

Direct Writing of Conductive Polymer tracks as part of an additive manufacturing process

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ABSTRACT: The use of electrically conductive polymers to construct heterogeneous structures via additive manufacturing is an attractive possibility. It maintains the all polymeric nature of such structures. In this work we discuss how this might be achieved in practical additive manufacturing equipment.

1 INTRODUCTION

Work on intrinsically conductive polymers was initiated by the pioneering work of Shirawaka on polyacetylene [Shirawaka 1977]. Shirawaka was able to use a precursor route which yielded highly conductive films of polyacetylene which were prone to oxidation which lead to a rapid reduction in conductivity when exposed to air. Subsequent to Shirawaka's work, other polymers were widely studied including polypyrrole, polythiophene and polyaniline [Wynne 1982]. All three have proved to have useful properties such as low density, easy to shape and are not affected by exposure to air. Polypyrrole can be synthesised by electrochemical means or through the use of a chemical oxidant. In this contribution we show how we can prepare conductive tracks in a patterned manner using a two stage additive approach.

1.1 Polypyrrole Chemistry

Pyrrole can be readily oxidized to form a polymer which consists of highly conjugated chains of pyrrole linked typically by 2,5 linkages. As shown in Figure 1. The polymerisation can be achieved in a number of ways, but common methods include electrochemical oxidation of a solution of pyrrole; in which case a polymer film is obtained on a suitable electrode material, or chemical treatment, with suitable reagents as outlined in Figure 1. Commonly pyrrole is prepared by reaction with ferric chloride; in such cases the resulting material is typically produced as a powder. Pyrrole itself is soluble in a range of organic solvents and is even soluble to a limited extent in water, it also has a relatively high vapour pressure at room temperature (boiling point 131), and thus it can be handled relatively easily, although it is moderately toxic. Polypyrrole in con-

trast is generally insoluble, and does not melt so its processing is problematic, as will be discussed in a subsequent section.

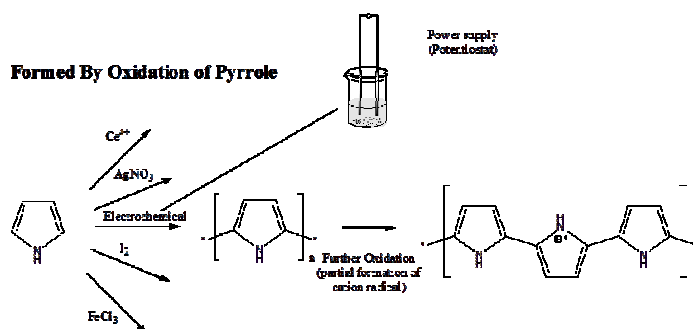


Figure 1. Routes to the preparation of polypyrrole; thin films of polypyrrole can be prepared electrochemically using an aqueous solution of pyrrole with an appropriate ionic charge carrier; alternatively a range of chemical oxidants can be used

Polypyrrole itself has a relatively low conductivity. The conductivity is increased by further oxidation of a fraction of the pyrrole units to form cation-radicals. These species act as charge carriers and their number will affect the conductivity, as will the morphology of the final polymer [Mitchell 1988, Kassim, 1992]. This presents additional challenges to the process over and above the nature of the polymer itself.

1.2 Additive Manufacturing technologies

In the Additive Manufacturing field, there are five main manufacturing processes: Fused Deposition Modelling (FDM) (3DF), 3D Fiber Deposition, 3D Printing, Stereolithography (STL), and Selective Laser Sintering (SLS). Nozzle-based technologies such as FDM process are based on molten polymers passing through a nozzle and a molten fibre is further deposited on the surface of a moving platform or

merges with the previous layer where it cools down and solidifies. Geometrical and morphological parameters of the object are influenced by the processing conditions, namely, nozzle diameter, writing speed, extrusion rate and polymer physics (de Mulder et al 2009).

3D printing creates tri-dimensional objects by depositing liquid binder onto a powdered bed. This liquid may act as glue or promote a reaction causing the particles to bind together. After each layer, a new powder bed is spread and the object is created by n cycles of this procedure. In this case, the unbounded particles aid the construction of the following layers as it provides temporary support to the object (Butscher, 2011).

Light-based technologies such as stereolithography and selective laser sintering are promising techniques to fabricate objects usually with a homogeneous composition. STL relies on the photo-curing process of a material by incidence of UV and/or IR radiation, whereas SLS uses IR lasers to heat up the powder beyond its melting point causing neighbouring particles to fuse forming a solid structure. When each layer is finished, a new powder layer is placed with a mechanical roller and the exceeding material from the previous layer provides in place to support the continuance of the process (Bártolo, 2009).

Inherently to each process, material physical properties are important characteristics to be considered. Clearly polypyrrole cannot be processed by techniques which involve heating to the molten phase such as FDM or SLS.

2 WRITING CONDUCTIVE TRACKS

2.1 Basic strategy

The intrinsic intractability of most conductive polymers presents a challenge to the writing technology required to deliver the conducting polymer. Thus the choices will involve the following:

- Modification of pyrrole to enhance solubility;
- Suspension of pyrrole particles in an appropriate matrix;
- Post casting oxidation.

Modification of pyrrole or other conducting polymers to enhance solubility can be achieved in a number of ways, but commonly this might involve the addition of substituents at (for example) the unreactive, 3 or 4 positions of the pyrrole (Langley 1997). Though such approaches may be rather time-consuming, and in our hands at least can yield materials with at best limited conductivity. A more realistic approach involves modification of the counter ion. Thus, for example pyrrole oxidised with ammonium persulphate in the presence of dodecylben-

zene sulphonic acid forms a soluble poly(pyrrole); the APS/DBSA system is also found to be conditionally soluble in chloroform when an equal amount of additional pure DBSA was added and sonicated. Figure 2 shows fibres prepared (by electrospinning) from a solution containing pyrrole and polyethylene oxide as a binder; the presence of the dopant can be seen from the elemental mapping of sulphur from the counter ion (dopant).

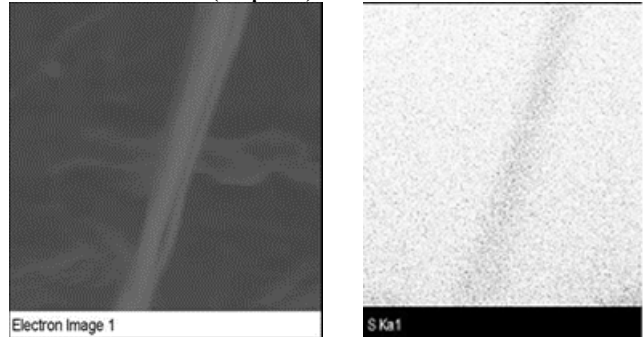


Figure 2 PEO/Polypyrrole (DBSA) composite fibres and X-ray mapping of PEO/ Polypyrrole composite fibres (Element map: Sulphur).

Suspension of particles in an appropriate carrier may allow suitable delivery, but may require rather high particle concentrations, and needs control of the particle size. With regard to the later point, it is worth noting that the particles with submicron dimensions can be obtained by the emulsion polymerisation of pyrrole with ferric using dodecyltrimethyl ammonium bromide (DTAB) to stabilise the emulsion, as shown in Figure 3.

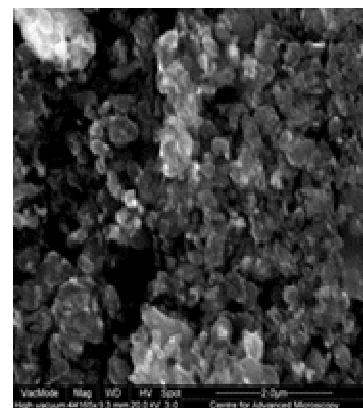


Figure 3 Polypyrrole particles prepared using an emulsion polymerisation stabilised with DTAB; the particles obtained had a good spherical morphology with sizes in the range of 100-200nm

We have explored the possibility of post-writing oxidation through experiments with electrospun fibres of polystyrene. Thus, polystyrene was dissolved in DMF with a range of concentrations of Ferric chloride. Fibres were spun from these to obtain yellow coloured composite fibres of polystyrene and ferric chloride. These fibres were then exposed

to Pyrrole vapour at different temperatures in the arrangement shown in Figure 4.

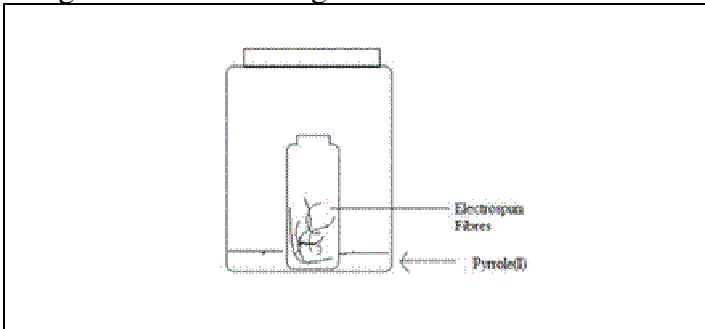


Figure 4 design of experiments to coat polystyrene/ ferric chloride composites with pyrrole through exposure to pyrrole vapour at elevated temperatures so as to ensure a sufficient amount of pyrrole vapour

At 60°C the fibres turned black within an hour and further exposure lead to the formation of nodules on the fibre surface as shown in Figure 5. After 24 hours the fibre structure was to some extent destroyed – presumably the action of the pyrrole vapour. Thus on this basis a simple design of a writing system would involve cycles of laying down polymeric material containing an oxidant and exposure to pyrrole for carefully controlled periods; too short a time and there would be insufficient deposition, whilst too long would allow the growth of significant defects through inhomogeneous layering.

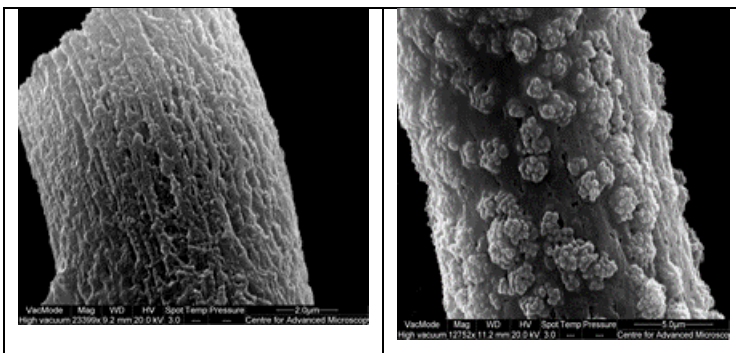


Figure 5 Polystyrene/FeCl₃ fibres electrospun from DMF, coated with Poly(pyrrole);, a : 2hrs, b: 3hrs, after exposure to Pyrrole vapour at 60°C

3 CASE STUDY

3.1 Polypyrrole-based conductive tracks in a PCL-based scaffolds

PCL-based scaffolds were obtained by fused-deposition method using the BIOEXTRUDER equipment developed at Institute Polytechnic of Leiria (Figure 6).

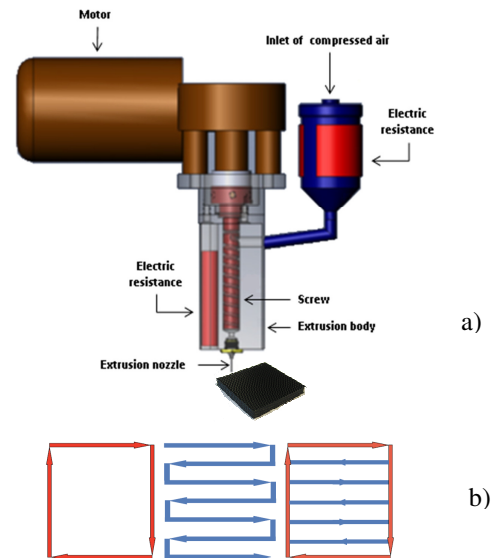


Figure 6. a) Bioextruder system and b) deposition trajectory of tri-dimensional scaffolds (Domingos et al 2009).

Finely ground ferric chloride was dispersed in the PCL by melt mixing using a high shear arrangement with different levels of loading ranging from 0.5 to 10%w/w. PCL/FeCl₃ strands were deposited on the previously written PCL strands which had a diameter of 300µm. The object was placed in a polypyrrole atmosphere as shown schematically in Figure 4 for varying periods of time.

4 CONCLUSIONS

We have developed a methodology for writing conductive tracks of polypyrrole which can be included in an additive manufacturing process cycle. The process is two stage and involves including a chemical oxidising agent in a conventional thermoplastic carrier. This can be deposited on to a structure using conventional 3-d printing technologies. A conducting track is developed on the surface using a vapour of pyrrole. Only where the oxidant is present will the pyrrole polymerised and become doped so that it is conducting. It is found that the exposure time to the pyrrole vapour needs to be controlled and limited to ensure a smooth film is obtained. We are currently optimising the delivery of the pyrrole vapour to enhance the qual-

ity of the resultant films and the efficacy of the manufacturing process. This opens up the possibility of manufacturing complex active all-polymer devices using additive manufacturing technologies.

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