Conducting nanofibres produced by electrospinning

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Abstract. Electrospun fibres based on polypyrrole have been prepared. The incorporation of preformed polypyrrole into fibres electrospun from a carrier polymer can only be achieved when materials are prepared with particulates smaller than the cross-section of the fibre; even so there are some problems, with the substantial loss of material from the electrode tip. As an alternative approach, soluble polypyrroles can be prepared but these are not of sufficient viscosity to prepare electrospun fibres, once again a carrier polymer must be employed. More effective loadings are gained by the process of coating the outer surface of a pre-spun fibre; in this way electrospun fibres coated with polypyrrole can be prepared. This approach has been adapted to produce silver coated polymer fibres by the use of copolymers of styrene and 3-vinyl benzaldehyde.

1. Introduction
Electrospinning is a technique which relies on the build-up of electrostatic forces on the surface of a drop to eject polymeric material, which on evaporation of the solvent, produces polymeric fibres with dimensions (of the order of 10s of nanometres to a few microns) largely inaccessible by alternative means [1]. The generation of such fibres has important implications in the field of nanotechnology in general [2], but more specifically in terms of potential applications; these include textiles, filters, catalysts, and a range of biomedical applications [3]. One particularly attractive possibility is the generation of conducting fibres with nanometre dimensions, and a number of workers have explored this possibility, through, for example, the incorporation of polyaniline [4] or through chemical or physical vapour deposition techniques [5]. Recently particular interest has been shown in the incorporation of polypyrrole into electrospun polymers, either through the introduction of the material prior to spinning, in a soluble form [6], [7], or through surface coating polymer composites containing an oxidant [8]. Polypyrrole is a particularly attractive material because of its ease of synthesis, the stability of the polymer and the possibility of chemical modification (for example through the incorporation of liquid crystalline groups [9]).

In this presentation we describe routes to producing conducting electrospun fibres. We describe initially routes towards the incorporation of polypyrrole into the fibres, through the dispersion of particles. Subsequently we explore the incorporation of a soluble polypyrrole derivative into fibres, and finally consider routes to the chemical deposition of polypyrrole on the surface. We further explore surface treatments by the preparation of copolymers of styrene with a reactive comonomer; in this case 3-vinylbezaldehyde. This method gives a more even surface coating for oxidised materials. This is demonstrated by reacting the aldehyde-containing polymer with a solution of silver as a reducing agent. The resulting material when analysed using SEM and in particular EDX is shown to
give an even surface coating, with control of the silver content being governed by preparation conditions.

2. Experimental

2.1 Materials
All materials were obtained from commercial suppliers and used without further purification except 3,4-diethylpyrrole, which was synthesised by a literature procedure [10], [11] and styrene copolymers, which were synthesised by free-radical polymerisation of mixtures of styrene and 3-vinylbenzaldehyde under reduced pressure at 55 C using azo-bis(isobutyronitrile) as the initiator. Pyrrole and 3,4-diethyl pyrrole were purified prior to use by distillation over calcium hydride under reduced pressure. The Polypyrrole synthesized using PVA as the steric stabiliser was isolated after centrifugation and then re-dispersed in 10ml of a 10% PVA solution; the solution was then stirred for 24hrs before electrospinning.

2.2 Electrospinning
Electrospinning was performed using a glass syringe mounted in a syringe pump fitted with a 22 gauge needle of length 2.5 cm and with an internal diameter of 0.71 mm together with a flat aluminium electrode placed normal to the needle at distances varying from 10 to 40 cm. A Glassman High Voltage power supply was used which allowed defined voltages over the range 7.5-20 kV.

2.3 Electron Microscopy
All electron microscopy was performed using a FEI Quanta FEG 600 Scanning Electron Microscope (SEM). Samples were coated with a thin layer of metal (gold) prior to analyses under high vacuum at an accelerating potential of 20kV and a working distance of 10mm. Alternatively, non-conducting samples were occasionally analysed under low-vacuum conditions without coating, when required, at an accelerating potential of 12.5kV and a working distance of 8mm. The SEM was fitted with an Oxford Instruments Energy dispersive X-Ray spectrometer which was used to confirm the presence of certain elements in addition to elemental mapping.

3. Results and Discussion

3.1 Dispersion of pyrrole particles.

Although previous workers have suggested that simple linear polypyrrole is not suitable for electrospinning, there is strong evidence that it is possible to produce fibres containing non-soluble materials through electrospinning a dispersion of solid particles in a polymer solution (see for example [12]). To this end we undertook preliminary experiments in which pyrrole prepared chemically through oxidation with either cerium (IV) or iron (III) was dispersed in an aqueous solution of either
poly(vinylalcohol) or poly(ethylene oxide). In line with expectations no evidence of fibres was obtained using a range of preparation and electrospinning conditions; instead there was substantial sparking during the process, solvent loss from the needle tip, and spots formed on surface of collector [figure 1] in some cases these then evolved spherulitic structures. On inspection of the chemically prepared polymer using SEM, it was found that the particulates produced were larger than the diameter typically obtained for the carrier polymer fibres (at the appropriate conditions), even after the material had been ground in a ball mill (figure 2).

In view of this problem, materials were prepared with controlled particle size. There are a number of approaches to this, but a particularly attractive one is through the use of poly(vinylalcohol) as a dispersant [13]. Using a modification to the literature method, polypyrrole with a particle size of between 50nm and 120 nm was prepared. In order to increase the concentration of the polypyrrole the material was isolated and re dispersed. In this way poly pyrrole fibres with an average diameter of 300 to 600nm were prepared; EDX analysis was used to map iron and chlorine in the fibres and confirmed the presence of polypyrrole on the basis of the presence of FeCl$_3$ in the polymer as shown in figure 3.

![Figure 3. PVA/Polypyrrole composite fibres (1:1, centre) with x-ray mapping showing chlorine content (left) and iron content (right).](image)

3.2 Soluble pyrrole
As an alternative to the addition of solid pyrrole-based particulates, the use of a modified pyrrole with solubilising features was considered. One example of this approach is to use poly(3,4-diethylpyrrole) prepared by oxidising 3,4-diethyl pyrrole with FeCl$_3$, as shown in figure 4. This approach yielded a polymeric material which was substantially soluble in a range of solvents. Homogenous solutions of up to 15%wt/vol in DMF were prepared and then used in the electrospinning process. However, no fibre structures were observed on the collecting electrode for a variety of tip to collector distances and working voltages; presumably the viscosity of the polymer was too low. Mixing with a carrier polymer, in this case polystyrene, in different ratios produced composite fibres with a deep brown/black colouration. SEM in conjunction with x-ray mapping confirmed the presence of Fe in the polymer. In this way it proved possible to produce materials with ratios of the pyrrole derivative of up to 1:2 w/w.

![Figure 4. Formation of poly(3,4-diethylpyrrole)](image)
3.3 Surface coating

Although both the approaches described above can be used to introduce polypyrrole into electrospun fibres, in both cases the amount of pyrrole incorporated is rather limited. This has clear consequences if high conductivity is required. As an alternative approach the formation of polypyrrole after the initial formation of the electrospun fibres is an attractive proposition; although weight for weight the loadings of conducting material might be equally small, the concentration of this on the surface will facilitate conductivity. There are a number of approaches to this; the simplest is to place fibres in a solution containing pyrrole and oxidant. Unfortunately this gave a rather poor and uneven coverage. Of a range of systems studied it was found that the most uniformly coated fibres were obtained when polystyrene was dissolved in DMF along with variable amounts of ferric chloride and then electrospun to obtain yellow coloured composite fibres of polystyrene and ferric chloride (figure 5). These fibres were then exposed to pyrrole at 60°C for 4-5 hours as shown in figure 6 (if the exposure to pyrrole vapour was substantially longer then disintegration of the fibre occurred as pyrrole vapour dissolved away the polystyrene).

![Figure 5: Polystyrene/FeCl₃ fibres electrospun from DMF](image1)

![Figure 6: Polystyrene/FeCl₃ fibres electrospun from DMF, coated with Polypyrrole.](image2)

The dissolution of the fibres observed during the preparation, as described above, leads to a route towards pure polypyrrole fibres. The composite fibres of polystyrene/polypyrrole were suspended in DMF at room temperature for a period of 24hrs, in order to selectively dissolve the polystyrene leaving behind a hollow polypyrrole fibre. Although in most cases the fibre structure broke down to give black particulates, for selected samples, a hollow fibres was obtained as shown in figure 7. The thickness of the polypyrrole layer shown in this example is approximately 300 to 400nm.

![Figure 7: Hollow polypyrrole fibre prepared by suspending a Polystyrene/Polypyrrole composite fibre in DMF at room temperature for 24hrs](image3)

3.4 Silver coated fibres pyrrole

An alternative oxidant for pyrrole is silver (I), our attempts to use this oxidant, by for example incorporating silver nitrate into polystyrene, whilst less promising for the generation of polypyrrole than the ferric chloride approach described above, did suggest a process which might provide an alternative type of conducting fibres; namely silver coated fibres. Thus, the methodology applied above was modified to the preparation of metallic coated fibres utilising the reaction between
ammonical silver nitrate and an aldehyde (figure 8), commonly known as Tollén’s test [14]. In this case investigations suggested that improved coatings were obtained by incorporation of the oxidant (typically glucose) as a co-solute during the electrospinning process.

In an extension to the silver coating approach, a range of copolymers were prepared based on polystyrene and poly(vinylbenzaldehyde) of the type shown in figure 9. These were prepared with compositions ranging from 10-50% aldehyde (w/w). Though there were some problems with partial cross-linking of the material containing greater proportions of the reactive unit, these materials were all spun successfully to form fibres (with typical diameters of ca. 2 µm). The quality of the silver coating was gauged by SEM and EDX. This was found to be highly dependant on the preparation conditions. However, for the conditions tried (concentration of reagent temperature etc.) it was noted that the most even coated material was one where the fibre contained ca. 50% aldehyde (Figure 10), while that with only 10% showed a rather more uneven distribution (figure 11). In this case attempts to remove the central core of the fibre (cf. figure 7) were unsuccessful. We attribute this to a rather thin coating, consistent with the oxidant being covalently bound to the polymer surface, with little possibility to diffuse through the silver coating.

![Figure 8: Reaction between Silver(I) and an aldehyde](image)

![Figure 9: Styrene/3-vinyl benzaldehyde copolymer](image)

![Figure 10: silver coated polystyrene fibre from a 50:50 styrene vinylbenzaldehyde copolymer](image)

![Figure 11: silver coated polystyrene fibre from a 50:50 styrene vinylbenzaldehyde copolymer](image)

4 Conclusions
A number of routes to composite electrospun fibres based on polypyrrole have been described. Polypyrrole particles can be incorporated provided that the dimensions of the particle are commensurate with the fibre diameter; large polypyrrole particles prevent the formation of fibres. However loading with sufficient concentrations of polypyrrole to render the fibres conductive may have consequences on the electrospinning. Soluble pyrrole-based polymers can also be incorporated into similar fibres, however the loadings may be limited and the low viscosity of the pure polymer solutions, at least in these investigations, prevented direct spinning of pure polypyrrole solutions. Surface coating offers a particularly versatile option, the results being particularly promising when the oxidant is contained in the fibres. In some cases part of the central core could be removed to produce...
essentially a pure polypyrrole hollow fibre. This approach has been extended to the production of oxidising copolymers; such polymers produce particularly uniform silver coated fibres. This post-processing approach offers a promising route to electrically conducting electrospun fibres.

5 References
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