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DEVELOPMENT AND CHARACTERISATION OF POLYANILINE - CARBON NANOTUBE CONDUCTING COMPOSITE FIBRES

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

DOCTOR OF PHILOSOPHY

From

UNIVERSITY OF WOLLONGONG

by

VAHID MOTTAGHITALAB

(B.Sc. Chemical Engineering; M.Sc. Polymer Engineering)

School of Material, Mechanical and Mechatronic Engineering

JUNE 2006

IN THE NAME OF ALLAH, THE MOST GRACIOUS, THE MOST MERCIFUL

This thesis is dedicated to:

My wife: Mahin

My son: Amir Reza

For their love, support and patience

and my Mother for her encouragement,

especially in memory of my father

and

To My Brothers

THESIS CERTIFICATION

I, Vahid Mottaghitalab, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the School of Material, Mechanical and Mechatronic Engineering, Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The thesis was completed under the supervision of Prof. Geoffery. M. Spinks and Prof. Gordon. G. Wallace and has not been submitted for qualification at any other academic institution.

Vahid Mottaghitalab

JUNE 2006

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PUBLICATIONS

Published Paper:

1. **V. Mottaghitalab**, G. M. Spinks and G. G. Wallace, The influence of carbon nanotubes on mechanical and electrical properties of polyaniline fibres, Synthetic Metals, 152, **(2005)**, 77-80.

2. G. M. Spinks, **V. Mottaghitalab**, M. Bahrami-Samani, P. G. Whitten and G. G. Wallace, Carbon Nanotube Reinforced Polyaniline Composite Fibres for High Strength Artificial Muscles, Advanced Materials, 18, (2006), 637.

In Press

1. **V. Mottaghitalab**, B. Xi, G. M. Spinks and G. G. Wallace, Polyaniline Fibres Containing Single Walled Carbon Nanotubes: Enhanced Performance Artificial Muscles, Synthetic. Metals. **(2006).**

2. **V. Mottaghitalab**, G. M. Spinks and G. G. Wallace, The development and characterization of polyaniline - single walled nanotube composite fibres using 2-acrylamido-2 methyl -1-propane sulfonic acid (AMPSA) through one step wet spinning process, Polymer, (**2006).**

Submitted to Journals:

1. C. Y. Wang, **V. Mottaghitalab**, C. O. Too, G. M. Spinks and G. G. Wallace, Investigation of Polyaniline fibre as battery material in ionic liquid, Journal of power source, **(2006).**

3. B. Xi, V.T. Truong, **V. Mottaghitalab**, P. Whitten, G. M. Spinks, G. G. Wallace, " Acctuation behavior of polyaniline films and tubes prepared by the phase inversion technique", Submitted , Smart Mater. and Struct.**(2005)**

<u>Conference papers:</u>

1. **V. Mottaghitalab**, B. Xi, G. M. Spinks and G. G. Wallace, "The influence of carbon nanotubes on mechanical, electrical and electrochemical properties of polyanline fibre", ICSM, Wollongong, Australia, **2004**, Session: Electronic Fibres and Other Unconventional Substrates.
2. **V. Mottaghitalab**, B. Xi, G. M.Spinks and G. G. Wallace, Polyaniline-single wall nanotube composite fibre: opportunities and challenges, Umist, Manchester, UK, **(2004).**session 7a-Nanostructured fibres I.

3. **V. Mottaghitalab**, G. M.Spinks and G. G. Wallace, A. R. Wilson, Polyaniline-nanotube multifunctional fibre: capabilities toward the manufacturing of smart fabric, 5648, SPIE, Sydney, Australia, **(2004).**385-396.

4. G. M. Spinks, **V. Mottaghitalab**, Binbin Xi, P. Whitten, G. Wallace, S. J. Kim, S. R. Shin and S. I. Kim, Carbon Nanotube Reinforcement of Conducting Polymers and Hydrogels for High Strength Actuators, MRS Fall Meeting, W6.2/V7.2, Boston , MA ,USA, **(2005)**.

5. G. Spinks, B. Xi, T. Campbell, P. Whitten, **V. Mottaghitalab**, M. Bahrami Samani and G. G. Wallace, In pursuit of high-force/high-stroke conducting polymer actuators (Invited Paper), Proceedings of SPIE-The International Society for Optical Engineering, 5759,**(2005)**, 314-321.

6. G. G. Wallace, **V. Mottaghitalab**, S. E. Moulton and a. G. M. Spinks., Synthesis and properties of organic, electronically conducting fibres: a platform for electronic textiles, Fr C3.2, Queenstown, New Zealand, **(2005).**

8. B. Xi, V.-T. Truong, **V. Mottaghitalab**, P. Whitten, G. M. Spinks and G. G. Wallace, Ed: S. F. Al-Sarawi, Actuation behaviour of polyaniline films and tubes prepared by phase inversion technique, 5649, SPIE, Sydney, Australia, (**2005**).436-444.

<u>Manuscript in preparation:</u>

1. **Vahid Mottaghitalab**, Philip G. Whitten, Geoffrey M. Spinks and Gordon G. Wallace , Nanotube orientation and load transfer in Polyaniline /Single Walled Carbon Nanotube Composite Fibre

2. **V. Mottaghitalab**, B. Xi, G. M. Spinks and G. G. Wallace, The study of electrical behavior of PAni- AMPSA fibre filled with CNTs: the enhanced metallic transport,

ABSTRACT

The present study describes methods for development and characterization of conducting electroactive polymer (CEP) fibre consisting of polyaniline (PAni) and single walled carbon nanotubes (SWNTs) which have potential applications as electronic devices to form building blocks of electronic textiles. The conducting composite fibres of PAni-SWNT were developed respectively using two steps (acid doping after fibre spinning) and one step methods (doping during preparation of spinning solution). The effectiveness of nanotube inclusion for improvement of mechanical, electrical and electrochemical properties was studied in each method. During development of the fibres, techniques such as UV-Vis-NIR, Raman spectroscopy, Dynamic light scattering and viscometery were used to characterise the quality of dispersion and spinning solutions. It has been shown that the N,N'-dimethyl propylene urea (DMPU) and dichloro acetic acid (DCAA) as solvents respectively for PAni in base and salt form are able to effectively disperse the pristine SWNTs to reach percolation level. The addition of nanotubes changes the rheological behavior of neat PAni spinning solution from a Newtonian to non-Newtonian shear thinning fluid based on power law regime which reflects nanotube-nanotube and/or nanotube-polymer physical entanglement. Several techniques including DMA, DSC, SEM, TEM, FIB, Raman spectroscopy, CV and four point probe electrical conductivity measurement were employed to characterize the various properties of the solid fibre. In both, one step or two steps methods, fibres containing SWNTs have superior tensile strength and elastic modulus compared with neat PAni fibre. The inclusion of SWNTs to PAni, however, decreases the elongation at break. These outcomes directly can be attributed to physical and/or chemical interfacial interaction between well distributed SWNTs bundles and the PAni matrix. The addition of nanotubes to the PAni matrix also increases the electrical conductivity and enhances the electrochemical redox process. However, the two step method was found to have some problem include low spinning rate, low flexibility and low conductivity and insufficient charge transfer along the fibre to be working electrode. These disadvantages were diminished by faster spinning of PAni-ES/2-acrylamido-2 methyl -1-propane sulfonic acid (AMPSA)/SWNT using the one step process with more than 5 times stretching ratio. An electronic conductivity percolation threshold of ~ 0.35 % w/w SWNTs was determined with fibres possessing electronic conductivity up to ~ 750 Scm^{-1}. The well defined electrochemical window for neat PAni-ES/AMPSA fibre and its composite containing SWNT either in aqueous or ionic liquid electrolyte, with wider electrochemical window, confirms the ease of charge transport through a new conduction path for the fibre formed from salt structure, which was enhanced by addition of nanotubes. The ultimate tensile strength, elastic modulus and elongation at break of PAni-ES/AMPSA/SWNT fibres containing 0.76 % w/w nanotubes respectively were obtained 255 ± 32 Mpa, 7.3 ± 0.4 GPa and 4 ± 1 % compared with 170 ± 22 MPa, 3.4 ± 0.4 GPa and 9 ± 3 % for PAni-ES/AMPSA fibre. The quantitative analysis of nanotube orientation and detection of load transfer from matrix to nanotubes were investigated in PAni-ES/AMPSA/SWNT composite fibre using Raman spectroscopy. It has been found that thermal stretching of as spun fibre mostly orients the nanotubes in a range of about ± 30° versus fibre axis which extremely increase the Herman orientation factor from 0.02 for as spun fibre to 0.43 for the 5x drawn fibre. Moderate orientation and Raman shift about 90- 130 cm^{-1} in D* band of SWNT also can

be correlated to effective but not prefect load transfer between PAni matrix and nanotubes. The result of temperature dependent electrical conductivity data was shown that the higher conductivity of PAni-ES/AMPSA/SWNT composite fibre compared to neat PAni-ES/AMPSA fibre also can be described by improvement of the metallic property in the crystalline areas and boosting of the metallic disorder contribution in amorphous area. The consequence of improvement of mechanical, electrical and electrochemical properties were a benefit for applying of PAni/ES-AMPSA fibre and its composite having SWNT in applications as actuator, power source and sensor. While the fibres showed great promise as actuators, their response as batteries and temperature/ humidity sensors was limited. The significant improvement was observed in actuator strength in excess of 100 MPa and work-per-cycle of over 300 kJ/m^3 through the incorporation of small amounts of SWNTs as reinforcement in the PAni matrix. This performance is 3 times higher than previously produced conducting polymer actuators and exceeds skeletal muscle in terms of stress generation by 300 times. PAni-ES/AMPSA/SWNT exhibited a higher charge/discharge capacity (12.4/11.2 mAhg^{-1}) compared with the neat PAni-ES/AMPSA (4.5/4.1 mAhg^{-1}). All the results show that solid polyaniline fibre can be used directly as electrode in ionic liquid of EMI.TFSI for wearable power source system. However its current performance is still well below conventional rechargeable battery systems. PAni fibre and its SWNT composite showed a nonlinear response with some delay to temperature signals. The PAni fibre incorporated with SWNTs showed lower sensitivity to change in humidity pulse compared with neat PAni fibre. This behavior has good opportunity for application in conducting yarn that needs the lowest variability in conductivity for transferring of electrical signal but clearly is not favored for sensing of humidity.

Abbreviations

Ch	Chiral vector
MWNT	multi wall carbon nanotubes
n	Power law index
NIBS	Non invasive backscattering
NIR	near infra red
NMP	N- methyl pyrrolidinone
n_R	The solvent refractive index
Nylon	11 - poly –ω-aminoundecanoyle
ODF	Orientation distribution function
PAN	Polyacrilonitrile
PAni	Polyaniline
PBO	Poly butyl oxide
PGB	Pernigraniline base
Pi (cosθ)	The Legendre polynomial of degree i
$<P_2 (\cos\theta)>$	The average amount of $P_2 (\cos\theta)$
$<P_4 (\cos\theta)>$	The average amount of $P_4 (\cos\theta)$
POT	polyoctylthiophene
PPMS	Physical property measurement system
PPy	Polypyrrole
Psi	Pound per square inch
PT	Polythiphene
PVA	Poly vinyl alcohol
Q	volumetric flow rate (cm^3/min)
R	Resistance(ohm)
RBM	Resonance breathing mode
S	Cross sectional area of fibre (cm^2)
SEM	Scanning electron microscopy

SWNT	single wall carbon nanotubes
$S\sigma$	the critical exponent at percolation
T	Temperature (K, °C)
TEM	Transmission electron microscopy
Tg	glass transition temperature (°C)
TGA	Thermogravimetric analysis
TM	Tangential mode (G band)
TPa	Tera pascal
Tt and Ts	tunneling parameters for transport model(K)
V	Voltage (V, mV)
V_d	Drawing velocity (m/min)
Vi	Injection rate (g/min)
V_t	Take up velocity (m/min)
α	Chiral angle
γ	Shear rate (s^{-1})
δ_b	Tensile strength at break (MPa)
$\varepsilon^{\cdot}_{c,m,f}$	Expected actuator strain of composite, matrix or filler
ε_b	Elongation at break (%)
η	Viscosity (mPa.s=cP)
η_0	Zero shear viscosity (mPa.s=cP)
θ	The scattering angle of laser beam
θ°	The angle between nanotubes and fibre axis
λ_2 and λ_4	The arbitrary parameter of orientation function
λo	The vacuum wavelength of the laser
ρ	Density (g/cm3)
ρ_i	Resistivity of a potion either amorphous or crystalline
σ	Conductivity (S/cm)
φ	Spin draw ratio
φ_{th}	Thermal draw ratio

ψ	The angle between the polarization plane and the fibre axis
υ_i	Volume fraction of component i
ω	SWNTs mass fraction in the solid fibre
ω_1	The contribution of metallic resistivity in bulk resistivity
ω_2	The contribution of nonmetallic resistivity in bulk resistivity
ω_c	critical weight percentage of SWNT at percolation
ω_p	weight fraction of polymer with regards to solvents

Table of Content

DEDICATION ……………………………………………………………………….II

CERTIFICATION…………………………………………………………………...III

ACKNOWLEDGMENTS……………………………………………………….....IV

PUBLICATIONS……………………………………………………………………..VI

ABSTRACT……………………………………………………………………......IX

ABBREVIATIONS………………………………………………………………XIII

LIST OF FIGURES …………………………………………………………….. XXVI

LIST OF TABLES……………………………………………..………..XXXVIII

LIST OF SCHEMES…………………………………………………………XLII

1. CHAPTER ONE…………………………………………………………1

General Introduction

1.1. Introduction ……………………….…………………………….………..2

1.2. Motivation…………………..………………….………..…………….……2

1.3. The aims of the project………………………………………..…..….……9

1.4. References………………………..……………………………..........12

2. CHAPTER TWO…….……………………………………….……17

Literature Review

2.1. The chemical structure of Polyaniline……………………………………………18

2.1.1. The solubility of polyaniline…..……………………………………....20

2.1.2. Aggregation and gel formation of polyaniline solution……………..……21

2.1.3. The solubility of PAni doped with sulfonic acid in organic acid…………24

2.2. Carbon Nanotubes……………………………………………………………...26

2.2.1. Discovery……………………………………………………………...26

2.2.2. Structure of carbon nanotubes………………………………………………28

2.2.3. The physical properties of SWNTs…………………………………………29

2.2.3.1. Aspect ratio…………….…………………………………….......29

2.2.3.2. Mechanical properties ……………………………………………30

2.2.3.3. Electrical properties………………………………………………...31

2.2.4. Properties and applications of self assembled SWNT material…………..32

2.2.5. SWNT-CEP composites……………………………………………………..33

2.3. Wet spinning of Polyaniline (PAni)………………………………………………35

2.3.1. General description of the wet spinning process…………………………35

2.3.2. A literature review for PAni fibre formation……………………………..37

2.4. References……………………………………………………………………..44

3. CHAPTER THREE……………………………………..….……….52

General Experimental Techniques

3.1. Introduction……………………………………………………………………….53

3.2. Preparation of spinning solution using ex-situ approach…………………………54

3.3. Characterisation of spinning solution…………………………………………….56

3.3.1. Elemental analysis………………………………………………………..56

3.3.2. Dynamic Light Scattering (DLS)…………………………………………56

3.3.2.1. Theoretical background……………………………………..56

        3.3.2.2. Sample preparation……………………………………………….57
        3.3.2.3. The measurement description…………………………………….58
    3.3.3. Viscometery…………………………………………………………59
    3.3.4. UV-Vis and UV-Vis- NIR spectroscopy………………………………60
3.4. General description of spinning process…………………………………61
    3.4.1. Spinning apparatus………………………………………………….61
    3.4.2. Drawing……………………………………………………………..63
3.5. Techniques for characterisation of solid fibre……………………………65
    3.5.1. Four probe electrical conductivity……………………………………65
    3.5.2. Cyclic voltammetry…………………………………………………66
    3.5.3. Dynamic mechanical analysis…………………………………………68
        3.5.3.1. Stress-strain (Mechanical test) in strain rate mode………………68
        3.5.3.2. Creep mode……………………………………………………69
        3.5.3.3. Viscoelasticity test………………………………………………70
    3.5.4. Differential scanning calirometry……………………………………...71
    3.5.5. Raman spectroscopy…………………………………………………...71
    3.5.6. Scanning Electron Microscopy………………………………………..72
    3.5.7. Transmission electron Microscopy……………………………………74
3.6. References……………………………………………………………..75

4. CHAPTER FOUR……………………………………………….…76

Development and Characterisation of Polyaniline (Leucoemeraldine base) / Single Walled Carbon Nanotubes Composite Fibre Prepared Using a Two Step Process

4.1. Introduction……………………………………………………………………77
4.2. Experimental………………………………………………………………….. 78
- 4.2.1. Materials and reagents…………………………………………………78
- 4.2.2. Instrumentation………………………….…………………………78
- 4.2.3. Comparison of the ability of NMP and DMPU to disperse SWNTs……. 79
- 4.2.4. Influence of polyaniline addition on the degree of SWNT aggregation…80
- 4.2.5. Use of DMPU for dispersing SWNTs at higher concentrations..………..80
- 4.2.6. Preparation of spinning solution…….…………………………………80
- 4.2.7. The fibre spinning process……………………..………………………81
  - 4.2.7.1. Effect of coagulation bath composition…………………………..82
  - 4.2.7.2. Effect of take up velocity…………………………………………82
- 4.2.8. Effect of CNT content…………………………………………………82
- 4.2.9. Post spinning treatments…………………………………………………83

4.3. Results and discussions……………………………………………………...83
- 4.3.1. The characterisation of SWNTs…………………………………………..83
  - 4.3.1.1. Elemental analysis………………………………………………..83
  - 4.3.1.2. Raman spectroscopy of the bulk SWNTs………………………...84
- 4.3.2. Characterisation of SWNT dispersions…………………………………..85
  - 4.3.2.1. UV-visible – NIR spectroscopy…………………………………..85
  - 4.3.2.2. Dynamic Light Scattering………………………………………...88
  - 4.3.2.3. Viscosity of SWNT/DMPU dispersions…………………………91
- 4.3.3. Viscometery of PAni-(LEB)-SWNT-DMPU spinning solution………....92
- 4.3.4. The effect of fibre spinning parameters on PAni/SWNT morphology…..98

4.3.4.1. Influence of solvent in the coagulation bath on morphology of as spun fibre……………………………………………………….99
4.3.4.2. The influence of take up velocity on morphology………………100
4.3.5. Thermal transition temperatures in as spun fibre………………………..102
4.3.6. Thermal stretching…………………………………………………103
4.3.7. Mechanical properties of thermally stretched PAni/SWNT fibres……...105
4.3.8. Flexibility of PAni/SWNT composite fibres……………………………111
4.3.9. Raman spectroscopy of PAni/SWNTs composite fibres………………..112
4.3.10. Electrical properties of PAni/SWNTs fibres……………………116
4.3.10.1. Electrical properties of PAni/SWNTs fibres before acid doping..117
4.3.10.2. Electrical properties of PAni/SWNTs fibres after acid doping….120
4.3.11. Cyclic voltammetry of PAni/SWNTs composite fibres………………...121
4.4. Conclusions……………………………………………………………...123
4.5. References………………………………………………………………126

5. CHAPTER FIVE………………………………………………….…...130

Development and Characterisation of PAni/SWNTs Composite Fibres Using 2-Acrylamido-2 Methyl -1-Propane Sulfonic Acid and a One Step Wet Spinning Process.

5.1 Introduction……………………………………………………………..131
5.2 Experimental…………………………………………………………132
5.2.1 Materials and Reagents………………………………………………132

5.2.2 Instrumentation……………………………………………………………132

5.2.3 Characterisation of SWNT dispersions…………………………………136

5.2.3.1 DCAA versus DMPU as solvent……………………………….. 136

5.2.3.2 Influence of AMPSA on degree of SWNT aggregation………... 136

5.2.3.3 Ability of DCAA to disperse higher concentration of SWNT…. 137

5.2.4 Preparation of composite spinning solutions……………………………137

5.2.5 The fibre spinning process………………………………………………139

5.3 Results and discussion…………………………………………………………..140

5.3.1 SWNTs dispersions……………………………………………………..140

5.3.1.1 UV-Vis– NIR spectroscopy of SWNT dispersions……………..140

5.3.1.2 Influence of AMPSA on degree of SWNT aggregation in DCAA…………………………………………………………...141

5.3.1.3 Effect of sonication time on SWNTs agglomeration in DCAA…143

5.3.1.4 Effect of SWNT concentration on aggregation of SWNTs in DCAA ……………………………………………………………..145

5.3.2 Characterisation of spinning solutions…………………………………..147

5.3.2.1 Determination of suitable PAni/AMPSA composition…………147

5.3.2.2 Viscometery of PAni-ES/AMPSA/SWNTs-DCAA spinning solutions………………………………………………………149

5.3.3 Preparation and characterisation of composite fibres …………………..151

5.3.3.1 Morphological properties of PAni-ES/AMPSA/SWNT as spun fibres……………………………………………………………151

5.3.3.2 Morphological properties of thermally stretched PAni-ES/AMPSA/SWNT……………………………………………...153
5.3.4 The mechanical properties of composite fibres…………………………156
5.3.5 Thermal analysis of the PAni-ES/AMPSA/SWNT composite fibres…...160
5.3.6 Electrical conductivity of PAni-ES/AMPSA-SWSNT composite fibres ……………………………………………………………………...164
5.3.7 Raman spectroscopy of PAni-ES/AMPSA/SWNTs fibres……………...166
5.3.8 Cyclic Voltammetry……………………………………………………..171
5.3.8.1 Cyclic voltammetry of PAni-ES/AMPSA/SWNTs composite fibres in HCl(aq)…………………………………………………………172
5.3.8.2 Cyclic voltammetry of PAni-ES/AMPSA/SWNTs composite fibres in ionic liquid electrolyte……………………………………………..173
5.4 Conclusions……………………………………………………………...178
5.5 References………………………………………………………………180

6. CHAPTER SIX. ….…..………………….....……………………....184

The Understanding Of the Mechanism of Strength Increase in the PAni-ES/AMPSA/ SWNT Composite Fibre

6.1. Introduction……………………………………………………………..185
6.2. Experimental……………………………………………………………186
6.2.1. Materials………………………………………………………......186
6.2.2. Instrumentation…………………………………………………....186
6.3. Results and discussion…………………………………………………..187

6.3.1. SWNTs orientation…………………………………………………...187

6.3.2. Load transfer Mechanism……………………………………………200

6.4. Conclusion……………………………………………………………203

6.5 References……………………………………………………………205

7. CHAPTER SEVEN……………………………………………………..207

Charge Transport Regime in the PAni-ES/AMPSA/SWNT Composite Fibre

7.1. Introduction…………………………………………………………..208

7.2. Experimental…………………………………………………………210

7.2.1. Material……………………………………………………………..210

7.2.2. Sample preparation …………………………………………………...210

7.2.3. Instrumental………………………………………………………211

7.3. Results and discussion…………………………………………………..211

7.3.1. Electrical transport analysis………………………………………..211

7.3.2. Heterogeneous model………………………………………………215

7.4. Conclusion……………………………………………………………222

7.5. References……………………………………………………………224

8. CHAPTER EIGHT…………………………………………………..…226

The Preliminary Studies into Applications of PAni-ES/AMPSA/SWNT Fibres

8.1. Introduction…………………………………………………………...227

8.1.1. Actuators: recent development and general requirement………………..227

8.1.2. PAni fibre electrode for application in rechargeable battery……………229

8.1.3. Sensitivity to temperature and humidity………………………………...230

8.2. Experimental……………………………………………………………….231

8.2.1. The actuation tests……………………………………………………231

8.2.1.1. Materials and reagents………………………………………….231

8.2.1.2. Instrumentation…………………………………………………232

8.2.2. Electrode material for rechargeable battery……………………….233

8.2.2.1. Materials and reagents…………………………………………...233

8.2.2.2. Fabrication of polymer electrode……………………………...233

8.2.2.3. Electrochemical characterisation……………………………...233

8.2.3. Tests for sensitivity to change of temperature and humidity…………..234

8.2.3.1. Material and reagents……………………………………………234

8.2.3.2 Instrumentation…………………………………………………...235

8.3. Results and discussion……………………………………………………..236

8.3.1. Actuation behavior……………………………………………………..236

8.3.2. Performance of PAni-ES/AMPSA and its composite containing SWNTs fibres as electrode material in rechargeable battery………………….243

8.3.2.1. Charge/discharge characteristics……………………………..243

8.3.2.2. Cycle life……………………………………………………….245

8.3.3. Performance of PAni-ES/AMPSA fibres with and without SWNTs as humidity and temperature sensors………………………………………246

8.3.3.1. Sensitivity to temperature………………………………………246

8.3.3.2. Sensitivity to relative humidity (% R.H.)………………………248

8.4. Conclusions……………………………………………………………...250

8.5. References……………………………………………………………….252

9. CHAPTER NINE…………………………………………………....256

General Conclusion

LIST OF FIGURES

Figure 1.1. U.S. Smart and Interactive Textile market by application segment, 2003-2009 ($ Millions) …………………………………………………………....8

Figure 1.2. The architecture of electronic textile based on component and function……9

****

Figure 2.1. The tubular structure of graphene layers of SWNT……. ………………..….27

Figure 2.2. Different arrangements of nanotubes (●) semiconducing (n,0) or (m,n) (○) metallic (n,n) or (m,n) [n-m = 3q] , q is integer……………………. 28

Figure 2.3. Schematic of the experimental setup used to make CNT fibres……………33

Figure 2.4. Schematic showing the set up used for wet spinning of fibres…………….36

****

Figure 3.1. Schematic of sonication unit for dispersion of nanotubes in the solvent…… 55

Figure 3.2. The schematic of blending unit for mixing of PAni and SWNT dispersion…56

Figure 3.3. Schematic diagram showing the measurement position for (a) small, weakly scattering samples and for (b) concentrated, opaque samples……………...57

Figure 3.4. The picture of spinning line apparatus has been used in this study (a) whole apparatus (b) pressure vessel (c) take up and drawing roller (d) spinneret…62

Figure 3.5. The experimental set up used for cyclic voltammtetry (a) cell set up (b) instrumental set up……………..……………………………………………..67

Figure 3.6. The SEM pictures obtained using (a) Hitach- S900 from internal microstroucture (b) Leica 440 from circular cross section……………….73

Figure 3.7. The images obtained from a sample of polyaniline fibre from different angle using FIB……………………………………………………………74

****

Figure 4.1. Raman spectrum of bulk SWNTs (λexc=632.8 nm)………………………...84

Figure 4.2. UV-Vis NIR spectra of SWNT (0.01% w/w) in (a) DMPU and (b) NMP after 2hrs sonication (A, B, C: refer to table 4.4)………………………………..86

Figure 4.3. Hydrodynamic diameter distribution of SWNT bundles in DMPU for different sonication times (triangle) 30 min (square) 60 min (circle) 120 min………88

Figure 4.4. Affect of standing time on the stability of SWNT dispersions and influence of PAni on stability of SWNT dispersion in (a) SWNT- DMPU (0.01 % w/w) (b) SWNT (0.01 % w/w)-PAni (0.01 % w/w) in DMPU. Photograph was taken 6 hr after sonication. Arrows indicate large agglomerates…………..89

Figure 4.5. Hydrodynamic diameter distribution of SWNTs in DMPU (0.01 % w/w) with (square) and without (inverted triangle) PAni. The distribution immediately after sonication is represented by filled symbols while the distribution measured 60 min after sonication was stopped is shown by unfilled symbols. ……………………………………………………………………..90

Figure 4.6. The size distribution of SWNTs bundle in DMPU for different concentrations of (Δ) 0.05 % w/w, (□) 0.10 % w/w and (□) 0.20 % w/w…………………91

Figure 4.7. Viscometry of SWNT (0.2 % w/w) in DMPU dispersions after different sonication times (a) 30 min, (b) 60 min and (c) 120 min…………………..92

Figure 4.8. Variation of viscosity of spinning solution of PAni (LEB) 10% w/w in DMPU containing (a) 0.00 % (b) 0.05 % (c) 0.10 % or (d) 0.20 % (w/w) of SWNT with regard to solvent. Shear rate = 1 s^{-1}………………………..93

Figure 4.9. Variation in viscosity of spinning solution based on PAni (LEB) 10 % w/w in DMPU containing (a) 0.00 % (b) 0.05 % (c) 0.10 % (d) 0.20 % (w/w) SWNT with regards to solvent, at different shear rates…………………………95

Figure 4.10. Viscosity versus SWNTs content at different shear rate………………….97

Figure 4.11. Cross sectional SEMs of PAni (a, b) and PAni/SWNTs (2.0 % w/w SWNTs (c, d) into a coagulation baths containing (a,c) 10 % w/w NMP in water or (b, d) water using take up velocity of 2 m/min. Scale bar 30 μm……………100

Figure 4.12. Cross sectional SEMs of PAni/SWNT fibres spun using different take up velocities for PAni(a, b) PAni/SWNTs containing 2 % w/w SWNT(c, d). Take up velocities were 3 m/min (a, c) or 6 m/min (b, d). Scale bar is 30 μm (a,c) and 10 μm (b, d)……………………………………………………101

Figure 4.13. DSC thermal analysis curve of neat as spun polyaniline (LEB) fibre under a N2 atmosphere first cycle (thick line); second (reheat) cycle (thin line) ……………………………………………………………………102

Figure 4.14. SEM micrographs of PAni/SWNTs fibres after thermal stretching containing (a) 0.0 %, (b) 0.5 %, (c) 1.0 % and (d) 2.0 % (w/w) SWNTs with respect to PAni…………………………………………………………………..104

Figure 4.15. Stress strain curves of PAni/SWNTs composite fibres with varying SWNTs content, before doping (thick lines) and after doping for 24 hrs in MSA(thin

lines). (a,a')Neat PAni, (b,b') PAni/SWNT (0.5 % w/w) (c,c') PAni/SWNT (1.0 % w/w) (d,d') PAni/SWNT(2.0 % w/w)…………………………106

Figure 4.16. SEM images showing a typical cross sectional surface of (a) neat PAni (b) PAni/ SWNT (2.0 % w/w)……………………………………………..108

Figure 4.17. SEMs of PAni/SWNTs composite fibres under flexural load with SWNTs of (a) 0.0 % w/w (b) 0.5 % w/w(c) 1.0 % w/w (d) 2.0 % w/w……………111

Figure 4.18. Enhanced Raman Spectra (before doping) of (a) neat SWNTs, (e) neat PAni and PAni/SWNTs fibres with varying SWNT content (b) 0.5 %w/w (c) 1.0% w/w, (d) 2.0% w/w (λexc=632.8)………………………………………112

Figure 4.19. The schematic illustrating the interaction of SWNTs with PAni through the quinoid rings of latter……………………………………………………114

Figure 4.20. Enhanced Raman Spectra(after doping in MSA solution for 24 hrs following by drying at 100 °C) of (a) neat SWNTs (e) neat PAni and PAni/SWNTs with varying SWNTs content (b) 0.5 % w/w, (c) 1.0 % w/w, (d) 2.0 % w/w…………………………………………………………………………115

Figure 4.21. The percolative behavior of SWNTs as filler in PAni matrix before doping ……………………………………………………………………………118

Figure 4.22. The Log-Log plot of conductivity vs reduced weight fraction of SWNTs. **……………………………………………………………………………118**

Figure 4.23.The EPR spectra of PAni/SWNTs composite fibres before doping containing varying amounts of SWNTs. (a) 0.0 % w/w (b)0.5 %w/w, (c) 1.0 % w/w and (d) 2.0 % w/w………………………………………………………………119

Figure 4.24. Cyclic voltametry of (a) neat PAni fibre (b) PAni/ SWNTs (2 % w/w) composite fibre. Scan rate= 50 mVs-1, electrolyte: 1.0 M HCl (aq)…….123

****

Figure 5.1. First step of FIB milling: labeling of working area………………………...134

Figure 5.2. Second step of FIB milling: (a) Pt deposition and (b) milling of sloping trenches……………………………………………………………………134

Figure 5.3. Third step: reduction of thickness of thin film……………………………..135

Figure 5.4. Fourth step of FIB milling: (a) Further thinning of the lamella and (b) cutting of holding edges…………………………………………………………135

Figure 5.5. Final step of FIB milling: (a) transfer of the thin film on a TEM grid using a micro robot (b) Schematic indicating a micro robot machine……………136

Figure 5.6. UV-Vis NIR spectra of SWNT (0.01 % w/w) in (a) DCAA after 30 min sonication (b) DCAA-AMPSA (2 % w/w) after 30 min sonication and (c) DMPU after 2 hrs sonication……………………………………………141

Figure 5.7. Influence of AMPSA concentration (% w/w) in DCAA on hydrodynamic diameter distribution of SWNT dispersions (0.05 % w/w). (□) 0 % w/w (□)1 % w/w (□) 2 % w/w. The results were obtained 30 min after samples preparation……………………………………………………………..142

Figure 5.8. Hydrodynamic diameter of SWNTs (0.05 % w/w) in DCAA with (□) and without (□) AMPSA (2 % w/w). Hydrodynamic diameters immediately after sonication are indicated by the filled symbols; while those measured 60 min after sonication was stopped are indicated by the unfilled symbols……..143

Figure 5.9. Influence of sonication time on homogeneity of SWNTs dispersion as gauged by fluctuation of viscosity versus shear rate. The dispersion contained 0.060 % w/w SWNT and 2 %w/w AMPSA relative to the DCAA solvent. ……………………………………………………………………...144

Figure 5.10. Average hydrodynamic diameter of SWNT dispersions for 5 repetitive experiments using either 10 min or 30 min sonication time. The dispersion contained 0.060 % w/w SWNT and 2 %w/w AMPSA relative to the DCAA solvent……………………………………………………………..145

Figure 5.11. Influence of SWNTs concentration in DCAA/AMPSA solution on hydrodynamic diameter (□) 0.030 %w/w (□) 0.045 %w/w (□) 0.060 %w/w (□) 0.090 %w/w………………………………………………………….146

Figure 5.12. Viscosity vs. shear rate for SWNTs dispersion in DCAA containing 2 % w/w AMPSA for various SWNT loadings from 0.00% w/w to 0.09 % w/w. ……………………………………………………………………….147

Figure 5.13. Influence of SWNTs content on viscosity of PAni-ES/AMPSA/SWNT solution versus shear rate. The total concentration of PAni and AMPSA was 11.5 % w/w……………………………………………………………….149

Figure 5.14. Time before gelation indicated by sharp rise in viscosity for (a)neat PAni-ES/AMPSA and (b) PAni-ES/AMPSA/SWNT (0.090 % w/w) SWNT spinning solutions. Shear rate =1 s^{-1}………………………………………………151

Figure 5.15. Typical SEM micrographs of as-spun fibres of (a) neat PAni-ES/AMPSA (b) PAni-ES/AMPSA/SWNT 0.76 %w/w…………………………………..152

Figure 5.16. Typical SEM micrographs of 5x thermally stretched fibre of (a) PAni-ES/AMPSA (b) PAni-ES/AMPSA/SWNT (0.76 % w/w).scale bar is 10 µm ……………………………………………………………………..153

Figure 5.17. SEM micro graph of the PAni-ES/AMPSA/SWNT (0.76 %w/w)(a) side wall (b) cross section parallel to fibre axis……………………………………154

Figure 5.18. TEM micrographs of thin film obtained by FIB milling, showing SWNTs dispersion within an PAni-ES/AMPSA matrix for (a) neat PAni-ESAMPSA (b) PAni-ES/AMPSA/SWNTs (0.76 %w/w SWNT………………………155

Figure 5.19. The typical stress – strain curve of PAni-ES/AMPSA fibre and its composites with different SWNT contents (D fibre=50±20 µm, strain rate= 500 µm /min)……..………………………………………………………..157

Figure 5.20. Strain recovery behavior of (□) neat PAni-ES/AMPSA fibre (□) PAni-ES/AMPSA/SWNT (0.76 % w/w) with cyclical application and removal of a 40 mN force………………………………………………………………158

Figure 5.21. SEM micrographs of full knots of (a) PAni-ES/AMPSA (b) PAni-ES/ AMPSA/SWNT (0.76% w/w). SEM micrographs of 16 ply twisted fibre of PAni-ES/AMPSA/SWNT (0.76 % w/w) fibre with (c) S shaped twisting (d) Z shaped twisting. The number of twist per inch was 36…………………159

Figure 5.22. (a)DSC thermogram of 5x drawn fibre (a) PAni-ES/AMPSA (b) PAni-ES/AMPSA/SWNT (0.76 %w/w). (b) The DSC thermogram for the first and second cycles of 5X drawn PAni-ES/AMPSA/SWNT…………………..161

Figure 5.23. (A) Storage modulus (B) the Tanδ (Loss modulus/Storage modulus) vs temperature curves for (a) PAni-ES/AMPSA and (b) PAni-ES/AMPSA - SWNTs (0.76 % w/w)……………………………………………………163

Figure 5.24. Influence of SWNTs content on the electrical conductivity of PAni-ES/AMPSA/SWNTs fibres………………………………………………164

Figure 5.25. log–log plot of electrical conductivity vs reduced mass fraction…………165

Figure 5.26. Enhanced Raman spectra (λexc = 632.8 nm) obtained for PAni-ES/AMPSA/SWNTs obtained containing various amounts of SWNTs (a) 0.00 % w/w (b) 0.26 % w/w) (c) 0.38 % w/w (d) 0.5 %w/w (e)0.76 % w/w and (f) SWNT bucky paper………………………………………………167

Figure 5.27. Enhanced Raman spectra (λexc =632.8) of neat PAni-ES/AMPSA (a) before deprotonation, (b) 3 hr after deprotonation and (c) 6 hr after deprotonation (d) Raman spectrum of PAni(EB).Arrow indicates the transition from the protonated ES form to the deprotonated EB form………………………..170

Figure 5.28. Enhanced Raman spectra (λexc= 632.8) of (a) Neat PAni-ES/AMPSA fibre before deprotonation, (b) Neat PAni-ES/AMPSA after 6 hrs deprotonation (c) PAni-ES/AMPSA/SWNT (0.76 % w/w) before deprotonation and (d) PAni-ES/AMPSA/SWNT (0.76 % w/w) after 24 hrs deprotonation…..171

Figure 5.29. CV characterization of (a) PAni-ES/AMPSA fibre (b) PAni-ES/AMPSA /SWNTs fibre 0.76 % w/w (b) in 1.0 M HCl (aq) electrolyte. 10 th cycle shown for each CV. Scan rate 10 mV/s. (L=10 mm, D= 70 μm)…………172

Figure 5.30. CV characterisation of fibres made of (a) PAni-ES/AMPSA/SWNT and (b) PAni-ES/AMPSA/SWNT (0.76 %w/w) in EMI.TFSI. potential cycled in

range of (±1.5), scan rate 50 mV/s, under 10 mN Load. (L=10 mm, D=70 μm)……………………………………………………………………..175

Figure 5.31. Comparison of the electrochemical stability of (a,b) PAni-ES/AMPSA and (c,d) PAni-ES/AMPSA/SWNT (0.76 % w/w) over potential ranges of (a,c) ±1.5 and ± 2 V (b,d)…………………………………………………….177

Figure 5.32. CV characterisation of the PAni-ES/AMPSA/SWNT fibre illustrating electrochemical stability over 30 successive cycles. scan rate 50 mV/s, under 10 mN Load. Potential cycled in range of (±2.0)…………………………178

****

Figure 6.1. Demonstration of SWNTs coordination (xyz) in PAni-ES/AMPSA-SWNTs composite fibre (XYZ coordinates) and the fibre arrangement in reference frame of the Raman sample stage (x'y'z' coordinates)……………………187

Figure 6.2. The Raman spectra under VV and VH configuration, ψ = the angle between fibre axis and polarization plane (a) PAni-ES/AMPSA fibre (5x drawn fibre) for ψ=0 ° and 90°. VV configuration (b) PAni-ES/AMPSA-SWNT (0.76 % w/w) composite fibre (as spun) VV configuration (c) PAni-ES/AMPSA-SWNT (0.76 % w/w) composite fibre (5x drawn) VV configuration.(d) PAni-ES/AMPSA-SWNT (0.76 % w/w) composite fibre (5x) VH configuration. From top to bottom, the angle between fibre axis and polarization plane is 0º, 30º, 45º, 60º, 75º and 90º………………………...189

Figure 6.3. The Raman spectra under VV and VH configuration for RBM band, ψ = the angle between fibre axis and polarization plane (a) PAni-ES/AMPSA fibre

(5x drawn fibre) for $\psi=0$ ° and 90°. VV configuration (b) PAni-ES/AMPSA-SWNT (0.76 % w/w) composite fibre (5x) VH configuration ……………191

Figure 6.4. The comparison of Ivv(ψ°)/Ivv 0° versus ψ in tangential mode (TM) and resonance breathing mode (RBM) modes for this work and references ….192

Figure 6.5. The orientation distribution function of SWNT in PAni-ES/AMPSA-SWNT (0.76 %w/w) composite fibres constructed with the orientation parameters, <P2(cosθ)> and <P4cos(θ)> listed in Table 6.1…………………………...197

Figure 6.6. Effect of mechanical strain on the frequency shift of D* band of SWNTs incorporated in PAni-Es/AMPSA matrix. (dashed line) before applying strain (solid line) after applying 3 % strain………………………………………200

Figure 6.7. The Raman shift of D* peak of nanotube under axial tension for two sample of SWNT (0.76 %w/w) in the PAni………………………………………201

Figure 6.8. Mechanical versus spectroscopic stress – strain curve…………………......202

****

Figure 7.1. Crystalline regions separated by disordered regions constitutes the heterogeneous morphology in composite fibre……………………………209

Figure 7.2. The temperature dependence conductivity for PAni-ES/AMPSA fibre and their composite containing 0.25% and 0.76 %w/w SWNT……………….212

Figure 7.3. Log-Log plot of reduced activation energy (W) vs. temperature (□) PAni-Es-AMPSA (Δ) PAni-Es-AMPSA-SWNT (0.25 % w/w) (□) PAni-Es-AMPSA-SWNT (0.76 % w/w)…………………………………………………...213

Figure 7.4. The resistance arrangement in the proposed model of charge transport described in equation 7.1……………………………………………….215

Figure 7.5. The fitting quality of experimental data and proposed model and residual amount of least square of fitting calculation……………………………219

****

Figure 8.1. Experimental set-up for actuation test in isotonic mode……………………232

Figure 8.2. Schematic shows the experimental set up used for measurement of resistance across the fibres for measurement of resistance in different humidity……236

Figure 8.3. The typical isotonic actuation data as a function of scanning potential in 1.0 M HCl at scan rate of 5 mV/s. Simultaneous demonstration of linear strain and cyclic voltammogram in one cycle for (a) Neat PAni-ES/AMPSA (b) PAni –ES/AMPSA/SWNT (0.76 % w/w)1 under 10 mN load…………………...237

Figure 8.4.Isotonic strains measured during cyclic voltammetry in 1M HCl at 5 mV/s between -0.2 and 0.5V (vs. Ag/AgCl reference). Open and filled symbols show the results from two separate samples. Square symbols are for neat PAni-ES/AMPSA fibres and circles are for SWNT-reinforced fibre……..239

Figure 8.5. Cyclic voltammograms showing current density (I) for potential (E) scans between -0.2V and +0.5V (vs. Ag/AgCl) in 1M HCl at 5 mV/s: a) neat PAni-ES/AMPSA and b) PAni-ES/AMPSA -SWNT fibres…………………….242

Figure 8.6. Charge/discharge curves of PAni –ES/AMPSA or PAni-ES/AMPSA/SWNT (0.76 % w/w) fibres (a) PAni-ES/AMPSA fibre charges (b) PAni-ES/AMPSA fibre

discharges(c) PAni –AMPSA-SWNT (0.76 % w/w) charges(d) PAni –ES/AMPSA-SWNT (0.76 % w/w) discharges………...244

Figure 8.7. Cycle life of (a) PAni-ES/AMPSA (b) PAni-ES/AMPSA/SWNT fibres…245

Figure8.8. The sensitivity of normalized resistivity versus (a) temperature by scan rate(3 °C/min) at constant humidity for (b)Neat PAni-ES/AMPSA (c) PAni-ES/ AMPSA-SWNT………………………………………………………...247

Figure 8.9 (a) Pulse in relative humidity at constant temperature. The variation of normalised resistance(R/R0) for (b) PAni-ES/AMPSA fibre and (c) PAni-ES/AMPSA /SWNT composite versus humidity pulse change …………249

****

Figure 9.1. The comparison of tensile strength versus elongation at break of PANi –CNT fibre with commercial yarns……………………………………………..261

Figure 9.2. The comparison of elastic modulus versus elongation at break of PANi –CNT fibre with commercial yarns……………………………………..…….261

LIST OF TABLES

Table 2.1. The solubility and conductivity of PAni cast from some typical protonic acids and solvents…………………………………………………………...........26

Table 2.2. Different chirality based on chiral angle ………..…………………………..29

Table 2.3. Typical mechanical properties of SWNTs compared with metals and carbon fibre……………………………………………………………………….30

Table 2.4. The mechanical and electrical properties of SWNT in the form of bucky paper (mat) and fibres…………………………………………………………32

Table 2.5. The mechanical and electrical properties of neat PAni fibre produced by the two step process……………………………………………………………37

Table 2.6. The mechanical and electrical properties of PAni fibre processed from one step process……………………………………………………………………..40

Table 2.7. The mechanical properties data of some synthetic and natural fibre ………...41

Table 2.8. The electrical and mechanical properties of composite of PAni and thermoplastic polymer……………………………………………………...42

****

Table 3.1. Viscosity ranges and spindles……………………………………………60

****

Table 4.1. Formulation of PAni (LEB)/SWNT-DMPU composite spinning solutions ……………………………………………………………………………81

Table.4.2. Elemental analysis of purified SWNTs prepared by Hipco@CNI(PO257)...... 84

Table 4.3. Vibrational modes observed for Raman scattering in SWNTs ………………85

Table 4.4. Electronic transitions reported for dispersed SWNTs and their occurrence in different solvents……………………………………………………………87

Table 4.5. Power law coefficients and exponents for PAni solution with different SWNT content in DMPU……………………………………………………...96

Table 4.6. The typical diameters, deniers and densities of thermally stretched 2x drawn PAni/SWNT fibre containing different amounts of SWNTs……………...105

Table 4.7. Influence of SWNTs loading on mechanical properties of PAni/SWNTs fibres before acid doping……………………………………………………..107

Table 4.8. Influence of SWNTs loading on mechanical properties of PAni/SWNT fibres after doping with MSA for 24 hr…………………………………………107

Table 4.9. The effective elastic modulus of SWNT bundles embedded in undoped and doped PAni matrix……………………………………………………….110

Table 4.10. Assignment of enhanced Raman spectra bands……………………………113

Table 4.11. Influence of drying temperature on four point probe conductivity of 2x PAni/SWNTs fibres (2X) with varying SWNT content after acid doiping ……………………………………………………………………..120

****

Table 5.1. Range of PAni and AMPSA contents used to prepare PAni-ES/AMPSA solutions in DCAA for fibre spinning. 20 g of DCAA was used for each. ………………………………………………………………………137

Table 5.2. Amount of PAni (EB), AMPSA and SWNTs used for the preparation of PAni-ES/AMPS/SWNTs spinning solution (each solution made up in 20 g DCAA solvent……………………………………………………………….138

Table 5.3. Summary of observations made during attempts to spin fibres from mixures "S1" to "S4"(refer Table 5.1)…………………………………………….148

Table 5.4. The power law index and consistency index for samples containing different amounts of SWNTs……………………………………………………….150

Table 5.5. The mechanical properties of PAni-ES/AMPSA fibre and its composites with different SWNT contents…………………………………………………157

Table 5.6. The influence of SWNT loading on four point probe conductivity of 5xdrawn fibre of PAni/AMPSA……………………………………………………165

Table 5.7. The assigned frequencies originated from PAni-ES/AMPSA and its SWNTs composite…………………………………………………………….168

Table 5.8. The chemical structure of the ionic liquids1-butyl-3-methyl imidazolium tetrafluoroborate (BMI.BF4) and ethyl methyl imidazolium bis (trifluoro methane sulfonyl) imide (EMI.TFSI)……………………………………..174

****

Table 6.1. The polarized Raman scattering intensity ratio of TM and RBM bands in VV configuration (θ=0°, 90°) versus VH configuration at θ=0° for as-spun and 5x drawn fibres of PAni-Es/AMPSA-SWNT (0.76 % w/w). Orientation order parameters are listed for construction of orientation distribution function….196

Table 6.2. The comparison of predicted elastic modulus from rule of mixture and experimental value…………………………………………………...199

****

Table 7.1. The conductivity parameters for PAni-ES/AMPSA fibre and its SWNT composite fibre……………………………………………………….214

Table 7.2. The sensitivity of the model to the initial starting values for the fitting…….217

Table 7.3. The fitting parameters presented in equation 7.2 for different samples…..220

Table 7.4. The contribution of metallic resistivity in bulk resistivity and the metallic disorder in amorphous resistivity………………………………………..221

****

Table 8.1. The description of aqueous solution required for preparation of different relative humidity in the conductivity chamber……………………………..235

Table 8.2. Measured and calculated properties of PAni-ES/AMPSA-SWNT fibre composites…………………………………………………………………...241

****

Table 9.1. The comparison of one step and two steps methods by considering economical and safety issues……………………………………………………..266

Table 9.2. The hazardous identification of non similar material used in one step and two steps methods…………………………………………………………..267

LIST OF SCHEME

Scheme 1.1. The schematic of the selection of conducting polymers…………..………...3

****

Scheme 2.1. (a)A general scheme for polymerisation of Aniline (b) different oxidation state of PAni ……………………………………………………………………...18

Scheme 2.2. Interconversions between different forms of polyaniline ………………….19

Scheme 2.4. The chemical structure of DMPU and NMP………………………………21

Scheme 2.5. Hydrogen bonding between PAni (EB) to DMPU………………………..21

Scheme 2.6. The interaction of LEB chain with carbonyl group of DMPU……………..23

Scheme 2.7. Some of sulfonic acid dopants used for one step PAni fibre processing…...25

****

Scheme 5.1. Polaronic (semiquinoid), bipolaronic and oxidized unit of PAni…..…….169

Scheme 5.2. The mechanism of electrochemical switching of PAni-ES/AMPSA between ES-LEB oxidation states in EMI.TFSA………………………………..176