Analysis of Electrospinning of nanofibers as a function of Polyacrylonitrile (PAN) concentration

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ABSTRACT
Carbon nanofibers find application in several fields, including nanoelectronics, photonics, and nanosensing. Previous results have demonstrated that they can be easily obtained by using a fabrication process including electrospinning of polymeric fibers followed by vacuum pyrolysis. In this paper we investigated the use of electrospinning using precursor solutions with different concentrations of polyacrylonitrile (PAN) (1% - 8% w/w) diluted in a fixed amount (10 mL) of N,N dimethylformamide (DMF). We explored the fact that differences in concentration reflect in differences of viscosity, what affects the characteristics of the deposited fibers. Fibers deposited with PAN concentrations higher than 3% are more uniform and present diameters in the range between 37 nm – 260 nm. For smaller concentrations the fibers present bead-like imperfections and AFM results demonstrated that fibers with diameters as small as 20 nm can be obtained, that are uniform for lengths in the range of microns.

II. INTRODUCTION
Carbon nanofibers can be easily obtained by using a fabrication process including electrospinning and vacuum pyrolysis. Using a PAN/DMF precursor solution (800 mg of polyacrylonitrile / 10 mL of N,N dimethylformamide) and performing vacuum pyrolysis at temperatures from 773 to 1273 K (0.5 to 5 h), Wang et al. [1] confirmed the formation of graphite carbon at near 873 K. Raman scattering analysis revealed the coexistence of graphitic and disordered carbons. These nanofibers exhibit interesting properties, as their conductivity increases monotonically with temperature, showing an apparently semiconducting behavior. Also, their conductivity increases with the external transverse magnetic field, revealing a negative magnetoresistance at temperatures between 1.9K and 10K [2].

Carbon nanofibers, like other quasi-one-dimensional (1D) nanostructures (nanowires, nanotubes and molecular wires), are receiving increased attention due to the possibility of applications in nanoelectronics, photonics, and nanosensing, among other fields [3-5].

Electrospinning is an easy and cost-effective process to obtain micro and nanofibers [6 – 8]. Huang et al. [6] compare in detail this technique with others used to obtain polymeric fibers and, also, give extensive information about the use of different types of polymers with electrospinning. Recent works have demonstrated the feasibility of obtaining self-alignment of fibers and structures (normally pads for electric contact) previously defined on the substrate [9, 10].

In this paper we investigate the characteristics of fibers electrospun using solutions with different concentrations of polymer, polyacrylonitrile (PAN) in solvent, N,N dimethylformamide (DMF), aiming at to obtain fibers with very reduced diameters (with tens of nanometers).

III. EXPERIMENTAL
The precursor solutions were prepared using different amounts of polymer (100, 200, 300, 400, 500, 600 or 800 mg, commercial polyacrylonitrile - PAN), and 10 mL of solvent (N,N dimethylformamide - DMF) in order to obtain concentrations ranging from 1 to 8% w/w. The solutions were stirred (900 rpm) during 24 hours, at room temperature before analysis or deposition.

The fibers were electrospun using a homemade apparatus, Fig. 1, composed of a DC power supply (Gamma High Voltage Research Inc., 0 – 30 kV), a syringe (volume of 3 cm³, needle type 26G(5/8)) and a collection screen (copper spiral covered with aluminum, placed at a horizontal distance of 15 cm from the tip) that sustained the substrates (silicon, <100>, 10–20 Ωcm, 1.5 cm x 1.5 cm). The samples were positioned in the center of the collection screen using a plastic tape with glue on both sides. The syringe was tilted at approximately 15º from horizontal so that a small drop was maintained at the capillary tip, due to the surface tension of the solution. We used a fixed potential difference of 15 kV between the tip and the grounded screen and a fixed deposition time of 20 s. Relative viscosities of the different precursor solutions were measured using a calibrated viscometer Ubbelohde, from Cannon.

![Fig. 1 - Electrospinning setup.](image-url)

Absolute viscosity was determined by using a viscometer Brookfield LVDV-III+. After deposition, the samples were analyzed by Scanning Electron Microscopy (SEM), Jeol – JSM 6360, and Atomic Force Microscopy (AFM), Digital Instruments – Dimension 3100.

For SEM images the fiber diameter was determined using an algorithm developed for Matlab. It permits to define two straight lines parallel to the fiber and calculates
the distance between these lines considering the number of pixels and their equivalent for distance.

The adhesion of samples to the substrate was analyzed using a profilometer (Alpha Step 500 – Tencor) stylus probe scanned horizontally with different loads.

IV. RESULTS

Figure 2 shows the relative viscosity obtained as a function of the concentration of PAN in the precursor solution. The absolute viscosity of the solution with 6% of PAN is 12.9 cP. It can be seen that working with amounts of PAN in the range between 1% to 8% causes measurable variations of the viscosity. Also, in this range, the viscosity has an almost exponential variation with concentration of PAN. As the viscosity has a very strong influence in the electrospinning process, these results show that different characteristics can be expected for the deposited fibers, accordingly to related works [11].

![Figure 2 - Relative viscosity as a function of the concentration of PAN in the precursor solution.](image)

A decrease of the concentration of PAN in the precursor solution causes a decrease of the amount of fibers that is deposited for a fixed time. Figure 3 compares the density of fibers obtained for a same area for solutions with 5% and 3% of PAN.

![Figure 3 - Density of fibers obtained for (a) 5% and (b) 3% of PAN in the precursor solution, using a fixed deposition time of 20 s.](image)

The use of higher concentrations of polymer is interesting when it is necessary to obtain mats of fibers. In this case fibers are deposited on fibers forming a tissue-like structure that can be easily removed from the substrate. The analysis of the adhesion of the fibers, by using a profilometer stylus probe scanned horizontally, reveals that some fibers can be removed by the substrate by using loads as low as 2 mg.

For precursor solutions with more than 2 % w/w the obtained fibers can be analyzed with SEM. Table 1 shows the range of variation of the diameter of the fibers as a function of the concentration of PAN. It can be observed a tendency to obtain fibers with smaller diameters as the concentration of PAN in the precursor solution decreases.

<table>
<thead>
<tr>
<th>PAN Concentration (w/w)</th>
<th>Range of Variation of the Diameters of the Fibers (nm)</th>
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<tbody>
<tr>
<td>5 %</td>
<td>109 - 260</td>
</tr>
<tr>
<td>4 %</td>
<td>37 - 94</td>
</tr>
<tr>
<td>3 %</td>
<td>35 - 88</td>
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</table>

Figure 4 compares the aspect of the fibers as a function of the concentration of PAN. Fibers prepared with precursor solutions with more than 3% of PAN are uniform and smooth for large lengths (in the millimeter range) as that presented in Figure 4a. Decreasing the concentration of PAN the fibers present diameter variations and imperfections as illustrated in Figure 4b. This result is explained by the decrease of viscosity. The formation of these imperfections occurs because of the capillary breakup during the spinning, due to variations of the surface tension. In the case of polymer solutions, there is a formation of small filaments between the droplets resulting in beads-on-string structures.

Thus, polymer molecules in the solution became an elongated and oriented network after the fiber solidifies and the jet radius driven by the surface tension causes the formation of beads [12].
devices, as we intend to explore further. Electrospinning is a very cost-effective process compared to other techniques (like CVD for example) to obtain fibers in the nanometric range. So, as we demonstrated in this work, it is possible through the control of the process parameters, to obtain fibers with different characteristics. This is an interesting feature of the electrospinning process when the objective is the application of the fibers in the sensors field, for example.

As it is possible to obtain the nanofibers as a non woven fabric and with different diameters, a potential application of these nanofibers is in the pre-concentration of liquid samples before insertion in an chemical sensor. Another interesting application is use these mats as filters. Both of these applications use the very high area to diameter ratio of the nanofibers.

V. CONCLUSION

We demonstrated the feasibility of obtaining fibers, using electrospinning, with diameters in the range between 20 nm and 260 nm by controlling the concentration of polymer (PAN) in the precursor solution, and correspondently the solution viscosity. Fibers deposited with PAN concentrations higher than 3% are more uniform and present diameters in the range between 37 nm – 260 nm. For smaller concentrations the fibers present bead-like imperfections and AFM results demonstrated that fibers with diameters as small as 20 nm can be obtained, that are uniform in the range of microns. The near 1-D confinement and high surface to volume atomic ratio in these materials produces a number of unique physical-chemical properties that we will continue exploring in future works.

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VII. REFERENCES


