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

Azadehsadat Mirabedini
University of Wollongong, am707@uowmail.edu.au

Javad Foroughi
University of Wollongong, foroughi@uow.edu.au

Gordon G. Wallace
University of Wollongong, gwallace@uow.edu.au

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Abstract

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.

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Developments in Conducting Polymer Fibres: From Established Spinning Methods toward Advanced Applications

Azadeh Mirabedini [a], Javad Foroughi[*a], Gordon G. Wallace[*a]

Inherently 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 of applications of them while focus on spinning methods related to conducting polymer fibres.

1. INTRODUCTION

1.1. Historical Background

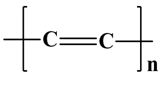
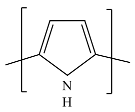
Although polymers have traditionally been considered to be electrical insulators, inherently conducting polymers (ICPs) were shown to exhibit semiconducting behaviour not long ago.[1,2] The fundamental feature of all conducting polymers is their extended conjugated π-system along the polymer backbone, which leads to metal-like electronic, magnetic and optical properties, while properties commonly associated with conventional polymers, such as flexibility, are maintained.[3,4] 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 so-called "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 engineering[19,20] to biomedical monitoring[4,21–23] and also diagnosis and treatment (including controlled drug delivery).[24–28]

1.2. Inherently Conducting Polymers

ICPs were discovered in 1977 with the 109 times increase in electrical conductivity (σ) of polyacetylene (PAc) through halogen doping to as high as 105 Scm^{-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, MacDiarmid and Heeger.[3,29] 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 **Figure 1**. The most significant conducting polymers with regard to technological fibres are PAni, PPy, PTh and PEDOT.

	
PAc	**PPy**

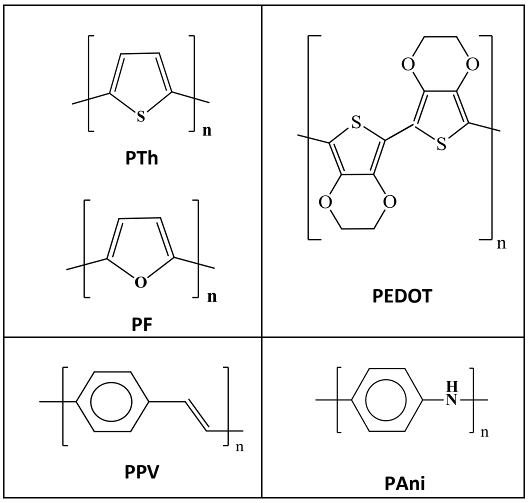


Figure 1 Inherently conducting polymer structures represented in their undoped forms.

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 energy characteristics. Printing technologies that require a printing plate are known as conventional methods and include lithography (offset), gravure, letterpress and screen-printing. 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 3D-printing 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 dry-wet 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 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 **Figure 2**.

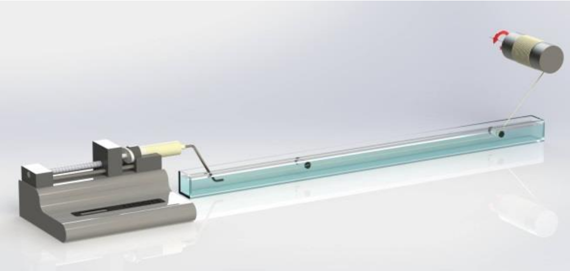


Figure 2 Schematic of a Lab scale wet spinning line.

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 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 ($2.9\times10{-}7$ Scm^{-1} with 40% wt. PPy). A schematic of melt spinning is presented in **Figure 3**.

Figure 3 Schematic of melt spinning.

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 dry-spinning 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 (**Figure 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 Scm^{-1}.[76]

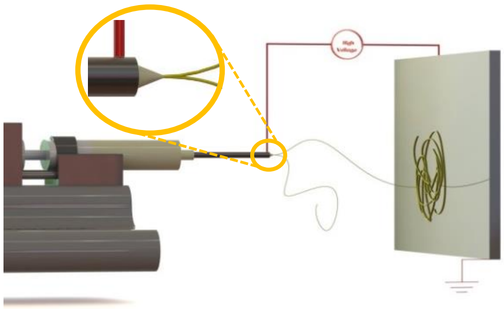


Figure 4 Schematic of electrospinning.

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 fibres[79] under an asymmetric reaction field consisting of chiral nematic liquid crystal. The prepared PAc helical fibrillar structure (**Figure 5**) may be considered as the only such structure to be reported so far. The relatively high electrical conductivities of ~1500-1800 Scm^{-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]

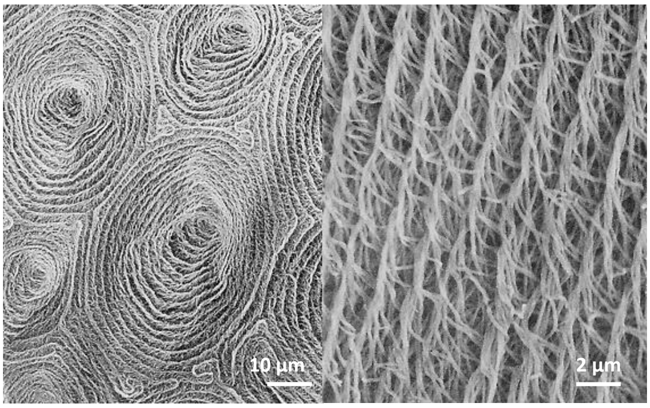


Figure 5 Scanning electron micrographs (at different magnifications) of helical polyacetylene films.[79] Reproduced with permission.[79] Copyright© 1998, American Association for the Advancement of Science

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 sp^2 hybridised state) or amine (sp^3 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 (**Figure 6**). 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.

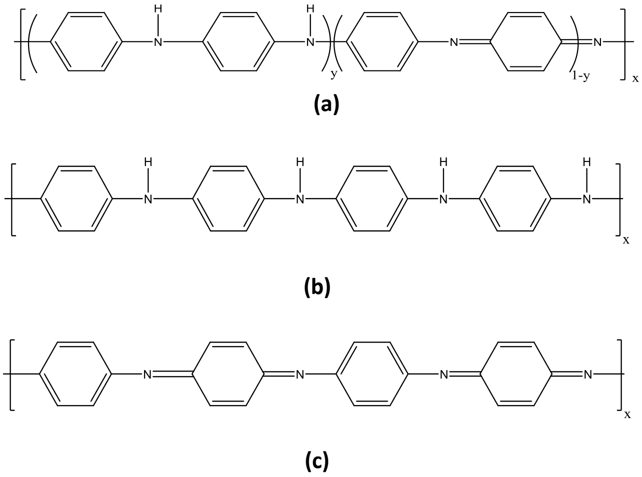


Figure 6 (a) emeraldine(y=0.5), (b) leucoemeraldine and (c) pernigraniline oxidation states of polyaniline.

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 Scm^{-1} and 157.8 Scm^{-1} of stretched fibres that had been doped with aqueous H2SO4 and HC1, respectively. To overcome the fast gelation of PAni, researchers found that selected Lewis-base organic solvents have a better solvency compared to N-methyl-2-pyrrolidinone (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) (**Figure 7**).[57,104]

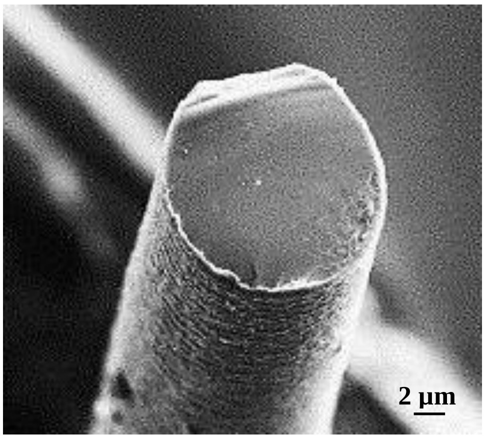


Figure 7. Scanning electron micrographs of cross-section of wet-spun polyaniline fibre[14] Reproduced with permission from Ref. [14] Copyright© 2006, Elsevier.

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 de-doping, 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-l-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 nano-sized PAni fibres.[90,91,106–109] Cárdenas *et al* were pioneers in the successful use of electrospinning to produce PAni nanofibres.[27] 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.

Table 1 Summary of polyaniline fibre production using different methods.

No.	**Dopants used**	**Focus of the resaerch**	**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 Scm^{-1}		100
2	NMP	Preparation of concentrated (10-25%) spinnable solutions of PAni in the emeraldine base form for fibre spinning	Dry-jet wet spinning	H_2SO_4 and HC1 are 320.5 and 157.8 Scm^{-1},	average tenacity of 3.9 gpd (~400 MPa),	101
3	NMP and DMPU	Improvement of solution stability and spinnability of concentrated PAni solutions	Wet spinning (DMPU, NMP, NMP/LICl)	---	Approaching that of Nylon6	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} Scm^{-1}-stretched acetic acid doped 10^{-6} Scm^{-1}-unstretched acetic acid doped ~1 Scm^{-1}- HCl and BPA doped	YM* 0.55-13.1 GPa US* ~2-9%	57
5	AMPSA	Production of PAni fibres A new acid processing route to produce in a one-step wet spinning process	Wet spinning (acetone, butyl acetate and 4-methyl-2-pentanone)	Max. 990 Scm^{-1}	YM 0.2 GPa UTS 50 MPa	95
6	AMPSA	Measuring electrical and mechanical properties of wet-spun PAni fibres in various coagulation solvents	Wet spinning (DCA)	70–150 Scm^{-1}	YM 40–60 MPa UTS 20–60 MPa	60
7	$HClO_4$	The development of a linear actuator prototypebased on PAni fibres	Wet spinning (water)	1-3 Scm^{-1}	YM ~2-3 MPa.	86
8	AMPSA	Study the processing routes for preparation of conducting PAni fibres	Wet spinning (acetone)	900-1500 Scm^{-1}	YM 0.2 GPa UTS* 97 MPa US ~550%	1
9	AMPSA	Study the temperature dependence of conductivity behaviour of the fibres	Wet spinning (acetone)	760-1060 Scm^{-1} at 363˚K	---	54
10	AMPSA	Introducing a new one-step acid-solution processing route for production of PAni fibres	Wet spinning (dichloroacetic acid)	70–150 Scm^{-1}	YM 40–60 MPa UTS 20–60 MPa US ~500%	29
11	NMP containing heptamethyleneimine as a gel inhibitor	Controlling macrovoid formation in wet-spun PAni fibres	Wet spinning (water)	---	YM 550-900 MPa UTS 5.9-12.8 MPa US ~1.1-1.45%	249
12	AMPSA	Electrochemically characterisation of PAni fibre microelectrodes for the first time	Wet spinning (dichloroacetic acid)	+0.20 to +0.60V versus SCE	---	30
13	CSA	Study the influence of dopants and cis-1,2-ethenesulfonate family of twin-tailed surfactants on properties of PAni nanofibre	Interfacial polymerisation	~ 1–5 Scm^{-1}	---	91
14	-	Using the electrospinning technique to produce sub-micron fibres of pure PAni	Electrospinning (acetone bath placed on the electrode)	10^{-3}–10^{2} Scm^{-1}	---	27
15	Sulfonated b-cyclodextrin and sulfonated a-cyclodextrin	Preparation and characterisation of PAni nanofibres containing sulfonated cyclodextrin group	Interfacial polymerisation	3.2x10^{-2}-8.5x10^{-3} Scm^{-1}	---	4
16	HCSA	Electrospinning and Evaluating PAni fibers doped with different levels of HCSA evaluated as chemiresistive gas sensors	Coaxial electrospinning	Up to 50 ± 30 Scm-1	---	112
17	APS	Controlling the morphological structure of the synthesized fibers by tuning the reaction time	Self-assembly process	Electroactive -0.6V- +0.3V	---	106

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),[113,114] chemical polymerisation (with prevention of secondary polymer growth),[115–118] nanofibre seeding through interfacial polymerisation,[119–121] 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.[122,123] 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 Scm^{-1} electrical conductivity, by electrolysis of a pyrrole solution in the presence of sulphuric acid in 1968.[124] 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 Scm^{-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.[123] 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.[123]

PPy demonstrates high electrical conductivity, good electrochemical properties, strong adhesion to substrates and thermal stability.[89,125] The heteroatomic and extended π-conjugated backbone structure of PPy provides it with chemical stability and electrical conductivity, respectively.[4,124] PPy exhibits a wide range of surface electrical conductivities (10–3 Scm^{-1} < σ < 100 Scm^{-1}) depending on the functionality and substitution pattern of the monomer and the nature of the counterion or dopant.[126] Not surprisingly therefore PPy has already been applied in a wide variety of areas such as rechargeable lithium batteries,[16,127] low temperature fuel cell technology,128 medical applications,[129,130] and volatile organic compound detection.[131,132] It has also been investigated as a material for "artificial muscles" that would offer numerous advantages over traditional motor actuation.[133,134]

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 a radical cation (polaron) or a dication (bipolaron), as depicted in **Figure 8**. In general, small anionic species are incorporated into the PPy chains upon oxidation and are expelled upon reduction in order to maintain charge neutrality.[124]

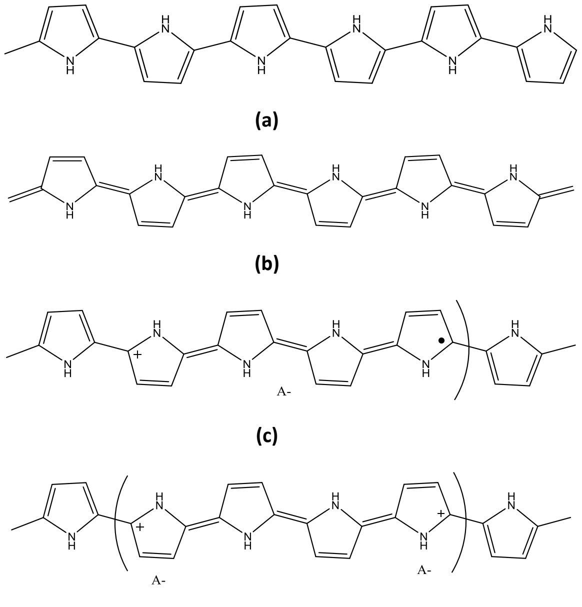


Figure 8 Chemical structures of polypyrrole in neutral (a) aromatic and (b) quinoid forms, and in oxidised (c) polaron and (d) bipolaron forms.

PPy usually takes the form of an intractable powder following chemical polymerisation and an insoluble film following electropolymerisation.[135] PPy prepared by conventional methods is insoluble in most organic solvents.[61,136] 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.[135] 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.[135] Another technique that has proven successful has been the use of long chain surfactant dopants such as sodium dodecyl benzene sulfonate (DDS),[137,138] di(2-ethylhexyl) sulfosuccinate sodium salt (DEHS),[139] and polystyrene sulfonate.[140] 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).[135]

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 µm and conductivity of ca. 0.5 Scm^{-1}. Chronakis *et al* used a different dopant and oxidant to similarly electrospun PPy nanofibres with diameters ranging between 70–300 nm.[141] 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.[142,143]

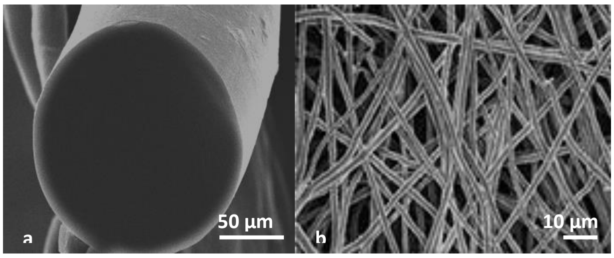


Figure 9 Scanning electron micrographs of (a) wet-spun polypyrrole fibre cross-section61 and (b) polypyrrole hollow fibres polymerised under ultrasonication.142 Reproduced with permission from Ref. 53 and 125. Copyright© 2008 and 2012; Elsevier and The Royal Society of Chemistry Publishing, respectively.

Few reports exist that consider the wet spinning of soluble PPy into continuous fibres, despite initial attempts.[144] 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 (**Figure 9**) through wet spinning,[61] which showed electrical conductivity of ~3 Scm^{-1} and elastic modulus of ~1.5 GPa. Later on the mechanical and electrical properties of these fibres were also studied.[145] 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**.

Table 2 Summary of previous studies into the preparation of polypyrrole fibres.

No.	Dopants used	Focus of the resaerch	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 polymerisation)	20 Scm^{-1}	---	[250]
2	DBSA as dopant,APS as the oxidant	Fabrication of electrically conducting PPy nonwoven web	Electrospinning	0.5 Scm^{-1}	---	[76]
3	DEHS	Fabrication of electrically conducting PPy	Electrospinning	2.7x10^{-2} Scm^{-1}	---	[141]
4	DEHS	Fabrication of continuous PPy fibre	Wet spinning (dichlroacetic acid (DCAA))	~3 Scm^{-1}	YM 1.5GPa UTS 25MPa US 2%	[61]
5	DEHS	Effect of synthesis conditions on the properties of wet spun PPy fibre	Wet spinning	---	YM 4.2GPa UTS 136MPa US 40% at 100°C	[62]
6	DEHS	Investigation of mechanical and the electrical properties of PPy fibres	Wet spinning	60<T<200, 566.8 Scm^{-1} T<60, 419.9 Scm^{-1}	YM ~4.2 GPa UTS 136 MPa US 5%	[145]

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 **Figure 10**).

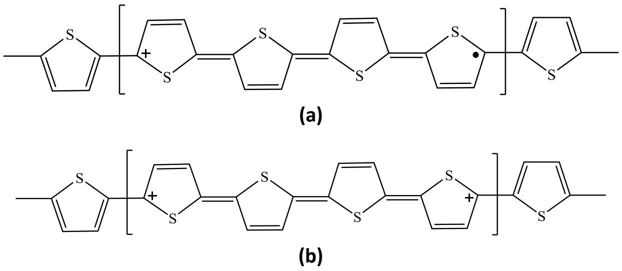


Figure 10 The mesomeric structures of polythiophene (a) polaron and (b) bipolaron.

PThs have been prepared since the 1980s by means of two main routes, namely chemical, and cathodic or anodic electrochemical synthesis.[146] The first chemical synthesis using metal-catalysed polymerisation of thermostable 2,5-dibromothiophene was reported by two research groups independently.[147,148] Yamamoto *et al* also reported on the polycondensation of 2,5-dibromothiophene catalysed by Ni(bipy)Cl_2.[147] Lin and Dudek have attempted several catalytic systems such as Ni, Pd, Co, and Fe salts.[148] 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.[146]

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. [149] This combined with favourable electrical and optical properties has led to the application of PThs in electrochromic displays, protection of semiconductors against photocorrosion, and energy storage systems.[150] 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.[151]

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.[152] PEDOT is characterised by stability, high electrical conductivity (up to 1000 Scm^{-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 resulting stable dark-blue aqueous dispersion of PEDOT:PSS is now commercially available and applied in antistatic coatings,[153] electrode materials,[154] organic electronics,[155] transparent electrodes, capacitors,[156] touchscreens, organic light-emitting diodes, microelectrodes and sensors.[152,157]

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.[158] Okuzaki and Ishihara later reported the first preparation of PEDOT:PSS microfibres via wet spinning with acetone as the coagulant (Figure11(a)),[159] where the effects of spinning conditions on fibre diameter (which ranged between 180-410μm), 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.[157] PEDOT nanofibres with diameters ranging between 100–180 nm were later produced using vanadium pentoxide nanofibres by a one-step nanofibre seeding method.[152] 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.[160] Shortly thereafter, Okuzaki *et al* fabricated highly conducting PEDOT:PSS microfibres with 5 μm diameter and up to 467 Scm^{-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 Scm^{-1} to 467 Scm^{-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 (**Figure 11**) 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 Scm^{-1} were achieved.[63] **Table 3** summarises efforts made in the preparation of PEDOT: PSS fibres.

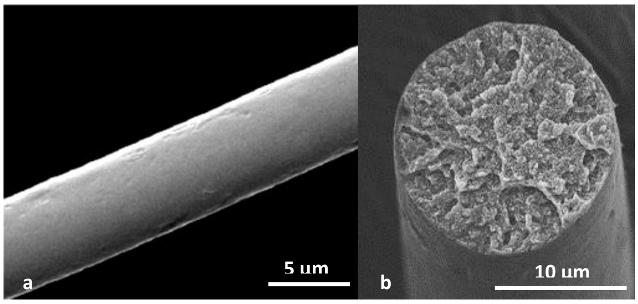


Figure 11 Scanning electron micrographs of (a) fibre surface of first wet-spun PEDOT:PSS microfibre,64 (b) cross-section of PEDOT:PSS fibre spun into acetone.63 Reproduced with permission from Ref. 55 and 56, Copyright© 2008 and 2011, Science Direct and 2011; WILEY-VCH Verlag GmbH & Co. , respectively.

Table 3 Summary of efforts made in the preparation of PEDOT: PSS fibres.

No.	Dopants used	Focus of the reseaerch	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)	~10^{-1} Scm^{-1}	YM 1.1 ± 0.3 GPa UTS 17.2 ± 5.1MPa US 4.3 ± 2.3%	159
2	poly(4-styrenesulfonate)	Fabrication microfibres of PEDOT:PSS	Wet spinning (acetone)	0.4-1 Scm^{-1}		251
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 Scm^{-1} (after post-treatment)	YM 4.0 GPa UTS130 MPa	64
4	Boron trifluoride	Synthesis of highly conducting poly(3,4-ethylenedioxythiophene) fibre by simple chemical polymerisation	*In-situ* polymerisation	In the range of 150–250 Scm^{-1}	---	160
5	---	Production of continuous PEDOT:PSS in both acetone/ IPA coagulation bathes	Wet spinning (acetone and isopropanol (IPA))	<264 Scm^{-1}	IPA: YM 3.3 ± 0.3 GPa UTS 125 ± 7 MPa US 15.8 ± 1.2% Acetone: YM 2.5 GPa UTS 98 MPa US 12.5%	63

2.2. Composite Conducting Fibres

Following the discovery of conducting polymers in 1977,[1,161] 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.[162] Segonds and Epstein prepared composite fibres from poly(paraphenylenediamine) (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.[162] 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-w-aminoundecanoyle in concentrated H_2S0_4. These fibres showed high strength and relatively high electrical conductivity (~10^{-7} Scm^{-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.[90,163,164] The highest electrical conductivity was stated from a wet-spun composite PAni fibre (~1000 Scm^{-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.[165] 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.[166] As-spun fibres demonstrated electrical conductivities in the order of ~10-2 Scm^{-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.[111,167] Nanofibrillar blends of a copolymer of PAni and benzoic acid and poly (lactic acid) (PLA) were also used as tissue engineering scaffolds.[168] Uniform electrospun fibres of PAni/poly[(L-lactide)-co-(e-caprolactone)] were developed for electrically conducting, engineered nerve grafts.[169] Electrospinning was also used to prepare photocatalytically active TiO_2/PAni composite fibres (**Figure 12(a)**).[170]

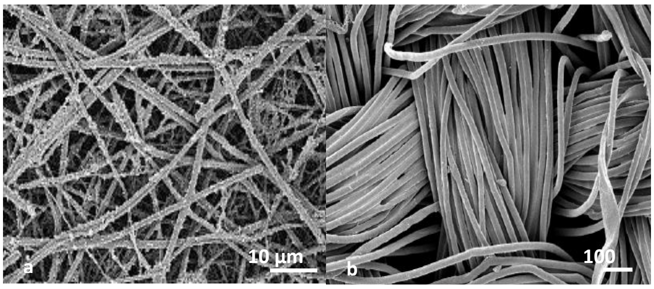


Figure 12 Scanning electron micrographs of (a) TiO_2/ polyaniline composite fibres 170 and (b) polyester fibres coated with polyaniline.171 Reproduced with permission from Ref. 148 and 149. Copyright© 2011and 2005; Elsevier and University of Bielsko-Biala, respectively.

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) (**Figure 12(b)**),[171] although no conductivity values were reported. In subsequent efforts, ultra-high molecular weight polyethylene, stainless steel, polycaprolactam and polyester were used as substrates on which a layer of PAni was coated.[172–175] *In-situ* oxidative polymerisation was used to prepare PAni-coated short nylon/natural rubber fibres,[176] while researchers have also employed this method to prepare conducting fibres based on polyurethane, kenaf, polyacrylamide, cellulose, coconut, Poly(methyl methacrylate) and detonation nanodiamond fibre substrates.[177–183] Recently, Polyaniline Nanofibre/ Silver Nanoparticle Composite Networks were prepared via well-known seeding polymerisation method with reported electrical conductivities in the range of 2×10^{-3} to 0.196 Scm^{-1} applied as an antibacterial agent.[184]

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.

Table 4 Summary of research concerning composite polyaniline fibres.

No.	Spinning solution blend	Focus of the resaerch	Sythesis method	Reported Conductivity / Conduction Potential Window	Mechanical properties	Ref.
1	PAni /PPD-T /H_2SO_4 spin dope	Preparation of composite fibres of poly(paraphenylenediamine) - terephthalic acid and emeraldine salt	Wet spinning (water)	---	YM* 62GPa UTS* 28GPa	[162]
2	Lyotropic PAni/poly(p-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 ~80˚C)	~0.1 Scm^{-1} (30% wt. PAn)	YM 270GPa	[252]
3	PAni/ poly-ω-aminoundecanoyle	Preparation of conducting PAni / poly-o-aminoundecanoyle fibre	Wet spinning (concentrated H_2SO_4)	~10^{-7} Scm^{-1} (5% wt. PAn)	---	[253]
5	PAni/ HCSA/polyethylene oxide blends	Electrostatic fabrication of ultrafine conducting fibres: PAni/polyethylene oxide blends	Electrospinning	~10^{-4}-10^{-1} Scm^{-1} (~20%-100% wt. Pan.HCSA)	---	[166]
4	PAni/polystyrene-polybutadiene-polystyrene (SBS)	Production of electrically conducting fibres in PAN-SBS blends	capillary extruded	~10^{-4} Scm^{-1} (~20% wt. PAn)	---	[164]
6	HCSA/PAni /polyethylene oxide (PEO)	Experimental observation of FET behavior in doped PAni/polyethylene oxide PAni/PEO nanofibre	Electrospinning	~10^{-3} Scm^{-1}	---	[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 × 10^{-7} Scm^{-1} (40% wt. PPy)	---	[70]
8	PAni doped with DBSA	Early attempts to obtain polyester (PET) fibres with antielectrostatic properties	Coating (fibres were padded with Pan.)	---	---	[171]
9	EB powder was dissolved in N-methyl-2-pyrrolidinone (NMP) to form a 5 wt.% solution	Actuation of PAni(AMPS) fibres	Wet spinning (2-butanone)	~1000 Scm^{-1} (200% stretched fibres)	Poor!	[93]
10	PAni/Naylon 6 in both concentrated sulphuric formic acids	Investigation on the coagulation rate of PAni/Naylon 6 fibre in different acids and the influence of Li_2SO_4 on mechanical properties of the fibres	Wet spinning (Li_2SO_4)	Electrical resistance 0.665-0.015 $\Omega.Cm^{-1}$ (~5-25% wt. PAn)	Improved using Li_2SO_4 in the bath	[163]
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) yarns	coating	~10^{-1}	---	[172]
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 *in-situ* oxidative polymerisation	2.856×10^{-2} Scm^{-1}	US* 0.39%	[254]
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	---	---	[255]
14	PAni film was deposited on the surface of stainless steel from H_2SO_4/aniline solution	Extraction of the target analytes from aqueous benzene derivatives systems in water samples using coated stainless steel with PAn	Coating	---	---	[173]
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 sensing.	Electrospinning	---	---	[111]
16	Poly(L-lactide-co-3-caprolactone)(PLCL)/PAni	Composite fibres of poly(L-lactide-co-3-caprolactone)(PLCL)/PANI for the culture of PC12 cells	Electrospinning	~0.1-0.15 Scm^{-1}	UEB*- 160±14.4% UTS* 15±3 MPa	-[169]
17	Poly(aniline-co-3-aminobenzoic acid)/HCl/ poly(aniline-co-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 engineering	Electrospinning	in the range of 0.9-8.1 m Scm^{-1}	---	[168]

18	PANI-EB in formic acid/PAni-coated Polycaprolactam (PA6) fibres doped by HCl, H_2SO_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 (Ω.cm=10^1-10^2)	---	174
19	Aniline in HCl /piece of TiO_2 multi-pore fibre film /APS in HCl was added to the aniline mixture	Preparation of TiO_2/PAni composite fibre	Electrospinning *in-situ* polymerisation.	---	---	170
20	aniline/ ammonium peroxydisulfate in the presence of short nylon-6 fibe	Preparation and characterisation of Natural rubber- PAni coated short nylon-6 fibre (PAni-N6) composites	*In-situ* oxidative polymerisation	~1.99×10^{-6} Scm^{-1}	Depend on Pan concentration	176
21	Aniline/potassium peroxydisulfate solution coated on polyester fabrics washed with an aqueous acid solution (H_2SO_4 or HCl)	Chemical and electrochemical characterisation of PAni coated conducting fabrics	Coating	-1 to +2V	---	175
22	HCPSA/ PAni/ PLCL dissolved in hexafluoropropanol (HFP)	Electroactive Electrospun PAni /Poly[(L- lactide)-co-(e-caprolactone)] Fibres for Control of Neural Cell Function	Electrospinning	~0.00641 Scm^{-1}	---	169
23	A blend of PP/PA6/PAni-complex (polypropylene/polyam- ide-6/ PAni-complex)	Preparation of conducting polyblend filaments by melt spinning of PP/PA6 blends /modified with poly- aniline–complex and characterised	Melt spinning	~10^{-3} Scm^{-1} (draw ratio of 5)	Tenacity < 28 cN/tex	256
24	PU fibres immersed in aniline/HCl solution	Preparation of PAni/PU fibre by *in-situ* chemical oxidative polymerisation of PAni on PU fibre and investigation of their piezoresistive properties	*In-situ* oxidative polymerisation	10^{-2} Scm^{-1}	US 400%	177
25	Kenaf fibres (UKF) in NaOH solution/aniline monomer in HCl/ APS	Modification of natural Kenaf fibre by PAni	*In-situ* oxidative polymerisation	~10^{-4}-10^{-3} Scm^{-1}	UTS 100±50 N/mm^2	178
26	Cellulose fibre in HCl/aniline and APS	Preparation of PAni/cellulose composite fibre for the treatment of Cr(VI)-contaminated water, and its effect	*In-situ* oxidative polymerisation	---	---	179
27	Cellulose acetate (CA)-PAni	Preparation of dual-layer hollow fibre of PAni –cellulose acetate	wet spinning (HCl and APS)	-2 to +2V	---	180
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	*In-situ* oxidative polymerisation	2.2 Scm^{-1}	---	181
29	Aniline in presence of detonantion nanodiamond (DND)/SDS/ APS	Characterisations of morphological, electrical and mechanical properties of PAni/DND nanofibres	Precipitation polymerisation technique	10-100 Scm^{-1}	---	182
30	Aniline in presence of CF using $FeCl_3.6H_2O$ or APS as oxidant	Investigation PAni-coated coconut fibres properties as additives in matrix of polyurethane	*In-situ* oxidative polymerisation	1.5×10^{-1} Scm^{-1} ($FeCl_3.6H_2O$) 1.9×10^{-2} (APS)	---	183
31	Silver nanoparticles embedded PAni ($AgNO_3$ aq soutions+ V_2O_5 nanofibrous seeding agent)	Synthesis and characterisation of PAni nanofiber/Silver composite networks as antibacterial agents	Seeding polymerisation reaction	2×10^{-3}-0.196 Scm^{-1}	---	184
32	PAni/HCSA	Electrospun PAni fibres as highly sensitive chemiresistive sensors for NH_3 and NO_2 gases	Electrospinning	2×10^{-6}-50 Scm^{-1}	---	112
33	PAni/HCSA blended with PMMA or PEO	Introduce a novel method to calculate fibre conductivity using IDE applied on electrospun conductive nanofibers	Coaxial electrospinning	Up to 50 Scm^{-1}	---	167
34	spherical-shaped Ag nanoparticles decorated PANI nanofiber	Preparation of Ag-decorated BDP fibres as a sensitive material for the detection of 4-mercaptobenzoic acid and rhodamine 6G	Solution dipping method	---	---	257
35	Acidic solutions of aniline in HCl polymerised on nonwoven electrospun PS mats	Preparation of hierarchical PAni–polystyrenecomposite for water remediation	*In-situ* polymerisation	---	---	258

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.185 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.[186] These substrates include carbon, graphite,[187] glass,[188] and polymeric fibres.[189,190] In general, the conductivity of PPy/fibre composites is directly related to PPy loading, ratio of oxidant to dopant, and fibre structure. [191]

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.[192] 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 35-160 Scm^{-1}.[193] Others have endeavoured to coat graphite fibres with PPy through this method.[187] 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.[194] Silver nanowires,[195] ultra-high molecular weight polyethylene fibre (Figure 13(a)),[196] silica short fibres,[28] cotton fibres[197] and yarns,[198] short nylon fibre/natural rubber,[199] cellulose[191] and banana fibres[200] 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 (**Figure 13(b)**).[201] Recently Wang *et al* described the preparation of novel actuators based on graphene fibres coated with electropolymerised PPy.[202]

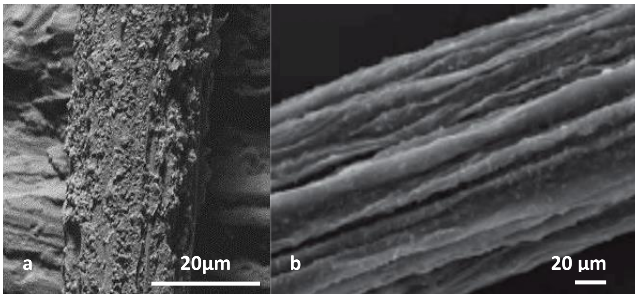


Figure 13 Scanning electron micrographs of (a) polypyrrole-coated ultra-high molecular weight polyethylene fibre,[196] (b) polypyrrole–(APS/DEHS)–alginate fibre.[201] Reproduced with permission from Ref. [172176], Copyrights© 2011; Elsevier and RSC Publishing, respectively

Chemical vapour deposition (CVD) (also known as vapour phase polymerisation) is another straightforward and rapid method to deposit PPy onto various substrates, and has been used widely to produce composite PPy fibres.[18,190,203–207] Although this method has the advantage of simplicity, the highest reported electrical conductivity of fibres prepared this way was only 0.68 Scm^{-1},[203] 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.[190] 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.[141] In 2007, a microfluidic approach was described by others for fabricating hollow and core/sheath PPy nanofibres by electrospinning.[208] 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.[209] It is worth noting that a large number of prepared PPy composite fibres have been employed for sensor applications.[18,132,210] An overview of the studies performed on composite PPy fibres is given in Table 5.

Table 5 Overview of composite polypyrrole fibres.

No.	Sample Name	Focus of the resaerch	Sythesis method	Reported Electrical Conductivity / Conduction Potential Window	Mechanical properties	Ref.
1	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	---	---	---	259
2	aqueous colloidal magnetite particles onto (polyester, nylon, cotton etc.) 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 Scm^{-1}	---	193
3	graphite fibre PPy coatings	Fabrication of graphite fibre PPy coatings by aqueous electrochemical polymerisation	Aqueous electrochemical polymerisation	---	---	187
4	PPy/Poly(p-phenylene terephthalamide)	continuous fast vapor phase polymerisation method to prepare electrically conducting PPy/PPTA	Vapor phase polymerisation	0.68 Scm^{-1}	UTS 2.644 KPa US 4.4%	203
5	Aramid fibres were immersed in $FeCl_3 \cdot 6H_2O$ 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	~$1.3x10^{-3}$ Scm^{-1}	---	204
6	insulating natural Cotton, silk, and wool fibres were electrochemically coated with pyrrole in acetonitrile (containing p-toluenesulfonic acid)	Fabrication of conducting fibres from natural polymers	Electrochemical polymerisation	---	---	260
7	PPycoated 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, etc	---	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	~10^{-3} Scm^{-1}	---	190
9	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	---	---	261
10	Organic solvent soluble PPy, $[(PPy3)^+(DEHS)^-]_x$ + NaDEHS	preparation of PPy nanofibres with the practical application for construction of nanoelectronic devices	Electrospinning	Pure $[(PPy3)^+(DEHS)^-]_x$ $2.7x10^{-2}$ Scm^{-1} For the composite fibre $3.5x10^{-4}$ Scm^{-1}	---	141
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	---	---	208
12	Pyrrole monomer+PAN polymers in DMF, H_2O_2 was slowly added depending on pyrrole amount	Fabrication of Polyacrylonitrile/PPy (PAN/PPy) composite nanofibres	Electrospinning	---	---	24
13	Fibres were dipped in solution of $FeCl_3$ anhydrous in dried acetonitrile and then	Preparation of continuous vapour deposited PPy-cotton and PPy-silk yarns	Vapour phase polymerisation	~ 10^{-4} Scm^{-1}	---	205

	exposed to pyrrole vapour					
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)	---	---	262
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	---	---	209
16	Polyamide 6/PPy nanofibres	Fabrication of composite polyamide 6/PPy conducting nanofibres	Electrospinning	---	---	189
17	pyrrole, N-methylpyrrole, 3-methylthiophene, poly 3,4-ethylene dioxythiophene, deposited on substrates (Pt, stainless steel)	Preparation of Poly-N-methylpyrrole microfibre	Electrodeposition	---	---	263
18	Silk fabrics were coated with electrically conducting doped PPy	Preparation of bio-based conducting composites ((PPy)-coated silk) fabrics	*In-situ* oxidative polymerisation	---	---	20
19	Ag nanowires (NWs) dispersed in solution of ($Cu(Ac)_2$), then oxidise pyrrole monomers to make uniform PPy sheath	Preparation of Ag/PPy coaxial nanocables	Ion adsorption /oxidative polymerisation	---	---	195
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 drugs	Solid-phase microextraction Electropolymerisation (SPME) coating	---	---	264
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)	---	UTS 304±61.0 MPa YM 10.4 ± 4.3 GPa	265
22	PPy/hexagonally ordered silica (PPy/SBA15) coated on stainless steel wire	Fabrication of PPy/hexagonally ordered silica nanocomposite for solid-phase microextraction	Vapour phase polymerisation	---	---	206
23	$Zn(S_2CNEt_2)_2$/pyrrole monomer	Spinning PPy/ZnS Core/Shell coaxial Nanowires	two-step process by anodic aluminum oxide (AAO) templates	---	---	266
24	$FeCl_3$-doped UHMWPE fibres soaked in an aqueous solution of hexahydrate (catalyst) treated by pyrrole monomer	Production of PPy-coated UHMWPE fibre to improve adhesion and structure properties of UHMWPE fibre	Oxidative polymerisation coating	---	---	196
25	Silica fibres treated with silane agent and then coated with PPy	Production of PPy-coated amorphous silica short fibres (PPy-ASF)	*In-situ* oxidative polymerisation coating	$0.32\ Scm^{-1}$	---	28
26	admixing silver nitrate and pyrrole in presence of cotton fabric at different mole ratios	Synthesis of PPy silver nanocomposite on cotton fabrics	*In-situ* oxidative polymerisation	$\sim 10^{-3}\ Scm^{-1}$	---	197
27	MWCNT fillers+ polystyrene matrix PPy was coated on fibres	Fabrication of conducting electrospun polymer fibres with nano features	Electrospinning/ In-situ polymerisation	$3.7x10^{-4}\ Scm^{-1}$	---	267
28	PPy coated layer on Ag-TiO_2 nanofibre	Protecting Ag nanoparticles from being oxidised by a PPy layer	Electrospinning	---	---	268
29	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	---	269
30	Pyrrole(Py) polymerised on Graphene fibres	Fabricating of novel electrochemical flexible and wearable graphene/PPy fibres as an actuator	*In-situ* oxidative polymerisation	Highly active within the ±0.8 V range	---	202
31	Py polymerised on the BF surface using ($FeCl_3.6H_2O$) as oxidant	Preparation and characterisation of PPy-coated Banana fibres	*In-situ* oxidative polymerisation	$1.8\ x10^5\ Scm^{-1}$ (electrical resistivity)	---	200

32	Py in presence of FeCl$_3$(oxidant)/p-toluene sulphonic acid (dopant)	Fabricating and characterising natural rubber/PPy and natural rubber/PPy/PPy-coated short nylon fibre	*In-situ* oxidative polymerisation	8.3x10^{-4} Scm^{-1} NR/PPy 6.25x10^{-2} Scm^{-1} (for NR/PPy/F-PPy)	---	199
33	FeCl$_3$ and anthraquinone-2- sulfonic acid sodium salt as oxidant/dopant	Preparation of PPy/cellulose fibre composites	*In-situ* oxidative polymerisation			191
34	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 *in-situ* polymerisation	---	---	142
35	Cotton, wool, polyester exposed to pyrrole using FeCl3(oxidant)	Investigation of the response of conductive woven, knitted, and nonwoven composite fabrics o pH, humidity, and mechanical strain	*In-situ* polymerisation	---	---	210
36	Aq Py with FeCl$_3$ (oxidant)/pTSA (dopant)	Fabrication of electroconductive cotton yarn	*In-situ* polymerisation	Resistivity 182.63 KΩm^{-1}	---	198
37	Aq Py with FeCl$_3$ (oxidant)/pTSA (dopant)	Preparation and characterisation of electrically conductive textiles for heat generation	*In-situ* polymerisation	Resistivity 1013.08 Ωm^{-1}	---	239
38	Aq Py with FeCl$_3$ (oxidant)/pTSA (dopant)	Investigation of chitosan/polypyrrole composite fiber as biocompatible artificial muscles	*In-situ* polymerisation	---	---	270
39	PPy coated with ferric tosylate (oxidant) /n-butanol/EDOT deposited	Soft Linear Electroactive Polymer Actuators based on Polypyrrole	Two-step chemical-electrochemical synthesis	---	---	207

2.2.1.3. Composite poly (3,4-ethylene dioxythiophene): poly(styrenesulfonic acid) Fibres

PEDOT is a well-studied intrinsically conducting polymer that is rendered solution-processable when doped with acidic PSS.211 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 Scm^{-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,[212] which was then used as a nitric oxide sensor for asthma monitoring. Recently, PEDOT:PSS-coated chitosan hybrid fibres was developed,[213] which showed relatively high conductivity values of ca. 60 Scm^{-1} (see Figure 14(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.[153,214,215]

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 (Figure 14(b)).[216] Not long ago, polyurethane/PEDOT:PSS elastomeric fibers with high electrical conductivities in the range of ca. 2-25 Scm^{-1} were reported.[217] Seyedin *et al* claimed as-prepared fibres as potential strain-responsive sensors. A summary of composite PEDOT:PSS fibre investigations is presented in **Table 6**.

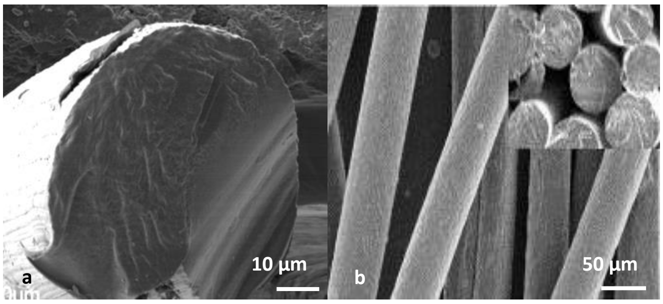


Figure 14 Scanning electron micrographs of (a) composite PEDOT:PSS/polyacrylonitrile conducting fibres with 0.38 wt.% PEDOT:PSS content 216 and (b) PEDOT:PSS-chitosan fibre.213 Reproduced with permission from Ref. [186] and [187]. Copyrights© 2013 and, Elsevier and WILEY-VCH Verlag GmbH & Co., respectively.

Table 6 Summary of composite PEDOT: PSS fibre investigations.

No.	Spinning or coating solution	Focus of the resaerch	Sythesis method	Reported Electrical Conductivity /Conduction Potential Window	Mechanical properties	Ref.
1	Ionomer mixture poly(3,4-ethylenedioxythiophene): 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 Scm^{-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 Scm^{-1}	UTS 1239 cN	245
3	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 Scm^{-1}	YM 2±0.3 GPa UTS 99±7 MPa, US 20.6±1.2%	213
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 Scm^{-1}	YM 3.32 cN/dtex UTS 0.36 cN/dtex US 36.73 %	216
5	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	---	---	212
6	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 Ωm^{-2}	---	153
7	Different compositions of PEDOT:PSS(2.9-25%) and PU	Preparation of highly conductive polyurethane/PEDOT:PSS elastomeric fibers for sensor applications	Wet spinning	2-25 Scm^{-1}	YM ~7.2 -247 MPa UTS ~0.5-9.1 MPa US up to ~400%	217
8	Polyvinyl alcohol (PVA) and PEDOT:PSS aq solution	Investigation of tensile strength and conductivity of PVA/PEDOT:PSS fibres	Wet spinning	10-79 Scm^{-1}	UTS ~39-84 MPa	271

2.2.2. *Conducting Polymer-Carbon Nanotube Fibres*

The combination of conducting polymers with carbon-based 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.[218] The first method employed to produce hybrid fibres from a combination of conducting polymers and CNTs was wet spinning. Mottaghitalab *et al* reported the wet spinning of PAni-CNT composite fibres, which exhibited excellent mechanical and electrical properties and were used as electrochemical actuators. Subsequent improvements in mechanical and electronic properties using different dopants have been described by several research groups.[219–222] A dual mode actuation was reported for the first time by Spinks and co-workers in a chitosan/PAni/single-walled 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.[223] Subsequently, Foroughi *et al* produced PPy-alginate-CNT conducting composite fibres [201] (**Figure 15**) 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.[201]

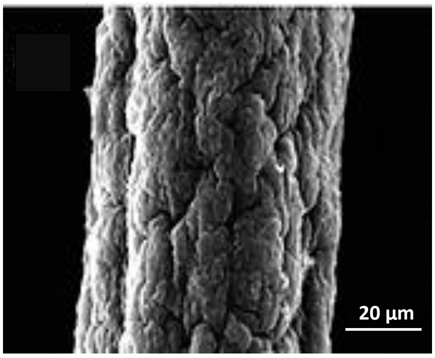


Figure 15 Scanning electron micrograph of an APS/DEHS-doped polypyrrole–alginate–carbon nanotube fibre.[201] Reproduced with permission from Ref. [176]. Copyright© 2011; The Royal Society of Chemistry

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.[224] Improvements in electrical and mechanical properties of electrospun PAni/PEO/MWCNT composite fibres were later described by Lin and Wu.[225] Zhang *et al* have recently reported on preparation of nanocomposite PAni/Polyacrylonitrile/Multiwalled Carbon Nanotubes fibres with conductivities up to 7.97 Sm-1 via electrospinning.[226]

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.[227,228] 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.[229] 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 (Figure 16(a)) may be used for applications where electrical conductivity and good mechanical properties are of primary importance.[230] 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 (Figure 16(b)).[231] Adhikari *et al* described PAni/MWCNT/chitosan nanofibres manufactured via polymerisation of PAni/MWCNT on wet-spun chitosan fibres.[232] These fibres yielded conductivities of ca. 5.3×10^{-2} Scm^{-1}. Table 7 summarises investigations into composite conducting polymer-carbon nanotube fibres.

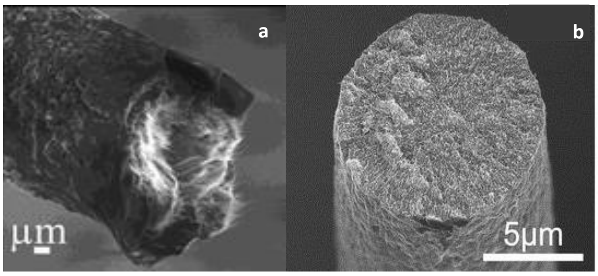


Figure 16 Scanning electron micrograph of (a) cross section of PPy-MWNT yarns[230] and (b) PEDOT:PSS/PEG-SWNTs composite fibre cross-section broken under tensile strain.[231] Reproduced with permission from Ref. [199] and [200]. Copyright© 2011 and 2013; The Royal Society of Chemistry and Nature Publishing Group's Reader Survey

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

No.	Spinning or coating solution	Focus of the research	Spinning method	Reported Electrical Conductivity /Conduction Potential Window	Mechanical properties	Ref.
1	---	Producing PAni-CNT composite fibres for potential use in e-textiles	Wet spinning	(2 wt.% CNT) 32±3	(2 wt.% CNT) After doping UTS 229±22 MPa YM 5.2±0.2 GPa US 8±3 %	[219]
2	2-acrylamido-2-methyl-1-propane sulfonic acid (AMPSA)	Producing PAni-SWCNT composite fibres for potential use in e-textiles	Wet spinning	750 S cm^{-1}	UTS 250–300 MPa YM 7–8 GPa	[220]
3	methane sulfonic acid (1M)	Improvement of electromechanical actuation of fibres when used as artificial muscles	Wet spinning	128.0 ± 25 S cm^{-1}	UTS 260 MPa YM 17 GPa	[221]
4	---	Producing high-strength conducting PAni-CNT composite fibres	Wet spinning	716 ± 36 S cm^{-1}	UTS 255±32 MPa US 4±0.6 % YM 7.3±0.4 GPa	[222]
5	1 M methanesulfonic acid (MSA) solution	Producing a fibre which shows both pH and electrochemical actuation	Wet spinning	1.8 S cm^{-1}	UTS 95 MPa US 60 %	[223]
6	(Oxidant/Dopant) APS/DEHS	Producing electrically conducting, robust fibre comprised of PPy-Alg-CNT	Reactive wet spinning	3.0±0.5 S cm^{-1}	UTS 250±5 MPa US10±1.3 % YM 10±0.5 GPa	[201]
7	(Oxidant/Dopant) $FeCl_3$/DEHS	Producing electrically conducting, robust fibre comprised of PPy-Alg-CNT	Reactive wet spinning	2.0±0.4 S cm^{-1}	UTS 95±4 MPa US 10±1.3 % YM 10±0.5 GPa	[201]
8	(Oxidant/Dopant) APS/*p*TS	Producing electrically conducting, robust fibre comprised of PPy-Alg-CNT	Reactive wet spinning	4.0±0.8 S cm^{-1}	UTS 250±5 MPa US 5±1 % YM 11.8±2 GPa	[201]
9	(Oxidant/Dopant) $FeCl_3$/ *p*TS	Producing electrically conducting, robust fibre comprised of PPy-Alg-CNT	Reactive wet spinning	10.0±1.5 S cm^{-1}	UTS 65±8 MPa US 4±0.7 % YM 3.7±0.8 GPa	[201]
10	---	Producing hybrid PAni/PEO/MWNT fibres with improved electrical properties using electrospinning	Electrospinning	Conductance (with 0.5 wt% MWNTs) : 8.89 µS	---	[224]
11	poly(ethylene oxide) (PEO)	to increase the electrical conductivity of PAni/PEO nanofibre	Electrospinning	(Electric conductance) Max. 2.77µS	---	[272]
12	---	Improving the electrical and mechanical properties of PAni/PEO/MWNT composite fibre	Electrospinning	9×10^{-6} cm^{-1}	YM 23.6 MPa	[225]
13	---	Producing CNT-PPY composite fibre	*In-situ* polymerisation	16 S cm^{-1}	---	[227]
14	---	Improvement in electrical, magnetic and thermal properties of CNTs by coating them with PPy	*In-situ* polymerisation	16 S cm^{-1}	---	[228]
15	---	Producing nano composite electrodes for supercapacitors	Electrospinning followed by *in-situ* chemical polymerisation	PPy/ACNF: 0.79 S cm^{-1} PPy/ACNF/CNT: 1.33 S cm^{-1}	---	[229]
16	Solutions of the PAni/PAN/MWCNTs in DMF DBSA (dopant)	Electrospinning and Microwave Absorption of Polyaniline/Polyacrylonitrile/ Multiwalled Carbon Nanotubes Nanocomposite	Electrospinning	Up to ~8 Sm^{-1}	---	[226]
17	PAni m-cresol solutions for coating carbon fabrics	Preparation of PAni/CF and characterization of them for removal of Cr(VI) from wastewater	Dip-coating	---	---	[273]
18	MWCNTs/aniline in HCl chemically deposited on chitosan fibres	Chitosan/polyaniline/MWCNT nanofibre as electrodes for electrical double layer capacitors	Chemical oxidative polymerization	5.3×10^{-2} Scm^{-1}	---	[232]
19	PPy coating on CF-filled polytetrafluoroethylene composites	Polypyrrole coating effect on mechanical properties of carbon fibre-filled polytetrafluoroethylene	Dip-coating	---	Very poor	[274]
20	---	Producing hybrid PPy-MWNT yarns with good conductivity and mechanical properties	Chemical and electrochemical polymerisation	**Electrochemically prepared PPy-CNT yarn** 220±9 S cm^{-1}	**Single PPy-CNT yarn (Chemically prepared PPy-CNT)** UTS 510±7 MPa US 2.5±0.4 % YM 35±3 GPa	[230]

				Chemically prepared PPy-CNT yarn	**Two-ply PPy-CNT yarn**	
				235±15 S cm^{-1}	***Chemically prepared PPy-CNT*** UTS 740±18 MPa US 1.5±0.6 % YM 57±6 GPa ----- ***Electrochemically prepared PPy-CNT*** UTS 273±9 MPa US 4.5±1 % YM 7.6±0.4 GPa	

3. CURRENT AND FUTURE APPLICATIONS OF CPFs

Thus far, conjugated conducting polymer fibers 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 multifunctions may be condensed into the two key classifications of energy and bionics devices development. In energy applications they have been incorporated into devices for a range of purposes from storage to conversion such as electrodes and batteries,[92,233,234] chemical sensors,[26,212,235] supercapacitors,[236–238] smart textiles,[172,239] actuators and artificial muscles.[134,240,241] It has also been suggested that they show promise for applications in photovoltaic (solar) cells,[83,154] electronic circuits,46 organic light-emitting diodes,[78,242] and electrochromic displays.[83,214] 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. 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] Today, the major bioapplications of CPFs are generally within the area of electrical stimulation and signal recording,[243–245] drug-delivery devices,[213] tissue-engineering scaffolds,[124,130,246] and biosensors.[23,247] 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] These functional aspects may also require the overlap of certain characteristics for example for uses in implantable batteries and bio-actuators.[23,248] In more detail, storage or conversion of energy and provide the required biocompatibility. Conversely, 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.

There exist potential applications of conducting polymer fibres in microelectronics, sensors, actuators and rechargeable batteries outside of those already discussed. Besides, conducting polymer fibres could be considered as candidates for interconnection technology. Furthermore, CPFs still lack desirable mechanical robustness comparing to common traditional textile fibres. 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.

Coclusions

Development of materials and methods for the preparation of conducting polymer fibres is an important enabling step towards their application, particularly in smart textiles. Wet-spinning is the preferred method for preparing conducting polymer 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. 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. Polythiophene is readily available in the water soluble form of PEDOT: PSS, which may be readily wet-spun. Electrospinning was used widely to produce nanoscale nonwoven fibres. The greatest improvements in conducting polymer fibre mechanical strength and electrical conductivity have been achieved through the incorporation of CNTs. 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.

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