RSC Advances



View Article Online

View Journal | View Issue

REVIEW



Cite this: RSC Adv., 2016, 6, 44687

Developments in conducting polymer fibres: from established spinning methods toward advanced applications[†]

Azadeh Mirabedini, Javad Foroughi* and Gordon G. Wallace*

Conducting polymers have received increasing attention in both fundamental research and various fields of application in recent decades, ranging in use from biomaterials to renewable energy storage devices. Processing of conducting polymers into fibrillar structures through spinning has provided some unique capabilities to their final applications. Compared with non fibrillar forms, conducting polymer fibres are expected to display improved properties arising mainly from their low dimensions, well-oriented polymer chains, light weight and large surface area to volume ratio. Spinning methods have been employed effectively to produce technological conducting fibres from nanoscale to hundreds of micrometre sizes with controlled properties. This review considers the history, categories, the latest research and development, pristine and composite conducting polymer fibres and current/future applications of them while focus on spinning methods related to conducting polymer fibres.

Received 3rd March 2016 Accepted 18th April 2016

DOI: 10.1039/c6ra05626a

www.rsc.org/advances

1. Introduction

1.1. Historical background

Although polymers have traditionally been considered to be electrical insulators, conducting polymers (CPs) were shown to exhibit semiconducting behaviour not long ago.^{1,2} The fundamental feature of all conducting polymers is their extended conjugated π -system along the polymer backbone, which leads to metal-like electronic, magnetic and optical properties, while

ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, AIIM Facility, University of Wollongong, Fairy Meadow, NSW 2519, Australia. E-mail: foroughi@uow.edu.au; gwallace@uow.edu.au

† Dedicated to Prof. Mojtaba Mirabedini for all his help and support during the whole period of my academic life.



Azadeh Mirahedini is an accomplished PhD candidate at Intelligent Polymer Research Institute (IPRI). She previously majored in polymer engineering and coatings at from Amirkabir University of Technology (Tehran Polytechnic), through her undergraduate (BSc). After undertaking a number of projects as a research assistant and tutoring several courses at the then university, she

commenced her master's studies at Iran Polymer and Petrochemical Institute (IPPI). Azadeh's research interests include polymer fibres and composites, conducting materials and nanomaterials. Her PhD project is about developing electroactive multiaxial fibres with great potential to be used as implantable electrodes or power sources.



Dr Javad Foroughi received the BS and MS degree in textile engineering in 1997 and PhD degree in material engineering from the University of Wollongong, Australia in 2009. He is currently working as an ARC senior research fellow at Intelligent Polymer Research Institute, University of Wollongong, Australia. His research interests include nanomaterials, electromechanical actuators (Artificial

Muscles) using inherently conducting polymers and/or carbon nanotubes, bionics and novel fibres spinning and the use of these in the development of smart materials and electronic textile. properties commonly associated with conventional polymers, such as flexibility, are maintained.^{3,4} Undoped forms of CPs represent semiconducting characteristics before they undergo a subsequent process so-called "doping" which involves oxidizing or reducing the material. Doping greatly increases the number of charge carriers within their internal structures for the purpose of modulating its electrical properties. ICPs have been studied extensively due to their intriguing electronic and redox properties, good environmental stability and numerous potential applications in many fields since their discovery in 1970s.^{5–7} The field has evolved from the early discovery of metallic conductivity in polyacetylene to a focus on soluble and processable polymers and copolymers.⁸

Knowledge surrounding the early developments in textiles is meagre due to insufficient records. Before the 18th century, all textile fabrics were made of natural fibres such as wool, silk, cotton and linen. Mass production of fibres and their fabrication into textiles grew out of the early stages of the industrial revolution as the demand for cloth increased.9 It was found that many physical and chemical properties of polymers are improved mostly due to the alignment of polymer chains along the fibre axis compared to the non fibrillar structures. To achieve that, a specialised form of extrusion using spinneret, known as spinning, was utilised extensively to form multiple continuous filaments. The subsequent merging of fibre spinning and conducting polymer technologies introduced a new era of socalled "electronic textiles".10 Polyaniline was the first among the conducting polymers to formed into a fibre.11 Thus far, CPFs have been produced and utilised for a wide range of applications such as energy storage (batteries, capacitors),12-16 energy conversion (photovoltaic, thermal energy harvesting),^{17,18} biology from tissue engineering19,20 to biomedical monitoring4,21-23 and also diagnosis and treatment (including controlled drug delivery).24-28

1.2. Conducting polymers

ICPs were discovered in 1977 with the 109 times increase in electrical conductivity (σ) of polyacetylene (PAc) through halogen



Professor Gordon Wallace is the Executive Research Director at the ARC Centre of Excellence for Electromaterials Science and Director of the Intelligent Polymer Research Institute. He is Director of the ANFF Materials node. He previously held an ARC Federation Fellowship and currently holds an ARC Laureate Fellowship. Professor Wallace's research interests include organic conductors, nanomaterials and

electrochemical probe methods of analysis, and the use of these in the development of Intelligent Polymer Systems. With more than 800 refereed publications, Professor Wallace has attracted some 27 000 citations and has an h-index of 69.



Fig. 1 Semiconducting polymer structures represented in their undoped forms.

doping to as high as 10⁵ S cm^{-1.7} To date, a tremendous amount of research has been carried out in the field of conducting polymers, while the broader significance of the field was recognised in the year 2000 with the awarding of the Nobel Prize for Chemistry to the three discoverers of ICPs, Shirakawa, Mac-Diarmid and Heeger.³ Since the discovery of conducting PAc, a number of additional ICPs have been developed, including polypyrrole (PPy),³⁰⁻³⁴ polyaniline (PAni),³⁵⁻³⁷ polythiophene (PTh),^{38,39} poly(*p*-phenylenevinylene) (PPV),^{40,41} poly(3,4-ethylene dioxythiophene) (PEDOT),^{3,42-44} and polyfuran (PF).⁴⁵ The structures of selected conducting polymers are illustrated in Fig. 1. The most significant conducting polymers with regard to technological fibres are PAni, PPy, PTh and PEDOT.

1.3. Current achievements in the fabrication of ICPs

Conducting polymers must undergo processing steps in order to attain the desired form. The precise nature of such processing steps is guided by the intended use.¹⁰ Printing and fibre spinning technologies are two of the most prominent methods which are being investigated for the development of devices based on ICPs.

Printing is a fast, old and inexpensive method that is used for mass fabrication of advanced conducting components.¹⁰ In recent years, increasing efforts have been focused on the printing of conducting polymer-based devices.⁴⁶ Printing is a reproduction process in which ink is applied to a substrate in order to transmit information such as images, graphics and text. Printed materials must form a solid, continuous conducting film following solvent removal. The solvent plays significant roles such as compatibility with the conducting polymer, stability in solution and appropriate rheological and surface

Review

energy characteristics. Printing technologies that require a printing plate are known as conventional methods and include lithography (offset), gravure, letterpress and screenprinting. Non-impact printing (NIP), such as inkjet printing or electrophotography, uses laser technology and does not require a printing plate.⁴⁷ Printing provides a convenient route to the deposition of conducting polymers with spatial resolution in the *x*, *y* plane in the order of tens of microns and makes layer thicknesses in the order of 100 nm feasible. The birth of 3Dprinting goes back to 1984 when as Charles Hull invented stereolithography which enabled a tangible 3D object to be created from a 3D model.⁴⁸ Varieties of conducting polymers have been processed earlier to become printable including PAni,^{49,50} PPy,^{51,52} and PTh.⁵³

Spinning of polymer fibres has witnessed great progress over the past few decades as an interdisciplinary field that applies the principles of engineering and material science toward the development of textile substitutes.54 It is a specialised form of extrusion that uses a spinneret to form multiple continuous filaments or mono filaments. All fibre forming processes regardless of the materials involved - are irreversible processes involving the rapid and continuous solidification of a liquid with a very restricted size in two directions. The solidification is brought about by the removal of heat and/or solvent by contacting the liquid with a suitable moving fluid, which can be a gas or a liquid. Considering fibres as continuous threadlike filaments with large L/Ds (typically L/D > 5), several other polymerisation methods reported for the production of short fibres are not considered in this review. The first step to produce fibres is to convert the polymer into a processable and spinnable state. Thermoplastic polymers can be converted into the melt-state and melt-spun. Other polymers may be dissolved in a solvent or chemically treated to form soluble or thermoplastic derivatives and subsequently spun via wet spinning, dry spinning or electrospinning.

Extensive advances have been made during the last three decades in the fundamental understanding of fibre spinning using conducting polymers. The very first attempts to achieve optimal conditions for the spinning of fibres from PAni were begun in the late 1980s.^{11,55,56} A few years later Mattes *et al.* pioneered the processing of PAni into fibre form through a drywet spinning process.⁵⁷ Yet to date, CPFs lack an inclusive published report which wraps the origins of their emergence, the fabrication methods and their developments from the beginning to recent time despite printed conducting polymers.⁴⁶ Hence, this paper attempted to provide an overview and perspective on the field of conducting polymer fibres with a particular emphasis on major spinning methods as key techniques to produce them.

1.3.1. Wet spinning. Of all the fibre spinning methods, solution spinning methods have the longest history. Wet spinning was one of the original methods for producing synthetic fibres and was first used in the late 19th century.⁵⁸ In wet spinning, the polymer dissolved in a suitable solvent is extruded directly into a coagulation bath containing a liquid which is miscible with the spinning solvent but a non-solvent of the polymer. This leads to solvent removal from the spinneret and



Fig. 2 Schematic of a lab scale wet spinning line.

solidification of the fibre as precipitation occurs. Wet spinning involves mass transfer of the solvent and non-solvent for fibre solidification, which is slower compared to the heat transfer process of cooling associated with melt spinning, and to the evaporation associated with dry spinning.⁵⁹ PAni was the first conducting polymer which was spun into a fibre by wet spinning.^{57,60} Later on, other conducting polymers including PPy^{61,62} and PEDOT : PSS^{63,64} were wet-spun. A schematic of wet spinning is shown in Fig. 2.

1.3.2. Dry spinning. Dry spinning is another type of solution spinning which was first employed around the same time as wet spinning.65 This old method for the preparation of synthetic fibres has many basic principles in common with wet spinning, including the requirement that the polymer needs to be dissolved in a solvent. Compared to wet spinning, solidification is achieved more easily through evaporation of the solvent, which must be highly volatile, and without requiring a coagulation bath. Dry spinning is suitable for polymers which are vulnerable to thermal degradation, cannot form viscous melts, and when specific surface characteristics of fibres are required.65 It is the preferred method for polyurethane, polyacrylonitrile, and fibres based on ophthalamide, polybenzimidazoles, polyamidoimides, and polyimides due to better physicomechanical fibre properties.66 However, since most conducting polymers show poor solubility in organic solvents, this method is generally not suited to the production CPFs.

1.3.3. Melt spinning. Most commercial synthetic fibres are produced by the melt spinning process. Melt spinning is a process in which dried polymer granules or chips are melted inside the extruder which is used afterward as the spinning dope. The obtained filament is quenched and solidified by cooling in a fast fibre solidifying process which is mainly due to the one-way heat transfer.67 Melt spinning is considered to be one of the simplest methods compared to other fibre manufacturing methods due to the absence of problems associated with the use of solvents.59 It is therefore the preferred method for spinning many polymers, provided the polymer gives a stable melt.68 However, there exist few reports of the melt spinning of CPFs due to some major limitations. These include decomposition at temperatures below the melting point, poor control over the exact temperature of the polymer melt during spinning, thermo-mechanical history of the melt, and final fibre structure. In addition there is a fundamental limitation concerning limited capability to produce very fine



Fig. 3 Schematic of melt spinning.



Fig. 4 Schematic of electrospinning

fibres.⁶⁹ Kim *et al.* were the first to report melt-spun CPFs based on a PAni/PPy blend, which were used in textile sensors.⁷⁰ However, the electrical conductivity was unsatisfactory due to homogeneity problems (2.9×10^{-7} S cm⁻¹ with 40% wt PPy). A schematic of melt spinning is presented in Fig. 3.

1.3.4. Electrospinning. Electrospinning is a versatile method for the preparation of long, continuous and fine (nano to sub-micron size range)⁷¹ nonwoven polymer mats or fibres known since early the 1930s.⁷² Electrospinning shares characteristics of both electro-spraying and conventional solution dryspinning methods.⁷³ Electrospun fibres possess properties not found in conventional fibres, including high surface to volume ratio, high aspect ratio, controlled pore size and superior mechanical properties.⁷⁴ A typical electrospinning setup (Fig. 4) consists of a capillary tube or syringe loaded with polymer solution, a metal collecting screen, and a high voltage supply.^{72,75} The pendant polymeric droplet at the tip of the needle, when subjected to an electric field in the kV range, will deform into a Taylor cone shape and form a liquid jet. This jet undergoes an electrically induced bending instability which results in strong looping

and stretching of the jet. Following solvent evaporation, ultrathin fibres are deposited on the collecting screen. Electrospun CPFs possess unique electronic and optical properties that can be tuned through doping, and have found application in chemical and biological sensors, light emitting diodes, rechargeable batteries nanoelectronic devices, electromagnetic shielding and wearable electronics.²⁵ Lee and his group were the first to report the electrospinning of PPy into a nonwoven web form, which contained individual fibre diameters of *ca.* 3 µm and exhibited electrical conductivities of *ca.* 0.5 S cm⁻¹.⁷⁶

2. Spinnable conducting polymers

Many researchers have investigated improved processing techniques for the preparation of conducting polymer fibrillar structures. Two main categories may be defined, the first being fibres spun purely from conducting polymers, termed "pristine conducting polymer fibres". The second category refers to composite fibres that are comprised of conducting polymer(s) and one or more other constituents. These may be fabricated either by blending of the components, or by coating, electrospraying or polymerising dissimilar materials onto the outer surface of a fibre. This category is referred to as "conducting composite fibres". The two main categories of conducting polymer fibrillar structures are described in detail below.

2.1. Pristine conducting polymer fibres

PAni may be the considered to be the first conducting polymer spun into a fibrillar form.⁵⁷ The spinning of PAc, PAni, PPy, PTh and PEDOT : PSS fibres is described in detail in the following sections.

2.1.1. Polyacetylene fibres. PAc was the first conducting polymer to be prepared.^{5,77} Interest in the conducting properties of oxidatively doped PAc was ignited in the mid-1970s with the accidental discovery of silvery, conducting PAc films up to 0.5 cm thick by the research group of Prof. Hideki Shirakawa. Multiple methods were employed after the discovery of PAc to improve its properties.^{78,79} The simple molecular framework and high electrical conductivity of PAc made it an interesting material for microelectronics. However, its insolubility, infusibility and poor environmental stability due to reactivity with air has rendered PAc rather unattractive for technological applications.⁸⁰

Due to the aforementioned processability issues surrounding PAc, few studies have reported on the successful preparation of PAc fibres. Sliva et al. first described a method for making continuous PAc fibres using a thin film evaporator to volatilise the reaction mixture of oxidatively coupled diethynyl organo compounds.⁸¹ The resulting concentrate could then be spun to produce PAc fibres that were easily converted into high strength carbon fibres. Akagi et al. reported the synthesis of hierarchical helical PAc fibres79 under an asymmetric reaction field consisting of chiral nematic liquid crystal. The prepared PAc helical fibrillar structure may be considered as the only such structure to be reported so far. The relatively high electrical conductivities of \sim 1500–1800 S cm⁻¹ obtained following iodine doping suggest that these fibres may find electromagnetic and optical applications.⁷⁹ Kim *et al.* attempted to prepare a PAc fibre network from a low density foam-like PAc later on.⁸²

2.1.2. Polyaniline fibres. PAni was first prepared by Letheby in 1862 using anodic oxidation of aniline in sulphuric acid, which resulted in the formation of a blue-black powder.⁸³ PAni stands out for its ability to form processable conducting forms at relatively low cost and in bulk amounts,⁸⁴ while it can be synthesised either by chemical or electrochemical methods. PAni has emerged as a promising candidate for practical applications including light emitting diodes, transparent electrodes, electromagnetic radiation shielding, corrosion protection of metals, gas and humidity sensing, and batteries.⁸⁵ An alternating arrangement of benzene rings and nitrogen atoms makes up PAni. The nitrogen atoms can exist in imine (in a sp² hybridised state) or amine (sp³ hybridised) form. Additionally it is the only ICP that can be doped by a protic acid such as HCl and exist in different forms depending on pH.⁸⁶

PAni may exist in one of three well-defined oxidation states: leucoemeraldine, emeraldine and pernigraniline (Fig. 5). Leucoemeraldine and pernigraniline are the fully reduced (all nitrogen atoms in amine form) and the fully oxidised (all nitrogen atoms in imine form) forms of PAni, respectively. Green, protonated emeraldine is the only conducting form of PAni, and contains reduced amine and oxidised imine nitrogens in equal amounts *i.e.* -NH-/-N= ratio ~ 0.5 .⁸⁷ The blue, insulating emeraldine form can be transformed into the conducting form by lowering the pH of the medium and vice versa.83 Another interesting feature is that using an organic counterion (X^{-}) as the dopant (e.g. camphor sulfonic acid), PAni may be retained in solution in the doped conducting form, further enhancing its versatility.88,89 PAni fibres may be spun from emeraldine base^{27,57,60,90} and leucoemeraldine base^{91–93} solutions and converted to the conducting form using aqueous protonating acids following processing.

Researchers have investigated various features of PAni, from stability in solution and different spinning methods through to electrochemical properties, actuating characteristics, and biomedical applications.^{57,60,90,91,94-100} Wet spinning has probably been the most important spinning method used to produce

PAni fibres.^{57,60,92,95,96,100} However, several processing problems were found, such as poor solubility in organic polymers and rapid polymer gelation at low solids content.11,56,101 Andreatta et al. reported the complete solubility of PAni (emeraldine salt or base) in concentrated sulfuric acid and demonstrated the feasibility of solution processing of crystalline, electrically conducting PAni fibres and films.¹⁰⁰ Hsu et al. were probably first to successfully spin the basic undoped form of PAni into fibre form,101 reporting electrical conductivity values of 320.5 S $\rm cm^{-1}$ and 157.8 S $\rm cm^{-1}$ of stretched fibres that had been doped with aqueous H₂SO₄ and HCl, respectively. To overcome the fast gelation of PAni, researchers found that selected Lewis-base organic solvents have a better solvency compared to N-methyl-2pyrrolidinone (NMP).^{102,103} Years later, the preparation of stable spinning solutions for low molecular weight emeraldine base was reported using N,N'-dimethyl propylene urea (DMPU) instead of NMP,⁵⁶ while Mattes et al. developed an approach to circumvent processing problems by addition of secondary amines to act as gel inhibitors in high molecular weight PAni solutions with concentrations of >20% (w/w) (Fig. 6).57,104

Up to the time of the work of Mattes et al.,57 the standard method for making conducting PAni fibres from the emeraldine base form was to convert to the conducting salt form using an aqueous protonic acid. This method had several difficulties, including inhomogeneous protonation, relative ease of dedoping, and adverse effects on material properties.¹⁰¹ In 1998, a new acid processing route to PAni was reported by Adams et al., using 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) as both protonating acid and solvating group, and dichloroacetic acid (DCA) as solvent.¹⁰⁵ One year later, in what may be considered as a first, PAni fibres were produced using a one-step wet spinning method,95 which eliminated the need for further protonation. Subsequently, various coagulation solvents (e.g. acetone, butyl acetate, 4-methyl-2-pentanone) were trialled in order to achieve a range of mechanical properties and electrical conductivities for different applications.⁶⁰

Many research groups have also attempted to fabricate nanosized PAni fibres.^{90,91,106-109} Cárdenas *et al.* were pioneers in the successful use of electrospinning to produce PAni nanofibres.²⁷



Fig. 5 (a) Emeraldine (y = 0.5), (b) leucoemeraldine and (c) pernigraniline oxidation states of polyaniline.



Fig. 6 Scanning electron micrographs of cross-section of wet-spun polyaniline fibre. Reproduced with permission from ref. 14 Copyright© 2006, Elsevier.

Published on 20 April 2016. Downloaded on 7/4/2018 1:33:04 AM.	

Table 1 Summary of polyaniline fibre production using different methods

No.	Dopants used	Focus of the research	Spinning method	Reported electrical conductivity/conduction potential window	Mechanical properties	Ref.
1	H_2SO_4	Preparation of conducting fibres of PAni from solutions in concentrated sulfuric acid	Wet spinning	$20-60~{ m S~cm^{-1}}$		100
0	NMP	Preparation of concentrated (10–25%) spinnable solutions of PAni in the emeraldine base form for fibre solutions.	Dry-jet wet spinning	${ m H}_2{ m SO}_4$ and HCl are 320.5 and 157.8 S cm ⁻¹	Average tenacity of 3.9 GPa (~400 MPa)	101
e	NMP and DMPU	Improvement of solution stability and spinnability of concentrated PAni solutions	Wet spinning (DMPU, NMP, NMP/LICI)	1	Approaching that of nylon- 6	56
4	BPA	Investigation of the effect of dopant on preserving the mechanical properties and improvement of conductivity values	Dry–wet spinning (water)	10^{-2} S cm ⁻¹ -stretched acetic acid doped 10^{-6} S cm ⁻¹ -unstretched acetic acid doped 1 S cm ⁻¹ -HCl and BPA doped	YM ^a 0.55–13.1 GPa, US ^a \sim 2–9%	57
IJ	AMPSA	Measuring electrical and mechanical properties of wet-spun PAni fibres in various coagulation solvents	Wet spinning (DCA)	$70-150 \text{ S cm}^{-1}$	YM 40-60 MPa, UTS 20-60 MPa	60
9	$HClO_4$	The development of a linear actuator prototype based on PAni fibres	Wet spinning (water)	$1-3 \mathrm{~S~cm}^{-1}$	$ m YM \sim 2-3~MPa$	86
7	AMPSA	Study the processing routes for preparation of conducting PAni fibres	Wet spinning (acetone)	$900-1500~{ m S~cm^{-1}}$	YM 0.2 GPa, UTS ^{a} 97 MPa, US ~ 550%	95
8	AMPSA	Study the temperature dependence of conductivity behaviour of the fibres	Wet spinning (acetone)	760–1060 S cm $^{-1}$ at 363 K	1	54
6	AMPSA	Introducing a new one-step acid- solution processing route for production of PAni fibres	Wet spinning (dichloroacetic acid)	70-150 S cm ⁻¹	YM 40–60 MPa, UTS 20–60 MPa, US \sim 500%	29
10	NMP containing heptamethyleneimine as a gel inhibitor	Controlling macrovoid formation in wet-spun PAni fibres	Wet spinning (water)	I	YM 550-900 MPa, UTS 5.9- 12.8 MPa, US ~ 1.1-1.45%	113
11	AMPSA	Electrochemically characterisation of PAni fibre microelectrodes for the first time	Wet spinning (dichloroacetic acid)	+0.20 to +0.60 V versus SCE	I	30
12	CSA	Study the influence of dopants and cis-1,2-ethenesulfonate family of twin- tailed surfactants on properties of PAni nanofibre	Interfacial polymerisation	\sim 1–5 S cm ⁻¹	1	91
13	I	Using the electrospinning technique to produce sub-micron fibres of pure PAni	Electrospinning (acetone bath placed on the electrode)	10^{-3} to 10^2 S cm ⁻¹	I	27

Table 1	. (Contd.)					
No.	Dopants used	Focus of the research	Spinning method	Reported electrical conductivity/conduction potential window	Mechanical properties	Rei
14	Sulfonated β - cyclodextrin and sulfonated α - cyclodextrin	Preparation and characterisation of PAni nanofibres containing sulfonated cyclodextrin group	Interfacial polymerisation	3.2×10^{-2} to 8.5 $\times 10^{-3}$ S cm ⁻¹	I	4
15	HCSA	Electrospinning and evaluating PAni fibres doped with different levels of HCSA evaluated as chemiresistive gas sensors	Coaxial electrospinning	Up to 50 \pm 30 S cm ⁻¹	I	112
16	APS	Controlling the morphological structure of the synthesized fibres by tuning the reaction time	Self-assembly process	Electroactive -0.6 V to +0.3 V	I	106
'A-MA _p	oung's Modulus, UTS-Ultima	te Tensile Stress, US-Ultimate Strain.				

View Article Online RSC Advances

This method produced fibres with diameters ranging from hundreds of nanometres to a few micrometres. This was a significant advance at the time, not only because pure PAni fibres were obtained, but also because the fibre was collected in an innovative manner involving the placement of an acetone bath on the electrode. In addition, the further treatment of fibres with radiation or gas without concern for side reactions with doping agents is an advantage. PAni fibres have found broad application, particularly sensors and biosensors,^{107,110-112} actuators^{15,93,99} and electrochemical mechanism investigations.⁹² A summary of PAni fibre production using different methods is presented in Table 1.

Although not considered in this review, it is worth noting that several other polymerisation methods have been reported for the production of discontinuous PAni nanofibres (diameter < 100 nm), such as photolithographic synthesis (ultraviolet irradiation of aqueous aniline solutions),^{114,115} chemical polymerisation (with prevention of secondary polymer growth),^{116–119} nanofibre seeding through interfacial polymerisation,^{120–122} and chemical oxidation polymerisation of doped aniline.⁸³

2.1.3. Polypyrrole fibres. Amongst the conducting polymers, PPy and its derivatives are of particular interest owing to rather straightforward synthetic procedures, reasonable stabilities in oxidised states in air and solvents, and availability of monomer precursors.^{123,124} However, it was not until 1977 that PPy attracted significant attention.3 Dall'Olio et al. published the first report of the synthesis of a PPy film, which exhibited 8 S cm⁻¹ electrical conductivity, by electrolysis of a pyrrole solution in the presence of sulphuric acid in 1968.125 The major breakthrough with regard to the routine synthesis of PPy, however, was achieved by Diaz et al. when they reported a highly conducting (100 S cm^{-1}), stable and flexible PPy film prepared by electrolysis of an aqueous solution of pyrrole.31 Chemical methods in addition to electrochemical methods have also been employed for the synthesis of PPy, such as photochemistry, metathesis, concentrated emulsion, inclusion, solid-state, plasma, pyrolysis and soluble precursor polymer preparation.¹²⁴ Nevertheless, it should be taken into account that electrochemical polymerisation provides a number of advantages over chemical methods, such as the final form of reaction product (an electroactive film attached to the electrode surface), high electrical conductivity, and control over film mass, thickness and properties.124

PPy demonstrates high electrical conductivity, good electrochemical properties, strong adhesion to substrates and thermal stability.^{89,126} The heteroatomic and extended π -conjugated backbone structure of PPy provides it with chemical stability and electrical conductivity, respectively.^{4,125} PPy exhibits a wide range of surface electrical conductivities (10^{-3} S cm⁻¹ < σ < 100 S cm⁻¹) depending on the functionality and substitution pattern of the monomer and the nature of the counterion or dopant.¹²⁷ Not surprisingly therefore PPy has already been applied in a wide variety of areas such as rechargeable lithium batteries,^{16,128} low temperature fuel cell technology,¹²⁹ medical applications,¹³⁰⁻¹³² and volatile organic compound detection.^{133,134} It has also been investigated as a material for



Fig. 7 Chemical structures of polypyrrole in neutral (a) aromatic and (b) quinoid forms, and in oxidised (c) polaron and (d) bipolaron forms.

"artificial muscles" that would offer numerous advantages over traditional motor actuation.^{135,136}

PPy may be switched between its oxidised and reduced states, thereby allowing dynamic control of electrical, chemical and mechanical properties. Reduced, non-conducting PPy has a resonance structure that resembles the aromatic or quinoid forms, and may be converted to the conducting form upon oxidation. The charge associated with the oxidised state is typically delocalised over several monomer units and can form



Fig. 8 Scanning electron micrographs of (a) wet-spun polypyrrole fibre cross-section and (b) polypyrrole hollow fibres polymerised under ultrasonication. Reproduced with permission from ref. 61 and 144 Copyright© 2008 and 2012; Elsevier and The Royal Society of Chemistry Publishing, respectively.

a radical cation (polaron) or a dication (bipolaron), as depicted in Fig. 7. In general, small anionic species are incorporated into the PPy chains upon oxidation and are expelled upon reduction in order to maintain charge neutrality.¹²⁵

PPy usually takes the form of an intractable powder following chemical polymerisation and an insoluble film following electropolymerisation.¹³⁷ PPy prepared by conventional methods is insoluble in most organic solvents.^{61,138} These characteristics may be largely attributed to the presence of strong interchain interactions and a rigid structure. Difficulties associated with poor processability have motivated researchers to identify methods to render PPy processable. These methods include direct polymerisation onto polymers sheets, glass, polymer and inorganic particles, clays, zeolites, porous membranes, fibres and textiles, and soluble matrices.¹³⁷ Furthermore attempts to improve polymer solubility have been made involving alkyl group substitution at the 3- and 4-positions or at the nitrogen atom of the pyrrole ring.¹³⁷ Another technique that has proven

Table 2 Summary of previous studies into the preparation of polypyrrole libr	Table 2	Summary of previous studie	es into the prepar	ration of polypyrrole	fibres
--	---------	----------------------------	--------------------	-----------------------	--------

No.	Dopants used	Focus of the research	Spinning method	Reported electrical conductivity/conduction potential window	Mechanical properties	Ref.
1	Sodium dodecyl sulfate (SDS)	Growth of dendrite-like fibres at PPy/Pt electrode interface	Electropolymerisation (galvanostatically	$20 \mathrm{~S~cm}^{-1}$	_	148
2	DBSA as dopant, APS as the oxidant	Fabrication of electrically conducting PPy nonwoyen web	Electrospinning	0.5 S cm^{-1}	_	76
3	DEHS	Fabrication of electrically conducting PPy	Electrospinning	$2.7 \times 10^{-2} \mathrm{~S~cm^{-1}}$	_	143
4	DEHS	Fabrication of continuous PPy fibre	Wet spinning (dichloroacetic acid (DCAA))	\sim 3 S cm ⁻¹	YM 1.5 GPa, UTS 25 MPa, US 2%	61
5	DEHS	Effect of synthesis conditions on the properties of wet-spun PPv fibre	Wet spinning	_	YM 4.2 GPa, UTS 136 MPa, US 40% at 100 °C	62
6	DEHS	Investigation of mechanical and the electrical properties of PPv fibres	Wet spinning	$60 < T < 200, 566.8 \text{ s cm}^{-1} T$ < 60, 419.9 S cm ⁻¹	YM ~ 4.2 GPa, UTS 136 MPa, US 5%	147

Review

successful has been the use of long chain surfactant dopants such as sodium dodecyl benzene sulfonate (DDS),^{139,140} di(2ethylhexyl)sulfosuccinate sodium salt (DEHS),¹⁴¹ and polystyrene sulfonate.¹⁴² PPy doped with such surfactants were soluble in a number of solvents including *m*-cresol, NMP, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and tetrahydrofuran (THF).¹³⁷

The fabrication of continuous electrically conducting PPy fibres was first achieved using electrospinning,⁷⁶ in contrast to PAni. The electrospun fibres were in a web form, with average diameter of 3 μ m and conductivity of *ca.* 0.5 S cm⁻¹. Chronakis *et al.* used a different dopant and oxidant to similarly electrospun PPy nanofibres with diameters ranging between 70 and 300 nm.¹⁴³ Recently solid-phase extraction was described based on electrospun conducting PPy hollow fibres for the extraction of different classes of compounds, where the application was attractive due to its low consumption of organic solvents, simplicity, high recovery and ease of automation and operation.^{144,145}

Few reports exist that consider the wet spinning of soluble PPy into continuous fibres, despite initial attempts.¹⁴⁶ This question was essentially abandoned for a number of years until Foroughi *et al.* published the first report on the production of continuous conducting PPy fibres (Fig. 8) through wet spinning,⁶¹ which showed electrical conductivity of ~3 S cm⁻¹ and elastic modulus of ~1.5 GPa. Later on the mechanical and electrical properties of these fibres were also studied.¹⁴⁷ Although a number of researchers continue to seek new methods to produce wet-spun PPy fibres, no additional reports have been published. Previous studies into the preparation of PPy fibres are summarised in Table 2.

2.1.4. Polythiophene fibres. PTh results from the polymerisation of thiophene, a sulfur heterocycle, which may be rendered conducting when electrons are added or removed from the conjugated π -orbitals *via* doping. Polyaromatic conducting polymers including PThs have a non-degenerate ground state and two limiting mesomeric structures, polaron and bipolaron (see Fig. 9).

PThs have been prepared since the 1980s by means of two main routes, namely chemical, and cathodic or anodic electrochemical synthesis.149 The first chemical synthesis using metal-catalysed polymerisation of thermostable 2,5-dibromothiophene was reported by two research groups independently.^{150,151} Yamamoto et al. also reported on the polycondensation of 2,5-dibromothiophene catalysed by Ni(bipy)Cl2.150 Lin and Dudek have attempted several catalytic systems such as Ni, Pd, Co, and Fe salts.¹⁵¹ Among the electrochemical synthesis methods, anodic electropolymerisation in particular presents several distinct advantages such as absence of catalyst, direct grafting of the doped conducting polymer onto the electrode surface, easy control of film thickness by controlling the deposition charge, and the possibility to perform in situ characterisation of the polymerisation process by electrochemical and/or spectroscopic techniques. The electropolymerisation of bithiophene was initially addressed in 1980.149

Amongst the wide variety of conducting polymers, those derived from thiophene and its derivatives show good stability toward oxygen and moisture in both doped and neutral states.¹⁵² This combined with favourable electrical and optical properties has led to the application of PThs in electrochromic



Fig. 9 The mesomeric structures of polythiophene (a) polaron and (b) bipolaron.



Fig. 10 Scanning electron micrographs of (a) fibre surface of first wetspun PEDOT : PSS microfibre, (b) cross-section of PEDOT : PSS fibre spun into acetone. Reproduced with permission from ref. 64 and 63 Copyright© 2008 and 2011, Science Direct and 2011; WILEY-VCH Verlag GmbH & Co., respectively.

displays, protection of semiconductors against photocorrosion, and energy storage systems.¹⁵³ Similarly to PPy, PTh is utilised in solid phase extraction applications. To the best of our knowledge, the only published work on the preparation of PTh fibres is by Zhang *et al.*, who described the preparation of PTh nanofibres *via* seeding as a general synthetic approach for bulk nanofibre production.¹⁵⁴

2.1.5. Poly(3,4-ethylene dioxythiophene). In the latter half the 1980s, scientists at the Bayer AG research laboratories developed the polythiophene derivative PEDOT (or PEDT), which was initially developed with the aim of providing a soluble conducting polymer.84 3,4-Ethylene dioxythiophene (EDOT) polymerises effectively, leading to PEDOT films that adhere well to typical electrode materials. PEDOT benefits from the absence of undesirable α,β - and β,β -couplings between monomer units, while its electron-rich nature plays a significant role in the optical, electrochemical, and electrical properties of subsequent polymers based around the PEDOT building block.155 PEDOT is characterised by stability, high electrical conductivity (up to 1000 S cm⁻¹), moderate band gap, low redox potential, and transparency in the oxidised state.84 Initially PEDOT was found to be insoluble in common solvents, however this was successfully overcome by using poly(styrenesulfonic acid) (PSS) as the dopant during its chemical synthesis. The Electrical conductivity of semiconducting PEDOT was also shown to become enhanced upon doping due to the interaction between PEDOT and PSS in the presence of organic compounds.156 The resulting stable dark-blue aqueous dispersion

No.	Dopants used	Focus of the research	Spinning method	Reported electrical conductivity/conduction potential window	Mechanical properties	Ref.
1	Poly(4- styrenesulfonate)	Fabrication and characterisation of conducting PEDOT : PSS microfibres	Wet spinning (acetone)	$\sim 10^{-1} { m S cm}^{-1}$	YM 1.1 \pm 0.3 GPa, UTS 17.2 \pm 5.1 MPa, US 4.3 \pm 2.3%	163
2	Poly(4- styrenesulfonate)	Fabrication microfibres of PEDOT : PSS	Wet spinning (acetone)	$0.4-1 \text{ S cm}^{-1}$		165
3	Poly(4- styrenesulfonate)	Fabrication of highly conducting PEDOT : PSS microfibres and study the effect of dip-treatment in ethylene glycol on its properties	Wet spinning (acetone)	74–467 S cm ⁻¹ (after post- treatment)	YM 4.0 GPa, UTS 130 MPa	64
4	Boron trifluoride	Synthesis of highly conducting poly(3,4- ethylenedioxythiophene) fibre by simple chemical polymerisation	<i>In situ</i> polymerisation	In the range of 150–250 S cm ⁻¹	_	164
5	_	Production of continuous PEDOT : PSS in both acetone/IPA coagulation bathes	Wet spinning (acetone and isopropanol (IPA))	$<264 \text{ S cm}^{-1}$	IPA: YM 3.3 ± 0.3 GPa, UTS 125 ± 7 MPa, US $15.8 \pm 1.2\%$, acetone: YM 2.5 GPa, UTS 98 MPa, US 12.5%	63

of PEDOT : PSS is now commercially available and applied in antistatic coatings,¹⁵⁷ electrode materials,¹⁵⁸ organic electronics,¹⁵⁹ transparent electrodes, capacitors,¹⁶⁰ touchscreens, organic light-emitting diodes, microelectrodes and sensors.^{155,161}

Initial attempts to prepare fibrillar structures from PEDOT started in 1994, when Sailor et al. reported electrosynthesis techniques for the fabrication of complex PEDOT interconnects on Pt arrays.¹⁶² Okuzaki and Ishihara later reported the first preparation of PEDOT: PSS microfibres via wet spinning with acetone as the coagulant (Fig. 10(a)),¹⁶³ where the effects of spinning conditions on fibre diameter (which ranged between 180 and 410 µm), electrical conductivity, microstructure and mechanical properties were investigated. The fabrication of nanotubes from electrochemically synthesised PEDOT using alumina as the template was subsequently addressed by Zhang et al. as another novel approach.¹⁶¹ PEDOT nanofibres with diameters ranging between 100 and 180 nm were later produced using vanadium pentoxide nanofibres by a one-step nanofibre seeding method.155 In this procedure EDOT is dissolved in aqueous camphorsulfonic acid (HCSA) together with a vanadium pentoxide nanofibre sol-gel, before radical cationic polymerisation was initiated by addition of ammonium persulfate (APS). Of special note in the preparation of PEDOT fibres is the work of Baik and co-workers, who developed a method to synthesise PEDOT nanofibres by simple chemical polymerisation without employing a template.¹⁶⁴ Shortly thereafter, Okuzaki et al. fabricated highly conducting PEDOT : PSS microfibres with 5 µm diameter and up to 467 S cm⁻¹ electrical conductivity by wet spinning followed by ethylene glycol post-treatment.⁶⁴ Dipping in ethylene glycol (two-step wet spinning process) resulted in a 2-6 fold increase in electrical conductivity from 195 S cm⁻¹ to 467 S cm^{-1} and a 25% increase in tensile strength after drying from 94 MPa to 130 MPa. Characterisation with X-ray photoelectron spectroscopy, X-ray diffractometry and atomic force microscopy led to the conclusion that the removal of insulating PSS from PEDOT : PSS grain surfaces and crystallization were responsible for the enhanced electrical and mechanical properties of the microfibres. This work opened a new way for scientists to prepare relatively long PEDOT: PSS fibres using a straightforward method. Jalili et al. simplified the method to a one-step process to prepare microfibres (Fig. 10) by employing a wet spinning formulation consisting of an aqueous blend of PEDOT : PSS and poly(ethylene glycol), where the need for post-spinning treatment with ethylene glycol was eliminated and fairly high electrical conductivities of up to 264 S cm⁻¹ were achieved.⁶³ Table 3 summarises efforts made in the preparation of PEDOT : PSS fibres.



Fig. 11 Scanning electron micrographs of (a) TiO_2 /polyaniline composite fibres and (b) polyester fibres coated with polyaniline. Reproduced with permission from ref. 175 and 176 Copyright© 2011 and 2005; Elsevier and University of Bielsko-Biala, respectively.

1:33:04 AM.
n 7/4/2018
Downloaded o
0 April 2016. E
Published on 20

Table 4 Summary of research concerning composite polyaniline fibres

No.	Spinning solution blend	Focus of the research	Synthesis method	Reported conductivity/ conduction potential window	Mechanical properties	Ref.
1	PAni/PPD-T/H2S04 spin dope	Preparation of composite fibres of poly(<i>para</i> -phenylenediamine)- terenkthalic acid and emeraldine salt	Wet spinning (water)	Ι	YM ^a 62 GPa, UTS ^a 28 GPa	167
7	Lyotropic PAni/poly(<i>p</i> -phenylene terephthalamide), PPD-T, sulfuric acid solutions	Preparation of PAni composite fibres are of lyotropic PAni/poly(p - phenylene terephthalamide), PPD-T, sulfuric acid solutions	Air-gap spinning (at \sim 80 $^\circ$ C)	\sim 0.1 S cm $^{-1}$ (30% wt PAn)	YM 270 GPa	190
3	PAni/poly-ഫ-aminoundecanoyle	Preparation of conducting PAni/poly- ω-aminoundecanovle fibre	Wet spinning (concentrated H ₂ S0 ₄)	${\sim}10^{-7}~\mathrm{S~cm}^{-1}~(5\%~\mathrm{wt~PAn})$	I	191
4	PAni/HCSA/polyethylene oxide blends	Electrostatic fabrication of ultrafine conducting fibres: PAni/polyethylene oxide blends	Electrospinning	$\sim 10^{-4}$ to 10^{-1} S cm ⁻¹ ($\sim 20^{-1}$ 100% wt PAn·HCSA)	I	171
2	PAni/polystyrene-polybutadiene- polvstyrene (SBS)	Production of electrically conducting fibres in PAn-SBS blends	Capillary extruded	${\sim}10^{-4}~\mathrm{S~cm}^{-1}~({\sim}20\%~\mathrm{wt~PAn})$	I	169
9	HCSA/PAni/polyethylene oxide (PEO)	Experimental observation of FET behavior in doped PAni/polyethylene oxide PAni/PEO nanofibre	Electrospinning	$ m \sim 10^{-3}~S~cm^{-1}$	I	108
7	PAni doped with DBSA, polypyrrole (PPy) and graphite	Electrical and morphological properties of PP and PET conducting polymer fibre	Melt spinning and coating process	$2.88 \times 10^{-7} \mathrm{S \ cm^{-1}} (40\% \ \mathrm{wt} \mathrm{PPy})$	I	70
×	Pani doped with DBSA	Early attempts to obtain polyester (PET) fibres with antielectrostatic properties	Coating (fibres were padded with PAn)	I	I	176
6	EB powder was dissolved in <i>N</i> - methyl-2-pyrrolidinone (NMP) to form a 5 wt% solution	Actuation of PAni (AMPS) fibres	Wet spinning (2-butanone)	$\sim 1000~{ m S~cm^{-1}}$ (200% stretched fibres)	Poor!	93
10	PAni/nylon 6 in both concentrated sulphuric formic acids	Investigation on the coagulation rate of PAni/nylon 6 fibre in different acids and the influence of Li_2SO_4 on mechanical properties of the fibres	Wet spinning (Li ₂ SO ₄)	Electrical resistance 0.665– 0.015 $\Omega \text{ cm}^{-1}$ (\sim 5–25% wt PAn)	Improved using Li ₂ SO ₄ in the bath	168
11	PAni-ES and DBSA mixtures dissolved in xylene and coated with the solution of UHMWPE	Preparation and characterisation of PAni-coated ultra-high-molecular- weight polyethylene (UHMWPE) varus	Coating	$\sim 10^{-1}$	I	177
12	Chitosan/acetic acid was wet-spun and aniline was polymerised on resulting fibres in the presence of HCl and APS	Electrochemical actuation in chitosan/PAni microfibres for artificial muscles	Wet spinning (NaOH) followed by <i>in situ</i> oxidative polymerisation	$2.856 imes 10^{-2} { m S} { m cm}^{-1}$	US ^a 0.39%	192
13	Two phase blend of PAni-complex and fibre grade polypropylene in melt-state	Investigation of different processing conditions such as mixing parameters (time and temperature) and draw ratio on polypropylene/PAni fibres	Melt spinning	1	I	193

Review

-
-
-2
-
C
- 2
•
. ١
(
~
-
~
1
. (
_
7
7

44698 | RSC Adv., 2016, 6, 44687-44716

Published on 20 April 2016. Downloaded on 7/4/2018 1:33:04 AM.

Table 4	(Contd.)				
No.	Spinning solution blend	Focus of the research	Synthesis method	Reported conductivity/ conduction potential window	Mechanical properties
14	PAni film was deposited on the surface of stainless steel from H ₂ SO ₄ /aniline solution	Extraction of the target analytes from aqueous benzene derivatives systems in water samples using coated stainless steel with PAn	Coating	Ι	I
15	PAni emeraldine base (PAni-EB)/ HCSA blended with (PEO, PVP and PS)	PAni fibres blended with different polymers were prepared to mimic structures like olfactory cilia possessing high surface to volume ratio. They were and tested for gas	Electrospinning	1	1
16	Poly(1-lactide-co-3-caprolactone) (PLCL)/PAni	Composite fibres of poly(L-lactide- <i>co</i> - 3-caprolactone) (PLCL)/PAni for the culture of PC12 cells	Electrospinning	\sim 0.1–0.15 S cm ⁻¹	UEB^a 160 \pm 14.4%, UTS^a 15 \pm 3 MPa
17	Poly(aniline- <i>co</i> -3-aminobenzoic acid)/HCl/poly(aniline- <i>co</i> -3- aminobenzoic acid)/pure poly(lactic acid) (PLA)	Fabrication of nanofibres of HCl- doped poly(aniline-co-3- aminobenzoic acid) (3ABAPANI) and poly(lactic acid) (PLA) blends and their potential applications in tissue envincerino	Electrospinning	In the range of 0.9–8.1 mS $\rm cm^{-1}$	I
18	PAni-EB in formic acid/PAni- coated polycaprolactam (PA6) fibres doped by HCl, H ₂ SO ₄ , HCOOH and TSA	The effect of solvent concentration and roller speed on the mechanical and electrical properties of PAni- coated PA6 fibre were discussed	Coating	PAni-coated PA6 fibre has good permanent conductivity volume resistivity ($\Omega \text{ cm} = 10^1$ to 10^2)	I
19	Aniline in HCl/piece of TiO ₂ multipore fibre film/APS in HCl was added to the aniline mixture	Preparation of TiO ₂ /PAni composite fibre	Electrospinning <i>in situ</i> polymerisation	Т	I
20	Aniline/ammonium peroxydisulfate in the presence of short nvlon-6 fibre	Preparation and characterisation of natural rubber–PAni coated short nvlon-6 fibre (PAni–N6) composites	<i>In situ</i> oxidative polymerisation	$\sim \! 1.99 \times 10^{-6} \mathrm{S cm^{-1}}$	Depend on PAn concentration
21	Aniline/potassium peroxydisulfate	Chemical and electrochemical	Coating	-1 to +2 V	I

-174

173

179

175

181

180

174

 ${\sim}0.00641~\mathrm{S~cm^{-1}}$

Electrospinning

Melt spinning

194

Tenacity < 28 cN per

 ${\sim}10^{-3}~{\rm S~cm^{-1}}$ (draw ratio of 5)

tex

Ref. 178 111

182

US 400%

 $10^{-2} \mathrm{S} \mathrm{cm}^{-1}$

In situ oxidative polymerisation

Preparation of PAni/PU fibre by in situ

complex and characterised

filaments by melt spinning of PP/PA6

blends/modified with poly-aniline-

Preparation of conducting polyblend $[(L-lactide)-co-(\varepsilon-caprolactone)]$ fibres Electroactive electrospun PAni/poly

A blend of PP/PA6/PAni-complex

23

hexafluoropropanol (HFP)

 22

(polypropylene/polyam-ide-6/

PAni-complex)

for control of neural cell function

characterisation of PAni coated

conducting fabrics

fabrics washed with an aqueous HCPSA/PAni/PLCL dissolved in

solution coated on polyester acid solution (H₂SO₄ or HCl) PAni on PU fibre and investigation of

their piezoresistive properties

chemical oxidative polymerisation of

This journal is © The Royal Society of Chemistry 2016

 24

PU fibres immersed in aniline/HCl

solution

1:33:04 AM.
on 7/4/2018
Downloaded
April 2016.
Published on 20

Table 4 (Contd.)

This journal is © The Royal Society of Chemistry 2016

No.	Spinning solution blend	Focus of the research	Synthesis method	Reported conductivity/ conduction potential window	Mechanical properties	Ref.
25	Kenaf fibres (UKF) in NaOH solution/aniline monomer in HCl/ APS	Modification of natural kenaf fibre by PAni	<i>In situ</i> oxidative polymerisation	${\sim}10^{-4}~{ m to}~10^{-3}~{ m S~cm}^{-1}$	$\rm UTS~100\pm50~N$ mm ⁻²	183
26	Cellulose fibre in HCl/aniline and APS	Preparation of PAni/cellulose composite fibre for the treatment of Cr(vı)-contaminated water, and its effect	<i>In situ</i> oxidative polymerisation	Ι	Ι	184
27	Cellulose acetate (CA)-PAni	Preparation of dual-layer hollow fibre of PAni-cellulose acetate	Wet spinning (HCl and APS)	-2 to +2 V	I	185
28	A blend of aniline, acrylamide and M acids/N,N0- methylenebisacrylamide (NMBA) and potassium peroxydisulfate (KPS) added	Synthesising hexagonal PAni fibres with polyacrylamide pendants in PAAm oligomer (oligo-PAAm) colloid	<i>In situ</i> oxidative polymerisation	$2.2~\mathrm{S~cm}^{-1}$	1	186
29	Aniline in presence of detonation nanodiamond (DND)/SDS/APS	Characterisations of morphological, electrical and mechanical properties of PAni/IDNU1 nanofihres	Precipitation polymerisation technique	$10{-}100~{ m S~cm^{-1}}$	I	187
30	Aniline in presence of CF using FeCl ₃ ·6H ₂ O or APS as oxidant	Investigation PAni-coated coconut fibres properties as additives in matrix of nolumethane	<i>In situ</i> oxidative polymerisation	$1.5 imes 10^{-1} { m S} { m cm}^{-1}$ $({ m FeCl}_3 \cdot { m 6H}_2 { m O}) 1.9 imes 10^{-2} ({ m APS})$	I	188
31	Silver nanoparticles embedded PAni (AgNO ₃ aq. solutions + V ₂ O ₅ nanofhrous caedino aront)	Synthesis and characterisation of PAni nanofibre/silver composite	Seeding polymerisation reaction	2×10^{-3} to 0.196 S cm ⁻¹	Ι	189
32	Hanolucious security agency PAni/HCSA	Electrospun PAni fibres as highly Electrospun PAni fibres as highly sensitive chemiresistive sensors for NH, and NO, cases	Electrospinning	$2 imes 10^{-6}$ to 50 S cm ⁻¹	Ι	112
33	PAni/HCSA blended with PMMA or PEO	Introduce a novel method to calculate fibre conductivity using IDE applied on electrospun conductive nanofibres	Coaxial electrospinning	Up to 50 S cm ^{-1}	I	172
34	Spherical-shaped Ag nanoparticles decorated PAni nanofibre	Preparation of Ag-decorated BDP fibres as a sensitive material for the detection of 4-mercaptobenzoic acid and rhofamine 6G	Solution dipping method	1	I	195
35	Acidic solutions of aniline in HCl polymerised on nonwoven electrospun PS mats	Preparation of hierarchical PAni- polystyrene composite for water remediation	In situ polymerisation	I	I	196
JA-WK a	oung's Modulus. UTS-Ultimate Tensile	Stress. US-Ultimate Strain. UEB-Ultimate E.	longation at Break			

20 <u>,</u> s, l 6 à

2.2. Composite conducting fibres

Following the discovery of conducting polymers in 1977,^{1,166} their processability has been one of the major barriers to their widespread use. Consequently, the combination of conducting polymers with other, more processable materials in composite structures has become one of the most effective ways to produce conducting fibres. By employing this approach, not only difficulties related to processability could be surmounted, but the complementary characteristics of other individual component(s) improved the final properties. Not surprisingly, a large proportion of reported high-quality conducting fibres have been composite fibres.

Techniques for preparing composite conducting fibres are diverse, from dispersing conducting fillers in a thermoplastic polymer via mechanical mixing and blending, to coating a layer of conducting polymer on a fibrillar substrate via chemical or electrochemical polymerisation of a suitable precursor. Based on a survey of the available literature, composite conducting polymers may be categorised into two main sub-groups. The first category may be referred to as "composite conducting polyblend fibres", that is fibres consisting of conducting polymers blended with natural/synthetic polymers. The second group encompasses composite fibres made by combining conducting polymers and carbon-based materials (carbon nanotubes (CNTs) in particular), which may be referred to as "conducting polymer-carbon nanotube fibres". Historical backgrounds and the most recent advances in the field are discussed in detail below.

2.2.1. Composite conducting polyblend fibres

2.2.1.1. Composite polyaniline fibres. Composite PAni fibres contain a natural or synthetic polymer in addition to PAni, and thus represent a large category of composite fibres. Composite PAni fibres were first reported in the late 1980s.167 Segonds and Epstein prepared composite fibres from poly(para-phenylenediamine) (PPD)-terephthalic acid (T) (Kevlar® aramid) and the emeraldine salt of PAni by mixing emeraldine base PAni in PPD-T/H₂SO₄ solution and extruding this solution via wet spinning.¹⁶⁷ Although the fibres showed insulating properties because of the low loading levels of emeraldine salt, the authors demonstrated the feasibility of making multicomponent systems. Years later, Zhang et al. prepared composite PAni fibres by wet spinning based on a blend of PAni and poly-ωaminoundecanoyle in concentrated H₂S0₄. These fibres showed high strength and relatively high electrical conductivity ($\sim 10^{-7}$ S cm⁻¹) compared to related fibres reported up to that time. Subsequently, various composite PAni fibres have been prepared using a range of polymers via wet spinning.90,168,169 The highest electrical conductivity was stated from a wet-spun composite PAni fibre (~1000 S cm⁻¹) belonged to 200% stretched PAni/Au bilayers which was doped with AMPSA.93

Most reports concerned with the electrospinning of conducting polymers focus on PAni and blends thereof.¹⁷⁰ This technique was especially used in recent years to produce nanofibrillar films for bio-related applications. The first report of composite PAni fibres prepared by electrospinning was that of HCSA-doped polyaniline (PAni·HCSA)/polyethylene oxide (PEO) blend nanofibres.¹⁷¹ As-spun fibres demonstrated electrical conductivities in the order of $\sim 10^{-2}$ S cm⁻¹, which was quite an achievement at the time.

Several applications of electrospun composite PAni fibres have been reported. PAni was blended with insulating polymer fibres (PEO, polyvinylpyrrolidone (PVP), and polystyrene (PS)) to prepare sensors with a range of response.^{111,172} Nanofibrillar blends of a copolymer of PAni and benzoic acid and poly(lactic acid) (PLA) were also used as tissue engineering scaffolds.¹⁷³ Uniform electrospun fibres of PAni/poly[(L-lactide)-*co*-(ɛ-caprolactone)] were developed for electrically conducting, engineered nerve grafts.¹⁷⁴ Electrospinning was also used to prepare photocatalytically active TiO₂/PAni composite fibres (Fig. 11(a)).¹⁷⁵

The approach of coating insulating fibres with conducting PAni as a route to conducting fibres was first considered in a report where PET fibres were coated with a layer of PAni/dodecylbenzene sulfonic acid (DBSA) (Fig. 11(b)),¹⁷⁶ although no conductivity values were reported. In subsequent efforts, ultrahigh molecular weight polyethylene, stainless steel, poly-caprolactam and polyester were used as substrates on which a layer of PAni was coated.^{177–180} *In situ* oxidative polymerisation was used to prepare PAni-coated short nylon/natural rubber fibres,¹⁸¹ while researchers have also employed this method to



Fig. 12 Scanning electron micrographs of (a) polypyrrole-coated ultra-high molecular weight polyethylene fibre, (b) polypyrrole–(APS/DEHS)–alginate fibre. Reproduced with permission from ref. 208 and 213 Copyrights© 2011; Elsevier and RSC Publishing, respectively.



Fig. 13 Scanning electron micrographs of (a) composite PEDOT : PSS/polyacrylonitrile conducting fibres with 0.38 wt% PEDOT : PSS content and (b) PEDOT : PSS-chitosan fibre. Reproduced with permission from ref. 239 and 242 Copyrights© 2013 and, Elsevier and WILEY-VCH Verlag GmbH & Co., respectively.

AM.
1:33:04
7/4/2018
on
Downloaded
Ξ.
2016
April
g
on
Published

Table 5 Overview of composite polypyrrole fibres

No.	Sample name	Focus of the research	Synthesis method	Reported electrical conductivity/conduction potential window	Mechanical properties	Ref.
7	PPy-polyester and PPy-quartz composite fibre	Utilization of time-of-flight secondary ion mass spectrometry to examine the nature of the aromatic sulphonate dopant anion(s) in PPy overlayers deposited onto both polyester fibres and quartz fibres	1	1	I	224
0	Aqueous colloidal magnetite particles onto (polyester, nylon, cotton <i>etc.</i>) fibres from utilising a simple dip-coat procedure and then treated them with a PPy coating	Preparation of superparamagnetic- conducting textile composites by a facile, two-step solution deposition process	Two-step solution deposition process	$35-160 \text{ S cm}^{-1}$	I	205
ŝ	Graphite fibre PPy coatings	Fabrication of graphite fibre PPy coatings by aqueous electrochemical polymerisation	Aqueous electrochemical polymerisation	I	I	199
4	PPy/poly(p-phenylene terephthalamide)	Continuous fast vapor phase polymerisation method to prepare electrically conducting PPy/PPTA	Vapor phase polymerisation	0.68 S cm^{-1}	UTS 2.644 kPa, US 4.4%	216
л	Aramid fibres were immersed in FeCl ₃ · $6H_2O$ solutions and were then exposed to pyrrole/ H_2O vapour at 20 °C	Preparation of conducting aramid/ PPy composite fibres by vapour-phase polymerisation	Vapour phase polymerisation	$\sim 1.3 \times 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$	I	217
Q	Insulating natural cotton, silk, and wool fibres were electrochemically coated with pyrrole in acetonitrile (containing <i>p</i> -toluenesulfonic acid)	Fabrication of conducting fibres from natural polymers	Electrochemical polymerisation	1	I	225
~	PPy coated fabrics (83% Tactel blended with 17% (40 denier) Lycra in)	Preparation of a flexible strain sensor from PPy-coated fabrics	Chemical vapour deposition (CVD)	Change with several factors such as dopant, temperature, <i>etc.</i>	I	18
8	PPy-poly(ethyl-ene oxide) (PPy- PEO) composite nanofibre	Fabrication of electrically conducting PPy-poly(ethylene oxide) composite nanofibre	Electrospinning and vapour phase polymerisation	$\sim 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$	I	202
6	Aqueous titanium tetraisopropoxide + ethanol contained polyvinylpyrrolidone (PVP), then exposed to the saturated pyrrole vapor	Fabrication and characterisation of coaxial nanocables of PPy (PPy)/TiO ₂ and their surface properties	Electrospinning followed by vapor-phase polymerisation	1	I	226
10	Organic solvent soluble PPy, [(PPy3) ⁺ (DEHS) ⁻] _x + NaDEHS	Preparation of PPy nanofibres with the practical application for construction of nanoelectronic devices	Electrospinning	Pure [(Ppy3) ⁺ (DEHS) $^{-1}$ x 2.7 × 10 ⁻² S cm ⁻¹ for the composite fibre 3.5 × 10 ⁻⁴ S cm ⁻¹	I	143

Review

				Reported electrical		
No.	Sample name	Focus of the research	Synthesis method	conductivity/conduction potential window	Mechanical properties	Ref.
11	A stock solution of PVP, pyrrole and FeCl ₃ in ethanol + DMF as the core channel layer device and PVP in ethanol + DMF as the sheath	Fabrication of core/sheath nanofibres of (PPy)/PVP	Electrospinning with multi- spinneret microfluidic devices	1		221
12	Pyrrole monomer + PAn polymers in DMF, H_2O_2 was slowly added depending on by pyrrole	Fabrication of polyacrylonitrile/PPy (PAn/PPy) composite nanofibres	Electrospinning	I	I	24
13	Fibres any pyrou annual Fibres were dipped in solution of FeCl ₃ anhydrous in dried acetonitrile and then exposed to wurnele variant	Preparation of continuous vapour deposited PPy–cotton and PPy–silk yarns	Vapour phase polymerisation	${\sim}10^{-4}~{ m S~cm^{-1}}$	I	218
14	Steel fibre coated with PPy (PPy) doped with polyphosphate	Development of polyphosphate- doped PPy coated on steel fibre for the GC determination of a group of organochlorine pesticides (OCPs) in water	Solid-phase microextraction (electrochemical coating)	1	I	227
15	Pyrrole, 3,4-diethyl pyrrole, PVA as the steric stabiliser polystyrene/ FeCl ₃ fibres coated with PPy polystyrene/PPy suspension fibre in DMF	Production of conducting nanofibres by electrospinning based on PPy	Electrospinning	1	I	222
16	Polyamide 6/PPy nanofibres	Fabrication of composite polyamide 6/PPy conducting nanofibres	Electrospinning	I	I	201
17	Pyrrole, <i>N</i> -methylpyrrole, 3- methylthiophene, poly(3,4- ethylene dioxythiophene), deposited on substrates (Pt, stainless steel)	Preparation of poly-M-methylpyrrole microfibre	Electrodeposition	1	I	228
18	Silk fabrics were coated with	Preparation of bio-based conducting	In situ oxidative	1		20
19	electricatly conducting doped <i>Pty</i> Ag nanowires (NWs) dispersed in solution of $(Cu(Ac)_2)$, then oxidise pyrrole monomers to make uniform Pty sheath	composites (trzy)-coated sink) raprics Preparation of Ag/PPy coaxial nanocables	polymensation Ion adsorption/oxidative polymerisation	Ι	I	207
20	PPy and PTh coating on stainless steels as working electrodes	Application of PPy and PTh as an adsorbent in solid-phase microextraction sampling of five adrenolytic drups	Solid-phase microextraction electropolymerisation (SPME) coating	1	I	229
21	FeCl ₃ -doped PPy into a collagen- based polyelectrolyte complexation (PEC) fibre	Fabrication of PPy-incorporated collagen-based fibres to make 3D electroactive fibrous scaffolds	Interfacial polyelectrolyte complexation (IPC)	1	UTS 304 ± 61.0 MPa, YM 10.4 ± 4 3 GPa	230

Published on 20 April 2016. Downloaded on 7/4/2018 1:33:04 AM.

Table 5 (Contd.)

Sample name	Focus of the research	Synthesis method	Reported electrical conductivity/conduction potential window	Mechanical properties	Ref.
PPy/hexagonally ordered silica (PPy/SBA15) coated on stainless	Fabrication of PPy/hexagonally ordered silica nanocomposite for	Vapour phase polymerisation	I	I	219
steel wire Zn(S ₂ CNEt ₂) ₂ /pyrrole monomer	solid-phase microextraction Spinning PPy/ZnS core/shell coaxial nanowires	Two-step process by anodic aluminum oxide (AAO)	I	Ι	231
FeCl ₃ -doped UHMWPE fibres soaked in an aqueous solution of hexahydrate (catalyst) treated by	Production of PPy-coated UHMWPE fibre to improve adhesion and structure properties of UHMWPE	templates Oxidative polymerisation coating	I	Ι	208
pyrrole monomer Silica fibres treated with silane	Tibre Production of PPy-coated amorphous	In situ oxidative	$0.32~\mathrm{S~cm^{-1}}$	Ι	28
agent and then coared with <i>PFY</i> Admixing silver nitrate and pyrrole in presence of cotton fabric at different mole ratios	suica snott nores (rry-Aər) Synthesis of PPy silver nanocomposite on cotton fabrics	porymensation coating <i>In situ</i> oxidative polymerisation	${\sim}10^{-3}~{ m S~cm}^{-1}$	I	209
MWCNT fillers + polystyrene matrix PPy was coated on fibres	Fabrication of conducting electrospun polymer fibres with nano features	Electrospinning/ <i>in situ</i> polymerisation	$3.7 imes10^{-4}~ m S~cm^{-1}$	I	232
PPy coated layer on Ag-TiO ₂ nanofibre	Protecting Ag nanoparticles from beine oxidised by a PPy laver	Electrospinning	I	I	233
PPy coated on E-glass fibre, FeCl ₃ (oxidant)/TsO ⁻ (dopant)	Fabrication of coaxial fibres to shield the house hold appliances	Vapor deposition	99.23% of the EM incident radiations can be blocked	I	234
Pyrrole (Py) polymerised on graphene fibres	Fabricating of novel electrochemical flexible and wearable graphene/Ppy fibres as an actuator	<i>In situ</i> oxidative polymerisation	Highly active within the ± 0.8 V range	I	214
Py polymerised on the BF surface using (FeCl ₃ ·6H ₂ O) as oxidant	Preparation and characterisation of PPy-coated banana fibres	<i>In situ</i> oxidative polymerisation	$1.8 imes 10^5$ S cm ^{-1} (electrical resistivity)	I	212
Py in presence of FeCI ₃ (oxidant)/ <i>p</i> -toluene sulphonic acid (dopant)	Fabricating and characterising natural rubber/PPy and natural rubber/PPy/PPy-coated short nylon fibre	In situ oxidative polymerisation	8.3 \times 10 ⁻⁴ S cm ⁻¹ NR/PPy 6.25 \times 10 ⁻² S cm ⁻¹ (for NR/PPy/F-PPy)	I	211
FeCl ₃ and anthraquinone-2- sulfonic acid sodium salt as oxidant/donant	Preparation of PPy/cellulose fibre composites	<i>In situ</i> oxidative polymerisation			203
PCL + dichloromethane and N,N- dimethylformamide (DMF), PPy was coated on fibres/FeCl ₃ as an oxidant	Fabrication of PPy hollow fibres to extract two important neuroendocrine markers from plasma samples	Electrospinning and <i>in situ</i> polymerisation	I	I	144
Cotton, wool, polyester exposed to pyrrole using FeCl ₃ (oxidant)	Investigation of the response of conductive woven, knitted, and nonwoven composite fabrics of pH, humidity, and mechanical strain	In situ polymerisation	1	I	223
Aq. Py with FeCl ₃ (oxidant)/ <i>p</i> TSA (dopant)	Fabrication of electroconductive cotton yarn	In situ polymerisation	Resistivity 182.63 k Ω m ⁻¹	I	210

View Article Online RSC Advances

No.	Sample name	Focus of the research	Synthesis method	Reported electrical conductivity/conduction potential window	Mechanical properties	Ref.
37	Aq. Py with FeCl ₃ (oxidant)/pTSA (dopant)	Preparation and characterisation of electrically conductive textiles for	In situ polymerisation	Resistivity 1013.08 $\Omega \text{ m}^{-1}$	I	235
38	Aq. Py with FeCl ₃ (oxidant)/pTSA (dopant)	Incar generation Investigation of chitosan/polypyrrole composite fibre as biocompatible artificial muscles	In situ polymerisation	I	I	236
39	PPy coated with ferric tosylate (oxidant)/ <i>n</i> -butanol/EDOT deposited	Soft linear electroactive polymer actuators based on polypyrrole	Two-step chemical- electrochemical synthesis	1	I	220
40	Pp, nanoparticles dispersed in aq. GO solution	Preparation of conductive composite fibres from reduced graphene oxide and polypyrrole	Wet spinning	$\sim 20~{ m S~cm^{-1}}$	YM 8 ± 4 GPa, UTS 175 ± 8 MPa	215

prepare conducting fibres based on polyurethane, kenaf, polyacrylamide, cellulose, coconut, poly(methyl methacrylate) and detonation nanodiamond fibre substrates.^{182–188}

Recently, PAni nanofibre/silver nanoparticle composite networks were prepared *via* well-known seeding polymerisation method with reported electrical conductivities in the range of 2 \times 10⁻³ to 0.196 S cm⁻¹ applied as an antibacterial agent.¹⁸⁹

Melt spinning is another method that has been used for making composite PAni fibres. However, the use of this method has been restricted because of several issues mentioned earlier, such as relatively low decomposition temperatures, poor control over the exact temperature of the polymer melt during spinning, thermo-mechanical history of the melt and final fibre structure. Kim *et al.* were the first to consider the spinning of a melted blend containing PAni, followed by a coating process.⁷⁰ Table 4 summarises research concerning composite PAni fibres.

2.2.1.2. Composite polypyrrole fibres. The low water solubility and poor processability of PPy mean that there are few reports of pristine PPy fibres.¹⁹⁷ It follows that PPy may be considered as the most utilised conducting polymer in making composite fibres. Over the past two decades, a variety of materials have been demonstrated as appealing substrates for PPy. Due to the good adhesion force between PPy and various substrates,¹⁸ conducting composites may be prepared that retain the inherent properties of both PPy and the substrate.¹⁹⁸ These substrates include carbon, graphite,¹⁹⁹ glass,²⁰⁰ and polymeric fibres.^{201,202} In general, the conductivity of PPy/fibre composites is directly related to PPy loading, ratio of oxidant to dopant, and fibre structure.²⁰³

In 1989 Kuhn et al. were the first to perform a remarkably effective, in situ, solution-based, and commercially feasible process for coating each individual fibre in woven, knitted or nonwoven textiles with a thin layer of PPy, with the results published some years later in 1993.204 This method was subsequently applied to a variety of textiles. Forder *et al.* applied the technique on polyester, nylon and cotton, leading to electrical conductivities ranging between 35 and 160 S cm⁻¹.²⁰⁵ Others have endeavoured to coat graphite fibres with PPy through this method.¹⁹⁹ One of the earliest reports of the deposition of PPy onto fibres involved a two-step process whereby the substrate was soaked in a ferric chloride solution before immersion in a pyrrole solution.²⁰⁶ Silver nanowires,²⁰⁷ ultra-high molecular weight polyethylene fibre (Fig. 12(a)),²⁰⁸ silica short fibres,²⁸ cotton fibres²⁰⁹ and yarns,²¹⁰ short nylon fibre/natural rubber,²¹¹ cellulose²⁰³ and banana fibres²¹² have been used as alternative substrates for the oxidative polymerisation process to create a PPy layer on them. Using reactive wet spinning, Foroughi et al. reported the fabrication of electrically conducting fibres comprised of an alginate biopolymer and PPy (Fig. 13(b)).²¹³ Recently Wang et al. described the preparation of novel actuators based on graphene fibres coated with electropolymerised PPy.²¹⁴ Furthermore, a wet spinning approach was lately employed to produce conductive composite fibres from reduced graphene oxide and polypyrrole nanoparticles resulted in conductivities of ~ 20 S cm⁻¹.²¹⁵

Chemical vapour deposition (CVD) (also known as vapour phase polymerisation) is another straightforward and rapid

RSC Advances

				Reported electrical conductivity/ conduction	Mechanical	
No.	Spinning or coating solution	Focus of the research	Synthesis method	potential window	properties	Ref.
1	Ionomer mixture poly(3,4-ethylenedioxy- thiophene) : poly(styrenesulfonate) (PEDOT : PSS. 1 : 2.5, w : w)	Preparation and characterisation of silk casted PEDOT : PSS fibres from a ethylene glycol solution	Dip-coating	8.5 S cm ⁻¹	UTS 1000 cN	17
2	PEDOT : PSS solution, mixed with 0.1% EDOT, which was infiltrated into silk thread	Preparation of composite fibres of PEDOT-PSS/silk for signal recording	Electrochemically deposition	0.102 S cm^{-1}	UTS 1239 cN	244
с,	Aqueous PEDOT : PSS dispersion injected into chitosan coagulation bath and then treated with ethylene glycol (EG)	Producing coaxial conducting polymer fibres loaded with an antibiotic drug by electropolymerisation for smart release applications	Dip-coating	56 ± 7 S cm ⁻¹	YM 2 ± 0.3 GPa, UTS 99 ± 7 MPa, US 20.6 ± 1.2%	239
4	PEDOT : PSS blended with polyacrylonitrile (PAn)	Characterisation of PEDOT : PSS-PAn composite fibre in terms of electrical conductivity, thermal stability and mechanical properties	Wet spinning	5.0 S cm ⁻¹	YM 3.32 cN per dtex, UTS 0.36 cN per dtex, US 36.73%	242
ى ا	Electrospun nanofibres of titania onto an interdigitated electrode (IDE) coated with an ultra-thin film of PEDOT : PSS	Preparation of a chemosensor as a potential sensing material for NO (asthma monitoring)	Electrospinning followed by dip-coating	I	I	238
9	Polyethylene terephthalate (PET) textiles coat with aq. PEDOT : PSS solutions	Fabrication of e-textiles based on polyethylene terephthalate (PET) textiles with different formulations of PEDOT : PSS	Knife-coating (direct), pad- coating (impregnation) and screen printing	Resistivity 10–20 Ω m ⁻²	I	157
Ч	Different compositions of PEDOT : PSS (2.9-25%) and PU	Preparation of highly conductive polyurethane/PEDOT : PSS elastomeric fibres for sensor applications	Wet spinning	2-25 S cm ⁻¹	YM ~ 7.2–247 MPa, UTS ~ 0.5– 9.1 MPa, US up to ~400%	243
8	Polyvinyl alcohol (PVA) and PEDOT : PSS aq. solution	Investigation of tensile strength and conductivity of PVA/PEDOT : PSS fibres	Wet spinning	$10-79~{ m S~cm^{-1}}$	UTS ~ 39 –84 MPa	245

Published on 20 April 2016. Downloaded on 7/4/2018 1:33:04 AM.

4

Table 6 Summary of composite PEDOT : PSS fibre investigations

method to deposit PPy onto various substrates, and has been used widely to produce composite PPy fibres.18,202,216-220 Although this method has the advantage of simplicity, the highest reported electrical conductivity of fibres prepared this way was only 0.68 S $\rm cm^{-1}$,²¹⁶ likely due to the formation of only a thin layer of conducting PPy. Nair and co-workers were the first to merge electrospinning with CVD for the synthesis of electrically conducting composite PPy nanofibres.²⁰² This approach provided the advantages of electrospinning while at the same time circumventing the intractability of PPy. A year later, Chronakis et al. reported for the first time a method to prepare nanofibres using a mixture of PPy and PEO.143 In 2007, a microfluidic approach was described by others for fabricating hollow and core/sheath PPy nanofibres by electrospinning.221 The benefits of using microfluidic devices for nanofibre synthesis include rapid prototyping, ease of fabrication, and the ability to spin multiple fibres in parallel through arrays of individual microchannels. PPy composite core-shell nanostructures were also successfully prepared using PAn, PS and polyamide 6 (PA6) solutions.²²² It is worth noting that a large number of prepared PPy composite fibres have been employed for sensor applications.18,134,223 An overview of the studies performed on composite PPy fibres is given in Table 5.

2.2.1.3. Composite poly(3,4-ethylene dioxythiophene): poly(styrenesulfonic acid) fibres. PEDOT is a well-studied semiconducting polymer that is rendered solution-processable when doped with acidic PSS.²³⁷ The processability of PEDOT : PSS has naturally meant that relatively few studies have considered PEDOT : PSS within composite fibres. Nevertheless, composite PEDOT : PSS fibres are at the centre of attention due to their high conductivity and multiple applications.

Dip-coating has been the main method used for preparing hybrid PEDOT : PSS fibres for the past few years. This method was first employed by Irwin *et al.* to deposit PEDOT : PSS onto silk fibres from an ethylene glycol solution,¹⁷ yielding a composite fibre exhibiting 8.5 S cm⁻¹ electrical conductivity, which was considerably higher compared to previous literature values for ICP-coated fibres. Zampetti *et al.* coated an electrospun titania membrane mesh with PEDOT : PSS using dip-coating,²³⁸ which was then used as a nitric oxide sensor for asthma monitoring. Recently, PEDOT : PSS-coated chitosan hybrid fibres was developed,²³⁹ which showed relatively high conductivity values of *ca.* 60 S cm⁻¹ (Fig. 13(a)). A few researchers have just addressed preparation of electrically conductive textiles based on poly(ethylene terephthalate) (PET), polyurethane and polyacrylate fabrics coated with PEDOT : PSS.^{157,240,241}

In recent time, limited cases described preparation of composite PEDOT : PSS fibres through wet spinning method. Liu and colleagues recently described a novel approach to prepare conducting fibres of PEDOT : PSS blended with PAn *via* wet spinning (Fig. 13(b)).²⁴² Not long ago, polyurethane/PEDOT : PSS elastomeric fibres with high electrical conductivities in the range of *ca.* 2–25 S cm⁻¹ were reported.²⁴³ Seyedin *et al.* claimed asprepared fibres as potential strain-responsive sensors. A summary of composite PEDOT : PSS fibre investigations is presented in Table 6.

2.2.2. Conducting polymer–carbon nanotube fibres. The combination of conducting polymers with carbon-based



Fig. 14 Scanning electron micrograph of an APS/DEHS-doped polypyrrole–alginate–carbon nanotube fibre. Reproduced with permission from ref. 213 Copyright© 2011; The Royal Society of Chemistry.



Fig. 15 Scanning electron micrograph of chemically prepared PPy– CNT yarn showing the surface morphology, scale bar shows 1 μ m; reproduced with permission from ref. 258 Copyright© 2012; The Royal Society of Chemistry.

materials, including carbon nanotubes and graphene, offers the possibility of improved properties combined with the introduction of new electronic properties based on interactions between the two components.²⁴⁶ Wet spinning was the first method employed to produce hybrid fibres from a combination of conducting polymers and CNTs. Mottaghitalab et al. fabricated wet-spun PAni-CNT composite fibres (containing 2% (w/w) CNTs) which exhibited excellent mechanical and electrical properties compared with the neat PAni fibers and used as electromechanical actuators.247 Subsequent improvements in mechanical and electronic properties using different dopants have been described by several research groups.247-250 A dual mode actuation was reported for the first time by Spinks and co-workers in a chitosan/PAni/singlewalled carbon nanotube (SWNT) composite fibre, which combined the benefits of the large, reversible swelling and biocompatibility of chitosan, actuation by control of pH or by electrochemical means, good solubility of PAni, and mechanical strength and good electrical conductivity of carbon nanotubes.251 Subsequently, Foroughi et al. produced PPy-alginate-CNT conducting composite fibres²¹³ (Fig. 14) using reactive wet spinning with different oxidants/dopants, which demonstrated promise for application in sensors, actuators and some biomedical applications, due to their suitable mechanical and electrical properties.²¹³

c Z	Sninning or coating solution	Enerts of the research	Sninning method	Reported electrical conductivity/ conduction potential window	Mechanical	Ref
.041	opinities of coantig solution	rocus of the recarding		MODITIA	br nhc nco	1001
ч	PAni-CNT-DMPU dispersion	Producing PAni-CNT composite fibres for potential use in e-textiles	Wet spinning	(2 wt% CNT) 32 ± 3 S cm ⁻¹	(2 wt% CNT) after doping UTS 229 ± 22 MPa, YM 5.2 ± 0.2 GPa, US 8 ± 3%	248
2	AMPSA	Producing PAni-SWCNT composite fibres for potential use in e-textiles	Wet spinning	$750~{ m S~cm^{-1}}$	UTS 250-300 MPa, YM 7-8 GPa	249
б	PAni-CNT-DMPU dispersion	Improvement of electromechanical actuation of fibres when used as artificial muscles	Wet spinning	$128.0 \pm 25~{ m S~cm^{-1}}$	UTS 260 MPa, YM 17 GPa	247
4	PAni (AMPSA)-CNT-DMPU dispersion	Producing high-strength conducting PAni-CNT composite fibres	Wet spinning	$716\pm36~\mathrm{S~cm^{-1}}$	UTS 255 \pm 32 MPa, US 4 \pm 0.6%, YM 7.3 \pm 0.4 GPa	250
5	Chitosan/PAni/SWNT (DCA- AMPSA)	Producing a fibre which shows both pH and electrochemical actuation	Wet spinning	$1.8~\mathrm{S~cm}^{-1}$	UTS 95 MPa, US 60%	251
9	Alg-PPy-CNT APS/DEHS (dopant) FeCl ₃ /DEHS (dopant) APS/pTS (dopant) FeCl ₃ /pTS (dopant)	Producing electrically conducting, robust fibres of PPy–Alg–CNT	Reactive wet spinning	$3.0\pm0.5~\mathrm{S~cm^{-1}}$	UTS 250 \pm 5 MPa, US 10 \pm 1.3%, YM 10 \pm 0.5 GPa	213
7				$2.0\pm0.4~\mathrm{S~cm^{-1}}$	UTS 95 ± 4 MPa, US $10 \pm 1.3\%$, YM 10 ± 0.5 GPa	
8				$4.0\pm0.8~\mathrm{S~cm^{-1}}$	UTS 250 \pm 5 MPa, US 5 \pm 1%, YM 11.8 \pm 2 GPa	
6				$10.0 \pm 1.5~{ m S~cm^{-1}}$	UTS 65 ± 8 MPa, US $4 \pm 0.7\%$, YM 3.7 ± 0.8 GPa	
10	PAni-polyethylene oxide (PEO)- MWNT	Producing hybrid PAni/PEO/MWNT fibres with improved electrical properties using electrospinning	Electrospinning	8.89 μS cm ⁻¹ (with 0.5 wt% MWNTs)	1	252
11	PAni-PEO-MWNT	To increase the electrical conductivity of PAni/PEO nanofibre	Electrospinning	Up to 2.77 $\mu S \text{ cm}^{-1}$	l	261
12	PAni-PEO-MWNT	Improving the electrical and mechanical properties of PAni/PEO/ MWNT composite fibre	Electrospinning	$9 imes 10^{-6}~\mathrm{S~cm^{-1}}$	YM 23.6 MPa	253
13 14	CNT-PPy (NH4,) ₂ S ₂ O ₈ (oxidant) CNT-PPy APS (oxidant)	Producing CNT–PPy composite fibre Improvement in electrical, magnetic and thermal properties of CNTs by coating them with PPy	<i>In situ</i> polymerisation <i>In situ</i> polymerisation	16 S cm ⁻¹ 16 S cm ⁻¹	1 1	255 256
15	PPy-activated carbon nanofiber (ACNF)-CNT	Producing nano composite electrodes for supercapacitors	Electrospinning followed by <i>in situ</i> chemical polymerisation	PPy/ACNF: 0.79 S cm ⁻¹ , PPy/ACNF/CNT: 1.33 S cm ⁻¹	I	257

Published on 20 April 2016. Downloaded on 7/4/2018 1:33:04 AM.

Table 7 Summary of investigations into composite conducting polymer-carbon nanotube fibres

This journal is © The Royal Society of Chemistry 2016

1:33:04 AM.
n 7/4/2018
Downloaded o
April 2016. I
Published on 20

Table 7 (Contd.)

Electrospinning was employed for the first time by Kim *et al.* for producing one-dimensional multi-walled carbon nanotube (MWNT)-filled PAni/PEO nanocomposite fibres with improved electrical properties.²⁵² Improvements in electrical and mechanical properties of electrospun PAni/PEO/MWCNT composite fibres were later described by Lin and Wu.²⁵³ Zhang *et al.* have recently reported on preparation of nanocomposite PAni/polyacrylonitrile/multiwalled carbon nanotubes fibres with conductivities up to 7.97 S m⁻¹ *via* electrospinning.²⁵⁴

In situ polymerisation of conducting polymers on CNTs is as another method used extensively to fabricate composite fibres. Fan et al. synthesised PPy on CNTs using (NH₄)₂S₂O₈ as the oxidant and reported modification of the electrical, magnetic and thermal properties of the CNTs by PPy.255,256 Ju et al. described a two-step method for producing aligned nano-sized PPy/activated carbon composite fibres for supercapacitor applications using electrospinning followed by an in situ chemical polymerisation method.257 Foroughi and co-workers prepared PPy-MWNT yarns by chemical and electrochemical polymerisation of pyrrole on the surface and within the porous interior of twisted MWNT yarns. The composite yarn produced may be used for applications where electrical conductivity and good mechanical properties are of primary importance.²⁵⁸ Wet spinning of composite formulations based on functionalised PEG-SWNT and PEDOT : PSS was investigated recently, yielding composite fibres exhibiting 22.8 GPa modulus and 254 MPa ultimate stress (Fig. 15(b)).259 Dorraji et al. described PAni/ MWCNT/chitosan nanofibres manufactured via polymerisation of PAni/MWCNT on wet-spun chitosan fibres.²⁶⁰ These fibres yielded conductivities of *ca.* 5.3×10^{-2} S cm⁻¹. Table 7 summarises investigations into composite conducting polymer-carbon nanotube fibres.

3. Current and future applications of CPFs

Thus far, conjugated conducting polymer fibres have found many applications due to combination of properties similar to those of metals along with their great formability via the variety of fabrication methods usually associated with conventional polymers. These fibres are being extensively studied to meet aesthetic demands and the needs of two key classifications of energy and bionics devices development. CPFs offer high conductivity, rapid charge-discharge rates, relatively inexpensive and simple large scale production, flexible and lightweight, and environmentally friendly devices known to form the next generation of energy suppliers. In energy applications they have been incorporated into devices for a range of purposes from storage to conversion such as electrodes and batteries, 92,264-266 sensors, 26,238,267 supercapacitors,268-270 chemical smart textiles,^{177,235,271-273} actuators and artificial muscles.^{136,250,274} For example, fabrication of polyaniline and polyaniline carbon nanotube composite fibers employing wet spinning as high performance artificial muscles have been reported previously by Spinks et al.²⁵⁰ The fibers have tensile strengths of 255 MPa and operate to stress levels in excess of 100 MPa, three times higher than previously reported for conducting-polymer actuators and 300 times higher than skeletal muscle. Furthermore, a wet spinning process was described to produce fiber capacitor electrodes of PAni-CNT which showed the maximum specific capacitance of 29.7 F cm⁻² in 1 M HCl solution.²⁷⁵ Conducting fibres also provide benefits for either their direct use as energy storage devices or to be integrated into fabrics to create multifunctional wearable smart textiles. This trend could facilitate the rapid development of portable and flexible electronic devices. However great efforts have been paid to investigate different aspects of the usage of CPFs in the field of energy, their electrochemical performance as well as mechanical properties are still far from satisfied, when compared to some other kinds of materials, such as CNT fibers. It has also been suggested that they show promise for applications in photovoltaic (solar) cells, 83,158 electronic circuits,46 organic light-emitting diodes,78,276 and electrochromic displays.83,240

Applications of CPFs in biological field were expanded later on with the discovery that these materials were compatible with many biological molecules in late 1980s.23 Most CPs present a number of important advantages for biomedical applications, including biocompatibility, ability to entrap and controllably release biological molecules, ability to transfer charge from a biochemical reaction, and the potential to alter the properties of the CPs to better suit the nature of the specific application.²³ Conducting fibres can provide self-supporting three-dimensional, flexible structures suitable for in vitro and in vivo bionic applications compared to the films. These functional aspects may also require the overlap of certain characteristics for example for uses in implantable batteries and bio-actuators.^{23,277} In more detail, storage or conversion of energy and provide the required biocompatibility. Today, the major bioapplications of CPFs are generally within the area of electrical stimulation and signal recording,244,278,279 drug-delivery devices,239 tissue-engineering scaffolds,125,132,280 and biosensors.^{23,281} Recently, there is a growing interest in using conducting fibres for neural tissue engineering applications. These conductive fibrillar pathways may provide appropriate replacements for nerve fibres after injuries. Electrical stimulation has been shown to enhance the nerve regeneration process and this consequently makes the use of electrically conductive polymer fibres very attractive for the construction of scaffolds for nerve tissue engineering. For instance, Li et al. investigated the feasibility to generate novel electrospun PAni-gelatin blended scaffolds as potential scaffolds for neural tissue engineering.170 They reported that as-prepared fibers are biocompatible, supporting attachment, migration, and proliferation of rat cardiac myoblasts. In another study, the feasibility of fabricating a blended fibre of PAni-polypropylene as a conductive pathway was studied for neurobiological applications.²⁸⁰ In addition, production of conducting fibres for controlled drug release applications is currently of particular interest of many research groups. Fabrication of PEDOT : PSS-chitosan hybrid fibres was described using a novel wet spinning strategy to achieve a controlled release of an antibiotic drug.239 Still, there remain limitations for use of CPs due to their manufacturing costs, material inconsistencies, poor solubility in solvents and

inability to directly melt process. Moreover, oxidative dopants could diminish their solubility in organic solvents and water and hence their processability.

Despite the above mentioned impressive achievements, further developments are needed for high-performance flexible conductive fibres that can simultaneously ensure high conductivity, excellent mechanical robustness and flexibility as well as high electrochemical performance for practical applications. There also exist potential applications of conducting polymer fibres in electrodes, microelectronics, sensors, actuators and rechargeable batteries outside of those already discussed. Besides, conducting polymer fibres could be considered as candidates for interconnection technology. However, to further improve the field of conducting polymer fibres, the following features could be potentially investigated and improved.

Great efforts have been paid to the field of fabrication of mechanically robust yet flexible robust conducting fibres; however, CPFs still lack desirable mechanical robustness comparing to common traditional textile fibres or some other kinds of polymers. Thus, there's an increasing tendency in recent years toward improving their toughness by producing composite fibres. This trend is expected to remain as the biggest challenge in their further development. There is also a necessity to establish a unified standard method to investigate mechanical flexibility of fibres.

Moreover, the trend for the development of smart textiles is to integrate or embed conducting fibres within common textile structures using facile knitting/braiding techniques to facilitate free and easy access to them while imparting a number of smart functionalities such as signalling, sensing, actuating, energy storage or information processing by creating hybrid systems. Some preliminary works have been carried out to study the incorporation of flexible conducting fibres into common textiles. However, integration of CPFs into the garments for practical applications is still a challenge.

4. Conclusions

Development of materials and methods for the preparation of conducting polymer fibres is an important enabling step towards their application, particularly in smart textiles. We have summarized the history of emergence of CPs, categories, preparation and spinning methods for the recent development of pristine and composite conducting polymer fibres as well as their current/future of applications. Wet spinning is the preferred method for preparing conducting polymer fibres. Electrospinning was also used widely to produce nanoscale nonwoven fibres. Due to the intractable nature of many conducting polymers, the first step to create fibres is the development of methods for the preparation of conducting polymer solutions. PAc was discovered in 1977 and was at the centre of attention for a time but its poor processability limited further development. PAni was the next conducting polymer of interest and drew much attention from the late 1980s, owing to its unique combination of processability and good electrical conductivity. It is readily soluble in emeraldine base and leucoemeraldine base forms, providing the opportunity to directly

spin fibres. However, such fibres displayed suboptimal properties due to their undoped state. This could be rectified by wet spinning the conducting emeraldine salt form from concentrated sulfuric acid. Better results were obtained using large molecule dopants that rendered the emeraldine salt form soluble in organic solvents. The highest conductivity values for PAni fibres were measured to be up to 150 S cm⁻¹. However, this value would be raised up to even 1500 S cm⁻¹ upon stretching or heating.54,95 The Young's moduli of these fibres were also reported to shift in the range of 0.5-13 GPa while stretched.57 Fibres prepared by such methods could be further improved by mechanical drawing and incorporation of CNTs. Similar approaches have been applied in the preparation of PPy fibres, while production of composite fibres have been focused on owing to the poor processability of PPy. The obtained electrical conductivities for polypyrrole fibres were appeared to be much lower compared to that of PAni fibres, up to the highest value of \sim 3 S cm⁻¹;⁶¹ however, higher Young's moduli was achievable with the maximum value of ~4.2 GPa.⁶² Polythiophene is readily available in the water soluble form of PEDOT : PSS, which may be readily wet-spun. PEDOT: PSS fibres indicated a better performance in contrast to the previously stated PAni and PPy fibres in terms of electrical conductivity and mechanical properties with the highest obtained conductivity of \sim 470 S cm⁻¹ and Young's moduli in the range of ~3.3-4.0 GPa.63,64

The greatest improvements in conducting polymer fibre mechanical strength and electrical conductivity have been achieved through the incorporation of CNTs. An enhanced electrical conductivity of \sim 750 S cm⁻¹ was determined for PAni fibres after addition of 0.3% w/w CNT.²⁴⁹ However, CNTs incorporation leads to relatively brittle fibres, with typical elongation at break values of less than 20%. Such brittleness is in contrast to common textile fibres such as nylons and polyesters, and limits the application of conducting polymer fibres. Therefore, the challenging task of improving the toughness of conducting polymer fibres needs to be a focus of future development. Although recent developments in CPFs appear extremely promising, there still remain challenges to improve their properties and performance to become adequate for practical and commercial applications.

Acknowledgements

This work was supported by funding from the University of Wollongong, Australian Research Council Centre of Excellence and Laureate Fellowships (G. G. Wallace) and the Australian Research Council under Discovery Early Career Researcher award (Javad Foroughi DE12010517). The authors would like to thank Mr Saber Mostafavian for his 3D set-up designs. The authors would also like to appreciate Dr George Tsekouras for his great help with critical revising and also Mr Sayamk Farajikh for his assistance.

References

1 D. Kumar and R. C. Sharma, *Eur. Polym. J.*, 1998, 34, 1053–1060.

- 2 H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1977, **16**, 578–580.
- 3 A. G. Macdiarmid, Angew. Chem., Int. Ed., 2001, 40, 2581–2590.
- 4 J. Foroughi, Development of novel nanostructured conducting polypyrrole fibres, PhD thesis, University of Wollongong, 2009, p. 210.
- 5 C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis,
 A. G. MacDiarmid, Y. W. Park and H. Shirakawa, *J. Am. Chem. Soc.*, 1978, 100, 1013–1015.
- 6 C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger,
 H. Shirakawa, E. J. Louis, S. C. Gau and
 A. G. MacDiarmid, *Phys. Rev. Lett.*, 1977, **39**, 1098–1101.
- 7 H. Derivatives, J. Louis and A. G. Macdiarmid, *J. Chem. Soc., Chem. Commun.*, 1977, **16**, 578–580.
- 8 T. C. Street and G. B. Clarke, *IBM J. Res. Dev.*, 1981, 25, 51–57.
- 9 G. Clark, Am. Econ. Rev., 2007, 90, 802-828.
- 10 G. G. Wallace, P. R. Teasdale, G. M. Spinks and L. A. P. Kane-Maguire, *Conductive electroactive polymers*, 2009.
- 11 J. E. Fischer, X. Tang, E. M. Scherr, V. B. Cajipe and A. G. MacDiarmid, *Synth. Met.*, 1991, **43**, 661–664.
- 12 L. Pan, H. Qiu, C. Dou, Y. Li, L. Pu, J. Xu and Y. Shi, Int. J. Mol. Sci., 2010, 11, 2636–2657.
- 13 J. Wang, C. Y. Wang, C. O. Too and G. G. Wallace, J. Power Sources, 2006, 161, 1458–1462.
- 14 C. Y. Wang, V. Mottaghitalab, C. O. Too, G. M. Spinks and G. G. Wallace, *J. Power Sources*, 2007, 163, 1105–1109.
- 15 A. Mazzoldi and D. Rossi, *Electro-active polymer fiber actuators polyelectrolyte gel fiber actuators conducting polymer fiber actuators*, 2003.
- 16 S. Kakuda, T. Momma and T. Osaka, *J. Electrochem. Soc.*, 1995, **142**, 1–2.
- 17 M. D. Irwin, D. A. Roberson, R. I. Olivas, R. B. Wicker and E. Macdonald, *Fibers Polym.*, 2011, 12, 904–910.
- 18 Y. Li, X. Y. Cheng, M. Y. Leung, J. Tsang, X. M. Tao and M. C. W. Yuen, *Synth. Met.*, 2005, 155, 89–94.
- 19 A. Granero, J. Razal, G. Wallace and M. Panhuis, J. Mater. Chem., 2010, 20, 7953–7956.
- 20 I. Cucchi, A. Boschi, C. Arosio, F. Bertini, G. Freddi and M. Catellani, *Synth. Met.*, 2009, **159**, 246–253.
- 21 S. Karamchandani, H. D. Mustafa, S. N. Merchant and U. B. Desai, *Sens. Actuators, B*, 2011, **156**, 765–772.
- 22 M. A. Mestrovic, Characterisation and Biomedical application of Fabric Sensors, Master's degree thesis, RMIT University, 2007, p. 162.
- 23 N. K. Guimard, N. Gomez and C. E. Schmidt, *Prog. Polym. Sci.*, 2007, **32**, 876–921.
- 24 X. Li, X. Hao, H. Yu and H. Na, *Mater. Lett.*, 2008, **62**, 1155–1158.
- 25 S. N. Khan, Electrospinning polymer nanofibers-electrical and optical Characterization, PhD thesis, Ohio University, 2007, p. 107.
- 26 T. Ahuja and D. Kumar, *Sens. Actuators, B*, 2009, **136**, 275–286.

- 27 J. R. Cárdenas, M. G. O. De França, E. A. De Vasconcelos,
 W. M. De Azevedo and E. F. Da Silva, *J. Phys. D: Appl. Phys.*, 2007, 40, 1068–1071.
- 28 C. Merlini, B. S. Rosa, D. Müller, L. G. Ecco,
 S. D. A. S. Ramôa and G. M. O. Barra, *Polym. Test.*, 2012,
 31, 971–977.
- 29 P. Chandrasekhar, *Conducting Polymers: Fundamentals and Applications*, Kluwer Academic Publishers, 1999.
- 30 G. G. Wallace and L. A. P. Kane-maguire, *Adv. Mater.*, 2002, 14, 953–960.
- 31 A. F. Diaz, K. K. Kanazawa and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 1979, 635–636.
- 32 G. M. Spinks, B. Xi, V. Truong and G. G. Wallace, Synth. Met., 2005, 151, 85–91.
- 33 J. Wang, C. O. Too, D. Zhou and G. G. Wallace, J. Power Sources, 2005, 140, 162–167.
- 34 Y. Lin and G. G. Wallace, *J. Controlled Release*, 1994, **30**, 137–142.
- 35 J. N. Barisci, R. Stella, G. M. Spinks and G. G. Wallace, Synth. Met., 2001, 124, 407–414.
- 36 L. A. Kane-Maguire, I. D. Norris and G. G. Wallace, Synth. Met., 1999, 101, 817–818.
- 37 L. A. P. Kane-maguire, A. G. Macdiarmid, I. D. Norris and G. G. Wallace, *Synth. Met.*, 1999, **106**, 171–176.
- 38 C. Wang, A. Ballantyne, S. Hall, C. Too, D. Officer and G. Wallace, J. Power Sources, 2006, 156, 610–614.
- 39 C. Liu, C. Lin, C. Kuo, S. Lin and W. Chen, *Prog. Polym. Sci.*, 2011, 36, 603–637.
- 40 C. Li, H. Bai and G. Shi, *Chem. Soc. Rev.*, 2009, **38**, 2149–2496.
- 41 M. Wan, Macromol. Rapid Commun., 2009, 30, 963-975.
- 42 J. Stejskal, I. Sapurina and M. Trchová, *Prog. Polym. Sci.*, 2010, 35, 1420–1481.
- 43 C. Laslau, Z. Zujovic and J. Travas-sejdic, *Prog. Polym. Sci.*, 2010, **35**, 1403–1419.
- 44 A. J. Heeger, Synth. Met., 2002, 125, 23-42.
- 45 B. Semire and O. A. Odunola, *Aust. J. Basic Appl. Sci.*, 2011, 5, 354–359.
- 46 B. Weng, R. L. Shepherd, K. Crowley, A. J. Killardb and G. G. Wallace, *Analyst*, 2010, 135, 2779–2789.
- 47 H. H. Kipphan, *Handbook of print media*, Springer Science & Business Media, 2001.
- 48 A. Earls and V. Baya, *Disruptive Manuf. Eff. 3D Print.*, 2014, p. 14.
- 49 T. C. Gomes, C. J. L. Constantino, E. M. Lopes, A. E. Job and N. Alves, *Thin Solid Films*, 2012, **520**, 7200–7204.
- 50 M. V. Kulkarni, S. K. Apte, S. D. Naik, J. D. Ambekar and B. B. Kale, *Sens. Actuators, B*, 2013, **178**, 140–143.
- 51 B. Weng, A. Morrin, R. Shepherd, K. Crowley, A. J. Killard, P. C. Innis and G. G. Wallace, *J. Mater. Chem. B*, 2014, 2, 793–799.
- 52 M. F. Mabrook, C. Pearson and M. C. Petty, *Sens. Actuators, B*, 2006, **115**, 547–551.
- 53 I. Zergioti, M. Makrygianni, P. Dimitrakis, P. Normand and S. Chatzandroulis, *Appl. Surf. Sci.*, 2011, 257, 5148–5151.

- 54 N. Farra, Development and Characterization of Conductive Polyaniline Fibre Actuators, Bachelor's degree thesis, University of Toronto, 2008, p. 40.
- 55 A. D. Jannakoudakis, P. D. Jannakoudakis, N. Pagalos and E. Theodoridou, *Electrochim. Acta*, 1993, **38**, 1559–1566.
- 56 K. T. Tzou and R. V. Gregory, Synth. Met., 1995, 69, 109-112.
- 57 B. R. Mattes, H. L. Wang and D. Yang, *Synth. Met.*, 1997, **84**, 45–49.
- 58 C. Woodings, Regenerated Cellulose Fibres, CRC Press, 2001.
- 59 M. N. Gupta, A. K. Sengupta and V. Kothari, *Manufactured Fibre Technology*, Springer Science & Business Media, 1997.
- 60 S. J. Pomfret, P. N. Adams, N. P. Comfort and A. P. Monkman, *Polym. J.*, 2000, **41**, 2265–2269.
- 61 J. Foroughi, G. M. Spinks, G. G. Wallace and P. G. Whitten, *Synth. Met.*, 2008, **158**, 104–107.
- 62 J. Foroughi, G. M. Spinks and G. G. Wallace, *Synth. Met.*, 2009, **159**, 1837–1843.
- 63 R. Jalili, J. M. Razal, P. C. Innis and G. G. Wallace, *Adv. Funct. Mater.*, 2011, 21, 3363-3370.
- 64 H. Okuzaki, Y. Harashina and H. H. Yan, *Eur. Polym. J.*, 2009, **45**, 256–261.
- 65 D. Zhang, Advances in Filament Yarn Spinning of Textiles and Polymers, Woodhead Publishing, 2014.
- 66 H. Wieden, J. Romatowski, F. Moosmueller and H. Lenz, Polyurethane spinning solutions containing ethylene diamine and bis-(4-aminophenyl)-alkane polyurethanes, US pat. 3485800 A, Bayer AG, Dec 23rd, 1969.
- 67 R. W. Moncrieff, Man-Made Fibres, Wiley, illustrate., 1970.
- 68 T. Huang, L. R. Marshall, J. E. Armantrout, S. Yembrick, W. H. Dunn, J. M. Oconnor, T. Mueller, M. Avgousti and M. D. Wetzel, Production of nanofibers by melt spinning, *US pat.* 8277711 B2, E I Du Pont De Nemours And Company, 2 Oct 2012.
- 69 J. Jia, MELT spinning of continuous filaments by cold air attenuation, PhD degree, Georgia Institute of Technology, 2010, p. 168.
- 70 B. Kim, V. Koncar, E. Devaux, C. Dufour and P. Viallier, Synth. Met., 2004, 146, 167–174.
- 71 D. H. Reneker and I. Chun, *Nanotechnology*, 1996, 7, 216–223.
- 72 Z. Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna, S. R. Zheng-Ming Huang, Y.-Z. Zhang and M. Kotaki, *Compos. Sci. Technol.*, 2003, 63, 2223–2253.
- 73 A. Ziebicki, *Fundamentals of Fibre Formation*, Wiley, London, 2010.
- 74 Y. Srivastava, M. Marquez and T. Thorsen, *Biomicrofluidics*, 2009, **3**, 12801.
- 75 J. Kameoka, R. Orth, Y. Yang, D. Czaplewski, R. Mathers, G. W. Coates and H. G. Craighead, *Nanotechnology*, 2003, 1124, 1124–1129.
- 76 T. S. Kang, S. W. Lee, J. Joo and J. Y. Lee, Synth. Met., 2005, 153, 61–64.
- 77 L. Dai, in *Intelligent Macromolecules for Smart Devices*, Springer Science & Business Media, 1975, vol. 1980, pp. 41–80.
- 78 A. Farcas and C. I. Simionescu, *Rev. Roum. Chim.*, 2006, 51, 1153–1156.

- 79 K. Akagi, G. Piao, S. Kaneko and K. Sakamaki, *Science*, 1998, 282, 1683–1686.
- 80 A. Pron, P. Rannou and Â. Synthe, *Prog. Polym. Sci.*, 2002, 27, 135–190.
- 81 D. E. Sliva, W. G. Selley, Continuous method for making spinnable polyacetylene solutions convertible to high strength carbon fiber, *US pat.* 3928516, General Electric Company, Schenectady, NY, Dec. 23rd, 1975.
- 82 G. T. Kim, M. Burghard, D. S. Suh, K. Liu, J. G. Park, S. Roth and Y. W. Park, *Synth. Met.*, 1999, **105**, 207–210.
- 83 N. Gospodinova and L. Terlemezyan, *Prog. Polym. Sci.*, 1998, 23, 1443–1484.
- 84 B. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, *Adv. Mater.*, 2000, **12**, 481–494.
- 85 A. A. Syed and M. K. Dinesan, Talanta, 1991, 38, 815-837.
- 86 S. Ramakrishnan, Resonance, 2011, 2, 48-58.
- 87 H. S. Kolla, S. P. Surwade, X. Zhang, A. G. Macdiarmid and S. K. Manohar, *J. Am. Chem. Soc.*, 2005, **127**, 16770–16771.
- 88 E. Peter Maziarz III, S. A. Lorenz, T. P. White and T. D. Wood, J. Am. Soc. Mass Spectrom., 2000, 11, 659–663.
- 89 S. Virji, J. Huang, R. B. Kaner and B. H. Weiller, *Nano Lett.*, 2004, 4, 491–496.
- 90 C. He, Y. Tan and Y. Li, J. Appl. Polym. Sci., 2003, 87, 1-4.
- 91 X. Zhang, R. Chan-Yu-King, A. Jose and S. K. Manohar, *Synth. Met.*, 2004, **145**, 23–29.
- 92 R. Pauliukaite, C. M. A. Brett and A. P. Monkman, *Electrochim. Acta*, 2004, **50**, 159–167.
- 93 E. Smela and B. R. Mattes, Synth. Met., 2005, 151, 43-48.
- 94 A. Mazzoldi, C. Degl'Innocenti, M. Michelucci and D. De Rossi, *Mater. Sci. Eng., C*, 1998, **6**, 65–72.
- 95 S. J. Pomfret, P. N. Adams, N. P. Comfort and A. P. Monkman, *Synth. Met.*, 1999, **101**, 724–725.
- 96 D. Yang, A. Fadeev, P. N. Adams and B. R. Mattes, in Smart Structures and Materials 2001: Electroactive Polymer Actuators and Devices, 2001, vol. 4329, pp. 59–71.
- 97 W. Lu and B. R. Mattes, Synth. Met., 2005, 152, 53-56.
- 98 X. Wang, J. Liu, X. Huang and L. Men, *Polym. Bull.*, 2008, **60**, 1–6.
- 99 N. C. S. U. Tushar K. Ghosh, T. Ghosh and M. Ramasubramanian, *Muscle Like Extruded Fiber Actuators*, 2009.
- 100 A. Andreatta, C. Yong, J. C. Chiang, A. J. Heeger and P. Smith, *Synth. Met.*, 1988, 26, 383–389.
- 101 C. H. Hsu, J. D. Cohen and R. F. Tietz, *Synth. Met.*, 1993, **59**, 37–41.
- 102 C. C. Han and R. L. Elsenbaumer, International Patent, WG92/11695, 1990.
- 103 S. Metals, Synth. Met., 1991, 41-43, 849-854.
- 104 B. R. Mattes, H.-L. Wang, Stable, concentrated solutions of high molecular weight polyaniline and articles therefrom, is patented in both US pat. (US6099907 A) and Europe (EP1008148 A1) invented by assigned to The Regents Of The University Of California, published on 16th Jun 1999 and May 29, 1997, respectively.
- 105 P. N. Adams, P. Devasagayam, S. J. Pomfret, L. Abell and A. P. Monkman, J. Phys.: Condens. Matter, 1998, 10, 8293– 8303.

- 106 Y. Chen, H. Zhao and B. Han, *Russ. J. Phys. Chem. A*, 2014, **88**, 2314–2317.
- 107 J. Huang, Pure Appl. Chem., 2006, 78, 15-27.
- 108 N. J. Pinto, A. T. Johnson, A. G. MacDiarmid, C. H. Mueller, N. Theofylaktos, D. C. Robinson and F. A. Miranda, *Appl. Phys. Lett.*, 2003, 83, 4244.
- 109 N. Ayu and K. Umiati, in ICITACEE, 2014, pp. 79-82.
- 110 C. M. A. Brett, R. Pauliukaite and A. P. Monkman, *Polyaniline Fibres as Substrates for Microsensors*, 2002, vol. 539.
- 111 A. Macagnano, E. Zampetti, S. Pantalei, M. Italia, C. Spinella and A. Bearzotti, in *CP1137*, Olfaction and Electronic Nose: Proceedings of the 13th International Symposium, 2009, pp. 373–377.
- 112 Y. Zhang, J. J. Kim, D. Chen, H. L. Tuller and G. C. Rutledge, *Adv. Funct. Mater.*, 2014, **24**, 4005–4014.
- 113 G. Jin, J. Norrish, C. Too and G. Wallace, *Curr. Appl. Phys.*, 2004, 4, 366–369.
- 114 F. D. Blum, S. K. Pillalamarri, L. K. Werake and J. G. Story, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 2006, 47, 2966.
- 115 L. K. Werake, J. G. Story, M. F. Bertino, S. K. Pillalamarri and F. D. Blum, *Nanomedicine*, 2005, **16**, 2833–2837.
- 116 X. Zhang and S. K. Manohar, J. Am. Chem. Soc., 2004, **126**, 12714–12715.
- 117 J. Huang and R. B. Kaner, *J. Am. Chem. Soc.*, 2004, **126**, 851–855.
- 118 U. Tamer, Ç. Kanbeş, H. Torul and N. Ertaş, *React. Funct. Polym.*, 2011, **71**, 933–937.
- 119 D. Li, J. Huang and R. B. Kaner, *Acc. Chem. Res.*, 2009, **42**, 135–145.
- 120 X. Zhang, W. Goux and S. Manohar, *J. Am. Chem. Soc.*, 2004, 126, 4502–4503.
- 121 A. Abdolahi, E. Hamzah, Z. Ibrahim and S. Hashim, *Materials*, 2012, 5, 1487–1494.
- 122 S. Xing, C. Zhao, S. Jing and Z. Wang, *Polym. J.*, 2006, 47, 2305–2313.
- 123 D. Han, H. J. Lee and S. Park, *Electrochim. Acta*, 2005, **50**, 3085–3092.
- 124 T. V. Vernitskaya and O. N. Efimov, *Russ. Chem. Rev.*, 1997, 443, 443–457.
- 125 A. Dall'olio, G. Dascola, V. Vacara and V. Bocchi, Resonance paramagnetique electronique et conductivite d'un noir d'oxypyrrol electrolytique, *CR Acad. Sci.*, 1968, **267**, 433-435.
- 126 J. Wu and J. Pawliszyn, J. Chromatogr. A, 2001, 909, 37-52.
- 127 D. Kim and Y. D. Kim, J. Ind. Eng. Chem., 2007, 13, 879-894.
- 128 C. J. Cui, G. M. Wu, H. Y. Yang, S. F. She, J. Shen, B. Zhou and Z. H. Zhang, *Electrochim. Acta*, 2010, 55, 8870–8875.
- 129 X. Yuan, X. Ding, C. Wang and Z. Ma, *Energy Environ. Sci.*, 2013, 1105–1124.
- 130 A. Mirabedini, J. Foroughi, T. Romeo and G. G. Wallace, Macromol. Mater. Eng., 2015, 300, 1217–1225.
- 131 E. W. H. Jager, C. Immerstrand, K. Magnusson, O. Inganas and I. Lundstrom, in Annual International IEEE-EMBS Special Topic Conference on Microtechnologies in Medicine & Biology, 2000, vol. c, pp. 58–61.

- 132 Z. B. Huang, G. F. Yin, X. M. Liao and J. W. Gu, Front. Mater. Sci., 2014, 8, 39–45.
- 133 H. Qin, A. Kulkarni, H. Zhang, H. Kim, D. Jiang and T. Kim, *Sens. Actuators, B*, 2011, **158**, 223–228.
- 134 S. Hamilton, M. J. Hepher and J. Sommerville, *Sens. Actuators, B*, 2005, **107**, 424–432.
- 135 B. E. Smela, Adv. Mater., 2003, 15, 481-494.
- 136 J. Foroughi, G. Spinks and G. Wallace, *Sens. Actuators, B*, 2011, **155**, 278–284.
- 137 P. Saville, Polypyrrole, Formation and Use, 2005.
- 138 N. M. Rowley and R. J. Mortimer, *Sci. Prog.*, 2002, **85**, 243–262.
- 139 C. Y. Kim, J. Y. Lee, D. Y. Kim, Soluble, Electroconductive polypyrrole and method for preparing the same, *US pat.* 005795953A, Korea Institute of Science and Technology. Seoul. Rep. of Korea, Aug 18, 1998.
- 140 G. J. Lee, S. H. Lee, K. S. Ahn and K. H. Kim, *J. Appl. Polym. Sci.*, 2002, **84**, 2583–2590.
- 141 E. J. Oh and K. S. Jang, Synth. Met., 2001, 119, 109-110.
- 142 Z. Qi and P. G. Pickup, Chem. Mater., 1997, 9, 2934-2939.
- 143 I. S. Chronakis, S. Grapenson and A. Jakob, *Polym. J.*, 2006, 47, 1597–1603.
- 144 T. Tian, J. Deng, Z. Xie, Y. Zhao, Z. Feng, X. Kang and Z. Gu, *Analyst*, 2012, **137**, 1846–1852.
- 145 E. M. Thurman and M. S. Mills, *Rapid Commun. Mass Spectrom.*, 1998, **12**, 988.
- 146 B. S. Li, C. W. Macosko and H. S. White, *Adv. Mater.*, 1993, 5, 575–576.
- 147 J. Foroughi, S. R. Ghorbani, G. Peleckis, G. M. Spinks,G. G. Wallace, X. L. Wang and S. X. Dou, *J. Appl. Phys.*, 2010, **107**, 103712.
- 148 M. A. De'Paoli, R. C. D. Peres and J. M. Pernaut, *J. Braz. Chem. Soc.*, 1990, **1**, 50–52.
- 149 J. Roncali, Chem. Rev., 1992, 92, 711-738.
- 150 T. Yamamoto, K. Sanechika and A. Yamamoto, *J. Polym. Sci.*, 1980, **18**, 9–12.
- 151 L. P. Dudek and J. W. P. Lin, *J. Polym. Sci.*, 1980, **18**, 2869–2873.
- 152 S. M. Unni, V. M. Dhavale, V. K. Pillai and S. Kurungot, J. Phys. Chem. C, 2010, **114**, 14654–14661.
- 153 A. M. Dadras and A. Entezami, *Iran. Polym. J.*, 1993, 3, 2–12.
- 154 X. Zhang, S. P. Surwade, V. Dua, R. Bouldin, N. Manohar and S. K. Manohar, *Chem. Lett.*, 2008, **37**, 526–527.
- 155 X. Zhang, A. G. Macdiarmid and S. K. Manohar, *Chem. Commun.*, 2005, 5328–5330.
- 156 H. Park, S. Ko, J. Park, J. Y. Kim and H. Song, *Sci. Rep.*, 2013, 3, 1–6.
- 157 M. Akerfeldt, *Electrically conductive textile coatings with PEDOT:PSS*, University of Boras, Faculty of Textiles, Engineering and Business, 2015, p. 46.
- 158 E. Environ, D. Alemu, H. Wei, K. Ho and C. Chu, *Energy Environ. Sci.*, 2012, **5**, 9662–9671.
- 159 X. Guo, X. Liu, F. Lin, H. Li, Y. Fan and N. Zhang, *Sci. Rep.*, 2015, **5**, 1–9.
- 160 M. M. Islam, A. T. Chidembo, S. H. Aboutalebi, D. Cardillo, H. K. Liu and E. Al, *Front. Mater. Sci.*, 2014, 2, 1–21.

- 161 Y. Zhang and K. S. Suslick, *Chem. Mater.*, 2015, 27, 7559–7563.
- 162 M. J. Sailor and C. L. Curtis, Adv. Mater., 1994, 6, 688-692.
- 163 H. Okuzaki and M. Ishihara, *Macromol. Rapid Commun.*, 2003, **24**, 261–264.
- 164 W. Baik, W. Luan, R. H. Zhao, S. Koo and K. Kim, *Synth. Met.*, 2009, **159**, 1244–1246.
- 165 T. Takahashi, M. Ishihara and H. Okuzaki, *Synth. Met.*, 2005, **152**, 73-76.
- 166 A. G. MacDiarmid, Curr. Appl. Phys., 2001, 1, 11-22.
- 167 P. V. Segonds and A. J. Epstein, *Synth. Met.*, 1991, 43, 1005–1008.
- 168 A. Mirmohseni, D. Salari and R. Nabavi, *Iran. Polym. J.*, 2006, **15**, 259–264.
- 169 R. H. Cruz-estrada and M. J. Folkes, *J. Mater. Sci.*, 2000, **35**, 5065–5069.
- 170 M. Li, Y. Guo, Y. Wei, A. G. Macdiarmid and P. I. Lelkes, *Biomaterials*, 2006, 27, 2705–2715.
- 171 I. D. Norris, M. M. Shaker, F. K. Ko and A. G. Macdiarmid, *Synth. Met.*, 2000, **114**, 109–114.
- 172 Y. Zhang and G. C. Rutledge, *Macromolecules*, 2012, 45, 4238–4246.
- 173 M. Gizdavic-Nikolaidis, S. Ray, J. R. Bennett, A. J. Easteal and R. P. Cooney, *Macromol. Biosci.*, 2010, **10**, 1424–1431.
- 174 S. H. Bhang, S. I. Jeong, T. Lee, I. Jun, Y. B. Lee, B. Kim and H. Shin, *Macromol. Biosci.*, 2012, **12**, 402–411.
- 175 Q. Yu, M. Wang, H. Chen and Z. Dai, *Mater. Chem. Phys.*, 2011, **129**, 666–672.
- 176 R. Fryczkowski, M. Rom and B. Fryczkowska, *Fibres Text. East. Eur.*, 2005, **13**, 141–143.
- 177 E. Devaux, V. Koncar, B. Kim, M. Rochery, C. Campagne and D. Saihi, *Trans. Inst. Meas. Control*, 2007, 29, 355–376.
- 178 Y. Wang, Y. Li, J. Feng and C. Sun, *Anal. Chim. Acta*, 2008, **619**, 202–208.
- 179 X. Jin, C. Xiao and W. Wang, Synth. Met., 2010, 160, 368-372.
- 180 J. Molina, M. F. Esteves, J. Fernández, J. Bonastre and F. Cases, *Eur. Polym. J.*, 2011, 47, 2003–2015.
- 181 S. Chandran and S. K. Narayanankutty, *Polym.-Plast. Technol. Eng.*, 2011, **50**, 37–41.
- 182 Q. Fan, X. Zhang and Z. Qin, *J. Macromol. Sci., Part B: Phys.*, 2012, **51**, 736–746.
- 183 S. Izwan, W. A. Wan, S. Hashim and M. Y. Yahya, *Compos. Interfaces*, 2012, **19**, 356–376.
- 184 X. Liu, W. Zhou, X. Qian, J. Shen and X. An, *Carbohydr. Polym.*, 2013, **92**, 659–661.
- 185 T. Takano, M. Tagaya and T. Kobayashi, *Polym. Bull.*, 2013, 70, 3019–3030.
- 186 X. Chen, H. Cai, Q. Tang, D. Liang, M. Wang and B. He, *Polym. Compos.*, 2013, **35**, 235–262.
- 187 D. Passeri, A. Biagioni, M. Rossi, E. Tamburri and M. L. Terranova, *Eur. Polym. J.*, 2013, **49**, 991–998.
- 188 P. Schmitz, C. Merlini, G. M. O. Barra, A. Silveira, T. Medeiros, S. D. A. S. Ram and A. Pegoretti, *Polym. Test.*, 2014, 38, 18–25.
- 189 S. Poyraz, I. Cerkez, T. S. Huang, Z. Liu, L. Kang, J. Luo and X. Zhang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 20025–20034.

- 190 C. Hsu, H. Shih, S. Subramoney and A. J. Epstein, *Synth. Met.*, 1999, **101**, 677–680.
- 191 Q. H. Zhang, Z. C. Sun, J. Li, X. H. Wang, H. F. Jin, X. B. Jing and F. S. Wang, *Synth. Met.*, 1999, **102**, 1198–1199.
- 192 Y. A. Ismail, S. R. Shin, K. M. Shin, S. G. Yoon, K. Shon, S. I. Kim and S. J. Kim, *Sens. Actuators, B*, 2008, **129**, 834– 840.
- 193 A. Soroudi and M. Skrifvars, *Preparation of melt spun* conductive polypropylene/polyaniline fibres for smart textile applications, 2008.
- 194 A. Soroudi and M. Skrifvars, *Polym. Eng. Sci.*, 2012, 1606–1612.
- 195 S. Mondal, U. Rana and S. Malik, *J. Appl. Mater. Interfaces*, 2015, 7, 10457–10465.
- 196 J. J. Alcaraz-espinoza, A. E. Cha, J. C. Medina-llamas,
 A. S. Andrade and C. P. De Melo, ACS Appl. Mater. Interfaces, 2015, 7, 7231–7240.
- 197 L. A. Mccullough, B. Dufour and K. Matyjaszewski, *Macromolecules*, 2009, **42**, 8129–8137.
- 198 S. Xing and G. Zhao, J. Appl. Polym. Sci., 2007, 104, 1987– 1996.
- 199 B. Grunden and J. O. Iroh, Polym. J., 1995, 36, 559-563.
- 200 O. Flores, A. Romo-Uribe, M. E. Romero-Guzman, A. E. Gonzalez, R. Cruz-Silva and B. Campillo, *J. Appl. Polym. Sci.*, 2009, **112**, 934–941.
- 201 F. Granato, A. Bianco, C. Bertarelli and G. Zerbi, *Macromol. Rapid Commun.*, 2009, **30**, 453–458.
- 202 S. Nair, S. Natarajan and S. Kim, *Macromol. Rapid Commun.*, 2005, **26**, 1599–1603.
- 203 H. Wang, N. Leaukosol and Z. He, *Cellulose*, 2013, **20**, 1587–1601.
- 204 H. H. Kuhn, W. C. Kimbrell, J. E. Fowler and C. N. Barry, *Synth. Met.*, 1993, 57, 3707–3712.
- 205 C. Forder, S. P. Armes, A. W. Simpson, C. Maggiore and M. Hawley, *J. Mater. Chem.*, 1993, 3, 563–569.
- 206 N. Balci, L. Topparet and E. Bayramlit, *Composites*, 1995, 26, 229–231.
- 207 T. Qiu, H. Xie and J. Zhang, J. Nanopart. Res., 2011, 13, 1175–1182.
- 208 X. Jin, W. Wang, L. Bian, C. Xiao, G. Zheng and C. Zhou, *Synth. Met.*, 2011, **161**, 984–989.
- 209 K. Firoz Babu, P. Dhandapani, S. Maruthamuthu and M. Anbu Kulandainathan, *Carbohydr. Polym.*, 2012, **90**, 1557–1563.
- 210 S. Maity and A. Chatterjee, J. Text. Sci. Eng., 2014, 4, 4-7.
- 211 D. S. Pramila Devi, P. K. Bipinbal, T. Jabin and S. K. N. Kutty, *Mater. Des.*, 2013, **43**, 337–347.
- 212 C. Merlini, S. Ramoa and G. M. O. Barra, *Polym. Compos.*, 2013, 537–543.
- 213 J. Foroughi, G. M. Spinks and G. G. Wallace, J. Mater. Chem., 2011, 21, 6421.
- 214 Y. Wang, K. Bian, C. Hu, Z. Zhang, N. Chen, H. Zhang and L. Qu, *Electrochem. Commun.*, 2013, **35**, 49–52.
- 215 K. S. U. Schirmer, D. Esrafilzadeh, B. C. Thompson, A. F. Quigley, R. M. I. Kapsa and G. G. Wallace, *J. Mater. Chem. B*, 2016, 4, 42–47.

- 216 C. Xu, P. Wang and X. Bi, *J. Appl. Polym. Sci.*, 1995, **58**, 2155–2159.
- 217 J. W. Cho and H. Jung, J. Mater. Sci., 1997, 32, 5371-5376.
- 218 A. Esfandiari, World Appl. Sci. J., 2008, 3, 470-475.
- 219 M. B. Gholivand, M. M. Abolghasemi and P. Fattahpour, *Anal. Chim. Acta*, 2011, **704**, 174–179.
- 220 A. Maziz, A. Khaldi, N. Persson and E. W. H. Jager, in *Proc.* of SPIE, 2015, vol. 9430, pp. 1–6.
- 221 Y. Srivastava, I. Loscertales, M. Marquez and T. Thorsen, *Microfluid. Nanofluid.*, 2007, 4, 245–250.
- 222 S. Sen, F. J. Davis, G. R. Mitchell and E. Robinson, *J. Phys.: Conf. Ser.*, 2009, **183**, 12–20.
- 223 S. Maity and A. Chatterjee, *J. Compos. Mater.*, 2015, **2015**, 1–6.
- 224 M. J. Hearn, I. W. Fletcher, S. P. Church and S. P. Armes, *Polym. J.*, 1993, **34**, 262–266.
- 225 S. N. Bhadani, M. Kumari, S. K. Sen Gupta and G. C. Sahu, *J. Appl. Phys.*, 1998, **64**, 1073–1077.
- 226 X. Lu, Q. Zhao, X. Liu, D. Wang, W. Zhang, C. Wang and Y. Wei, *Macromol. Rapid Commun.*, 2006, **27**, 430–434.
- 227 A. Mollahosseini and E. Noroozian, *Anal. Chim. Acta*, 2009, **638**, 169–174.
- 228 A. D. Kammerich, Y. Srivastava, K. N. Hargett, V. S. R. Harrison and J. F. Rubinson, *J. Electrochem. Soc.*, 2009, **156**, P68.
- 229 P. Olszowy, M. Szultka, T. Ligor, J. Nowaczyk and B. Buszewski, J. Chromatogr. B: Anal. Technol. Biomed. Life Sci., 2010, 878, 2226–2234.
- 230 S. Yow, T. Lim, E. Yim, C. Lim and K. Leong, *Polymers*, 2011, 3, 527–544.
- 231 D. Zhang, L. Luo, Q. Liao, H. Wang, H. Fu and J. Yao, *J. Phys. Chem. C*, 2011, **115**, 2360–2365.
- 232 J. Wang, H. Naguib and A. Bazylak, *Behavior and mechanics of multifunctional materials and composites*, 2012, vol. 8342, pp. 1–13.
- 233 Y. Yang, J. Wen, J. Wei, R. Xiong, J. Shi and C. Pan, *Appl. Mater. Interfaces*, 2013, 5, 6201–6207.
- 234 A. Malik, R. Abbasi and J. Militky, J. Chem. Eng., 2013, 7, 256–259.
- 235 S. Maity, A. Chatterjee, B. Singh and A. P. Singh, *J. Text. Inst.*, 2015, **5000**, 887–893.
- 236 S. Lee, B.-J. Yi, K.-Y. Chun, J. Lee, Y. T. Kim, E.-J. Cha and S. J. Kim, *J. Nanosci. Nanotechnol.*, 2015, **15**, 2537–2541.
- 237 I. F. Perepichka, M. Besbes, E. Levillain, M. Salle and J. Roncali, *Chem. Mater.*, 2002, **14**, 449–457.
- 238 E. Zampetti, S. Pantalei, A. Muzyczuk, A. Bearzotti, F. D. Cesare, C. Spinella and A. Macagnano, *Sens. Actuators, B*, 2013, **176**, 390–398.
- 239 D. Esrafilzadeh, J. Razal, S. Moulton, E. Stewart and G. Wallace, *J. Controlled Release*, 2013, **169**, 313–320.
- 240 Y. Ding, M. A. Invernale and G. A. Sotzing, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1588–1593.
- 241 M. Stra and A. Maria, Text. Res. J., 2013, 83, 618-627.
- 242 Y. Liu, X. Li and J. C. Lu, *J. Appl. Polym. Sci.*, 2013, **130**, 370–374.
- 243 M. Z. Seyedin, J. M. Razal, P. C. Innis and G. G. Wallace, *Adv. Funct. Mater.*, 2014, 24, 2957–2966.

- 244 S. Tsukada, H. Nakashima and K. Torimitsu, *PLoS One*, 2012, 7, 1–10.
- 245 H. Miura, K. Morohoshi, J. Okada, B. Lin and M. Kimura, *Cellul. Ind.*, 2010, **66**, 280–283.
- 246 R. Y. Suckeveriene, E. Zelikman, M. Narkis and L. Nicolais, in *Wiley Encyclopedia of Composites*, John Wiley & Sons, Inc., 2011.
- 247 V. Mottaghitalab, B. Xi, G. M. Spinks, G. G. Wallace and G. G. Wallace, *Synth. Met.*, 2006, **156**, 796–803.
- 248 V. Mottaghitalab, G. M. Spinks and G. G. Wallace, *Synth. Met.*, 2005, **152**, 77–80.
- 249 V. Mottaghitalab, G. M. Spinks and G. G. Wallace, *Polym. J.*, 2006, **47**, 4996–5002.
- 250 G. M. Spinks, V. Mottaghitalab, M. Bahrami-samani,
 P. G. Whitten, G. G. Wallace, B. G. M. Spinks,
 V. Mottaghitalab, M. Bahrami-samani, P. G. Whitten and
 G. G. Wallace, *Adv. Mater.*, 2006, 2522, 637–640.
- 251 G. M. Spinks, S. R. Shin, G. G. Wallace, P. G. Whitten, I. Y. Kim, S. I. Kim, S. J. Kim and S. Jeong, *Sens. Actuators, B*, 2007, **121**, 616–621.
- 252 Y. J. Kim, M. K. Shin, S. J. Kim, S.-K. Kim, H. Lee, J.-S. Park and S. I. Kim, *J. Nanosci. Nanotechnol.*, 2007, 7, 4185–4189.
- 253 Y. Lin and T. Wu, J. Appl. Polym. Sci., 2012, 126, E123-E129.
- 254 Z. Zhang, F. Zhang, X. Jiang, Y. Liu, Z. Guo and J. Leng, *Fibres Polym.*, 2014, **15**, 2290–2296.
- 255 J. Fan, M. Wan, D. Zhu, B. Chang, Z. Pan and S. Xie, *Synth. Met.*, 1999, **102**, 1266–1267.
- 256 J. Fan, M. Wan, D. Zhu, B. Chang, Z. Pan and S. Xie, *J. Appl. Polym. Sci.*, 1999, **74**, 2605–2610.
- 257 Y. Ju, G. Choi, H. Jung and W. Lee, *Electrochim. Acta*, 2008, 53, 5796–5803.
- 258 J. Foroughi, G. M. Spinks, S. R. Ghorbani, M. E. Kozlov, F. Safaei, G. Peleckis, G. G. Wallace and R. H. Baughman, *Nanoscale*, 2012, 4, 940–945.
- 259 R. Jalili, J. M. Razal and G. G. Wallace, Nature, 2013, 3, 1-7.
- 260 M. S. S. Dorraji, I. Ahadzadeh and M. H. Rasoulifard, *Int. J. Hydrogen Energy*, 2014, **39**, 9350–9355.
- 261 M. K. Shin, Y. J. Kim, S. I. Kim, S. Kim and H. Lee, *Sens. Actuators, B*, 2008, **134**, 122–126.
- 262 B. Qiu, C. Xu, D. Sun, H. Wei, X. Zhang, J. Guo and Q. Wang, *RSC Adv.*, 2014, 4, 29855–29865.
- 263 H. Chen, X. Cai and X. Bi, J. Thermoplast. Compos. Mater., 2014, 27, 1065–1073.
- 264 D. Wei, D. Cotton and T. Ryhänen, *Nanomaterials*, 2012, 2, 268–274.
- 265 R. Pauliukaite, C. M. A. Brett and A. P. Monkman, *Electrochim. Acta*, 2004, **50**, 159–167.
- 266 A. Mirabedini, J. Foroughi, B. Thompson and G. G. Wallace, *Adv. Eng. Mater.*, 2015, **18**, 284–293.
- 267 S. Seyedin, J. M. Razal, P. C. Innis, A. Jeiranikhameneh, S. Beirne and G. G. Wallace, ACS Appl. Mater. Interfaces, 2015, 7, 21150–21158.
- 268 J. M. Chem, K. Jost and Y. Gogotsi, *J. Mater. Chem. A*, 2014, 2, 10776–10787.
- 269 L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy,H. Sun and C. Gao, *Nat. Commun.*, 2014, 5, 1–10.

- 270 D. Yu, K. Goh, H. Wang, L. Wei, W. Jiang, Q. Zhang, L. Dai and Y. Chen, *Nat. Nanotechnol.*, 2014, **9**, 555–562.
- 271 Z. Xu and C. Gao, Acc. Chem. Res., 2014, 47, 1267-1276.
- 272 Z. Li, Z. Liu, H. Sun and C. Gao, *Chem. Rev.*, 2015, **115**, 7046-7117.
- 273 B. Fang, L. Peng, Z. Xu and C. Gao, *ACS Nano*, 2015, **9**, 5214–5222.
- 274 T. F. Otero and J. M. Sansinena, Adv. Mater., 1998, 10, 491-494.
- 275 A. Mirmohseni, M. S. S. Dorraji and M. G. Hosseini, *Electrochim. Acta*, 2012, **70**, 182–192.
- 276 S. J. Wang, Y. Geng, Q. Zheng and J. Kim, *Carbon*, 2010, **8**, 1815–1823.

- 277 S. Li, K. Shu, C. Zhao, C. Wang, Z. Guo, G. Wallace and H. K. Liu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 16679–16686.
- 278 B. A. F. Quigley, J. M. Razal, B. C. Thompson, S. E. Moulton, M. Kita, E. L. Kennedy, G. M. Clark, G. G. Wallace and R. M. I. Kapsa, *Adv. Mater.*, 2009, **21**, 1–5.
- 279 G. G. Wallace, G. M. Spinks, A. P. Leon and P. R. Teasdale, Conductive Electroactive Intelligent Materials Systems, 2003.
- 280 D. K. Cullen, A. R. Patel, J. F. Doorish, D. H. Smith and B. J. Pfister, *J. Neural. Eng.*, 2008, 5, 374–384.
- 281 L. Xia, Z. Wei and M. Wan, *J. Colloid Interface Sci.*, 2010, 341, 1–11.