Nano and Micro Fibers for Conductive Applications

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ABSTRACT
Micro- and nanofibers have been obtained by melt-spinning or electrospinning. Melt-spinning uses mechanical forces to stretch fibers while electrospinning allows the production of fibers using the force of an electric field to stretch them. The study focuses on the production of conducting fibers by processing intrinsically conducting polymers (ICPs) or conventional polymers containing carbon nanotubes. The fibers were characterized by electron microscopy (SEM, TEM) as well as 4-point probe conductivity measurements.

Keywords
Nanofibers, melt-spinning, electrospinning, conductivity, conducting polymers, carbon nanotubes, nanocomposites.

INTRODUCTION
The textile industry is currently moving towards more and more sophisticated applications with the addition of specific high-end functionalities, including health monitoring[1-3], sports[4], heat control[5-7], electronics[8, 9], fashion[10, 11], etc. For the majority of these applications, data and energy communication within the fabric are major issues and require adequate conductive pathways. However, conducting materials, typically metals or carbon, are usually rigid and present limited flexibilities.

Different approaches have been studied to incorporate conductive fibers into textile fabrics: the use of ultrathin metal fibers[12], coating of textile fibers with thin layersof metal[13-15], carbon[16], or intrinsically conducting polymers[17]. However, these approaches have several drawbacks such as the wear-out of the coatings with time, the oxidation of the metal layers, or the rigidity of the conductive fibers[18]. 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.

The most widely used polymer fiber production process is fiber spinning, a process that allows manufacturing of fibers with diameters down to ten(s) of microns. During the last decade, the electrospinning process has been investigated to obtain fibers with diameters down to tens of nanometers[19, 20]. These nanofibers are obtained in the form of non-woven mats and present considerable potential for various applications including sensors, ultrafiltration, biological cell growth, functional textiles etc. In this process, the fiber formation and stretching is obtained by the application of an electric field between the solution-containing syringe and the fiber collector. Polymers are usually electrospun from solutions but can be also melt-processed[21]. The set-up built at NRC-IMI is illustrated in Figure 1.

Functional polymers and polymer nanocomposites are increasingly attracting the attention of the textile industry because of their promising functional applications, which can maximize properties such as mechanical, thermal, barrier, electrical or piezoelectric properties and/or allow the development of new properties, such as lighting (photoluminescence, electroluminescence), color change (photo or electrochromism), thermoregulation, etc…

This paper describes several projects carried out at NRC-IMI that aim at the development of polymeric nano and microfibers which present electric conductive properties. Fibers were obtained either by electrospinning or melt-spinning processes. The conductivity was obtained by adding carbon nanotubes into non-conductive polymers or by processing directly intrinsically conducting polymers (ICPs). The fibers were characterized by microscopy techniques (SEM, TEM), and 4-points probe conductivity measurements.

EXPERIMENTAL
Materials. Regio-random poly-3-hexylthiophene (P3HT) was chemically synthesized using the $FeCl_3$ oxidation method, as described elsewhere[22] (Mw = 43,700 g/mol, PS standard; PDI = 2.8 as determined by gel permeation chromatography in THF ; 72 % head-to-tail diads content). Polyethylene oxide (PEO, Mw 1,000,000 g/mol – *Polysciences*) and polyacrylonitrile (PAN, Mw 150,000 g/mol – *Sigma-Aldrich*) were used as received. Carbon nanotubes (MWNTs purity > 95 % from *Helix Corporation*, USA and purified SWNTs (> 95 %), *Bucky USA*, USA) were used as received or chemically modified with triphenylphosphines (TPP) according to a reported procedure[23]. Polymer masterbatches containing 15 wt% of MWNTs – polycarbonate (PC), polyethylene terephthalate (PET) and polyamide 6,6 (PA) – were obtained from *Hyperion Catalysis*, USA and used as received or melt-diluted through twin screw compounding with corresponding homopolymers.

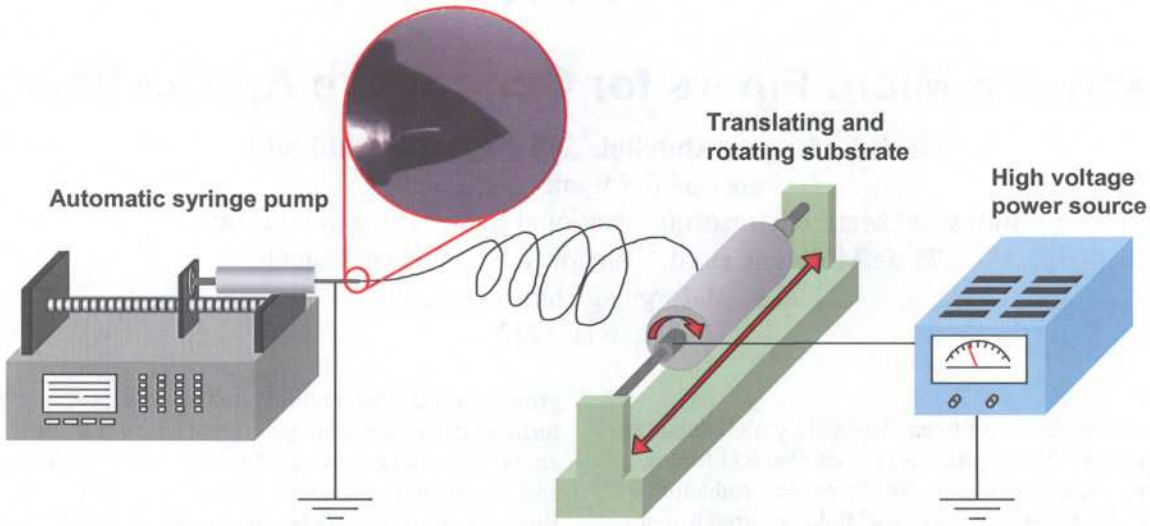

Figure 1. Electrospinning setup at NRC-IMI. Inset is a photograph of the Taylor cone at the end of the needle caused by the electric field, where the drop breaks into a jet flying towards the substrate (jet to small to be visible in the picture) .

Electrospinning. The electrospinning solutions were prepared by dissolving the polymers into appropriate solvents and stirring for a minimum of 12 hours with the aid of gentle heating. P3HT and PEO were dissolved in chloroform.

The polymer solutions were filled into a glass syringe terminated by a stainless steel needle. The syringe was placed in an automatic pump (Harvard Apparatus PHD 440) and grounded (cf. Figure 1). A stainless steel target on which the fibers were collected was connected to a high voltage power supply (Gamma High Voltage Research Model ES75P-10W). Nanofibers mats for electrical conductivity measurements were electrospun on a non-conductive polyimide sheet (50 µm thick), which served as a rigid substrate easier to handle than the unsupported mat.

Characterization. Scanning electron microscopy observations were performed on a Hitachi S4700 microscope. The diameter analysis, histograms were built using SEM image analysis on a minimum of 50 fibers taken at several positions on the sample.

Electrical conductivity measurements were carried out under ambient conditions by the four-point probe method using a Bekktech conductivity cell and a VMP3 multipotenstiostat (Princeton Applied Research, USA).

Transmission electron microscopy (TEM) was performed on a JEOL JEM2000FX operated at 80 kV. For TEM observation, the electrospun mats were embedded into an epoxy resin and cut into 50 to 80 nm lamellas using a Leica Ultracut UCT ultramicrotome equipped with a EM FCS cryochamber. The samples were observed after I_2 staining (15 min to 1 hour).

RESULTS AND DISCUSSION

1. P3HT fibers by electrospinning.

P3HT is one of the most studied ICPs due to its good solubility in common organic solvents such as THF or chloroform. Main applications include sensors[24], solar cells[25] and organic field effect transistors (OFETs)[26]. P3HT has a very rigid backbone structure that prevents reaching the degree of chains entanglement that is required to form fibers through the electrospinning process. To be able to obtain fibers, high molecular weight PEO was added to help the formation of fibers. Figure 2 shows an optical micrograph of fibers containing 75 wt% of P3HT and 25 wt% of PEO. They have the bright red colour typical of P3HT.

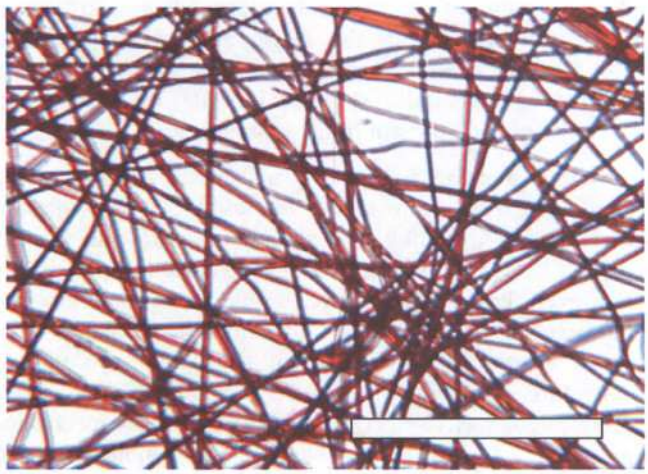

Figure 2. Optical microscopy of electrospun nanofibers containing 75 wt% of P3HT. Scale bar represents 50 µm.

A number of different parameters can be used to control and modify the fiber properties, such as distance from needle to collector, voltage, solution viscosity, pump flow rate, needle size, blend ratio, etc… An optimisation of the processing conditions was performed. For example, the strict control of voltage was found critical for the formation

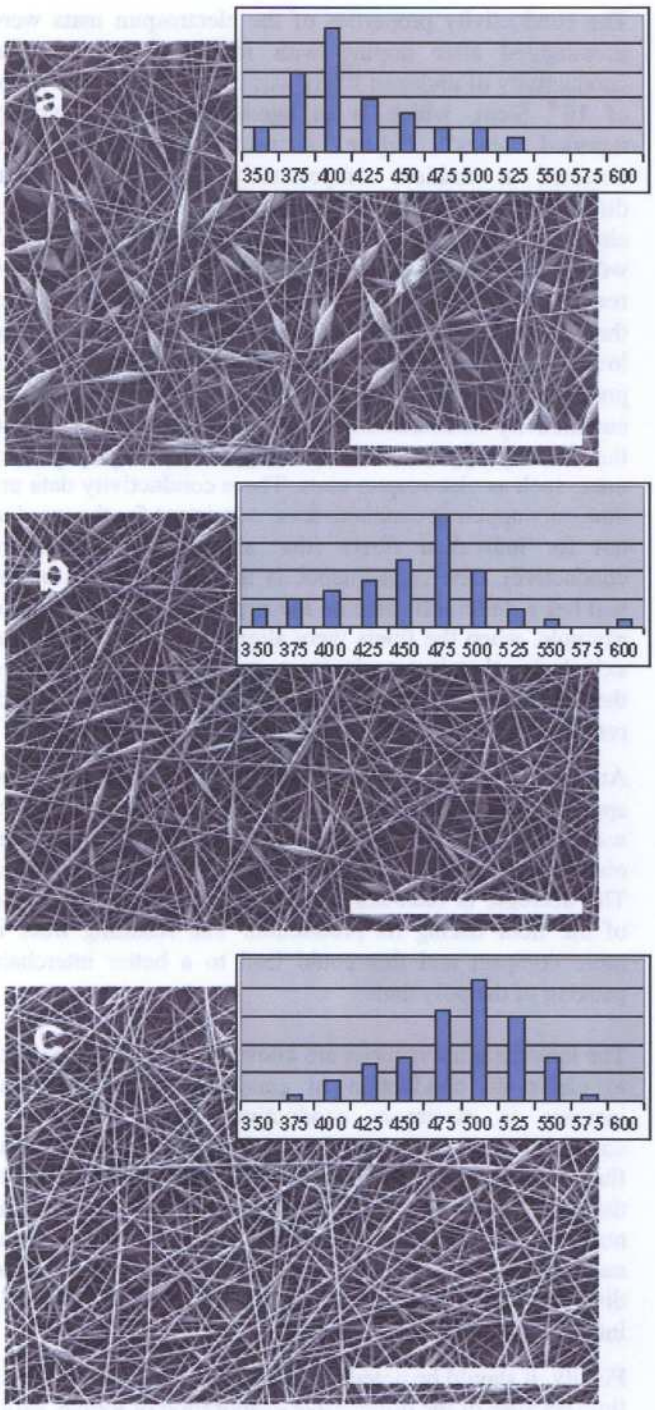

Figure 3. SEM micrographs of nanofibers containing 75 wt% of P3HT, obtained at different voltages: 14 kV (a), 18 kV (b) and 22 kV (c). Inset are the histograms of the fibers diameters (in nm). Scale bar represents 10 μm.

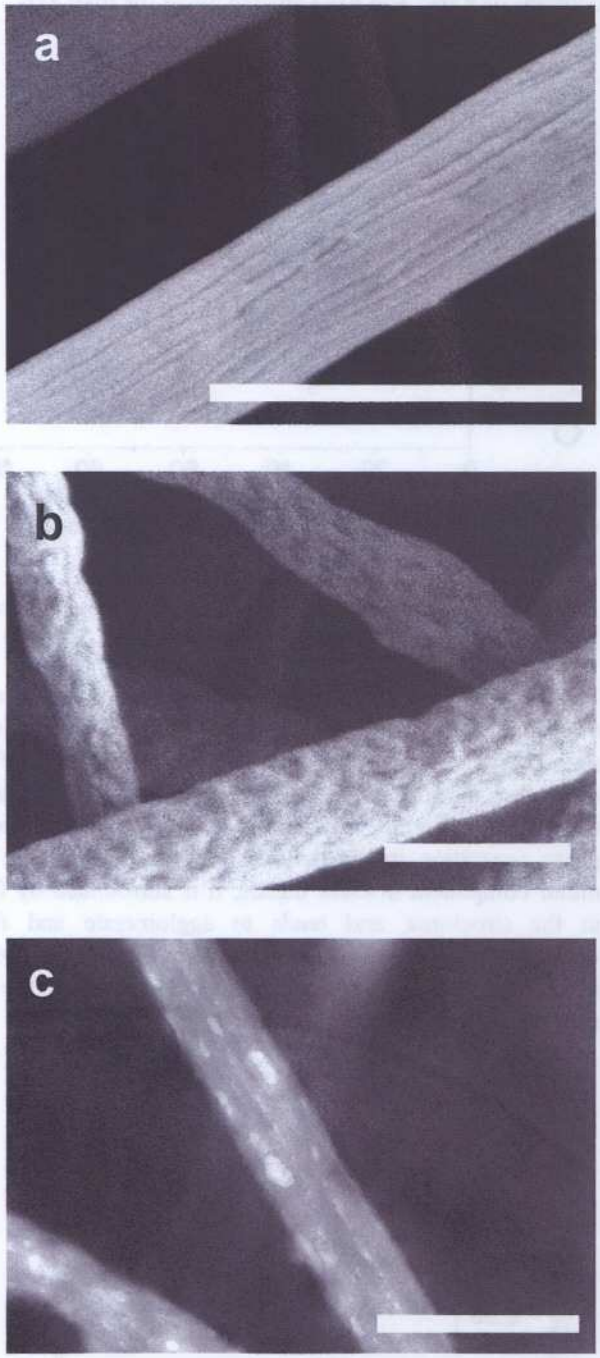

Figure 4. SEM micrographs of nanofibers with a P3HT content of 75 wt% (a) and 33 wt% (b) and TEM micrograph of a nanofiber containing 75 wt% of P3HT (c). All scale bars represent 1 μm.

of perfect (non-beaded) nanofibers, as can be observed on Figure 3.

When the voltage was to low, beaded fibers were obtained as a consequence of the surface tension instability of the polymer solution drop coming out of the needle tip. By increasing the voltage, the beads progressively disappeared from the fibers and above 22 kV non-beaded fibers were obtained. As can be seen on the histograms of the fibers' diameter, the size of the fibers increased with the progressive disappearance of the beads, as a consequence of the incorporation of the polymer material of the beads into the fibers.

When P3HT was the major component in the fibers, their surface was striated as can be seen on Figure 4a. This tends

to indicate that the structure was composed of segregated domains of P3HT and PEO aligned along the fiber axis.

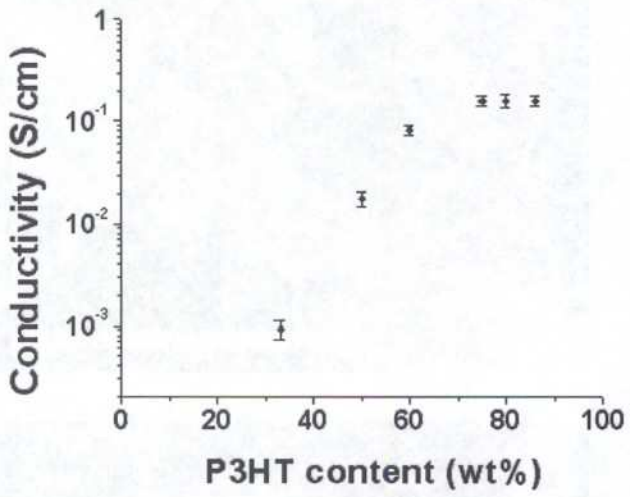

Figure 5. Apparent conductivity of iodine-doped nanofibers at different P3HT contents.

TEM experiments (cf. Figure 4c) confirmed the alignment of clear PEO domains in a darker P3HT matrix (selectively stained by iodine). When the P3HT content in the fiber decreased, the surface became rough and no striations were observed (cf. Figure 4b). This is believed to be related to phase separation in the polymer blends. P3HT being the minor component in these blends, it is surrounded by PEO in the structures, and tends to agglomerate and form irregular nodules, as already observed in electrospun blends involving P3HT and other polymers[27]. Its rigid structure can explain this agglomeration behaviour.

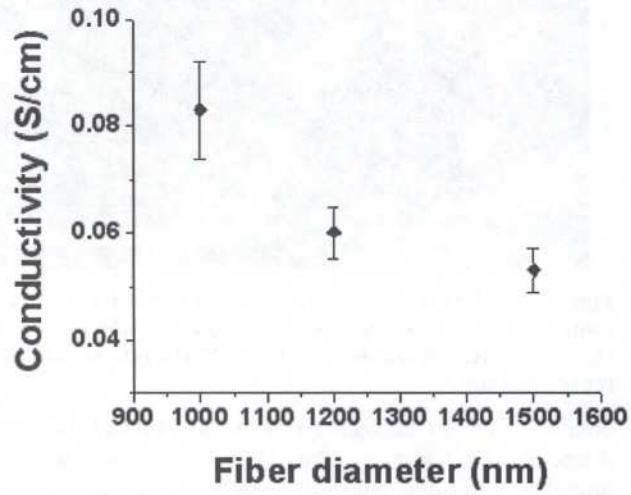

Figure 6. Apparent conductivity of iodine-doped nanofibers at different fiber diameters. (P3HT content = 60 wt%).

The conductivity properties of the electrospun mats were investigated after doping with iodine vapours., The conductivity of undoped fibers was found to be in the range of 10^{-9} S/cm, which is in agreement with previously reported values[28]. Figure 5 shows the conductivity values obtained at ambient temperature for doped fibers at different P3HT contents. The electrical percolation was already obtained at low P3HT content in the fibers (33 wt%). The conductivity increased progressively and reached a plateau at 0.16 S/cm for P3HT contents higher than 75 wt%. This value is about one order of magnitude lower than the conductivity measured on a P3HT film prepared by casting. It is important to note that the 4-points conductivity measurement method is a volumetric method that usually applies to bulk samples, not highly porous ones, such as electrospun mats. These conductivity data are thus only apparent conductivities, consistent for the mat but not for individual fibers (that should be much more conductive). One consequence is that the structure of the mat has a direct influence on the apparent conductivity. For example, when the fibers were aligned along a preferential axis during the electrospinning process, the conductivity in the direction of this axis was increased by a factor two, reaching 0.3 S/cm.

Another interesting phenomenon was observed: the apparent conductivity increased when the fiber diameter was decreased, as can be seen on Figure 6. A similar observation was already made on electrospun nanofibers. The decrease in diameter is due to an increased stretching of the fiber during its production. The resulting fiber is more compact and this could lead to a better interchain packing of the polymers.

The interchain interactions are known to be the main barrier to electronic conduction in conducting polymers. The increase in electronic conductivity could thus be a consequence of the compaction of the polymer chains in the fiber. Alternatively, this phenomenon could be attributed to the increase in the number of electronic paths through the mat, given that the lower the diameter, the higher the number of fibers you can put in a given volume. The discrimination between both explanations would be highly interesting and is presently investigated.

Finally, it should be noted that iodine doping is not stable in time because of the progressive evaporation of iodine. More stable dopants have to be used in order to achieve stable conducting polythiophene nanofibers. P3HT nanofibers have potential applications in sensors, thermochromic and electrochromic textiles.

2. CNT-polymer nanofibers by electrospinning.

One much studied way to induce electronic conductivity to polymers is to incorporate carbon nanotubes (CNTs) into conventional polymer matrixes. Percolation thresholds well below 1 wt% have been reported in the literature[29, 30]. However, the key point is the dispersion of the CNTs into

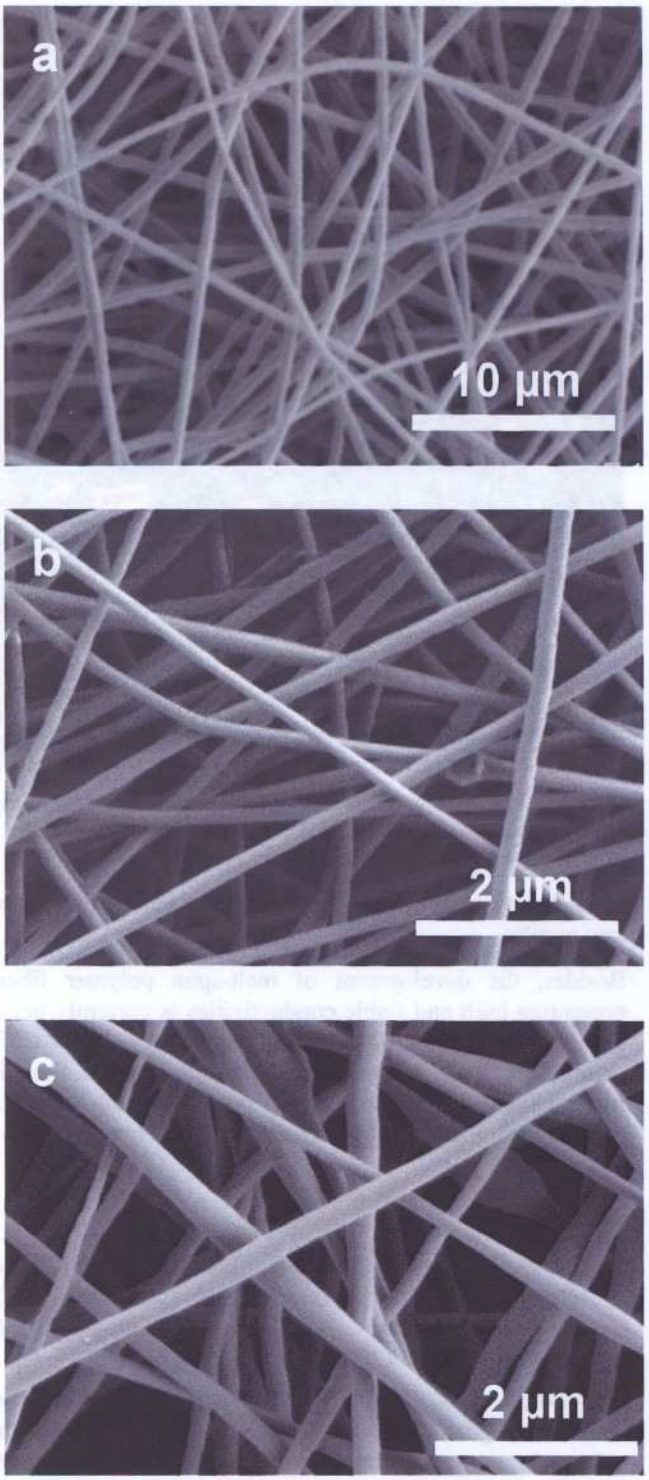

Figure 7. SEM micrographs of polystyrene (a) and polyacrylonitrile (b,c) nanofibers containing 10 wt% of MWNTs (a,b) and SWNTs (c).

the polymer, and this represents a significant challenge. Usually, chemical surface modification of the CNTs is needed to be able to de-agglomerate them. Other alternatives include the addition of dispersing agents, like surfactants or block copolymers that will help the dispersion of the CNTs. For example, arabic gum was successfully used for the dispersion into water-soluble polymers[29].

However, CNTs dispersion into organic solvents is much more difficult and strong acid treatments are usually required, in order to incorporate alcohol and carboxylic groups at the surface of the CNTs, which will improve the interactions between the nanotubes and the solvent molecules. It is important to note that the acid treatment partially destroys the surface of the carbon nanotubes, causing a degradation of the electronic properties. Moreover, only multi-walled carbon nanotubes can be treated, the single-walled nanotubes being totally destroyed in the process.

Several approaches are currently under investigation at NRC-IMI to disperse CNTs into polymer nanofibers by using block copolymers as dispersing agents or by chemical functionalization under mild conditions.

Figure 7 presents electrospun mats of different polymers containing 10 wt% of MWNTs dispersed using two methods. In the first case (Fig. 7a), PS was dissolved jointly with the nanotubes and a small amount of a block copolymer. In the second case (Fig. 7b,c), CNTs were first chemically modified with triphenylphosphines, following a recently published procedure[23]. This procedure being non-destructive, it can be applied to both multi-walled and single-walled nanotubes. However, the measured conductivities were in the range of 10^{-5} - 10^{-4} S/cm, lower than expected. It shows that the dispersion of the CNTs is still not sufficient to achieve a good electronic percolation in the nanofibers. These studies are in progress with the aim to achieve electronic conductivities in the range of 10^{-2} - 10^{-1} S/cm.

3. Conductive polymer fibers by melt-spinning.

Melt-spun conducting polymer fibers have a great potential of rapid market introduction, thanks to the already huge usage of melt-processes in the industry and hence the straightforward scale-up possibilities. Up to now, carbon-polymer conductive composites have not been able to be melt-spun because high contents of carbon filler are needed to obtain a conductive percolation (especially in stretched materials), at the detriment of mechanical properties of the fibers. However, the use of carbon nanotubes can overcome this problem. CNTs have very high aspect ratio and with an adequate dispersion, electric percolation can be achieved even at very low contents in the polymer matrix[31].

Several polymer masterbatches containing mult-iwalled CNTs are being studied at NRC-IMI for the development of conductive fibers. These masterbatches possess a high MWCNTs content (~15 wt%) and conductivities in the range of 0.1 to 1 S/cm. However, when melt-processed as received, their mechanical properties are very poor, leading to brittle, non-usable materials.

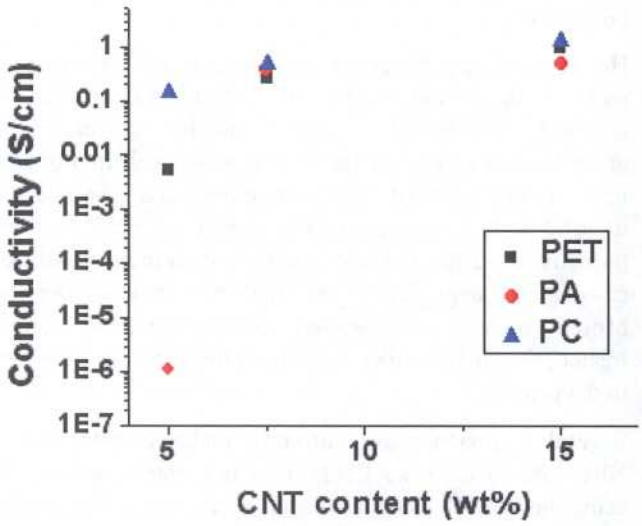

Figure 8. Conductivity of polymer/MWNTs composite films. PET: polyethylene terephthalate; PA = polyamide 6,6; PC = polycarbonate.

They were then melt-diluted using the corresponding homopolymer using both single-screw (5 wt%) or twin-screw extruders (7.5 wt%). The conductivity of the composites was first measured on thin hot-pressed films and is displayed in Figure 8. At 5 wt%, the conductivity droped to 5.10^{-3} and 1.10^{-6} S/cm for PET and PA composites, respectively, while the conductivity of the PC composite remains high.. However, especially with PA composites, a heterogeneous dispersion of the masterbatch into the homopolymer could also influence this decrease in conductivity. At contents lower than 10 wt%, the mechanical properties of PA and PC composites improved significantly whereas the PET composites were still very brittle.

The composites were melt-spun into single filaments without post-stretching, to yield conductive fibers having diameters around 1 mm using a Randcastle multi-material processing system equipped with a multilayer fiber spinning die (cf. Figure 9). Conductivities of the unstretched filaments were in the same order of magnitude than the thin films. These first results are promising. 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.

CONCLUSIONS

Two fiber spinning techniques were used to produce conducting fibers that could be incorporated into smart textiles.

Electrospinning leads to nanofiber mats that are difficult to handle as individual fibers but could be incorporated into garments as sensing zones for different applications, like textrodes in health monitoring textiles. Nevertheless, more work has to be carried out to ensure higher and more stable conductivity before these fibers can be successfully used into textiles.

Figure 9. Photograph of the monofilament multilayer spinning set-up designed at NRC-IMI and capable of spinning fibers with up to three coaxial layers of three different materials.

Besides, the development of melt-spun polymer fibers presenting high and stable conductivities is currently being carried out at NRC-IMI. The first results on polymer-CNT composites look promising and should lead to flexible fibers having conductivities as good as the bulk material, ensuring a higher stability than fibers possessing conductive coatings.

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