Strategies for the Fabrication and Characterization of Conductive Fibers Using Electrospinning and Melt-spinning Techniques

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ABSTRACT

This paper describes two approaches studied at NRC-IMI in order to produce polymeric conductive fibers : the use of melt-spinning and electrospinning techniques.

Melt-spinning is a widely used technique for the fabrication of microfibers whereas electrospinning allows the production of fibers with diameters down to tens of nanometers. The first one is a melt-state technique that uses mechanical forces to stretch the fibers and the second one is a solvent-based technique that uses the force of an electric field to stretch the fibers (cf. Figure 1).

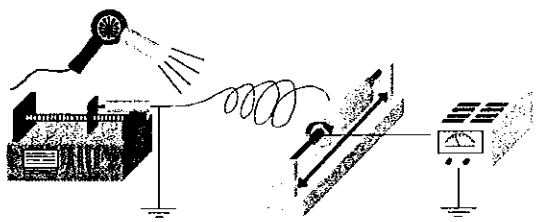

FIGURE 1. Electrospinning setup at NRC-IMI: the syringe pump is grounded and the substrate is connected to a high voltage power source. An optional heat gun can be used to increase the polymer solution temperature.

INTRODUCTION

The development of flexible and conductive fibers is a major challenge for smart textiles applications. All the approaches that have been used to incorporate conductive fibers into textile fabrics have important drawbacks: metallic fibers are rigid and are thus woven with much difficulties within the textile; conductive coatings tend to wear-out with friction and time, etc...). Therefore, the development of new materials is needed to produce conductive fibers that would match the mechanical properties of textiles and ensure a stable conductivity with time.

This study details several projects aiming at the production of conductive fibers obtained either by electrospinning or melt-spinning processes. The conductive materials were polymer-carbon nanotubes (CNTs) composites or polythiophene derivatives, a well known family of intrinsically conducting polymers (ICPs).

RESULTS AND DISCUSSION

1. Electrospinning of conductive polythiophenes nanofibers.

Polythiophenes are very rigid and insoluble in the conductive state. Two approaches were then studied to electrospin conductive polythiophene fibers: the first approach is the electrospinning of a soluble polythiophene (poly-3-hexylthiophene, P3HT) in its non-conductive (undoped) state, followed by its doping to render it conductive. The second approach is a two-step method involving electrospinning of a polymer precursor and a subsequent base inhibited vapour-phase polymerization (BI-VPP) [1], to obtain conductive fibers of poly(3,4-ethylenedioxythiophene) (PEDOT).

1.1 P3HT nanofibers

Even if P3HT is soluble in common organic solvents such as chloroform or tetrahydrofuran, the rigidity of its chains does not allow the formation of nanofibers by the electrospinning technique, due to a lack of entanglements that hinders the formation of the fibers. The addition of a polymer carrier of high molecular weight is needed to produce continuous fibers, as can be seen in Figure 2.

The addition of a small amount of high molecular weight PEO resulted in the production of nice nanofibers with diameters around 500 nm [2]. The alignment of the polymer domains along the fiber axis was observed by SEM and TEM (cf. Figure 3).

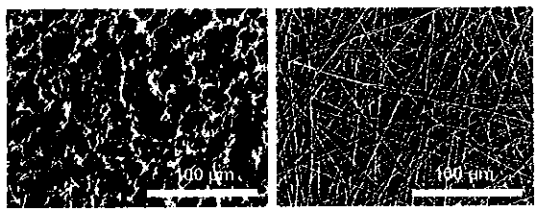

FIGURE 2. SEM images of P3HT samples electrospun without (left) and with (right) addition of PEO.

The fibers were doped with iodine vapours and conductivities around 0.16 S/cm were measured. However, this conductivity was not stable in time

due to the continuous dedoping of the P3HT with time.

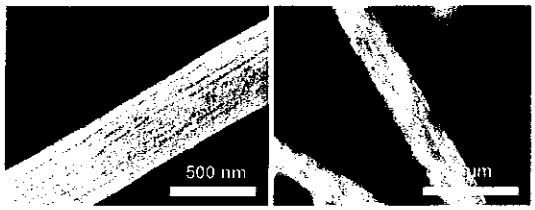

FIGURE 3. SEM (left) and TEM (right) images of P3HT nanofibers. In the TEM picture, white domains are PEO whereas gray domains are P3HT.

1.2 PEDOT nanofibers

PEDOT is one of the most widely used ICP, due to its high conductivity and oxidative stability. PEDOT is not electrospinnable by itself because of its total insolubility. A two-step technique was then investigated to circumvent this issue: an alcohol solution containing the oxidant used in the polymerization of PEDOT (ferric tosylate, FeTos), and a small amount of PEO (600,000 g/mol) was first electrospun into nanofibers (cf. Figure 4a). A small amount of pyridine was also added as a base inhibitor during the following polymerization. The light orange color is characteristic of the oxidant solution. The fibers were then transferred into a reaction chamber filled with argon and containing the EDOT monomer. The monomer temperature was increased to 55°C and the polymerization took place during 80 min. The fibers color turned to blue, the characteristic color of PEDOT (cf. Figure 4b). After washing with methanol to get rid of the unreacted chemicals (monomers?), the fiber mat was dried under a nitrogen stream.

The electrical conductivity of the nanofiber mats was measured to be 200 ± 50 S/cm, which is the highest value ever reported to our knowledge for polymer nanofibrous materials. As the dopant (tosylate ion) is not volatile, the conductivity is expected to be very stable in ambient conditions.

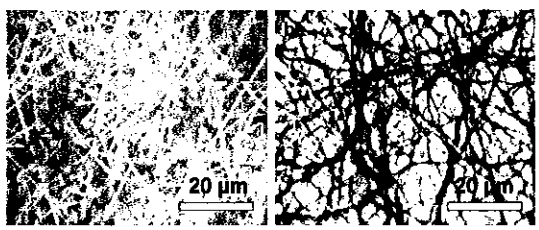

FIGURE 4. Optical images of the FeTos/Pyridine/PEO nanofibers (a) and of the PEDOT nanofibers obtained after BI-VPP (b).

2. Melt-spinning of polymer-CNTs composites

Several polymer masterbatches containing 15 wt% of multiwalled CNTs were obtained from Hyperion Catalysis. However, when melt-processed as received, their mechanical properties were very poor, leading to brittle, non-usable materials. They were melt-diluted to 7.5 wt% using the corresponding homopolymer in a twin-screw extruder to obtain composites with enhanced mechanical properties. They were melt-spun into single filaments with minimal post-stretching to yield conductive fibers having diameters around 500 µm. (cf. Figure 5). Average conductivities of the filaments were 2.10^{-2} S/cm for PET and PC composites and 4.10^{-7} S/cm for the PA composite showing a loss of electrical percolation in the latter case. PET fibers were still brittle whereas the PC and PA fibers possessed good mechanical properties. Next steps will include post-stretching of the fibers and the study of both mechanical properties and conductivity at varying fiber diameters and processing conditions.

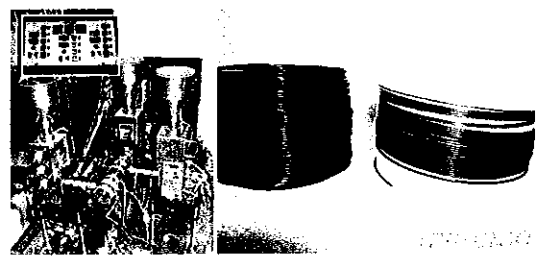

FIGURE 5. Left : Melt-spinning line at NRC-IMI capable of spinning fibers with up to three coaxial layers of three different materials. Right : PC-MWNTs composite fibers.

CONCLUSIONS AND PERSPECTIVES

Different strategies are being studied at NRC-IMI to obtain conductive fibers for textile applications. First results are very promising and future work includes optimization of the processes and further characterization of the fibers.

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[1] Winther-Jensen, B., Chen, J., West, K., Wallace, G. , "Vapor-Phase Polymerization of 3,4-Ethylenedioxythiophene: A Route to Highly Conducting Polymer Surface Layers", *Macromolecules,* 37, 2004, 4538-4543.

[2] Laforgue, A., Robitaille, L., "Fabrication of poly-3-hexylthiophene / polyethylene oxide nanofibers using electrospinning", *Synthetic Metals*, doi:10.1016/j.synthmet.2008.04.004