



Original research article

# Production of conductive electrospun polypyrrole/poly(vinyl pyrrolidone) nanofibers

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## ABSTRACT

This article reports on a new method for the production of Polypyrrole/Poly(vinyl pyrrolidone) nanofibers via the electrospinning of pyrrole solution and subsequent oxidation. The low solubility of polypyrrole makes its electrospinning very difficult. However, low viscosity of pyrrole makes it also unsuitable for electrospinning as well. It was found that increasing the viscosity of pyrrole by adding poly(vinyl pyrrolidone) (PVP) (9% w/w), makes its electrospinning possible. The electrospun pyrrole – PVP nanofibers were collected in a solution of FeCl<sub>3</sub>·6H<sub>2</sub>O (2% w/v) and dopant in ethanol and oxidized in-situ, in other words polymerized to PPy (one step method). In another method (two step method), the electrospun pyrrole-PVP-dopant nanofibers were collected on an aluminum foil and then detached from it. To polymerize pyrrole, the nanofibrous mats were immersed in FeCl<sub>3</sub>·6H<sub>2</sub>O (2%w/v) solution. P-toluene sulfonic acid (PTSA) and anthraquinone-2-sulfonic acid sodium salt (AQSA) were employed as dopant. The SEM micrographs showed that PPy-PVP nanofibers with an average diameter as low as 440 nm could be prepared. X-ray diffraction patterns showed a crystallinity of about 25.7% for the PPy-PVP nanofibers. FTIR analysis proved the formation of PPy as well as the absence of any considerable reaction between PPy and PVP. The highest electrical conductivity recorded for the AQSA doped PPy-PVP nanofibers with an average diameter of around 830 nm was  $5.22 \times 10^{-1} \text{ S cm}^{-1}$  which is higher than the highest conductivity of  $0.5 \text{ Scm}^{-1}$  reported for PPy fibers (average diameter = 3 μm) in the literature.

## 1. Introduction

Polypyrrole (PPy) is one of the most important intrinsic conductive polymers (ICPs). The alternate single and double bonds (conjugate bonding) in the backbone of the molecular chain, constitute the main characteristic of ICPs. Conjugate bonding makes the electrical charge movement along the polymer chain possible. In fact, the charge movement occurs as a result of dislocation of the electrons of double bonds [1]. It is well known that the electrical conductivity of ICPs can be enhanced by applying chemicals known as dopant. Dopants lead to the formation of counterions through an oxidation or a reduction process [2]. High electrical conductivity, biodegradability, relatively easy synthesis and long-term stability in ambient conditions constitute the main merits of PPy. Basically, ICPs have attracted the attention of many researchers for a wide range of applications such as chemical sensors, electronic devices, drug release, tissue engineering, antistatic, electromagnetic shielding, actuators, heat generation, artificial muscle and batteries [3–6]. However, the poor solubility of PPy in common solvents is a major drawback which restricts practical applications of PPy

in some fields [3]. Electrospinning of PPy is an example of this. It must be pointed out that apart from very low solubility, other factors such as low molecular weight and high molecular chain rigidity can be considered as responsible for the difficult electrospinning of PPy [3,7].

Up to the present time, the following attempts have been made to obtain electrospun PPy nanofibers by dissolving the polymer. A brief summary follows next. Kang et al. [8] have reported the electrospinning of PPy in chloroform solution with extra amount of dodecyl benzene sulphonic acid (DBSA) as dopant. The average fiber diameter and the electrical conductivity of the electrospun fibers have been reported as 3 μm and  $0.5 \text{ Scm}^{-1}$ , respectively. It is claimed that the extra dopant reduces the intermolecular interactions and as a result the electrospinning of PPy becomes easier. Chronakis et al. [7] report the electrospinning of PPy after functionalization with sodium salt of di(-2ethyl hexyl) sulfosuccinate  $[(\text{PPy}3)^+(\text{DEHS})^-]_x$  first and then dissolution in dimethyl formamide (DMF). Other researchers have mixed a second polymer with PPy solution to make PPy electrospinnable. The electrical conductivity reported in these cases is not high. Ju et al. [9] electrospun the solution of PPy/sulfonated-poly(styrene-ethylene-butylenes-

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styrene) in chloroform or DMF. The electrospun fibers had an average diameter of 300 nm and electrical conductivity of  $0.52 \text{ Scm}^{-1}$ . Cetiner et al. [10] electrospun the solution of PPy/Poly(acrylonitrile-co-vinyl acetate) in DMF and obtained fibers with an average diameter of 200–400 nm and electrical conductivity of  $10^{-7} \text{ Scm}^{-1}$ . In this case, the low conductivity has been related to the low portion of PPy in the electrospinnable solution. Kai et al. [11] produced nanofibrous scaffolds of PPy/poly( $\epsilon$ -caprolactone)/gelatin from hexafluoro-2-propanol (HFP). The best fibrous webs are reported to be obtained from the solution containing only 15% PPy. The average nanofiber diameter and the electrical conductivity values are reported to be 216 nm and  $1.3 \times 10^{-7} \text{ Scm}^{-1}$ , respectively. Yanilmaz et al. [12] electrospun the solution of PPy/polyurethane in DMF. In this case, the average diameter of electrospun fibers was around  $2 \mu\text{m}$  and the electrical conductivity was  $1.4 \times 10^{-6}$ , respectively.

Merelini et al. [13] synthesized PPy particles in  $\text{FeCl}_3$  with DBSA as dopant. These particles were added to poly(vinylidene fluoride) (PVDF) solution. The resulting solution was electrospun to obtain nanofibers. The sample with the highest amount of PPy (23%) had an average diameter of 460 nm. Merelini, et al. [14] also studied the effect of compressive stress on the electrical resistivity of PVDF-PPy blends.

Finally, the third group of researchers have coated nanofibers with PPy for different applications, namely heat generation, radiation absorption [15] and tissue engineering [16]. Using pyrrole, Han and Shi [17] employed vapor phase deposition technique to coat electrospun sodium 1,4-bis(2-ethylhexyl) sulfosuccinate - ferric chloride nanofibers with PPy. The average diameter of these coated electrospun fibers was  $5 \mu\text{m}$ .

Considering the above literature, this study aimed at a completely new route for producing PPy nanofibers via electrospinning pyrrole monomer first, followed by oxidation (polymerization) to achieve PPy nanofibers. This idea constitutes the novelty of this article.

## 2. Experimental

### 2.1. Materials

Pyrrole ( $\geq 97\%$ ) as monomer, ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) as oxidant, anthraquinone-2-sulfonic acid sodium salt (AQSA) as dopant, poly(vinyl alcohol) (PVA) ( $M_w = 72 \text{ kDa}$ ), ethanol (100%), methanol (99.9%), were purchased from Merck, Germany. *p*-Toluene sulfonic acid (PTSA) monohydrate as dopant, glycerol ( $\geq 99\%$ ), poly(ethylene oxide)(PEO) ( $M_w = 400 \text{ kDa}$ ) flakes, poly(vinyl pyrrolidone) (PVP) ( $M_w = 360 \text{ kDa}$ ) was purchased from Sigma-Aldrich. All chemicals were used as received.

### 2.2. Preparation of nanofibrous mats

The electrospinning set up employed in this work consisted of a dosing pump (TERUMO, STC-527 Japan) with feeding capacity of 0–60 ml/h, a high voltage supply (Emersun, 220 V, AC input – up to 35 kV DC output) and a 1 ml syringe with a blunt tipped needle (internal diameter = 0.5 mm). The positive electrode was connected to the needle tip and the aluminum foil collector was connected to negative electrode.

As apart from volatility, the low viscosity of 1.35 cP [18] and surface tension of 37.1 dyn/cm of pyrrole [19] (in ambient temperature) rendered its electrospinning difficult, it was tried to improve its electrospinnability by increasing its viscosity through adding an additive to its electrospinning solution. Adding the solution of glycerol (viscosity = 1412 cP [20]) in ethanol to pyrrole, in different proportions, proved fruitless, in spite of applying the whole range of electrospinning conditions. It is worth mentioning that both pyrrole and glycerol are soluble in ethanol and their solution in ethanol enjoys stability. Although poly(vinyl alcohol) (PVA) proved to be more positive, however, proper electrospinning of pyrrole-PVA solution was not possible either.

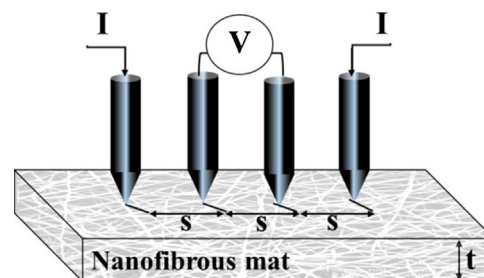


Fig. 1. The schematic of 4-point probe set up for the measurement of the electrical conductivity of the samples.

In further attempts to enhance the electrospinnability of pyrrole, polyethylene oxide (average molecular weight of 400 kDa) as well as poly(vinyl pyrrolidone) (PVP) (average molecular weight of 360 kDa) was added to pyrrole. Both PEO [21] and PVP [22] are soluble in ethanol and can be electrospun relatively easily [23]. PEO did not help the electrospinnability of pyrrole greatly; however, the addition of PVP to the solution of pyrrole in ethanol proved fruitful and pyrrole-PVP solution was electrospun successfully. It was also observed that PVP dissolved in pure pyrrole quite easily. To prepare this solution with concentration in the range of 5–10 (% w/w), PVP was added to pyrrole and stirred overnight. The viscosity of the ideal solution which led to proper electrospinning (PVP-pyrrole (9%–91%)) was measured by rotational viscometer LDVD-II+PRO, Brookfield USA. The viscosity of this solution was 429.9 cP. It is worth mentioning that lower concentrations of PVP in the electrospinning solution led to the formation of beaded nanofibers. To obtain PPy nanofibers, two approaches were considered and named one-step and two-step process.

In the one step process, the electrospun pyrrole-PVP nanofibers were directly collected in an oxidizing bath of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in ethanol (2% w/w) containing dopant, if required. In the two step process, the electrospun pyrrole-PVP-dopant nanofibrous webs were detached from the aluminum foil and then immersed in an oxidizing bath containing the solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in ethanol. It is worth mentioning that it was also tried in vain to collect PPy nanofibers from electrospun pyrrole on a  $\text{FeCl}_3$  coated aluminum foil. This failure can be related to the difficulty of oxidant reaching the deposited pyrrole nanofibers to fulfill its oxidation (polymerization) role. Both of the one and two step methods have the advantage of providing enough oxidant solution for a thorough polymerization. The electrospinning conditions are mentioned in the results and discussion parts.

### 2.3. Loading efficiency of pyrrole on electrospun nanofibers

As pyrrole is relatively volatile, it would be interesting to know its loading efficiency before polymerization. Loading efficiency is calculated with the assumption that all the pyrrole existing in the electrospun nanofibers before polymerization is polymerized into PPy during oxidation process. So, the weight of PPy in nanofibers is assumed to show the weight of pyrrole in nanofibers before oxidation. This assumption is based on the fact that pyrrole is polymerized into PPy through addition polymerization [24,25]. It has been assumed that there was no PVP or dopant loss during the flight of the jet in the electrospinning field. The pyrrole loading efficiency was calculated as follows:

$$\text{Pyrrole loading efficiency} = \left[ 1 - \frac{W_{\text{Py}} - W_{\text{PPy}}}{W_{\text{Py}}} \right] \times 100$$

Where;

$W_{\text{Py}}$ : Weight of the consumed pyrrole in the electrospun solution after 20 min.

To measure  $W_{\text{Py}}$ , the weight of the syringe after 20 min was subtracted from the weight of the syringe before starting electrospinning.

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