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Characterization of an Electrospinning Process using Different PAN/DMF Concentrations

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Abstract: We performed an extensive characterization of an electrospinning process to evaluate how the process parameters and precursor solution characteristics affect the fibers morphology. The work was conducted using precursor solutions with different concentrations of polyacrylonitrile (PAN) diluted in a fixed amount of N,N dimethylformamide (DMF). Fibers obtained with this process can find important applications in the field of nanosensors. The characteristics of the electrospun fibers were analyzed as a function of the solution viscosity, applied voltage and distance between the needle tip (positive electrode) and the collector plate (grounded electrode). The electrical current was monitored during the deposition process and its behavior was correlated with the characteristics of the fibers obtained. Our results demonstrate that the diameter of the fibers increases with increasing viscosity and applied voltage. The number of deposited fibers also increases with the applied voltage. Also, viscosity and applied voltage strongly affect the shape, length and morphology of the fibers. Of particular interest, we demonstrated that by monitoring the electrical current it is possible to control the fibers morphology and bead concentration. The distance between tip and collector plate determines the way the fibers arrive on the collector plate. A main contribution of this study was the definition of conditions to controllably obtain fibers that are smooth and that present diameters in the range between 140 and 300 nm.

Keywords: *Nanofibers (A), electrospinning (E), nanostructure (A).*

Introduction

The electrospinning process has been largely used by industries in order to produce filters, membranes, optical and electronics applications, among others. It is an easy and cost-effective process to obtain micro and nanofibers[1-3]. Huang et al.[1] 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[4,5].

The electrospinning process, depicted in Figure 1, 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[6,7]. The solvent evaporates as the jet travels in air, leaving behind charged polymer fibers that lay themselves randomly on a collecting metallic electrode[8]. It is well known that the morphology of the resulting fibers is determined by a synergetic effect of solution parameters and electrostatic forces[9]. 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 acceleration voltage. Also, ambient parameters including temperature, humidity and air velocity in the electrospinning chamber influence the results.

Controlling the parameters described above, the fibers can be electrospun from different precursor solutions and their melts, like water soluble polymers, biopolymers, etc. Also, the electrospinning process may easily incorporate particles of materials such as pigments, carbon particles and many others into the nanofibers that are being produced.

Electrospun fibers may have diameters ranging from 0.05 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

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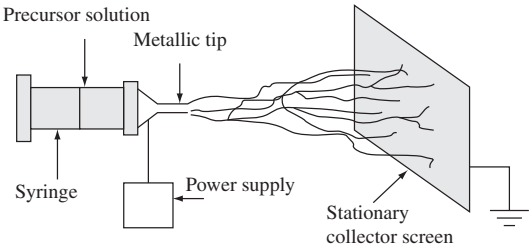


Figure 1. Electrospinning setup.

the fibers, make then a good choice to be used in sensors technology. 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[10].

Carbon nanofibers can be easily obtained by using a fabrication process including electrospinning and vacuum pyrolysis[11,12]. 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[13-15].

Thus, in this work, we performed an extensive characterization of an electrospinning process using precursor solutions with different concentrations of polyacrylonitrile (PAN) (2-10% w/w) diluted in a fixed amount (10 ml) of N,N dimethylformamide (DMF). With this purpose we investigated the influence of the applied voltage and of the distance between the needle tip (positive electrode) and the collector plate (grounded electrode). The electrical current was monitored during the deposition process. We aimed at obtaining the window process to controllably obtain uniform nanofibers that can be used for sensors applications.

Experimental

The polymeric fibers were electrospun using a homemade apparatus, composed of a DC power supply (Gamma High Voltage Research Inc., 0 – 30 kV), a syringe (volume of 3 cm^3, needle type $26G^{5/8}$) and a collection screen (copper plate) that sustained the substrates (silicon, <100>, 1.5 x 1.5 cm). In order to maintain the reproducibility, the samples were positioned in the center of the collection plate. The syringe was tilted at approximately 15° from horizontal so that a small drop was maintained at the capillary tip, due to the surface tension of the solution. In order to maintain a stable and reproducible drop at the tip a constant pressure was applied over the polymer solution. With this purpose an apparatus was built which consists in a small pump connected to the end of the syringe with a small polyethylene tube and a valve. The air flux was controlled using the valve until a reproducible drop was achieved.

The precursor solutions were prepared using different amounts of polymer (200, 400, 600, 800 mg, and 1 g of commercial polyacrylonitrile - PAN), dissolved in 10 ml of solvent (N,N dimethylformamide - DMF) in order to obtain concentrations ranging from 2 to 10% w/w. The solutions were stirred (900 rpm) during 24 hours, at room temperature before analysis or deposition. The distance between tip and collector plate ranged between 2 to 20 cm and the applied voltage ranged from 2 to 20 kV.

Relative viscosities of the different precursor solutions were measured using an Ubbelohde type viscometer, from Cannon. After deposition the samples were analyzed by Scanning Electron Microscopy (SEM).

The fiber diameters were determined acquiring the image using an image editor. Two straight lines parallel to the fiber were determined and the distance between these lines was calculated considering the number of pixels in the image and correlating it to their equivalent as distance. All diameters were taken considering only the smooth portion of fibers.

The electrical current during the electrospinning process was determined by Ohm's law by measuring the voltage on a 10 MΩ resistor that was placed between the collector screen and the ground.

Results and Discussion

Figure 2 shows that for the used solutions the viscosity increases exponentially with the increase of the concentration of PAN.

SEM images of resulting fibers electrospun from less concentrated solution are shown in Figure 3. A high concentration of beads can be observed and the fibers are thin and short. The concentration of beads and also the number of fibers increases as a function of the applied voltage. As the viscosity has a very strong influence in the electrospinning process, these results confirm that different characteristics can be expected for the deposited fibers, accordingly to related works[9]. It has been reported in the literature that

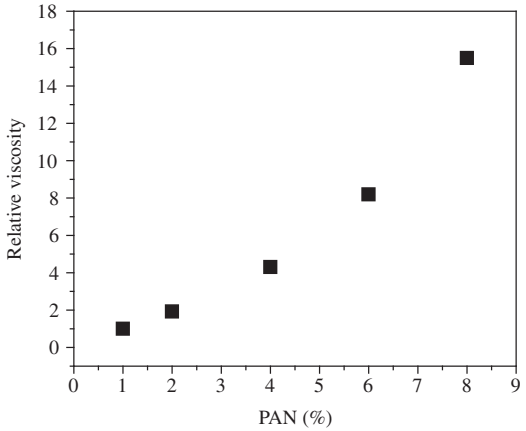
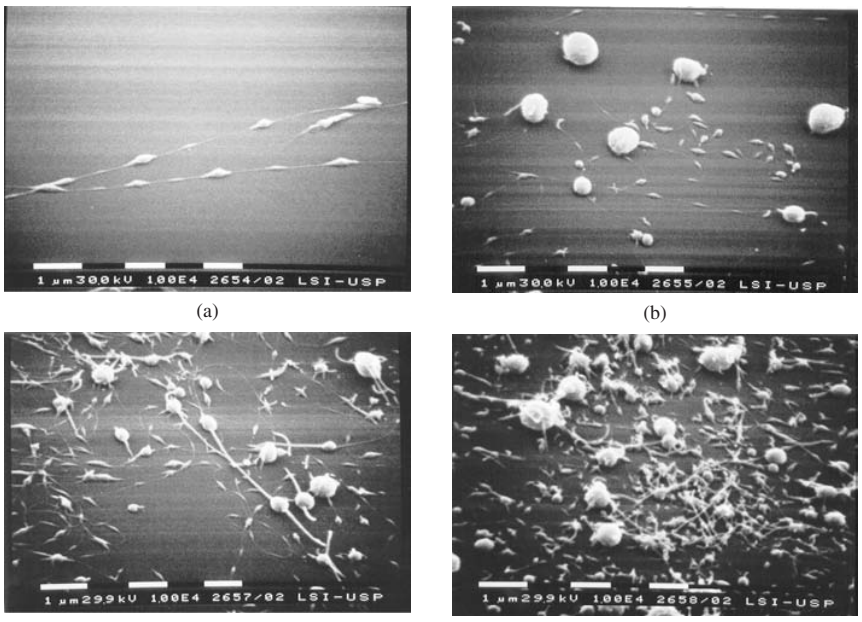


Figure 2. Precursor viscosity as a function of the PAN concentration.

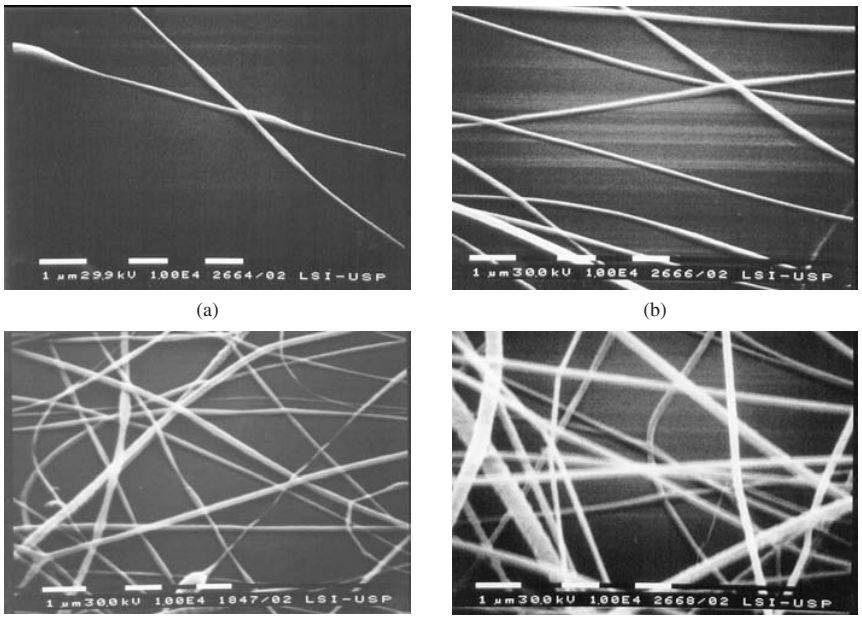
the solution composition has strong influence on the fibers morphology and in the formation and concentration of beads. As discussed by Deitzel[16] the solution surface tension and viscosity play important roles in the electrospinning process, determining the concentration for which is possible to obtain continuous fibers by electrospinning. Deitzel establishes that for viscosities lower than 1 poise the surface tension is the main influence on the fibers morphology and below certain viscosity values only drops are obtained. For viscosities higher than 20 poise is impossible to obtain fibers because the control of polymer solution through the tip is difficult.

Figure 4 shows SEM images of fibers electrospun using a 6% solution. The fibers are smooth and some variations in the fibers diameters in the same sample are observed. However, in average, the fibers diameters and the number of fibers increase as a function of the applied voltage.



(a) (b) (c) (d)

Figure 3. SEM images from the fibers electrospun as a function of applied voltage, for solution concentration of 2% and a fixed distance from the tip to collector plate of 15 cm. a) 4 kV; b) 8 kV; c) 16 kV; and d) 20 kV.



(a) (b) (c) (d)

Figure 4. SEM images from the fibers electrospun as a function of applied voltage, for a solution concentration of 6% and a fixed distance from the tip to collector plate of 15 cm. a) 4 kV; b) 8 kV; c) 16 kV; and d) 20 kV.

Figure 5 clearly illustrates the effects of the viscosity and applied voltage in the fibers diameters. It also points out that the diameter variation is less pronounced for the fibers obtained from less viscous solutions independently of the applied voltage.

The work from H. Fong and coworkers[17] correlates the viscosity and the applied voltage to the shape of nanofibers. They show that the viscosity and surface tension of the solution and the net charge density carried by the electrospinning jet are the main factors that affect the formation of nanofibers with or without beads. For the polymer solution with low viscosity the formation of the beads are caused by the capillary breakup of the jet during the electrospinning by surface tension. In this case the filaments formed between the beads are stabilized and the beads form on a string like structure as that observed in Figure 3.

In the electrospinning process the fibers transport charge across the gap between the charged needle and the grounded collector plate, closing the circuit. As reported by Fong and coorkers[17] and Deitzel and coorkers[16], during the electrospinning process the electric current due to ionic conduction of charge in the polymer solution is so small that is considered negligible, so the only mechanism of charge transport is the flow of polymer from the tip to the collector plate. Thus, an increase in the electrospinning current generally reflects an increase in the mass flow rate from the capillary tip to the grounded target when all other variables (conductivity and flow rate of the solution) are held constant.

For the PAN/DMF system studied in this work it can be observed that current increases with the applied voltage as shown in Figure 6. It is observed that there is no significant change in the current value for the processes performed with low voltage values (from 4 to 8 kV). The fibers obtained in this range of voltage have beads and an irregular shape, as shown in Figure 3 and 4. A significant increase in the current is observed for processes performed with applied voltages higher than 12 kV. Also, the current values are higher for the more viscous solutions. The fibers obtained in this range are smooth and no beads are observed (Figure 3 and 4). So, monitoring the spinning current it is possible to control the fibers morphology and beads concentration.

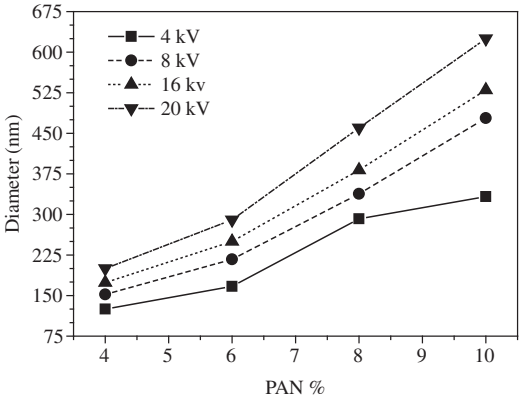


Figure 5. Fibers diameter variation as a function of the precursor solution concentration and applied voltage.

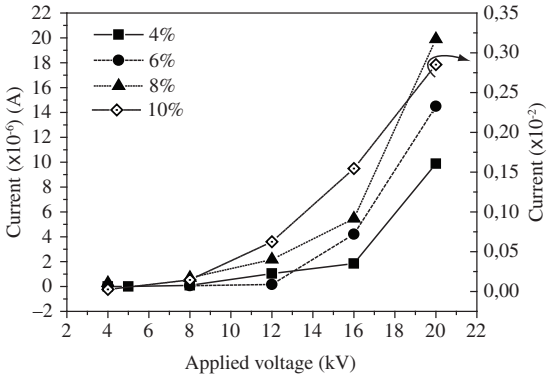


Figure 6. Current measured during the electrospinning process as a function of applied voltage and solution concentration.

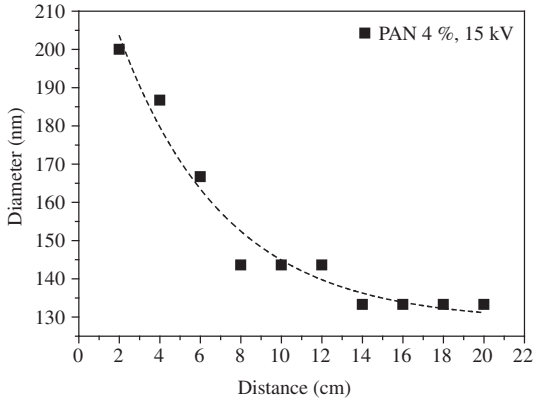
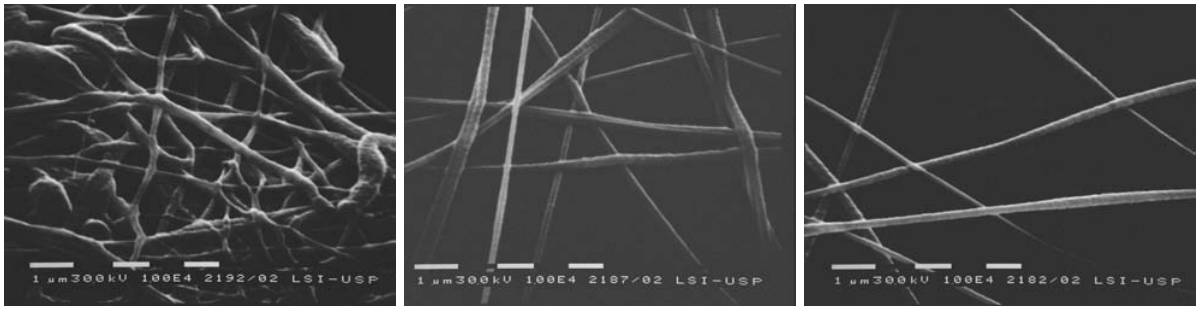


Figure 7. Influence of the distance between tip and collection plate on the fibers diameters. These results were obtained for the fibers electrospun from precursor solution with 4% and applied voltage of 15 kV.

Figure 7 shows the fibers diameters as a function of the distance between the tip and the collection plate. For distances higher than 14 cm there is no measurable variation in the fibers diameter. The SEM images show that the processes performed with shorter distances (2 to 8 cm) result in thick and curled fibers. Also, the collected structure has a sponge like appearance. This occurred because the polymer did not have time to dry before reaching the collector plate and the fibers were collected wet (Figure 8a). However in the Figure 8b) and c) is shown that there is no significant difference between the fibers diameter electrospun with 8 and 12 cm of distance.

Conclusion

Electrospinning is an easy and cost-effective process to obtain micro and nanofibers. In this paper we explored the fact that the process parameters and precursor solution characteristics have a strong influence on the fibers morphology. Thus we performed an extensive characterization of an electrospinning process using precursor solutions with concentrations of polyacrylonitrile (PAN) (2-10% w/w) diluted in



(a) (b) (c)

Figure 8. SEM images from the fibers collected with distances of a) 2 cm; b) 8 cm; and c) 12 cm.

a fixed amount (10 ml) of N,N dimethylformamide (DMF). Besides investigating the influences of different polymer concentrations, which lead to changes in viscosity, we also analyzed the effects of the applied voltage and of the distance between the needle tip (positive electrode) and the collector plate (grounded electrode). The electrical current was monitored during the deposition process and its behavior was correlated with the characteristics of the obtained fibers. Our results demonstrate that the fibers diameters increase as a function of the viscosity and applied voltage. The number of deposited fibers also increases with the applied voltage. This is a demonstration that viscosity and the applied voltage determine the mass flow through the tip, a behavior reflected in the electrical current. Also, viscosity and applied voltage strongly affect the shape, length and morphology of the fibers. Of particular interest, we demonstrated that monitoring the electrical current it is possible to control the fibers morphology and bead concentration. The distance between tip and collector plate determines the way the fibers arrive on the collector plate. A main contribution of this study was the definition of conditions to controllably obtain fibers that are smooth and that present diameters in the range of 140 to 300 nm. Fibers obtained with this process can find important applications in the field of nanosensors.

Acknowledgments

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