Materials Research, Vol. 8, No. 1, 105-108, 2005 © 2005

Electrostatic Deposition of Nanofibers for Sensor Application

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Received: October 29, 2003; Revised: November 22, 2004

This work addresses the formation of nanofibers (with hundred of nanometers) by using electrospinning (electrostatic deposition) aiming at applications as sensors. Different quantities of a colloidal dispersion of graphite particles were blended with polyacrylonitrile (PAN) and N,N dimethylformamide (DMF), resulting in a series of solutions with carbon concentrations ranging from 0 to 25%. Precipitation was observed depending on the concentration of carbon added to the precursor blend. As a consequence, the relative viscosity decreases, due to PAN molecules removal from the solution by carbon particles adsorption, forming precipitates. The resulting fibers show an irregular shape, as observed by SEM and the diameters decrease with the increase of the carbon concentration in the precursor blend. The incorporation of carbon particles in the fibers was confirmed by FTIRS and Raman spectroscopy.

Keywords: *electrospinning, nanofibers, sensors, polyacrylonitrile, carbon nanofibers*

1. Introduction

The electrospinning process (electrostatic deposition) has been largely used in order to produce filters, membranes, optical and electronics applications, among others[1,2]. This process occurs when the electrical forces at the surface of a polymer solution overcome the surface tension and cause an electrically charged jet to be ejected. The solvent evaporates as the jet travels in air, leaving behind charged polymer fibers that lay themselves randomly on a collecting metallic electrode[3].

It is well known that the morphology of the resulting fibers is determined by a synergetic effect of solution parameters and electrostatic forces[4]. These parameters include viscosity, surface tension, concentration and dielectric properties of the spinning solution and process parameters such as the feed rate of the solution to the tip and electric field. Also, ambient parameters including temperature, humidity and air velocity in the electrospinning chamber influence the results. Controlling these parameters, the fibers can be electrospun from different precursor solutions and their melts, like water soluble polymers and biopolymers. Also, the precursor solution can include pigments, carbon particles and many others materials that can be incorporated in the resulting fibers[5,6].

Electrospun fibers may have diameters ranging from less than 50 nm to 5 μm. The small diameters provide high surface area to volume and high length to diameter ratios. These characteristics together, associated to the easy way to obtain the fibers, makes the nanofibers a good choice to be used in sensors technology[1,6,7]. Other applications may be devised, such as separation membranes and non-woven fabrics. Otherwise, the non-woven fabrics obtained with the electrospun process may be coated with a metal layer and, subsequently, be used as an electrode in a dye based photovoltaic cell and other different kinds of sensors[8,9].

This work addresses the preparation and characterization of the polymer blends and the resulting nanofibers. The incorporation of carbon particles in the fibers during the deposition process may facilitate the conversion to carbon after subsequent thermal annealing and also improve their electrical characteristics[10,11], as we want to explore further. Given the broad distribution of the carbon particle size in the colloidal dispersion that we are using (300 nm to 1.5 μm)[12], we are looking forward to obtain process conditions that can lead to composite fibers with diameters in the range of hundreds of nanometers.

2. Experimental

Fibers were electrospun using a homemade apparatus, schematized in Figure 1, composed of: a DC power supply, a syringe (volume of 3 cm^3, needle type 23G1 - 0.6 mm x 25 mm) and a collection screen (copper plate placed at a horizontal distance of 15 cm from the tip) that sustained the samples (silicon, <100>, 10 – 20 Ωcm, 1.5 cm x 1.5 cm). The syringe was tilted at approximately 15° from the horizontal so that a small drop was maintained at the capillary tip, due to the surface tension of the solution. We worked with a fixed potential difference of 15 kV between the tip and the grounded screen.

The polymer solutions were prepared with 600 mg of commercial polyacrylonitrile (PAN) and 10 ml of N,N dimethylformamide (DMF)[13]. Different quantities of a colloidal dispersion of graphite particles[12], with diameters ranging from 300 nm to 1.5 μm, were blended with the polymer solution, resulting in a series of solutions with carbon concentrations ranging from 0 to 25%. The precursor solutions were stirred (900 rpm) during 24 hours, at room temperature, but some difficult was encountered to dissolve the PAN into DMF. Due to the presence of precipitate, just before filling the syringe the solutions were stirred (900 rpm) during 1 hour, to perform the electrospinning process.

The viscosities of the different solutions were measured using a calibrated viscometer Ubbelohde, from Cannon. Relative viscosity was determined dividing the flow time of the solutions with carbon by the flow time of the solution without carbon. After deposition, the

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Article presented at the II SBPMat, Rio de Janeiro - RJ, 26-29/October/2003

fibers were analyzed by Scanning Electron Microscopy (SEM) to evaluate the fibers shape and diameter. The chemical bonds and carbon incorporation into the fibers were analyzed by Fourier Transform Infrared Spectroscopy (FTIRS) and Raman Spectroscopy.

3. Results

Figure 2 presents SEM images of fibers that were electrospun using different concentrations of carbon particles in the blend. Figure 2a shows that for a concentration of 0% the fibers result very smooth and uniform in diameter. In this case, diameters lower than 100 nm can be easily obtained. With the addition of a small concentration of carbon particulates to the blend, as for example 1%, Figure 2b, the fibers present a more irregular shape. Increasing further the carbon particle concentration, for example to 7% as presented in Figure 2c, the fibers get a curled shape and the presence of beads and agglomerates can be noticed. For concentrations higher than 15% no fiber is deposited at all and one observes only the presence of the agglomerates.

It is reported that the solution characteristics like viscosity, conductivity and charge density are factors that strong influence the formation of beaded fibers[4,14].

In order to understand how the solution characteristics influence the electrospinning process and the resulting fibers, the solution viscosity, the weight of precipitates in the solution and the current during the electrospinning process were evaluated.

Figure 3 shows that the relative viscosity decreases, following an exponential behavior, as the concentration of carbon particles increases. If the solution viscosity is decreasing as the carbon concentration increases, it can be assumed that the concentration of PAN in the solution is decreasing. These results are in accordance with those obtained from the analysis of the weight of the precipitates as a function of the carbon concentration, as shown in Figure 4.

Examining the results presented in Figures 3 and Figure 4, one has to consider that the carbon particles used to prepare the precursor solutions are very small and have charge on the surface to avoid the precipitation and to maintain the colloidal structure. Also, the PAN molecules have dipoles due the presence of nitrile groups. Therefore, a charge imbalance appears into the solution as a consequence of the electrostatic forces between the charged carbon particle and the PAN molecules, leading these particles to agglomerate. If the solution is left resting during some hours, a precipitation is observed. As a consequence of the precipitation and because the polymer molecules are being removed from the solution by the carbon particles, there is less PAN molecules dissolved in a same volume of solvent, so the hydrodynamic volume occupied by PAN molecules decreases resulting in a lower viscosity. As a result, the fibers diameters decrease as a function of the carbon concentration as show in Figure 5.

Curled fibers with the presence of beads, as those observed in the Figure 2c, can be related to a low solution viscosity in accordance with the results in the Figure 3. Also, this phenomenum can be attributed to the fact that the applied voltage is too high for the used solution viscosity[6].

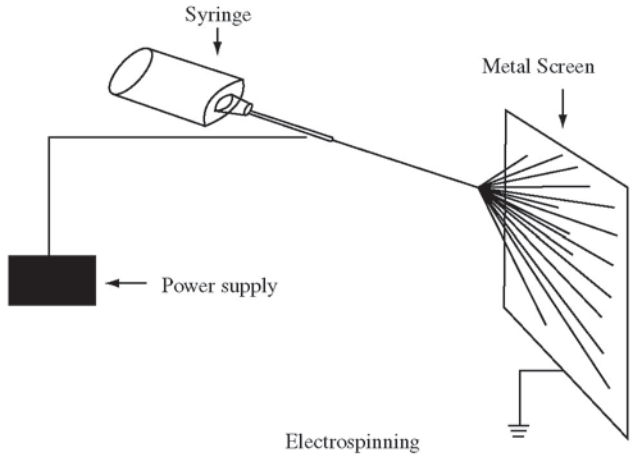
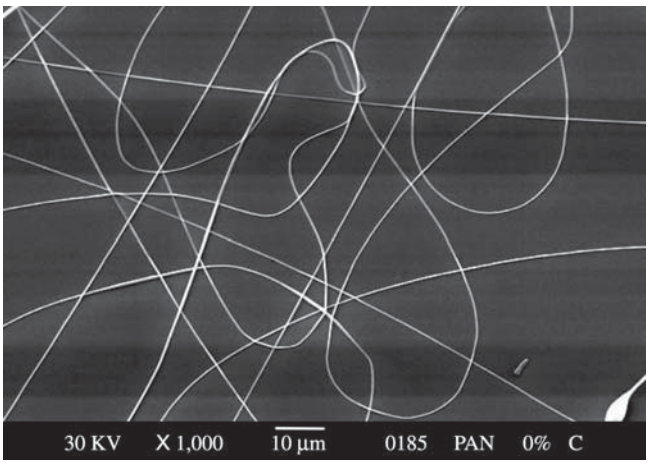
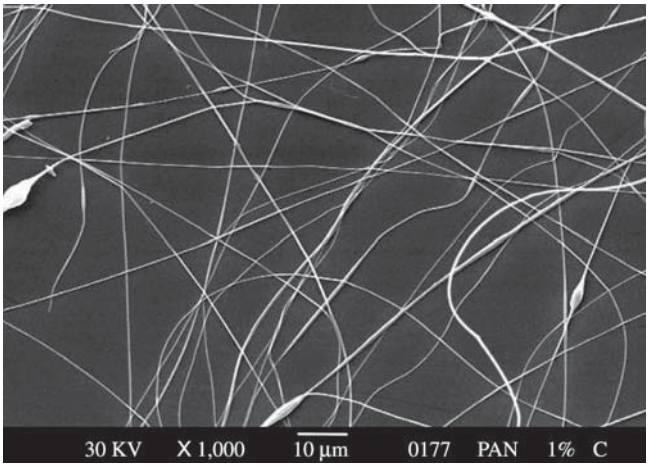


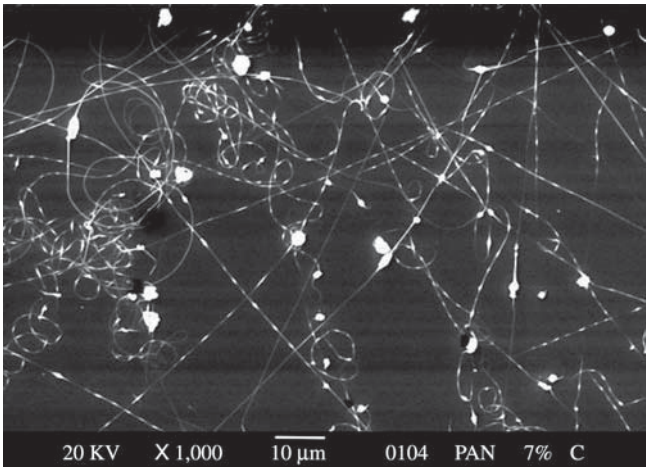
Figure 1. Electrospinning setup.



(a) 0%



(b) 1%



(c) 7%

Figure 2. SEM pictures illustrating the behavior of the fibers as a function of the concentration of carbon particles in the blend.

In order to investigate how the involved electrical charges are influencing the electrospinning process, the current was measured during the process for the different solutions prepared. The current value increases as a function of the carbon concentration for an applied voltage of 15 kV, as shown in Figure 6. An increase in the current value means an increase in the mass flow rate from the tip to the grounded target, considering all the other process parameters constant[7]. This increase in the mass flow rate can be explained considering that adding more conductive particles more charge is being generated, facilitating the electrospinning process.

The presence of carbon particles inside the fibers is confirmed by FTIRS and Raman analysis. In the FTIRS analyses, shown in Figure 7, a band in 1580 cm^{-1} is observed, which can be attributed to C=C bonds. The carbon particles have a C=C double bond that is not observed in the PAN monomer.

Figure 8 shows the Raman spectra, in a range of 1000 to 3000 cm^{-1}, considering fibers electrospun from blends with 0%, 1% and 10% of carbon. The spectrum obtained from the continuous layer of carbon and DMF is shown only for comparison. In these spectra there are two broad peaks centered on 1360 and 1590 cm^{-1}, which are the D and G peaks which are characteristic of disordered carbon and graphite, respectively, and are attributed to sp^2-bonding. In the spectra obtained from the fibers electrospun from solutions with 1 and 10% of carbon two overlapping broad bands can be observed, which can be attributed to the G and D carbon peaks. These peaks are well aligned with the peaks obtained using a carbon film. As no band can

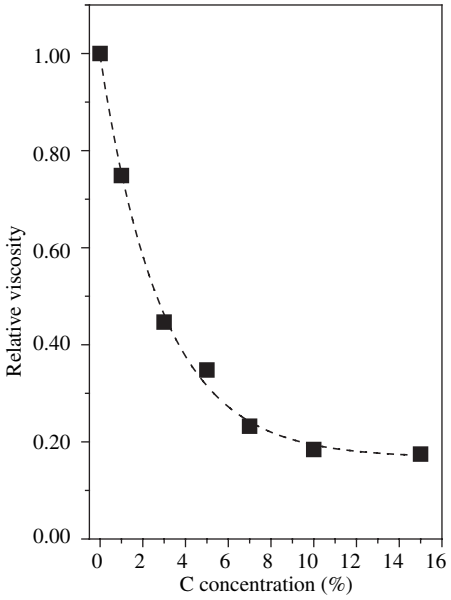


Figure 3. Relative viscosity as a function of the concentration of carbon particles.

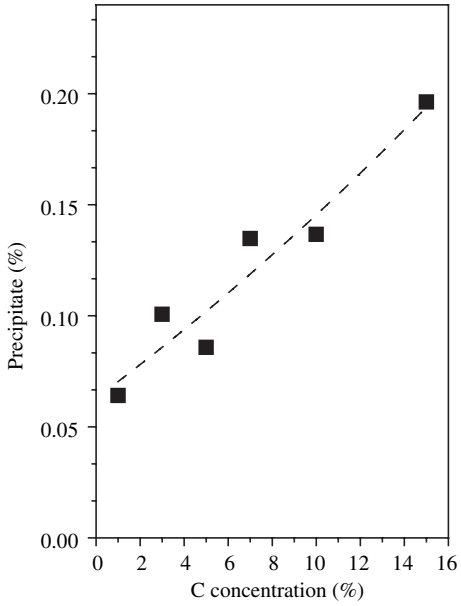


Figure 4. Precipitate percentage as a function of the concentration of carbon particles.

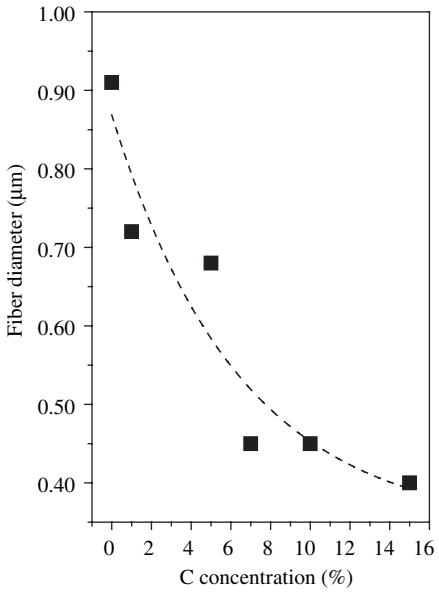


Figure 5. Fiber diameter as a function of the carbon concentration.

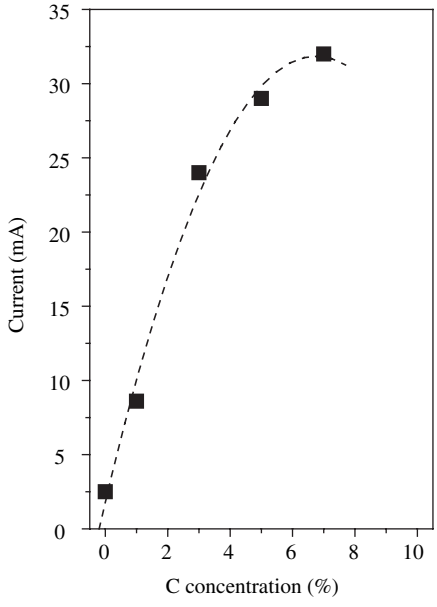


Figure 6. Current as a function of the carbon concentration for a fixed applied voltage of 15 kV.

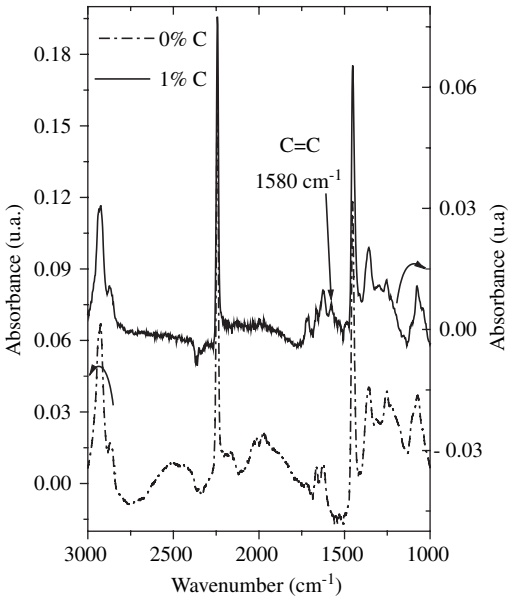


Figure 7. FTIRS spectra obtained from the fibers with 0% and 1% w/w of carbon particles added to the precursor solution.

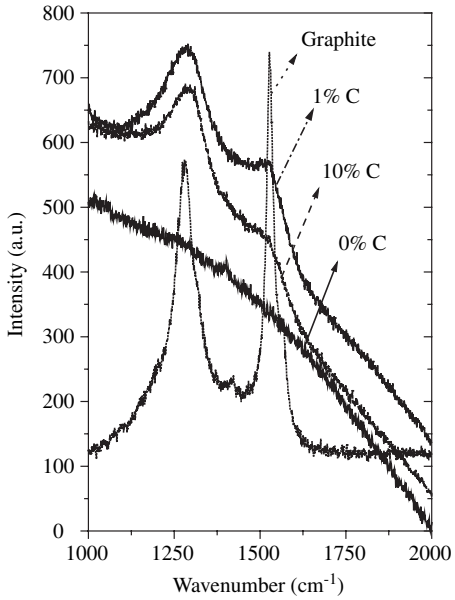


Figure 8. Raman spectra obtained from the fibers with 0%, 1% and 10% w/w of carbon particles added to the precursor solution. The spectrum obtained from the continuous layer of carbon and DMF is included only for comparison.

be observed in the spectrum taken from the fibers electrospun without carbon, it can be concluded that the carbon particles are really incorporated into the fibers.

Thus, the analysis of the precursor solutions reveals that due to the variation in the viscosity and the precipitate formation, the solutions prepared with more than 1% of carbon particles are not suitable for the electrospinning process. Also, the fibers electrospun from these solutions have beads and diameter variations that may affect the electrical behavior of these fibers.

4. Conclusion

The feasibility of incorporating carbon microparticles in fibers deposited using electrospinning is reported. The influence of the preparation method of the precursor solution was also discussed. A precipitation is observed as a function of the concentration of carbon added to the solution. As a consequence, the viscosity of the solution decreases because the PAN molecules are removed from the solution by the carbon particles, forming precipitates. For carbon concentrations higher than 15% the solution becomes not appropriate to perform electrospinning. The fibers with incorporated carbon show an irregular shape, as observed by SEM, and the variations in the diameter of their smooth sections decrease with the increase of the carbon concentration in the blend. The incorporation of carbon particles in the fibers was confirmed by FTIRS and Raman spectroscopy.

Acknowledgment

This work was supported by NSF-DMR-0353730 and NSF-SBE-0123654. We kindly acknowledge Acheson Colloids Company for providing colloidal dispersion of graphite microparticles. We would like also to acknowledge the Materials Characterization Center (MCC), at UPR-Rio Piedras, for the FTIRS and Raman analysis, and the IQ-USP for Raman analysis.

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