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# Development of novel nanostructured conducting polypyrrole fibres

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# Development of Novel Nanostructured Conducting Polypyrrole Fibres

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

DOCTOR OF PHILOSOPHY

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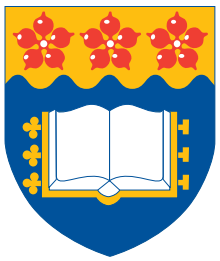

by

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September 2009

*To my parents for their endless love.*

*To my country IRAN*

# CERTIFICATION

I, ***Javad Foroughi***, declare that this thesis, submitted in fulfilment of the requirements for the award of ***Doctor of Philosophy***, in the ***Faculty of Engineering***, 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.

Javad Foroughi
September 2009

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# PUBLICATIONS

## Journal:

1-Javad Foroughi, G. Spinks, G. Wallace," A Reactive Wet Spinning Approach to Polypyrrole Fibres", to be submitted.

2- Javad Foroughi, G. Spinks, G. Wallace," Effect of Synthesis Conditions on the Properties of Wet Spun Polypyrrole Fibres", Synthetic Metals, 2009 159(17-18): p. 1837-1843

3-Javad Foroughi, G. Spinks, P. Whitten, G. Wallace," Production of polypyrrole fibres through a wet spinning process", Synthetic Metals, 2008 158(3-4): p. 104-107

## Conferences:

1- Javad Foroughi, Geoffrey M. Spinks and Gordon G. Wallace, " A Novel Approach to Produce Polypyrrole Biopolymer Nano-Composite Fibres", Electromaterials Symposium 2009(ACES) " Nanostructured Electromaterials", Australia, 4-6 Feb. 2009.

2- Javad Foroughi, Geoffrey M. Spinks and Gordon G. Wallace, "A comparison of chemically prepared and electrochemically prepared polypyrrole films and fibres for artificial muscles", The NanotxUSA'08, International Nanotechnology conference and trade Expo, Dallas, Texas, USA 2-3 October 2008.

3- Javad Foroughi, Geoffrey M. Spinks, Xiao Liu and Gordon G. Wallace, "Towards to Development of NanoBionics Using Polypyrrole-Biopolymer Fibres", Asia Pacific symposium on Nano Bionics, Australia, 22-25 June 2008.

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6- Javad Foroughi, Geoffrey M. Spinks, Philip G. Whitten and Gordon G. Wallace, "Highly flexible and conducting electropolymerized polypyrrole film", 3rd International Electromaterials Science Symposium (Advanced materials for energy storage and generation), Monash University, Australia, 21-22Feb 2008.

7- Javad Foroughi, Geoffrey M. Spinks, Philip G. Whitten and Gordon G. Wallace, "A new opportunity for conducting polymers using polypyrrole fibres", 3rd International Electromaterials Science Symposium (Advanced materials for energy storage and generation), Monash University, Australia, 21-22Feb 2008.

8- Javad Foroughi, G. Spinks, C. Lynam, P. Whitten, G. Wallace, "The development of Polypyrrole single walled carbon nanotube composite fibres through wet spinning process", 2nd International Symposium on Electromaterials Science, Australia, 7-8 Feb 2007.

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12- Javad Foroughi, G. Spinks, G. Wallace, "Development of e-Textiles using conducting polymers", HDR Conference, University of Wollongong, Sep. 2006.

## Manuscript in preparation:

1-Javad Foroughi, G. Spinks, G. Wallace," A novel DEHS doped Polypyrrole", Manuscript in preparation, 2009.

2-Javad Foroughi, G. Spinks, G. Wallace," A New Opportunity for Bionics Using DEHS Doped Polypyrrole", Manuscript in preparation, 2009.

# Abstract:

Polypyrrole (PPy) as a conducting polymer has potential applications in electrical and electronic devices because of its high electrical conductivity, environmental stability and redox activity. There have been many attempts to endow electrically PPy with processibility. Although some success has been achieved *via* synthesising soluble PPy, there have remained difficulties to fabricate this material through fibre spinning due to its low molecular weight and poor mechanical properties. Prior to this thesis, there was no report of the production of PPy fibres. This project therefore aimed to produce novel *"polypyrrole fibres via the development of nanostructured conducting polypyrrole"* by fibre spinning of PPy and to investigate the formed fibres for applications such as actuators, e-textiles, batteries, sensors and biomedical areas.

As a result of the research conducted for this thesis, polypyrrole fibres have been produced for the first time. The initial wet-spinning process was enabled by the use of highly soluble non-functionalised PPy using di-(2-ethylhexyl)sulfosuccinate (DEHS) dopant, and the generation of a spinning solution of the PPy-DEHS in dichloroacetic acid (DCAA) solvent. Subsequent work sought to improve the properties of these first generation PPy-DEHS fibres by increasing the molecular weight, addition of carbon nanotubes (CNTs) and addition of a supporting polymer (alginate). The use of the host polymer also enabled a new fibre spinning method to be developed that included an *in situ* polymerization process. Carbon nanotubes additions were achieved in two ways: firstly by adding small amounts of CNTs to the spinning dope; and secondly, a completely novel approach was developed whereby PPy was polymerized onto and into a CNT yarn.

Each of the methods used to generate PPy fibres gave different performances in terms of mechanical strength / stiffness; electrical conductivity and electroactivity. Generally, it was found that adding of carbon nanotubes to the PPy improved the strength, stiffness and conductivity. The highest conductivity and Young's modulus of any conducting polymer based fibre reported to date was obtained by incorporating PPy into a CNT yarn. The more robust fibres were assessed as mechanical actuators and a maximum strain of 2.5% was produced from the high molecular weight PPy-DEHS fibre.

In summary, a range of novel fibrous PPy materials have been developed for possible use in applications such as actuators, sensors, artificial muscles, batteries and biomedical applications. The main aim of the thesis was to develop methods for continuous production of doped PPy fibres. This aim was successfully completed with a variety of different fibre compositions and properties demonstrated using a range of different fibre processing methods.

# ABBREVIATIONS

| | |
|---|---|
| A | Ampere |
| $A^-$ | Anion |
| AC | Alternating current |
| ACN | Acetonitrile |
| Ag/Ag+ | Silver/silver ion reference electrode |
| Ag/AgCl | Silver/silver chloride reference electrode |
| BMI.BF4 | 1-Butyl-3-methyl-imidazolium tetrafluoroborate |
| C | Coulomb |
| cm | Centimetre |
| conc. | Concentration |
| CV | Cyclic voltammetry |
| D | Diffusion coefficient |
| DBS- | Dodecylbenzene sulfonate |
| $e^-$ | Electron |
| E | Potential |
| $E_{app}$ | Applied potential |
| $E_C$ | Electrochemical/Electrochemistry |
| $E_f$ | Final potential |
| $E_i$ | Initial potential |
| E' | Loss modulus |
| E" | Storage modulus |
| F | Faraday constant |
| g | Gram |
| i | Current |
| L | Litre |
| M | Molar |
| mA | Milliampere |
| min | Minute |
| ml | Millilitre |
| mV | Millivolt |
| MWNT | multi wall carbon nanotubes |

| | |
|---|---|
| n | Number of electrons |
| NIR | Near infra red |
| NMP | N-methyl pyrrolidinone |
| PAni | Polyaniline |
| PC | Propylene carbonate |
| PF6- | Hexafluorophosphate |
| PPy | Polypyrrole |
| PPy/Cl | Polypyrrole chloride |
| PPy/ClO4 | Polypyrrole perchlorate |
| PPy/NO3 | Polypyrrole nitrate |
| PPy/DBS | Polypyrrole Dodecylbenzenesulfonate |
| PPy/PF6 | Polypyrrole hexafluorophosphate |
| PPy/pTS | Polypyrrole p-toluene sulphonate |
| Psi | Pound per square inch |
| PTh | Polythiophene |
| PVA | Polyvinyl alcohol |
| Pt | Platinum |
| *p*TS.Na | p-toluene sulphonic acid sodium salt |
| Q | Charge |
| R | Resistance (ohm) |
| s | Second |
| S | Siemens |
| SEM | Scanning electron microscopy |
| SWNT | Single wall carbon nanotubes |
| S/N | Sulphur to nitrogen atomic ratio |
| t | Time |
| T | Temperature |
| TEM | Transmission electron microscopy |
| Tg | Glass transition temperature |
| TGA | Thermogravimetric analysis |
| TM | Tangential mode (G band) |
| TPa | Tera pascal |
| TBA.PF6 | Tetrabutylammonium hexafluorophosphate |
| TFSI- | (bis) trifluoromethanesulfonimide |

| | |
|---|---|
| V | Volt |
| $V_d$ | Drawing velocity (m/min) |
| $V_i$ | Injection rate (g/min) |
| $V_t$ | Take up velocity (m/min) |
| μ | Micro (prefix) |
| υ | Scan rate |
| γ | Shear rate (s-1) |
| η | Viscosity (mPa.s = cP) |
| ρ | Density (g/cm3) |
| σ | Conductivity (S/cm) |
| $X^+$ | Cation |

# LIST OF FIGURES AND TABLES

## Chapter 1



## Chapter 2

## Chapter 3



## Chapter 4

## Chapter 5

## Chapter 6

## Chapter 7

## Chapter 8

## Tables

## Schemes

# Contents