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Polyaniline Nanofibers: Towards Pure Electrospun PANI

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Abstract. Nanofibers of conducting polymers, as polyaniline (PANI), have received a great deal of attention by the scientific community for their potential applications (electronic, magnetic, biomedical, optical fields). Recently the electrospinning has emerged as a promising technique to produce wires and fibers of polymers with diameters ranging from 10 nm to 10μm. PANI has poor processability by electrospinning due to its poor solubility in common solvents, but it is possible to spun polyaniline nanofibers adding another polymer to the organic solutions. The presence of an insulator copolymer decreases the fibers/wires conductivity.
In this work we report the preparation of highly pure polyaniline fibers by electrospinning process.
PANI powder has been characterized by FT-IR, UV-VIS, and X-Ray diffraction. The spun sample obtained have been characterized by SEM to evaluate the wire morphology and complex impedance spectroscopy (EIS) in order to measure the electrical conductivity.
We observed that, reducing the amount of PEO in the PANI/PEO blend organic solution, the fiber sizes decreased from 421nm for higher content of PEO (PANI: PEO= 1: 1, w/w) to 230 nm (PANI: PEO= 1: 0.1, w/w).
The way to collect the fiber has been also investigated. Using a rotanting collector we observed a stretching effect on the fibers which promotes a narrow distribution of fibers dimension with respect to the fibers obtained with static collector.

Keywords: polyaniline, nanowires, electrospinning.
PACS: Nanotechnology 81.16.-c, 81.07.-b; Nanofabrication, methods of, 81.16.-c

INTRODUCTION

Conducting organic polymers constitute an attractive class of materials for many applications (electronic, magnetic, biomedical and optical fields).[1-3]

Among them, polyaniline (PANI) is particularly investigated for its electrical properties, which are reversibly controlled by both changing the oxidation state of the main chain [4] and the protonation of the imine nitrogen atoms.[5]

Nanowires and nanofibers of polyaniline can be produced by numerous chemical and physical methods, including polymerization in nanoporous templates,[6] dip-pen nanolithography [7] and self-assembly.[8]

Electrospinning method has emerged as a promising technique to produce well aligned wires and fibers with nanometric diameters that magnifies the intrachain percolation especially in conductive polymers.[9]

The method [10] consists of applying a strong electrostatic field between a capillary, connected to a syringe containing a polymer solution or melt, and a grounded collector.

The polymeric chains are first polarized and consequently attracted by the electric field creating the Taylor cone. When the electric field is high enough to overcome the surface tension, a jet is formed and accelerated by the high voltage towards a collector. Before reaching the collector screen, the solution jet evaporates and the remaining material is collected as an interconnected net of small fibers (fig. 1).

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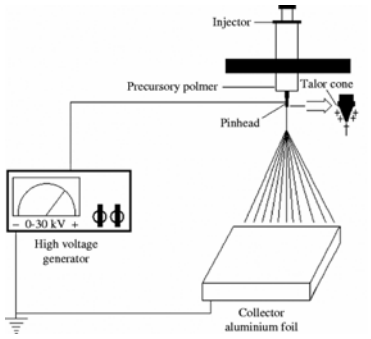


FIGURE 1. Schematic diagram of the electrospinning set-up

This process can be adjusted to control the fiber diameter.

Because of its poor solubility in common solvents, PANI cannot be directly processed by electrospinning but must be doped by organic acids, able to increase its solubility in common organic solvent. Generally, a copolymer is necessary to assist in fiber formation.[11] It is known that the presence of an insulator copolymer reduces the fiber properties.[11] Here we report a route to prepare PANI fibres reducing the PEO amount from 1 to 0% w/w with respect to the amount of PANI. The results are then discussed.

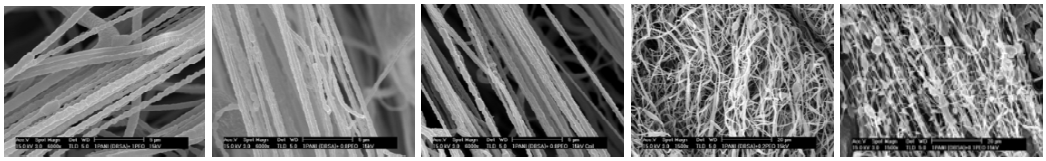
RESULTS AND DISCUSSION

Fibers were spun from PANI/PEO blends, reducing the PEO content from 1 to 0% (w/w) with respect to the amount of PANI. Polyaniline was synthesized *via* the chemical oxidative polymerization of aniline in HCl solution using $(NH_4)_2S_2O_8$ as the oxidant, according to a method reported in the literature.[5] PANI powder, in form of hydrochloric salt (PANI_HCl, emeraldine salt), was undoped in NH_4OH solution and then redoped with dodecylbenzenesulfonic acid (DBSA) to produce PANI_DBSA.

The PANI-DBSA solution was stirred in chloroform for 12 hours in the presence or in the absence of PEO. We obtained the homogeneous solutions that did not show any phase separation before use.

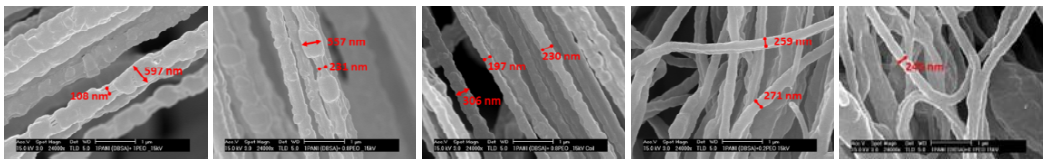
The electrospinning parameters maintained as a constant in this work are: temperature of 21°C; injection rate of 0.707ml/hr; target-capillary distance of 12 cm and relative humidity (RH) <40%. Only the way of fiber collection has been varied, in particular we have used a static collector and a rotating collector (the rotation speed of the drum was 300 rpm).

The fibers morphology was characterized using scanning electron microscopy (SEM) at low magnification (series figures 2 a, b, c, d, e) and at high magnification (series figures 3 a, b, c, d, e).



2a 2b 2c 2d 2e

FIGURE 2. SEM images at low magnification of a) sample PANI_DBSA-PEO 1:1, b) sample PANI_DBSA-PEO 1:0,8 static collector ,c) sample PANI_DBSA-PEO 1:0.8 rotating collector, d) sample PANI_DBSA-PEO 1:0.2 rotating collector, e) sample PANI_DBSA-PEO 1:0.1 rotating collector



3a 3b 3c 3d 3e

FIGURE 3. SEM images at high magnification of a) sample PANI_DBSA-PEO 1:1, b) sample PANI_DBSA-PEO 1:0,8 static collector ,c) sample PANI_DBSA-PEO 1:0.8 rotating collector, d) sample PANI_DBSA-PEO 1:0.2 rotating collector, e) sample PANI_DBSA-PEO 1:0.1 rotating collector

It is possible to observe that by increasing the concentration of PANI_DBSA in the solution (practically, by reducing the PEO amount in the solution) the fiber sizes decreased. As seen in Fig. 3, a quantitative analysis of at least 30 fibers from 2–3 independent samples indicates that the mean fiber size decreased from 421nm, for higher content of PEO, to 230 nm for 1:0.1 PANI_DBSA-PEO blend fibers.

As also shown in Fig. 3, the way to collect the fiber concentration affects the fiber formation: the rotanting collector favors a stretching effect on the fibers (fig. 3b) which promotes a narrower distribution of fibers dimension if compared to the fibers obtained with the static collector (fig. 3c).

Some defects such as beads occur in the polymer nanofibers when the PEO concentration is low (fig 2e). Their formation is due to the capillary instability of the spinning jet by surface tension.

CONCLUSIONS

In summary, electrospinning has been used to produce continuous nanofibers from the polymer solutions of pure PANI_DBSA and its blend with PEO in lower content.

We observed that the fiber diameters decrease by increasing of the PANI_DBSA concentration. Furthemore, the use of a rotating collector allows a narrower distribution of the fiber diameters with respect to the ones achieved by employing a static collector.

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