first cycle compared to the second cycle. In about four cycles, repeatable resistance-strain responses can be observed (Figure 5.15). The initial increase in resistance (eg. Figure 5.14) is mainly due

to the change of the fabric from a fully relax state to a gradually tense (stretched) state. In the relax state, all fibres rest against each other and are in a natural contracted position. At the beginning of stretching, the fibres temporarily lose contact with each other resulting in an increase of resistance. All fibres will gradually get closer upon further stretching; as a result, its overall resistance is decreased.

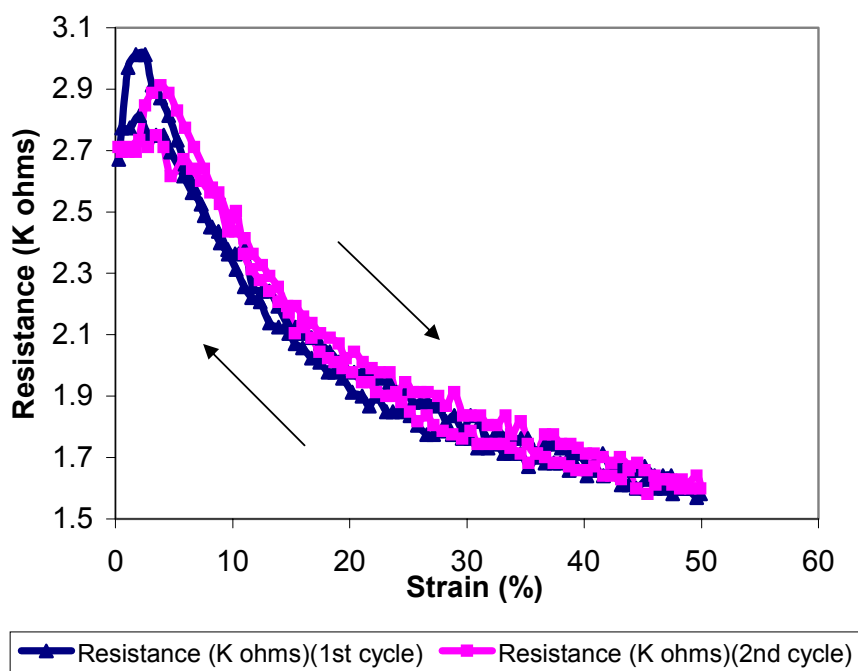


Figure 5.14. Resistance-strain of PPy-coated nylon Lycra fabric for the first two cycles when stretched to 50%. PPy-coated nylon Lycra was prepared using conditions as described in Chapter 3 (Section 3.2.3.3.1).

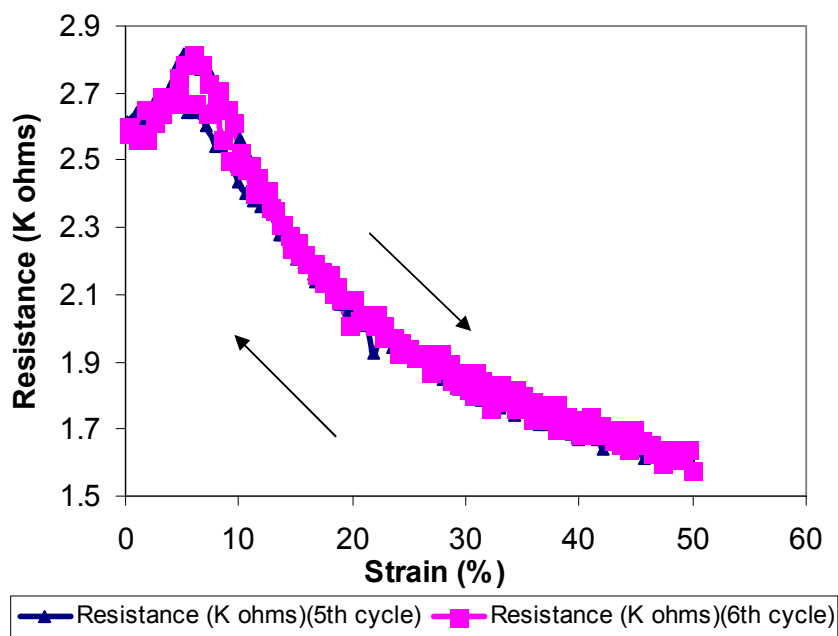


Figure 5.15. Resistance-strain of PPy-coated nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50%. PPy-coated nylon Lycra was prepared using conditions as described in Chapter 3 Section 3.2.3.3.1.

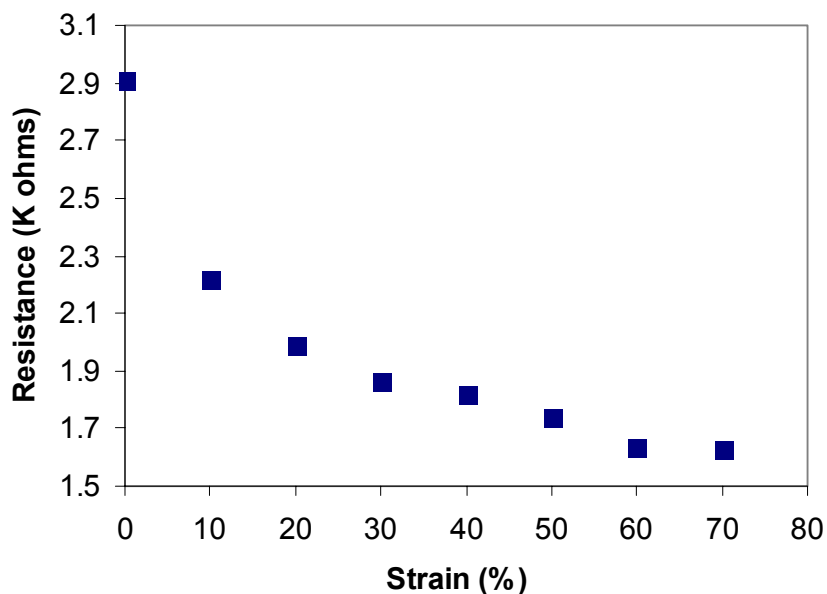


Figure 5.16. Resistance-strain on PPy-coated nylon Lycra fabric in the wale direction at different strains.

Figure 5.16 shows the changes in resistance of PPy-coated nylon Lycra fabric in the wale direction at different strain ranges from 0 to 70%. The results indicate that the resistance of PPy-coated nylon Lycra fabric decreases from 2.91 K Ω to 1.63 K Ω when stretched to 70%. Only a small change from 1.68 K Ω to 1.63 K Ω is observed between 50% and 70% of strain. By combining Figure 5.5 and Figure 5.16, it can be seen that PPy-coated nylon Lycra fabric is suitable for applications as a strain gauge that require measurement of a strain up to 50%.

5.3.2.2. Templated PAn-coated Wool Nylon Lycra

Typical resistance-strain responses of PMAS templated PAn-coated wool nylon Lycra fabric under different cycles are given in Figure 5.17 and Figure 5.18. The resistance-strain responses for the first two cycles between 0% and 50% of strain in the wale direction for PMAS templated PAn-coated fabric are presented in Figure 5.17. The resistance-strain responses of the fifth and the sixth cycles for the same coated fabric are given in Figure 5.18. The change in resistance-strain response between the first cycle and subsequent cycles is linked to a change in the mechanical property of the coated fabric, as shown in Figure 5.10. It is found that the wool nylon Lycra has more stiffness during the first cycle compared to the second cycle. After about four cycles, repeatable resistance-strain responses can be observed in Figure 5.18. The initial increase in resistance, associated with the initial strain applied to the coating, is attributed to deformation of the coating on the fabric surface. The initial increase in resistance of PAn-coated fabric (eg. Figure 5.17) similarly as observed with PPy-coated textile, is mainly due to the change in the fabric from a fully relax state to a stretched state. In the relax state, all fibres rest against each other and are in a natural contracted position. At

the beginning of stretching, the fibres temporarily lose contact each other, resulting in an increase in resistance. All fibres will gradually get closer upon further stretching; as a result, its overall resistance is decreased.

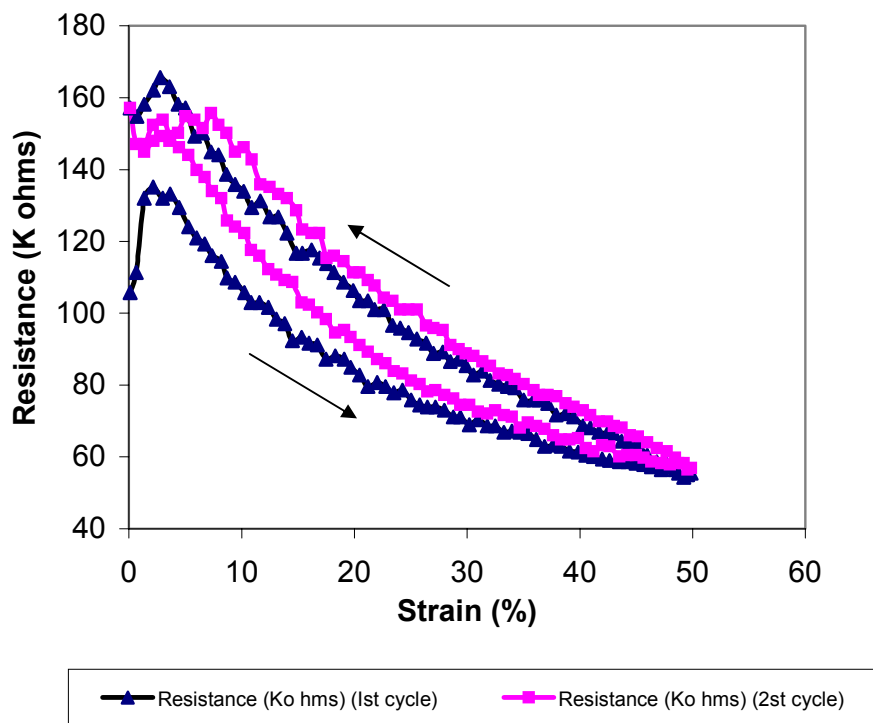


Figure 5.17. Resistance-strain of PMAS templated PAn-coated wool nylon Lycra fabric for the first two cycles when stretched to 50% (Details on preparation can be found in Chapter 4 Section 4.2.3.2).

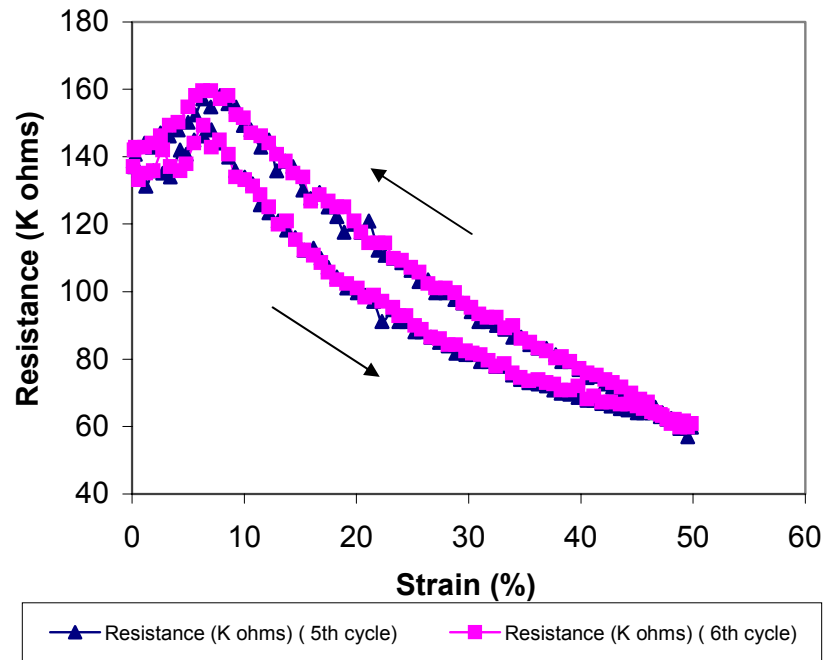


Figure 5.18. Resistance-strain responses of PMAS templated PAn-coated wool nylon Lycra fabric for the fifth and the sixth cycles when stretched to 50% (Details on preparation can be found in Chapter 4 Section 4.2.3.2).

Figure 5.19 shows the changes of resistance on PMAS templated PAn-coated wool nylon Lycra fabric in the wale direction at different strain ranges from 0 to 70%. Result indicates that resistance on the PMAS templated PAn-coated fabric decreases from 93.4 K Ω to 50.8 K Ω when stretched to 70%. By combining Figure 5.12 and Figure 5.19, it can be seen that templated PAn coated wool nylon Lycra fabric is suitable for applications as a strain gauge that require measurement of a strain of up to 70%.

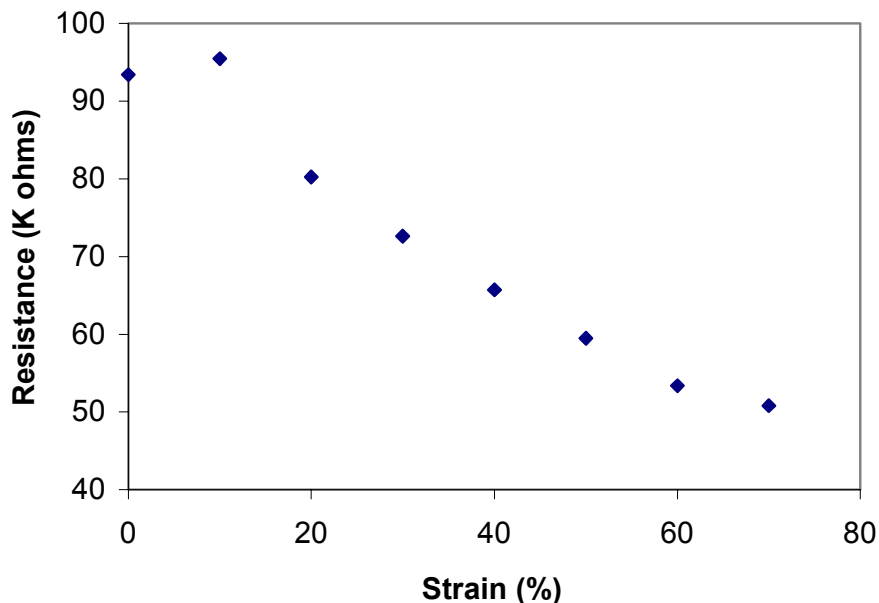


Figure 5.19. Resistance-strain responses for PMAS templated PAn-coated wool nylon Lycra 7010 fabric in the wale direction at different strain.

Strain gauge characteristics of PPy-coated nylon Lycra and templated PAn-coated wool nylon Lycra textiles have been investigated using the Instron 4302 tensile tester. Results previously described indicate that both of the conductive polymer coated fabrics can be used as strain gauges. The ratio of change in average resistance to initial resistance ($\Delta R/R_i$) of PPy-coated nylon Lycra at different strains ranging from 0 to 50% is given in Figure 5.20. The gauge factor of PPy-coated nylon Lycra fabric was obtained as 0.75 (absolute value) when the coated fabric was stretched to 50%. Results from Figure 5.1 indicate that the sensitivity of PPy-coated fabric strain gauge is better at the lower strain range (eg. between 0 to 10%). The resistance of polypyrrole coated textile changes significantly at low strains due to the improvement of alignment of the polypyrrole chains within the coated fabric. When the fabric was stretched to a large strain, a maximum degree of alignment of the polymer chains within the coated textile was

attained. Thus the resistance of the PPy-coated nylon Lycra fabric did not change any further. Therefore PPy-coated nylon Lycra is suitable to be used as a strain gauge when stretched up to 50%.

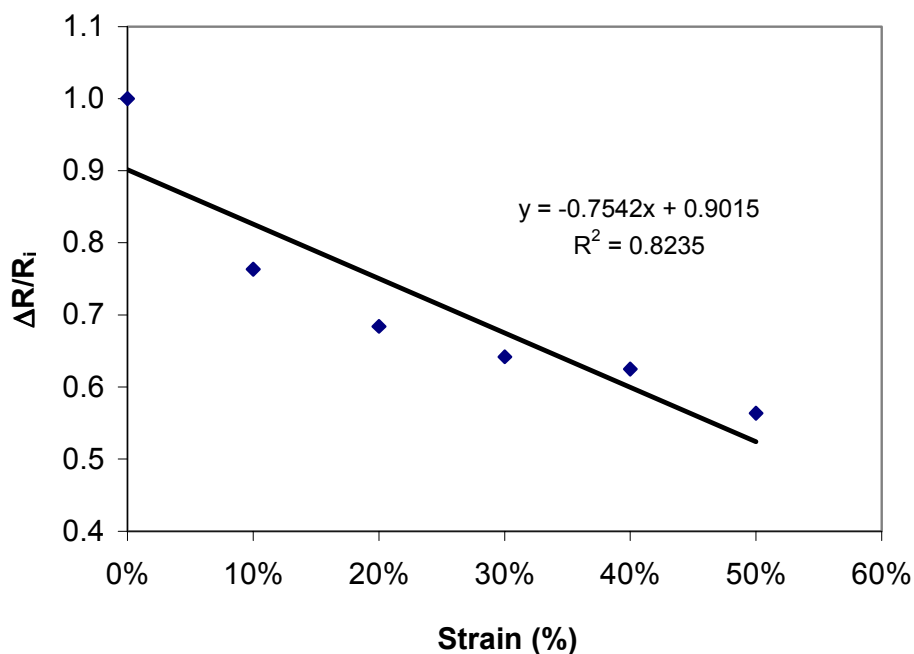


Figure 5.20. Ratio of change in resistance to initial resistance ($\Delta R/R_i$) of PPy-coated nylon Lycra when stretched to 50%.

The ratio of change in average resistance to initial resistance ($\Delta R/R_i$) of PMAS templated PAn-coated nylon Lycra at different strains ranging from 0 to 70% is given in Figure 5.21. The gauge factor of PMAS templated PAn-coated nylon Lycra was 0.74 (absolute value) when the coated fabric was stretched to 70%. Compared with the PPy-coated nylon Lycra fabric, the linear strain range of PAn-coated fabric can be extended up to 70%. So the PMAS templated PAn-coated wool nylon Lycra can be used as a strain gauge at high strains.

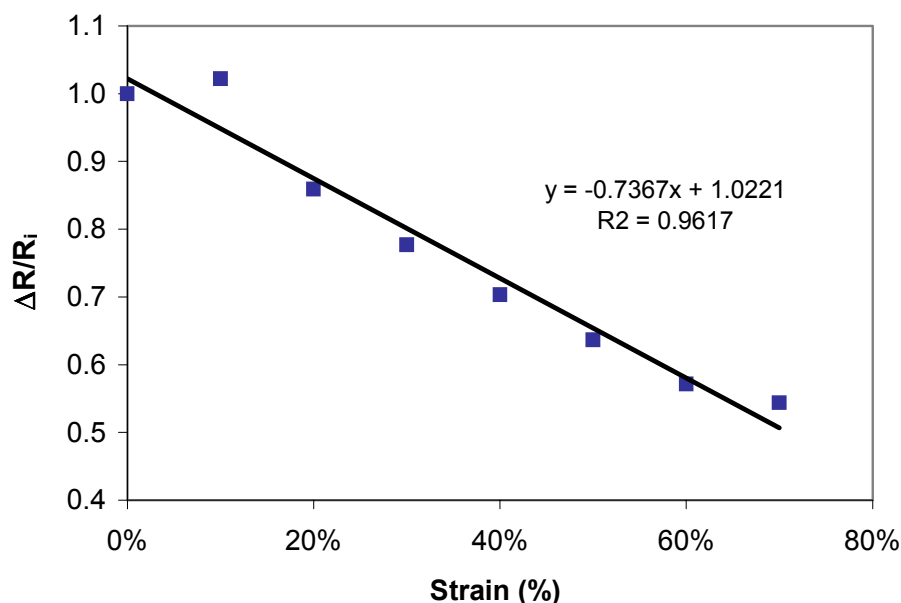


Figure 5.21. Ratio of change in resistance to initial resistance ($\Delta R/R_i$) of PMAS templated PAn-coated wool nylon Lycra when stretched to 70%.

5.3.3. Strain Gauge Response of Polymer-coated Fabrics at Different Frequencies

Strain gauge characteristics of PPy-coated nylon Lycra and PMAS templated PAn-coated wool nylon Lycra fabrics have been investigated using the dynamic calibration “SmartMotor” system that was previously described in Chapter 2. The coated fabrics undergo changes in resistance when stretched. Multi-cycled resistance-strain has been performed at different frequencies from 0.5 Hz to 1.5 Hz because the custom designed smart motor cannot operate at higher frequencies over large/ moderate distances (3.0 cm length).

5.3.3.1. PPy-coated Nylon Lycra

Strain Gauge Responses at 1 Hz: Typical electronic signal responses of PPy-coated nylon Lycra at 1 Hz obtained from the “SmartMotor” system are shown in Figure 5.22. Changes in resistance on PPy-coated fabrics in the wale direction at different strain ranges from 10% to 70% at 1 Hz are shown in Figure 5.23. Figure 5.22 shows that the double peaks occurred at the beginning of the strain. The double peaks are due to the temporary relaxation of the fabric. There is a momentary stop at the end of a stretch whether using Instron or “Smartmotor”. As the fabrics approach to their rest position, their electrical contact increase and resistance decrease. When stretching starts again, the rest position is broken and the contact starts to part.

Initial resistance of the coated fabric is hard to measure during dynamic calibration. In general, strain gauge performance on coated fabric has been investigated from 10% to 70% strains with the “SmartMotor”. Results show that the resistance on the PPy-coated nylon Lycra fabric decreases from 1.63 K Ω to 1.50 K Ω when stretched from 10% to 70%. When stretching is continued to a large strain, the resistance decreases slowly. After the coated fabric is stretched more than 50%, the resistance remains the same. This result is similar to that from the Instron machine (which had been operated at much lower frequency, 0.03 Hz). In summary, PPy-coated nylon Lycra fabric is suitable for use as a strain gauge from 10% to 50% in the “SmartMotor” system.

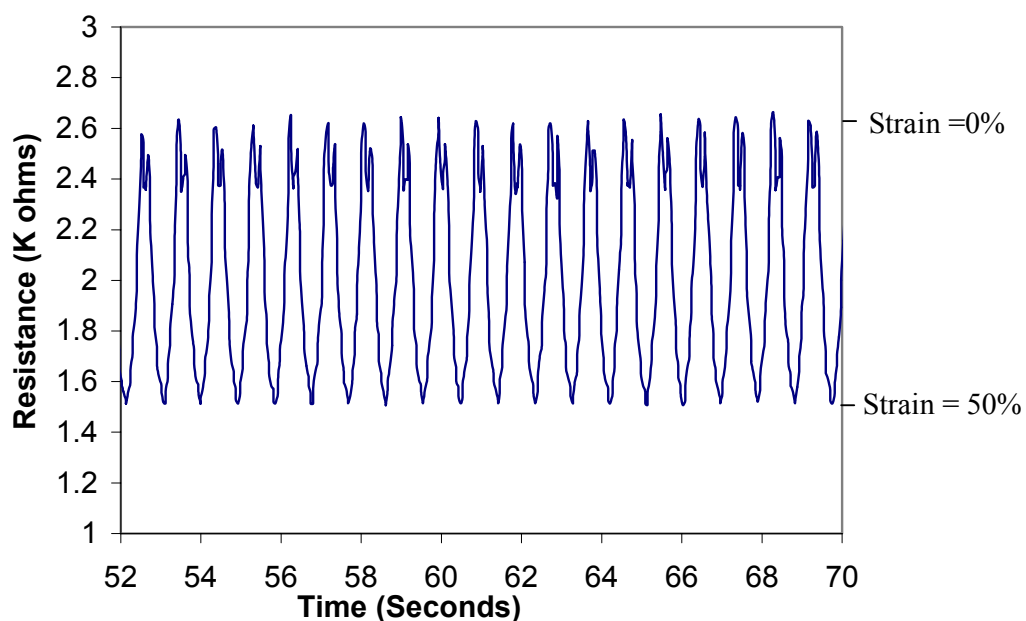


Figure 5.22. Electronic signal of resistance response on PPy-coated nylon Lycra at 1 Hz when stretched to 50%. PPy-coated nylon Lycra was prepared using conditions as described in Chapter 3 Section 3.2.3.3.1.

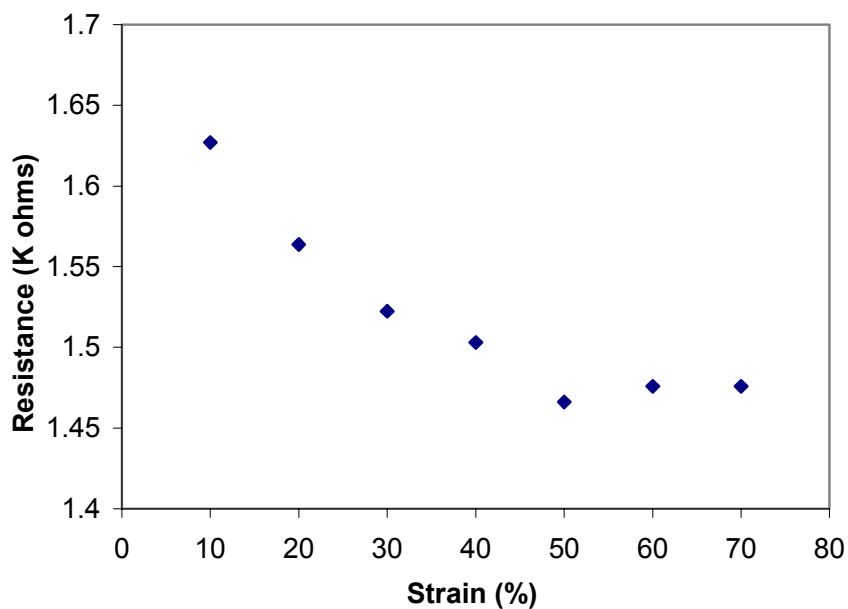


Figure 5.23. Changes in resistance of PPy-coated nylon Lycra fabric in the wale direction at 1 Hz under different strains (Details refer to Section 3.2.3.3.1 in Chapter 3).

Strain Gauge Responses at Different Frequencies:

PPy-coated fabric

samples were tested at different frequencies varied from 0.5 Hz to 1.5 Hz. Figure 5.24 shows the changes in resistance of PPy-coated nylon Lycra fabric in the wale direction at different frequencies under different strains.

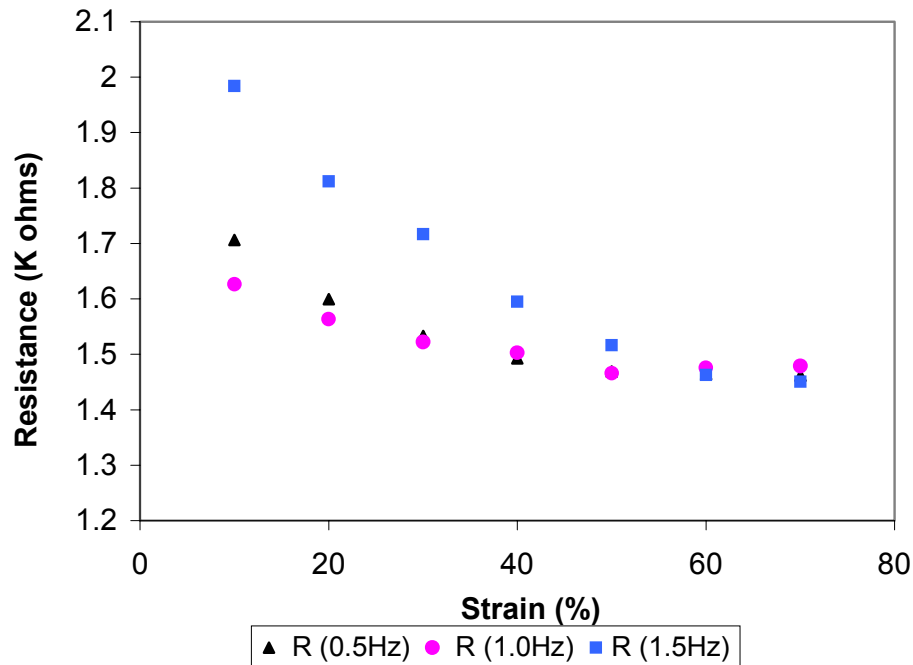


Figure 5.24. Changes in resistance of PPy-coated nylon Lycra fabric in the wale direction at different frequencies under different strains. PPy-coated nylon Lycra was prepared using conditions as described in Chapter 3 Section 3.2.3.3.1.

The variation of fabrics may also result in a difference. As a general rule, more stretching caused a larger change in resistance. Similar resistance-strain responses can be observed using frequencies of 0.5 Hz and 1.0 Hz respectively. Different resistance-strain response is obtained using a frequency of 1.5 Hz due to the different initial resistance of the fabric. Normally 1.0 Hz can be used in the “SmartMotor” system to measure the strain gauge on coated fabrics in this work.

5.3.3.2. Templated PAn-coated Wool Nylon Lycra

Typical electronic signal responses of PMAS templated PAn-coated wool nylon Lycra at 1Hz from the “SmartMotor” are shown in Figure 5.25. Changes in resistance for the coated fabric in the wale direction at different strain ranges from 20% to 70% is shown in Figure 5.26.

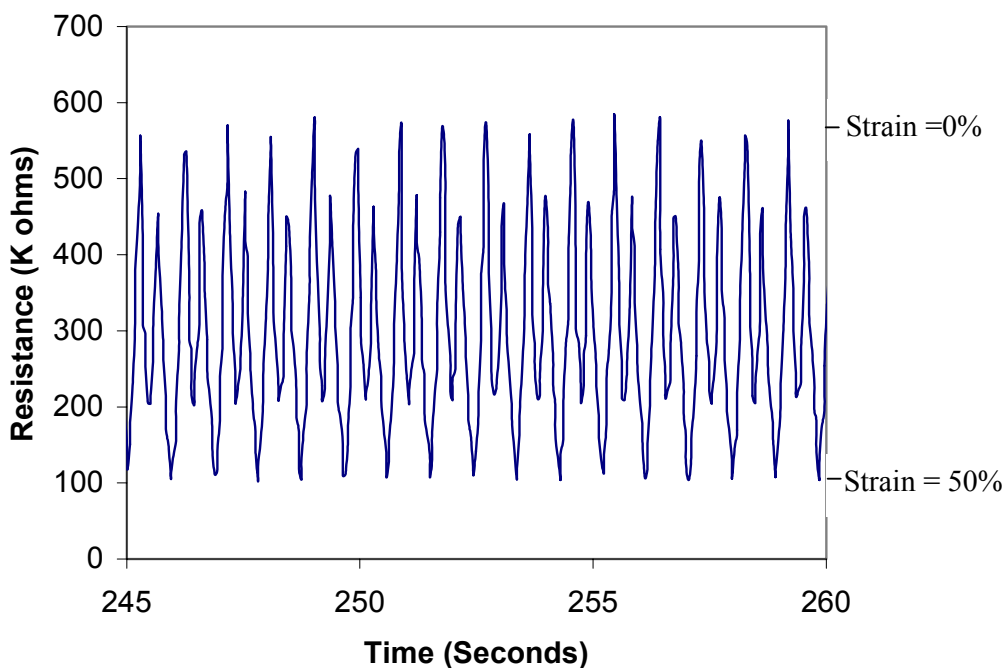


Figure 5.25. Electronic signal of resistance responses on PMAS templated PAn-coated wool nylon Lycra at strain=50%. (Details on preparation can be found in Chapter 4 Section 4.2.3.2).

There are two resistance minima in one cycle: one close to 200 K Ω and another 100 K Ω in Fig 5.25. The double peaks are due to the temporary relaxation of the fabric. There is a momentary stop at the end of a stretch whether using Instron or “Smartmotor”. As the fabrics approach to their rest position, their electrical contact increase and resistance

decrease. When stretching starts again, the rest position is broken and the contact starts to part. The linear relationship between the applied strain and resistance was determined by plotting the average of the valley resistance values against the average of each strain interval using “Smartmotor”.

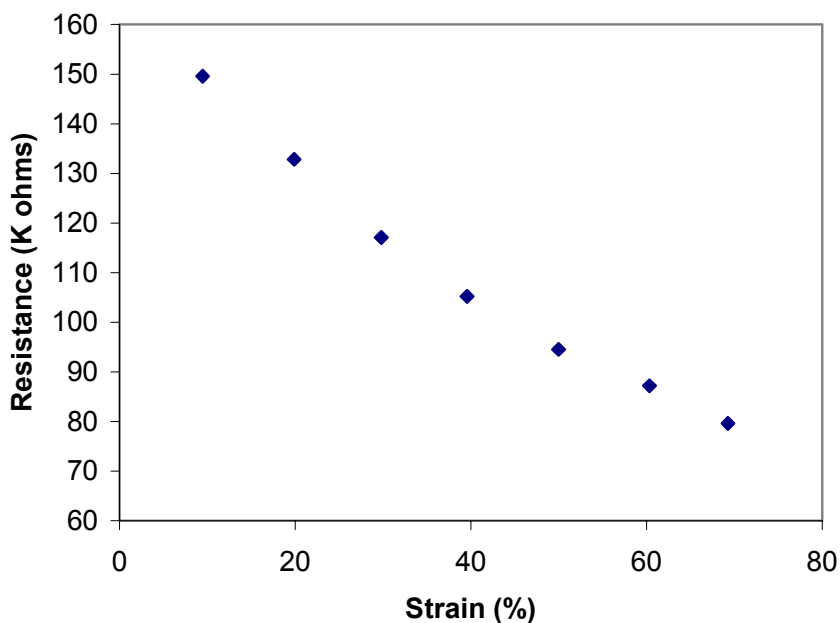


Figure 5.26. Changes of resistance on PMAS templated PAn-coated wool nylon Lycra fabric in the wale direction at different strain.

Results from the “Smart-Motor” indicate that the resistance of the PMAS templated PAn-coated wool nylon Lycra fabric decreases from 149.6 KΩ to 79.6 KΩ when stretched from 10% to 70%. Compared with the PPy-coated nylon Lycra fabric, when stretching the fabric is continued to a large strain, the linear relationship between resistance and strain is found in Figure 5.27. This result is similar to that from the Instron machine (which had been operated at much lower frequency, 0.03 Hz). As a result, PMAS templated PAn-coated wool nylon Lycra fabric is suitable for use as a strain gauge from 10% to 70% strains in the “Smart-Motor” system.

Strain gauge characteristics of PPy-coated nylon Lycra and templated PAn-coated wool nylon Lycra textiles have also been investigated using the dynamic calibration SmartMotor” system at 1Hz. Results previously described indicate that both conductive polymer coated fabrics can be used as strain gauges.

The ratio of change in average resistance to initial resistance ($\Delta R/R_i$) of PPy-coated nylon Lycra at different strains ranging from 10% to 50% is given in Figure 5.27. Results from Figure 5.23 show that a significant change in resistance of PPy-coated fabric is observed at a lower strain range (below 50%). After being stretched to 50%, the resistance of the PPy-coated nylon Lycra fabric did not change any further. Similar results from the Instron system was also obtained showing that PPy-coated nylon Lycra is suitable for use as a strain gauge at strains below 50%. The gauge factor of the PPy-coated nylon Lycra fabric was calculated to be 0.23 (absolute value) from Figure 5.27, when the coated fabric was stretched from 10% to 50%. Due to the initial resistance of the coated fabric is hard to measure during dynamic calibration; the gauge factor measured by “Smartmotor” is smaller than that from Instron system. This means that the resistance of polypyrrole coated textile changes significantly at the initial strain stage (between 0 to 10%). Figure 5.27 shows a linear strain range from 10% to 50% and indicates that this coated fabric can be used as a strain gauge from 10% to 50%.

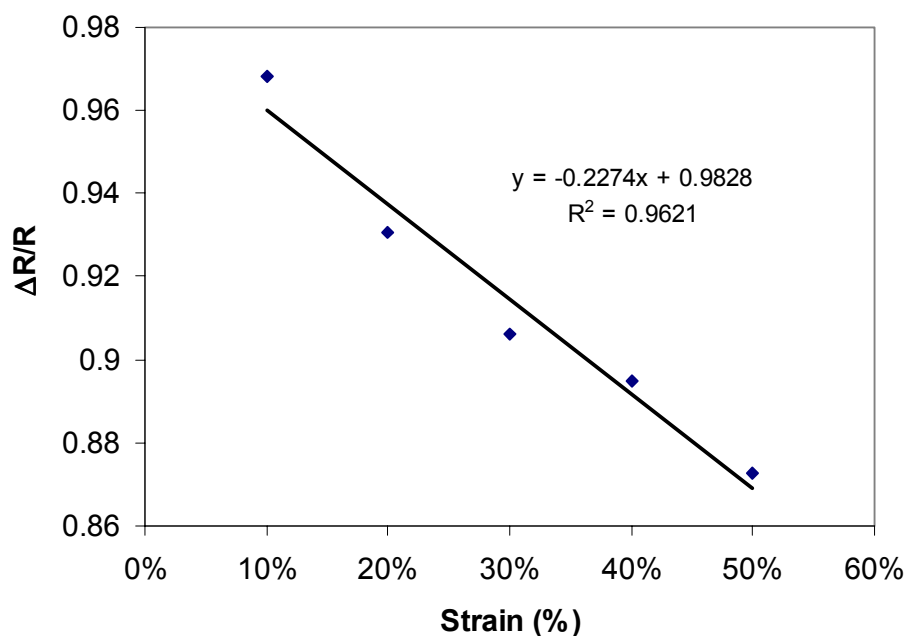


Figure 5.27. Ratio of change in resistance to initial resistance ($\Delta R/R_i$) of PPy-coated nylon Lycra when stretched from 10% to 50%.

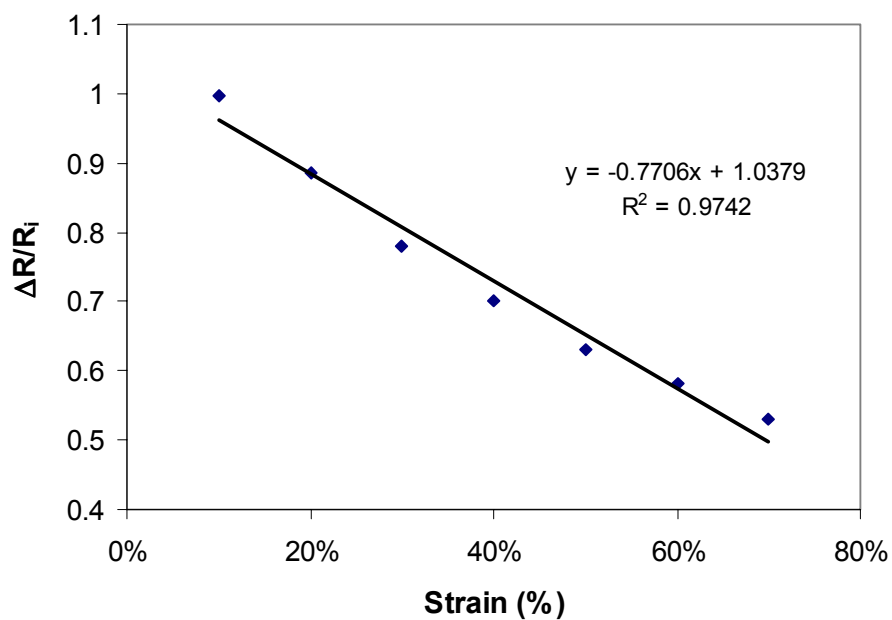


Figure 5.28. Ratio of change in resistance to initial resistance ($\Delta R/R_i$) of PMAS templated PAn-coated wool nylon Lycra when stretched from 10% to 70%.

The ratio of change in average resistance to initial resistance ($\Delta R/R_i$) of PMAS templated PAn-coated wool nylon Lycra at different strains ranging from 10% to 70% is given in Figure 5.28. The linear relationship between the resistance and the strain range has been found in Figure 5.28. The gauge factor was calculated to be 0.77 (absolute value) when the coated fabric was stretched from 10% to 70% strains. This result is similar to that (0.74) from the Instron system. Compared with the PPy-coated nylon Lycra fabric, the linear strain range of PAn-coated fabric can be extended from 10% up to 70%. As a result, the PMAS templated PAn-coated wool nylon Lycra can also be used as a strain gauge to higher strains (up to 70%) in the dynamic calibration “Smart-Motor” system.

5.4. CONCLUSION

Mechanical properties of conducting polymers are very poor. But by introducing conductive polymer into fabrics, mechanical properties of the coated fabrics have minor variations depending on process conditions.

Investigation of conductive polymer coated textiles has shown that their conductivity changes when the fabrics are stretched using Instron 4302 tensile tester. The sensitivity of a PPy-coated nylon Lycra fabric strain gauge is better in a lower strain range especially when stretched to 10%. There are only minor variations on the resistance of the coated nylon Lycra fabric when stretched to more than 50%. With increasing strain, the resistance of PMAS templated PAn-coated wool nylon Lycra fabric decreased. It has been found that a repeatable response can be achieved after four cycles. The linear relationship between the resistance and strain has been found when the fabric was

stretched to 70%. By comparing the strain performance of PPy-coated and templated PAN-coated textiles, it is evident that both polypyrrole and templated polyaniline coated fabrics can be applied as strain gauges, especially the PMAS templated PAN-coated wool nylon Lycra that can be stretched to 70%.

The strain gauge performance has also been investigated using a “SmartMotor” system. Initial resistance on the coated fabric is hard to measure during dynamic calibration. It has been found that the resistance of PPy-coated nylon Lycra decreases slowly when stretched to a large strain (70%). After PPy-coated fabric is stretched more than 50%, the resistance remains the same. Effect of different frequencies on the strain gauge performance has been studied using a “SmatMotor” system. Results indicate that gauge factors can be changed on the different initial resistance on the fabric. Normally 1.0 Hz was used in the “SmartMotor” system to measure the strain gauge on the coated fabrics in this work. Thus PPy-coated nylon Lycra fabric can be used as strain gauge from 10% to 50% strains in the “SmartMotor” system. Strain gauge performance of the PMAS templated PAN-coated wool nylon Lycra fabric has also been investigated using the “SmartMotor” system. Similar results with the Instron system indicate that the resistance of the coated wool nylon Lycra decreases when stretched at frequency spanning 1 Hz. A wide strain range was found (from 10% to 70%) using the “SmartMotor”.

The two strain gauge measurements show that PPy-coated and templated PAN-coated textiles are suitable for application as strain gauges. The “SmartMotor” system used for the strain test is very useful and convenient during dynamic measurement, allowing a

change in the strain frequencies to suit different applications such as for body movement in sport.

5.5. REFERENCES

1. H. L. Trietley, *Transducers in Mechanical and Electronic Design*, Marcel Dekker, Inc., New York, USA, 1986, pp 47-51.
2. X. Luo, D. D. Chung, *Journal of Intelligent Material Systems and Structures*, 8 (1993) 3539.
3. P. Pramanik, D. Khastagir, *Journal of Materials Science*, 28 (1993) 3539.
4. A. Mazzoldi, D. De Rossi, F. Lorussi, E. P. Scillingo and R. Paradiso, *AUTEX Research Journal*, 2 (2002) 4.
5. D. De Rossi, A. Della Santa and A. Mazzoldi, *Mater. Sci. Eng.*, C7 (1999) 31.
6. M. Couper, "Polyurethane Elastomeric Fibers", *High Technology Fibers Part A, Handbook of Fiber Science and Technology: Volume III*, Marcel Dekker, Inc., New York, 1985.
7. H. H. Kuhn, A. D. Child and W. C. Kimbrell, *Synth. Met.*, 71 (1995) 2139.
8. Y. Chen, R. Qian, G. Li and Y. Li, *Polym. Commun.*, 32 (1991) 189.
9. D. S. Kelkar and N. V. Bhat, *Polymer* 34 (1983) 986.
10. P. Whitten, *BEng Thesis*, University of Wollongong, Australia, 1998.

CHAPTER 6

APPLICATION OF CONDUCTING POLYMER

COATED FABRICS

6.1. INTRODUCTION

In recent years, conducting polymer coated textiles have attracted much attention due to the ease of synthesis, high conductivity and low cost. It has been recognised that the properties of conducting polymer can be exploited by incorporating them into the fabric structure to provide unique mechanical and physical properties for applications. Many applications of conductive polymer coated fabrics have been proposed; including static dissipation, EMI shielding, energy storage fabrics, composite structure, military application, strain gauge performance.

Static Dissipation: Electrostatic charge (ESC) and electrostatic discharge (ESD) constitute a serious and expensive problem for many industries. To protect devices against ESC and ESD, conducting materials are used. For example, conductors are incorporated into plastic packages which are used to transport sensitive electronic chips or modules. Currently conducting polymer offer a new alternative for ESD protection. The conductivity of these polymers such as polypyrrole and polyaniline can be tuned and easily meet the high end of the dissipative range. Fabrics can be coated with conducting polymers enabling their use in anti-static applications. Customers of Milliken Research Corporation report that polypyrrole-coated fabrics show instant dissipation of static electricity with excellent tunnelling characteristics [1]. These properties allow a number of industry applications in conducting polymer coated textiles such as, abrasive belts, conveyor belts, high speed composite rollers, carpets, upholstery fabrics, uniforms, gloves, wrist straps and filtration. Contex fabrics marketed by Milliken Research Corporation have been suggested for use as wrist rest mats to dissipate static charging near computer keyboards [1,2].

EMI Shielding: Electromagnetic radiation that negatively affects device performance is usually termed EMI (ElectroMagnetic Interference). Many electronic devices not only emit electromagnetic fields that cause interference in other systems, but are also affected by the electromagnetic fields generated by other electronics. Higher frequency communications and faster rise-time chips, each capable of generating its own EMI, create potential problems that must be addressed. Hence EMI shielding solutions will become more important. Simply stated, EMI shielding is the use of conductive materials to reduce EMI, radio frequency interference or radiation by either absorption and /or reflection.

For more effective low frequency EMI shielding applications, surface resistivity below $1 \Omega/\square$ are needed. Polypyrrole-coated textiles have been shown to be fairly transparent to the magnetic component of electromagnetic radiation below 100 MHz [1]. Even though metal-coated textiles are preferred in these applications, several other applications are still useful such as a higher surface resistance in gaskets or when corrosion or adhesion prevents the use of metal-coated fabrics [1].

Energy Storage Fabrics: Conducting polymer coated textiles can also provide energy storage or energy conversion such as batteries, capacitors, photovoltaic devices that can help people living and travelling in remote areas. The use of wearable textile electrodes with conducting polymers and combined with appropriate electrolytes can give an efficient electrochemical cell and impart long cycle life to a rechargeable battery [3]. An area of current intense research interest is the development of multifunctional textiles where there is the possibility and feasibility of producing textile

based conducting polymer photovoltaic wearable devices and other photovoltaic textile products such as tents, blankets and curtains [4].

Thermal Control: The range of resistances makes inherently conducting polymer (ICP) coated textiles suitable for resistive heating applications. A conductive fabric offers many potential advantages over traditional heaters consisting of rigid resistive wires. Not the least of these is the diffuse nature of the conducting surface, which gives rise to fast, even heating over the entire surface and low power density [1]. ICPs coated substrates are suitable for a large range of applications such as heating sheets for car seats, heating winter sports wear and heating gloves for medical use [5].

Reinforced Composite: Textile fabrics coated with polypyrrole and polyaniline have wide applications in fibre reinforced composite structures as used with epoxy resins, polyimide resins, polyester resins and others [6]. One of these applications is the use of Contex fabrics to be examined by General Dynamics in aircraft wings. It has been shown that polypyrrole treated quartz fabric in an epoxy laminate has strength properties comparable to the untreated materials [6]. The use of conducting polymer-coated fabrics can be used in the manufacture of composite structures as reinforcement materials for thermoset resins due to the highly efficient microwave absorbance characteristics of conducting polymers [1]. Polypyrrole-coated quartz fabrics embedded in epoxy resins have shown sufficient stability in accelerated aging test [7].

Radar -Absorbing Materials: There can be made from polypyrrole or polyaniline coated textiles due to the range of conductance attainable with polypyrrole or polyaniline. It is desirable to minimise the radar signature by the use of so called

edge cards. They allow a smooth transition around sharp edged surface by having a gradient in conductivity, going from metallic to insulating properties [6]. Conventionally these gradients are produced by sputtering metal in varying thickness on a substrate film. Conductive polymer coated fabrics are able to produce similar microwave properties combined with the strength of supporting properties of the textile [6]. This type of fabric can be prepared by either weaving or knitting yarns of various conductivities into the fabric structure. Another approach is to immerse a polypyrrole coated fabric into a reducing agent yielding a progressive decrease in conductivity. Details have been described in some US patents [6].

The microwave attenuation can easily be modified by the selection of the base fabric and the thickness of the polypyrrole coating. Thicker fabric can be employed in applications where high levels of attenuation are desired. Tighter constructions are used when the attenuation at high frequencies is an issue, because the attenuation is affected by the opening size of the textile structure [1]. The microwave response of fabrics in the range from 10 to $10^3 \Omega/$ seems to be ideal for camouflage, decoys and other military applications. Multispectral fabrics combining the radar properties of Comtex fabrics with visible, near infrared and thermal camouflage properties are used to produce camouflage nets for military applications [6].

Other Applications:

Conducting polymers such as polypyrrole-coated textile fabrics have been investigated for their gas sensing capabilities by monitoring conductivity changes, e.g. detection of species, such as $\text{HCl}/\text{N}_2/\text{NH}_3/\text{N}_2$ is possible [8]. On the other hand, polypyrrole coated polyester fabrics with the value of surface resistivity in the range 10^4 - $10^5 \Omega/$ are considered to be attractive biomaterials for

biomedical applications and tissue engineering [9]. Electrically conducting polypyrrole-coated woven polyester fabrics have recently been investigated to induce undesirable effects on endothelial cell behaviour in terms of cell growth, migration and viability [10]. *In vitro* biocompatibility studies of electrically conductive polypyrrole-coated polyester fabrics indicate that PPy-coated polyester fabrics did not cause hemolysis nor did they alter the blood coagulation properties. This study investigated the basic biocompatibility aspects of two types of PPy-coated polyester fabrics for possible use as vascular prostheses [11].

The application of stretchable conductive textiles is reported in this Chapter. A preliminary study to assess the feasibility of a strain gauge produced from conducting polymers coated fabrics, the possibilities and potential for further study in this field will be described in the following sections.

6.2. DEVELOPMENT OF STRETCHABLE CONDUCTIVE TEXTILES

6.2.1. Strain Gauge Performance in Sport Training

A wearable strain gauge produced from conducting polymer-coated textile fabrics can be applied instead of conventional strain gauge for movement measuring at different strain range. Conventionally the digital imaging of high speed video can be used to measure functional dynamic range of the motion of a human body. To do so, it is necessary to place high contrast markers at pre-determined reference points on the subject body. A high speed video camera records the activity undertaken by the subject body and then digitised by a computer. There is a major advantage of digital imaging

having a visual image of the subject, but there are some problems associated with digital imaging including the cost to purchase the expensive equipment, impossibility of *in-situ* analysis data, a time-consuming process to digitise the video image and to track the high contrast markers. The distance between the video and high contrast markers needs to be kept constant for accurate digital imaging. It is very difficult for recording and studying three-dimensional motions for relatively high speed sport.

It is necessary to design an advanced device which can measure and record the functional dynamic range of motion as an alternative to high speed video imaging technology. This device can be used in sport testing applications where the object is restricted by recording in a video camera. A flexible strain gauge is a simple method to measure and record the functional dynamic range motion. Most strain gauges convert an applied strain directly into electrical resistance [12]. Strain is calculated by measuring the change in resistance. In general, materials used for strain gauges retain a linear relationship with the change of resistance in a small strain scale, such as most metallic materials. Flexible strain gauges using conducting polymer coated textiles have been investigated by De Rossi and co-workers [13,14]. It is reported that the presence of conductive elements gives these coated materials piezoresistive properties and enables the detection of local strain on the fabric [13]. Polypyrrole-coated nylon Lycra fabric used to predict the joint angle of the knee during a traditional style-racing bike was investigated at the University of Wollongong [15]. The joint angle ϕ of the knee is shown in Figure 6.1. A piece of PPy-coated nylon Lycra with 13 cm x 2 cm was attached to the skin at two points. The joint angle of knee flexion and extension can be calculated by measuring the changes in resistance when the coated fabric was stretched during cycling [15].

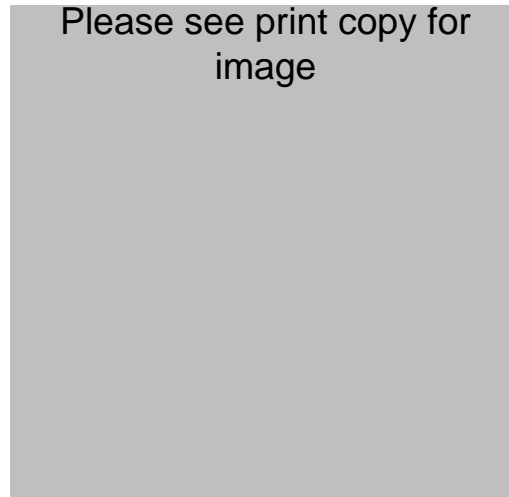


Figure 6.1. The joint angle, ϕ , for the knee [15].

A wearable strain gauge has been demonstrated by an “Intelligent Elbow Strain Gauge”; which can monitor arm motion during sporting activities. Figure 6.2 shows an “Intelligent Elbow Strain Gauge”. Conducting fabric sensor such as polypyrrole coated nylon Lycra fabric is hooked into a telemetry device, which can collect data and relay to a computer *in-situ*. Information is gathered and stored on a tiny microchip that signals the polymer fabric to expand and contract in response to arm movement. The change in resistance of PPy-coated nylon Lycra strip used for the “Intelligent Elbow Strain Gauge” is shown in Figure 6.3.



Figure 6.2. “Intelligent Elbow Strain Gauge”

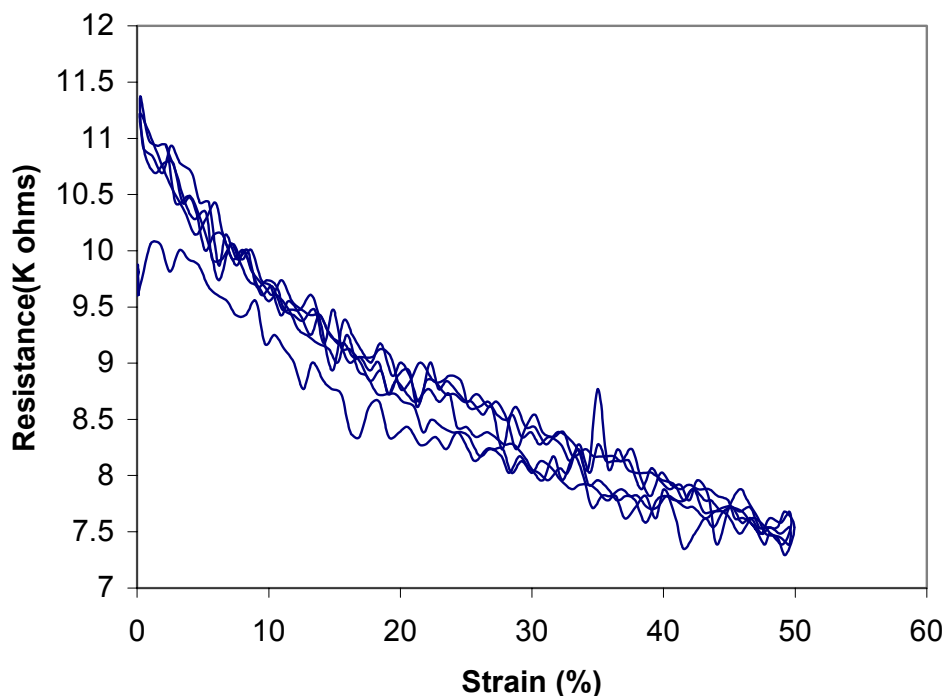


Figure 6.3. Changes in resistance of PPy-coated nylon Lycra strip on the “Intelligent Elbow Strain Gauge” under different strain ranges. PPy-coated nylon Lycra fabric was prepared by an *in-situ* polymerisation process for 2 hours at room temperature. The polymerisation solution consisted of 0.015 M pyrrole monomer, 0.04 M FeCl_3 and 0.005 M dopant NDSA.

Intelligent Knee Sleeve: Non-contact rupture of the anterior cruciate ligament (ACL) is one of the most common disabling injuries an athlete can sustain. ACL rupture frequently results from poor landing technique and accounts for a quarter of all sports injury costs in Australia [16]. As a result, an intelligent knee sleeve has been currently developed between the Intelligent Polymer Research Institute and Biomedical Science at the University of Wollongong and CSIRO Textile & Fibre Technology. This knee sleeve is comprised of a strip of Lycra coated with a thin layer of conducting polypyrrole and can provide feedback to players by emitting an audio

tone (Figure 6.4). This is because the knee sleeve is a dynamic electronic component within an electronic circuit. When the coated fabric is stretched, changes in resistance of the textile results in changes of the output of an electronic circuit. So different sounds will be emitted according to the strain from the coated fabrics.

The use of the “intelligent knee sleeve” (Figure 6.5) can teach people, such as AFL footballers, skiing or netball players, how to land correctly depending on the different type of tone they hear. The Geelong football team have used this intelligent knee sleeve in training routines (Figure 6.6). With its help, football players can protect against sporting injuries and save great amount money in medical costs. Intelligent knee sleeve and its electronic components are shown in Figure 6.4 and Figure 6.5.

Layout of the components

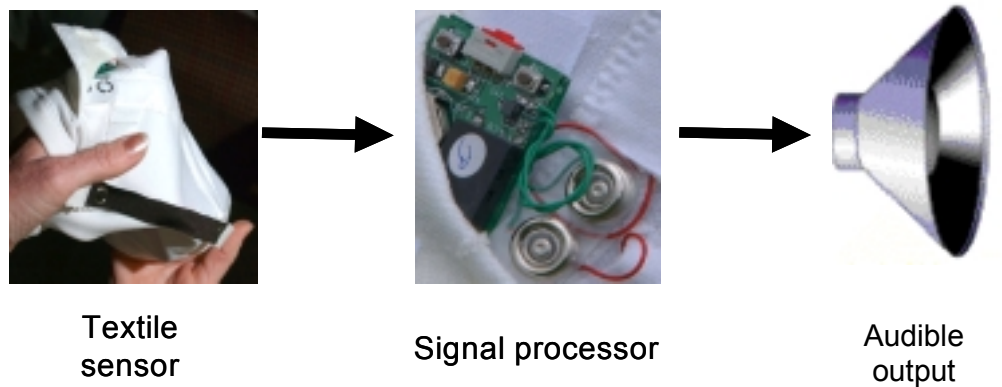


Figure 6.4. Knee sleeve system.



Figure 6.5. Intelligent Knee Sleeve.



Figure 6.6. Football player wearing the “intelligent knee sleeve” and training to land correctly to protect his knee from potential ligament damage.

6.2.2. Conductive Stretchable Textiles for Sensors and Actuators

Stretchable textiles coated with conducting polymers can also be applied in the field of rehabilitation, motion control and medical treatment due to their piezo- and thermo-resistive properties [14]. It was reported by D. De Rossi and co-workers that smart textiles for wearable motion capture systems had been used as kinaesthetic and haptic interfaces in surgery and rehabilitation [13]. Some prototypes were made to show reasonable capabilities of detecting and monitoring body segment position by reading the mutual angles between the bones including a sensorised glove and a sensorised leotard [13].

Electromechanical actuators are being investigated for a wide range of applications in medical, electronic and industrial areas. One attractive application is to incorporate conductive polymer fibre actuators into fabrics for use in prosthetic applications. The design of polypyrrole fibre actuators for use in a glove to open and close the human hand has been described by G.M. Spinks and co-workers [17]. Another aspect of the practical use of actuator materials is their control. The simple strain sensors based on conductive polymer-coated stretch fabrics has been developed [18]. Calibration of these materials shows a wide linear range and high gauge factor. Combining fabric strain gauges with polymer actuators is a convenient means for providing feedback control to the actuating element [18]. The use of electromechanical actuators based on conducting polymers has been currently investigated at the “Intelligent Polymer Research Institute” of the University of Wollongong. Coated fabric strips are sewn across the proximal interphalangeal joint in this rehabilitation glove and bending of the finger causes a measurable change in fabric resistance [17]. Figure 6.7 shows this rehabilitation glove

in collaboration with The Royal North Shore Hospital (Sydney, Australia). The actuators (not shown) can be integrated throughout the wearable glove structure to provide assisted movement during rehabilitation [19].



Figure 6.7. The rehabilitation glove with PPy-coated fabric sensor strips on each finger.

Following injury or surgical intervention, most patients suffer an asymmetric loss of joint mobility, deficits in proprioception and muscle weakness. Wearable sensing systems such as the “intelligent knee sleeve” may assist patients to learn how to move their joints through a desirable range of motion throughout typical rehabilitation exercise and may promote the recovery of joint range of motion and function [16].

Electrical conducting polymer coated stretchable fabrics have been used in medical treatments such as electrotherapy. Electrotherapy using electric pulses is increasingly being used in physiotherapy and rehabilitation to reduce pain, enhance healing, and improve patient’s mobility [20]. Conductive materials used for electric stimulation

electrodes are usually manufactured by the post-treatment of fabric or addition of conductive fillers to the fabric finishing process. Among the various approaches, use of a conducting polymer coating is easy to produce and does not detract from the inherent flexibility and durability of the bare fabric. Changes in conductivity with repeated fabric extension can improve the properties of conductive electrode pad materials to be adaptable for human body movement during electrotherapy [20]. In addition, changes in conductivity with a direct current are observed to generate heat from a long period of treatment current for electrotherapy [20]. Currently electroconductive stretchable fabrics have been prepared by coating of conductive PPy and electroless copper plating on nylon/spandex stretchable fabric to pursue feasibility of the conductive electrode pad materials for electrotherapy. Performance of prepared stretchable conductive fabric pad was evaluated in terms of conductivity changes as a function of extension and continuous current application time, and clinical effect [21].

6.2.3. Further Potential Applications

Conductive PPy-coated stretchable textiles have potential further applications in the field of biomechanics to monitor the kinematics and kinetic characterising of human performance. They may be widely used in sports such as kicking a football, bowling a cricket ball, hitting a tennis ball and sorting out the golf swing. These unique wearable systems with a large dynamic range can be integrated directly into existing clothing and equipment without changing the properties and functions of the materials and may not interfere with normal human motion. This technique will be widely applied for injury prevention, rehabilitation and technique modification and so on.

Golf has been rated as the fastest growing sport played by people of different ages and levels in the world. The golf stroke involves coordinated movement of the whole body. Without correct swing technique, a player may be injured during the golf stroke. It is anticipated that conductive wearable sensing systems can be incorporated into sports such as golf to assist players to learn the correct mechanics of a golf swing as well as facilitate the prevention of golf-related injuries [16]. There are some advantages in this system that can provide immediate, individual and objective biofeedback to the wearer during the movement. It will not impede the body movement and can help people reinforce the correct technique to optimise performance or prevent injuries in activities of daily living, work and recreation.

6.3. CONCLUSIONS

Traditional, conductive polymer coated textile fabrics have been widely used for static dissipations, EMI shielding, heating elements composite structures and many military applications. New techniques can produce energy textiles to generate and store electricity from the fabrics, build conductive fibres into garments to use in the area of biomedical monitoring and medical applications. Current research is focusing on development of conducting polymer coated wearable strain gauges to be used for biomechanical monitoring (eg. intelligent knee sleeve).

Conducting polymer coated textile fabrics are easily prepared and integrated into truly wearable clothing and garments to create strain sensors with a wide dynamic range. Functional wearable textile sensing systems can monitor human motion, provide immediate, individual and objective biofeedback to the wearer without changing

properties and functions of fabric materials and without interfering with normal human body motion. This innovative technique can be widely used for injury prevention, rehabilitation, sport techniques modification and medical treatment. It will have a number of further potential applications to be used for daily living, work and recreation in the future.

6.4. REFERENCES

1. H. H. Kuhn and A. D. Child, “*Electrically Conducting Textile*”, *Handbook of Conducting Polymers, Second Edition*, Marcel Dekker, Inc. New York, 1998. pp 994.
2. H. H. Kuhn, A. D. Child and W. C. Kimbrell, *Synth. Met.*, 71 (1995) 2139.
3. J. Mazurkiewicz, M. Forsyth, P. Innis, D. MacFarlane, C. Too and G. Wallace, *2003 IPRI International Workshop “Electronic Fibre & Textiles”*.
4. J. Chen, A. Burrell, W. Campbell, D. Officer, C. Too and G. Wallace, *2003 IPRI International Workshop “Electronic Fibre & Textiles”*.
5. J. P. Boutrois, R. Jolly and C. Petrescu, *Synth. Met.*, 85 (1997) 1405.
6. H. H. Kuhn, Characterization and application of polypyrrole-coated textiles, in *Intrinsically Conducting Polymers* (M. Aldissi, ed.), Kluwer, Dordrecht, 1993, pp 25.
7. H. H. Kuhn, W. C. Kimbrell, G. Worrell and C. S. Chen, *Tech. Pap.-Soc. Plast. Eng.* 37 (1991) 760.
8. D. Kincal, A. Kumar, A. D. Child and J. Reynolds, *Synth. Met.*, 92 (1998) 53.
9. D. Tessier, L. Dao, Z. Zhang, M. King and R. Guidon, *J. Biomater. Sci. Polymer Edn.*, 11 (2000) 87.
10. B. Jakubiec, Y. Marois, Z. Zhang, R. Roy, M. Sigot-Luizard, F. Dugre, M. King, L. Dao, G. Laroche and R. Guidoin, *J. Biomed Mater Res*, 41 (1998) 519.
11. Z. Zhang, R. Roy, F. Dugre, D. Tessier and L. Dao, *J. Biomater. Sci. Polymer Edn.*, 57 (2001) 63.

12. H. Trietley, *Transducer in Mechanical and Electronic Design*, Butterworth & Co. Ltd, London, Great Britain, 1985, pp 66.
13. A. Mazzoldi, D. De Rossi, F. Lorussi, E. P. Scillingio and R. Paradiso, *AUTEX Research Journal*, 2 (2002) 4.
14. D. De Rossi, A. Della Santa and A. Mazzoldi, *Mater. Sci. Eng.*, C7 (1999) 31.
15. P. Whitten, *Bachelor Thesis*, University of Wollongong, Australia, 1998.
16. B. J. Munro, J. R. Steele, G. G. Wallace and T. E. Campbell, *2003 IPRI International Workshop "Electronic Fibre & Textiles"*.
17. G. M. Spinks, G. G. Wallace, L. Liu and D. Zhou, *Macromol. Symp.* 192 (2003) 161.
18. G. M. Spinks, G. G. Wallace, L. Liu and D. Zhou, *Mat. Res. Soc. Symp. Proc.* 698 (2002) 5.
19. G. G. Wallace, G. M. Spinks, L. A. P. Kane-Maguire, P. R. Teasdale, *Conductive Electroactive Polymers, Intelligent Materials Systems, Second Edition*, CRC Press LLC, 2003.
20. K. W. Oh, H. J. Park and S. H. Kim, *J. Appl. Polym. Sci.*, 88 (2003) 1225.
21. S. H. Kim, K. W. Oh and J. H. Bahk, *J. Appl. Polym. Sci.*, 91 (2004) 4064.

CHAPTER 7

GENERAL CONCLUSIONS

The synthesis, characterisation and application of conducting polymer coated textile fabrics were the main objectives of this work. Several strategies were investigated to obtain conducting polymer coated fabrics with studies into the electrical and mechanical properties for different applications. In one approach conducting polypyrrole coated textile fabrics were prepared using an *in-situ* chemical oxidation process. Surface resistivity and gauge factor can be tailored by varying polymerisation conditions such as polymerisation time, reaction temperature and concentration of reactants. Individual fibres were coated with a thin uniform polypyrrole layer with the nodules between ca 200 nm to 500 nm. UV-Visible studies confirm that the nylon Lycra fabric was coated with a thin layer of polypyrrole. The degradation of polypyrrole on the coated fabric was reduced by storing the coated fabrics in a desiccator to avoid oxidative reaction in air. PPy-coated nylon Lycra fabric was observed to be electroactive with one pair of redox peaks due to oxidation/reduction of the polymer. The thermal stability of PPy/NDSA coated nylon Lycra is less than the uncoated fabric with a mass loss of 6.3% at 350 °C due to the break down of the polypyrrole backbone and/or chemical decomposition of the dopant NDSA.

Fabrics can also be made conductive using coating techniques that involve template molecules such as water-soluble poly(2-methoxyaniline-5 sulfonic acid) (PMAS) followed by the introduction of conducting polyaniline. Pre-treatment of fabrics, lower reaction pH and higher dyeing temperature used in the dyeing process can significantly increase the exhaustion of PMAS from the dye bath. More efficient exhaustion resulted in an increased PMAS loading on the fabric and an increase in the fabric conductivity. With template polymerisation, a molar ratio of 1:2:0.5 between PMAS, aniline and APS was found to be optimal and produced more conductive templated polyaniline coated

wool nylon Lycra fabrics. Lower polymerisation temperatures were observed to result in a more conductive fabric.

Templated polyaniline coated wool nylon Lycra fabrics are less stable in air. The degradation of polyaniline on the coated fabric can be reduced by storing the coated fabrics in a sealed plastic bag rather than exposure to the air. SEM studies show a thin, uniform and coherent polyaniline layer has been formed on the single fibre after the templating polymerisation process. PMAS templated PAn coated wool nylon Lycra fabric is electroactive due to one pair of redox peaks as monitored by cyclic voltammetry. UV-Vis spectrum for PMAS templated PAn coated wool nylon Lycra fabric exhibited two peaks at ca. 445 nm and 480 nm, assigned as a low wavelength polaron $\rightarrow \pi^*$ band transition from PAn emeraldine salt and a $\pi - \pi^*$ transition band transition from PMAS. A broad band around 800 nm and a strong free carrier tail, corresponding to conductive PAn emeraldine salt on the wool nylon Lycra fabric was also observed. The thermograms of all coated fabric samples including PMAS-treated and PMAS templated PAn coated wool nylon Lycra 7010 fabrics demonstrate similar characteristics to the uncoated wool nylon Lycra fabric. Therefore the thin layer of conductive PAn emeraldine salt does not affect the thermal stability of the natural wool nylon Lycra fabric.

Mechanical properties of conducting polymers are generally poor. By introducing conductive polymer into fabrics, mechanical properties of the coated fabrics shows little change compared to uncoated fabrics.

Investigation of conductive polymer coated textiles has shown a resistance change vs strain when the fabrics are stretched using an Instron 4302 tensile tester (Chapter 5). The sensitivity of the PPy-coated nylon Lycra fabric strain gauge is higher in low strain ranges (<10%). There are only minor variations on the resistance of the coated nylon Lycra fabric when stretched over the strain of 50%. With increased strain, the resistance of PMAS templated PAn-coated wool nylon Lycra fabric decreases. A linear relationship between the resistance and strain was in the range 10 - 70%. By comparing the strain performance of PPy-coated and templated PAn-coated textiles, it was found that both polypyrrole and templated polyaniline coated fabrics was used as a strain gauge. The gauge factor of PPy-coated nylon Lycra fabric was 0.75 (absolute value) when coated fabric was stretched to 50%. The wide strain range was found using the PMAS templated PAn-coated wool nylon Lycra fabric. The gauge factor was 0.74 (absolute value) when it is stretched to 70%.

Strain gauge performance was investigated using a “SmartMotor” system. It was found that the resistance of PPy-coated nylon Lycra decreases when stretched. After straining to greater than 50%, the resistance remains the same value. Multi-cycle resistance-strain measurements were performed at different frequencies from 0.5 Hz to 1.5 Hz. Results indicate that gauge factors change depending on the different initial resistance on the fabric. Strain gauge performance of the PMAS templated PAn-coated wool nylon Lycra fabric has also been investigated using the “SmartMotor” system. Similar results with the Instron system indicate that the resistance of the coated wool nylon Lycra decreases when stretched. The wide strain range was determined to be from 10% to 70% using the “SmartMotor”.

PPy-coated and templated PAn-coated textiles were found to be both suitable for application as the strain gauges using both the Instron machine and the “SmartMotor”. The “SmartMotor” system used for the strain test proved very useful during dynamic measurement at higher frequencies as the strain frequencies could be modified to suit different applications such as for body movement in sport.

Current focus in my work is on development of conducting polymer coated wearable strain gauge to be used for biomechanical monitoring (eg. intelligent knee sleeve).

Conducting polymer coated textile fabrics are easily prepared and integrated into truly wearable clothing and garments to create strain sensors with a wide dynamic range. Functional wearable textile sensing systems can monitor human motion, provide immediate, individualise and objective biofeedback to the wearer without changing properties and functions of fabric materials and without interfering normal human body motion. This innovative technique can be widely applied for injury prevention, rehabilitation, sport techniques modification and medical treatment.

In this thesis, although all the techniques produced and characterised conducting polymer coated textiles with widespread applications, further studies are recommended for further improvement in potential applications. My recommendations are:

- Synthesis of new types of textiles coated with different conducting polymer using various techniques.
- Development of strain gauge characteristics on different conducting polymer coated textile fabrics.

- Investigation of potential applications of conducting polymer coated textile in a number of area including daily living, work and recreation.