Study of Nanofiber Formation by Injecting Polymeric Solutions Inside Intense Electric Fields Using Different Electrode Configurations

R. Furlan[1], S. V. Arroyo[2], R. O. F. Torres[3], J. A. M. Rosado[4], A. N. R. da Silva[5]

[1,2,3,4]Department of Physics and Electronics, University of Puerto Rico at Humacao, Humacao, PR, USA
[5]Department of Engineering of Electronic Systems, University of Sao Paulo, Sao Paulo, Brazil
rogerio.furlan@upr.edu

ABSTRACT

Electrospinning has been considered a straightforward way of producing nanofibers. In this work we are analyzing non-conventional approaches of the electrospinning process to better understand and explore the effect of electrostatic interactions. The processes we are investigating include the insertion of polymer inside the electric field keeping the capillary for polymer injection at a floating potential. Also, we are investigating different electrode configurations including: same as electrospinning (with and without polarization of the capillary for polymer injection), parallel macro electrodes and, microelectrodes (with tip to tip alignment). Image analysis reveals the occurrence of instabilities/oscillations of the polymer flow (caused by redistribution of charges). Improvement of polymer flow directionality and fiber diameter reduction are observed in comparison with conventional electrospinning. Fiber orientation can be obtained using parallel macro electrodes and micro electrodes.

Index Terms: nanofibers, electrospinning, fiber orientation, polymeric fiber.

1. INTRODUCTION

Electrospinning has been considered a straightforward way of producing nano and micro fibers which find applications in widely different areas such as photonic structures, micro and nano fluidics, catalysis, sensors, medicine, to name just a few [1].

The electrospinning process [2, 3], depicted in Figure 1, occurs when the electrical forces at the surface of a polymer solution (drop at the output of a polarized capillary) overcome the surface tension and cause an electrically charged stream of polymer to be ejected. The solvent evaporates as the stream travels. Depending on process conditions charged polymer fibers can be collected on a grounded metallic electrode (collector screen), with a random distribution.

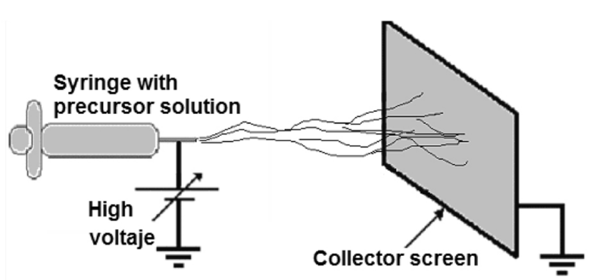


Figure 1. Schematic representation of the typical electrospinning processes.

Different configurations of electrospinning setups have been considered [4-6] aiming at obtaining: aligned fibers, mixing of fibers of different materials, control of the area covered by the deposited fibers, high production of fibers, definition of fiber patterns, coaxial fibers, smooth fibers and single fibers made of two different materials.

These configurations employ additional electrodes, rotating mechanisms and/or multiple capillary for solution injection.

In this paper we explore a novel modification of the conventional electrospinning process by injecting polymeric solutions inside the intense electric field keeping the capillary for polymer injection (syringe needle) at a floating potential. In this way we are investigating different mechanisms of effective charge formation/redistribution.

We are also using different setup configurations to explore the effects of electric field distribution/intensity. These configurations include: same as electrospinning (with and without polarization of the capillary for polymer injection), parallel macro electrodes, and micro electrodes (with tip to tip alignment).

2. EXPERIMENTAL

Figure 2 shows the setups that were used, including conventional electrospinning (Figure 2a), for comparison, and processes that use capillary for polymer injection (syringe needle) at a floating potential: modified electrospinning (Figure 2b), parallel macro electrodes (Figure 2c), and micro electrodes with tip to tip alignment (Figure 2d).

For setups of Figures 2a and 2b the distance from positive electrode (tip of syringe needle) to collector (aluminum foil) was 20 cm. The area of the collector was 20 cm x 20 cm. The applied voltage had values between 2 kV and 30 kV. When polymer was injected inside the electric field, as in Figure 2b, the tip of the capillary for injection (tip of the tuberculin syringe needle) was kept 2 cm far from the tip of the positive electrode and 1 cm above. These setups were examined using aqueous solutions (1 wt% to 7 wt%) of polyethylene oxide (PEO, molecular weight: 2,000,000).

The setup of Figure 2c used rectangular aluminum electrodes (5 cm x 2.5 cm x 1.2 cm). Different distances between electrodes were examined (from 10 cm to 20 cm). The applied voltage was in the range between 10 kV and 30 kV. The tip of the capillary for injection (tip of the tuberculin syringe needle) was placed 0.5 cm to 2 cm from the border positive electrode and from 1 cm to 5 cm above. Aqueous PEO solutions were tested but better results were obtained with PEO dissolved in 10 ml of chloroform (0.25 wt%, 0.5 wt%, 1 wt%, and 2%). The collection of fibers was conducted manually using a silicon substrate after deposition. In this way the fibers stick to the substrate keeping their orientation.

Figure 2d presents the setup with carbon microelectrodes (carbon fibers extracted from a fishing cane) (average width of ~ 420 μm, length between 1 cm and 2 cm and average thickness of ~ 100 μm). The electrodes were placed on a glass substrate and aligned in a straight line. The tips have a separation in the range between 1.5 cm and 3 cm. Electric contact with the electrodes was made with aluminum foils of 1.5 cm by 2.5 cm. A voltage between 5 kV and 20 kV was applied to these electrodes. The tip of the capillary for polymer injection (tip of the tuberculin syringe needle) was placed close to the edge of the positive electrode. Solutions with different concentrations of polyethylene oxide (molecular weight: 900,000) and 10 ml of water (1 wt% to 4 wt%) and, also, solutions with different concentrations of polyacrylonitrile (PAN) dissolved in 10 ml of N,N dimethylformamide (DMF) (1 wt% to 10 wt%) were used. The study of formation of PAN fibers is important because they can be converted to carbon fibers (a material with a wide range of applications) using vacuum pyrolysis [3, 7].

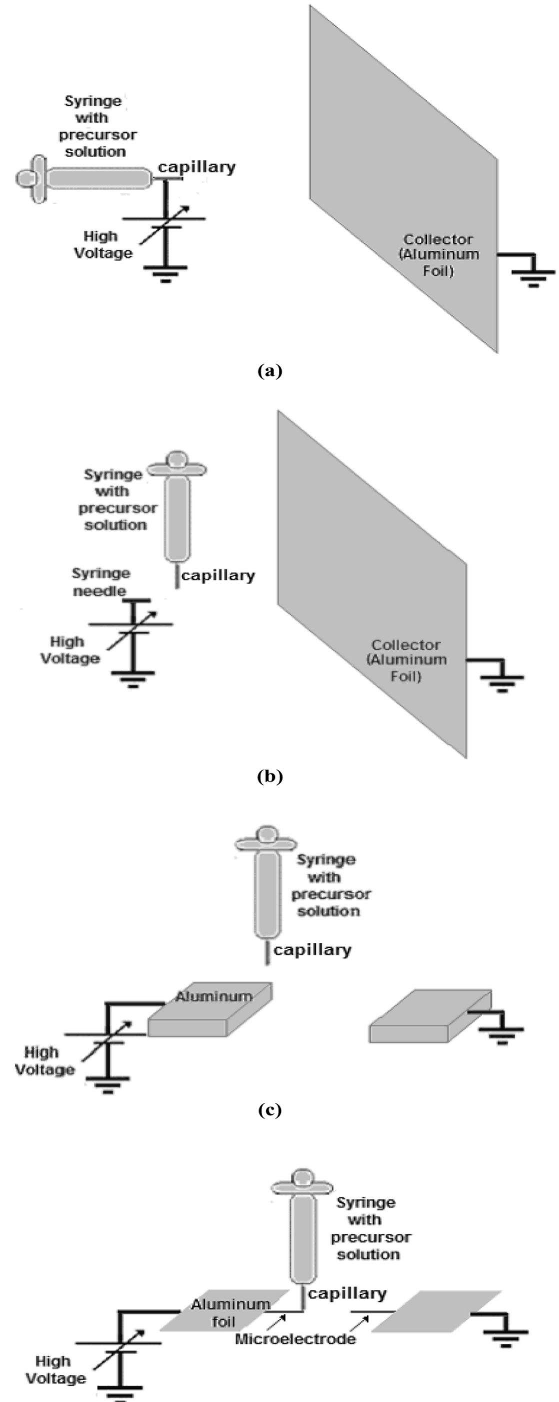


Figure 2. Schematic representation of the used setups: **(a)** conventional electrospinning, **(b)** modified electrospinning, **(c)** parallel macro electrodes, and **(d)** micro electrodes with tip to tip alignment. Setups b,c, and d use capillary for polymer injection (syringe needle) at a floating potential.

Polymer flow images were taken (30 frames per second) using a digital camera (Leica Dicomar). They were analyzed frame by frame using appropriate software (Roxio Easy Media Creator). The negative of the images are presented to facilitate the observation of details. A large amount of polymer was injected when the images were taken in order to facilitate visualization.

Deposited fibers were analyzed using optical microscopy (ME600, Nikon) and Scanning Electron Microscopy (SEM) (JSM 6360, Jeol).

3. RESULTS AND DISCUSSION

The results obtained for the different setup configurations in terms of polymer flow directionality, fiber characteristics and orientation are discussed below.

A. Conventional Electrospinning

Figure 3 shows images of the polymer flow for conventional electrospinning (setup of Figure 1a) when a large amount of polymer is injected to facilitate visualization. For both cases (Figures 3a and 3b) PEO aqueous solution (2.5 wt%,) and an electrode separation of 20 cm were used. In Figure 3a, where a higher voltage (25 kV) is used, the trend of the polymeric jet is to go backwards. Decreasing voltage (5 kV) (Figure 3b) the jet tends to go to the front, in the direction of the grounded electrode. These visual results confirm the ones obtained in reference [8] where directionality was analyzed in terms of amount of fibers that arrived at the substrate placed on the collector. Reference [8] also points out that fibers deposited using voltages between 2 kV and 5 kV can be easily collected and present uniform diameter, typically in the range between 600 nm and 700 nm.

B. Modified Electrospinning

Figure 4 presents the typical behavior observed for modified electrospinning (setup of Figure 1b). In this case a PEO aqueous solution (3 wt%) was injected inside the electric field using an applied voltage of 25 kV. When the polymer drop is inserted, the polymer stream is attracted to the grounded electrode (Figure 4a – 4f). After this, a rearrangement of effective charges occurs and the polymer is attracted to the syringe needle connected to the positive electrode and ejected again to the grounded electrode (Figures 4g - 4i) and an oscillating behavior is observed. In this process polymer streams travel towards the grounded electrode and fibers can be easily collected placing a sample (e.g. silicon) on this electrode.

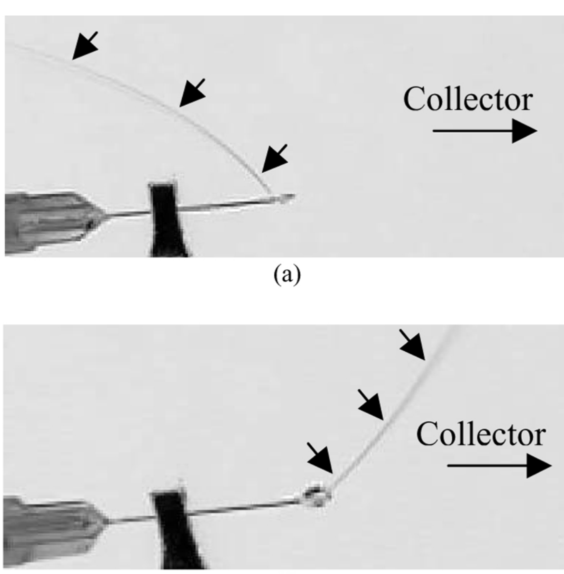


Figure 3. Polymeric streams observed as a function of voltage for conventional electrospinning (PEO aqueous solution of 2.5 wt% and electrodes separation of 20cm): **(a)** 25 kV and **(b)** 5 kV. Small arrows indicate the position of the polymer stream.

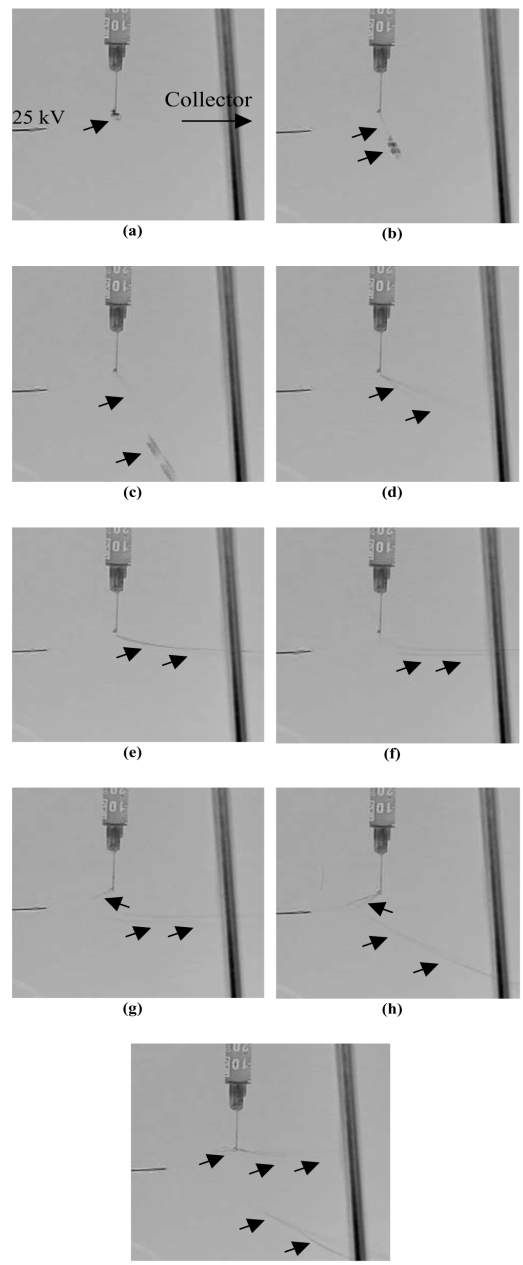


Figure 4. Sequential snapshots taken after injection of PEO aqueous solution (3 wt%), applied voltage of 25 KV, and electrodes separation of 20 cm. The arrows indicate the polymer streams.

An analysis of the effect of the intensity of the electric field reveals that using PEO aqueous solutions directionality (polymer flow traveling to the collector) is obtained with voltages in the range between 25 kV and 30 kV.

This behavior is different from that observed for conventional electrospinning for which directionality is achieved with lower voltages (as low as 2 kV, as observed in reference [8]). Also, using the setup of Figure 2b a larger variation of the diameters of the fibers is observed, but thinner fibers can be obtained (diameter as small as ~150 nm), Figure 5, compared to conventional electrospinning, as described above, for which typical diameter are of the order of 650 nm.

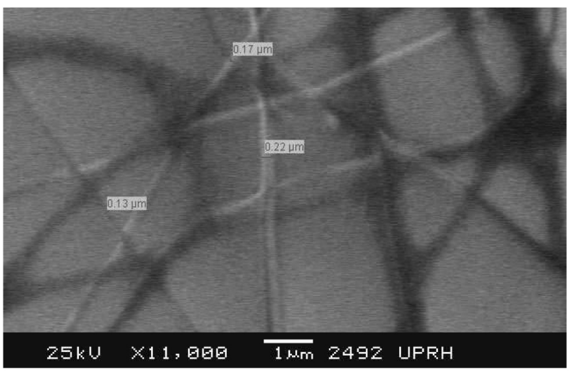


Figure 5. Fibers deposited using electrospinning with capillary for polymer injection at a floating potential, PEO aqueous solutions (2.5 %wt), 30 kV, and 20 cm of separation.

C. Parallel Macro Electrodes

The typical behavior for parallel macro electrodes, using solutions with PEO and chloroform, is depicted in Figure 6. Injecting a large amount of polymer, to facilitate visualization, the formation of a fine stream of polymer that initially moves towards the positive electrode (Figure 6a) can be observed. From the positive electrode a stream is formed and it goes to the grounded electrode (Figure 6b). Then another stream is ejected from the tip of the syringe needle and both streams formed stretch following electric field lines (Figure 6c). This process is repeated several times within an interval of time of approximately one second, resulting in an oscillating behavior of the polymer flow. Fibers collected on a substrate placed between electrodes present a good degree of orientation, following the electric field lines that go straight from the positive to the grounded electrode.

The rate and intensity of the polymer stream oscillations are proportional to the applied voltage. Values higher than 25 kV resulted in more pronounced instability (oscillations) and a loss of a practical degree of fiber orientation. Applied voltages in the range between 20 kV and 25kV and electrodes distance between 12 cm and 14 cm allowed obtaining oriented microfibers and nanofibers (typical diameter of 600 nm). These fibers can have lengths of several centimeters what represent an advantage over oriented fibers obtained with the use of conventional electrospinning with additional electrodes [4, 9].

Figure 7a shows nanofibers collected sequentially resulting in a perpendicular configuration. The detail presented in Figure 7b shows that the fibers result not uniform.

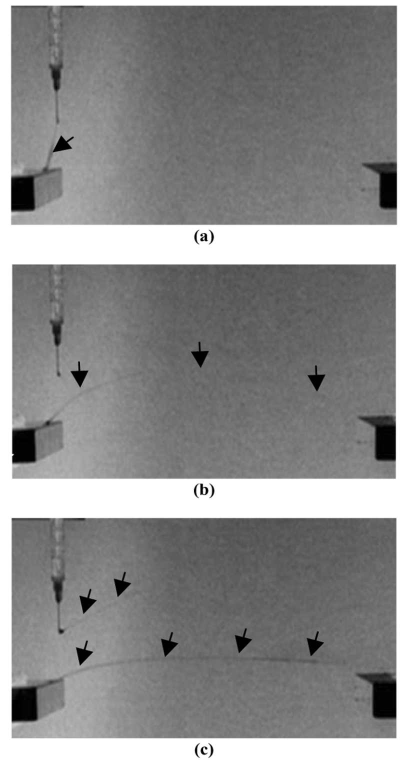


Figure 6. Sequential images for the injection of solutions with PEO and chloroform (1 wt%), applied voltage of 20 KV, and electrodes separation of 14 cm. The arrows indicate the polymer streams.

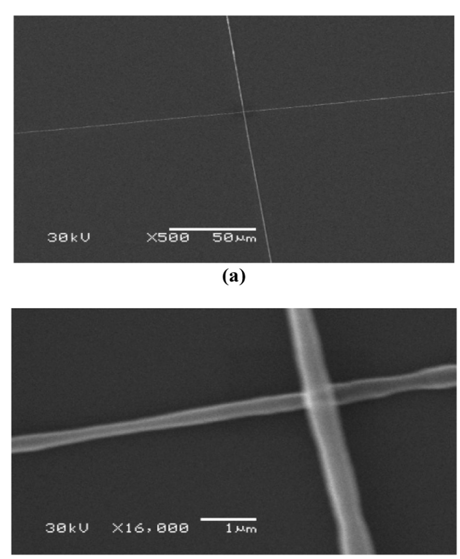
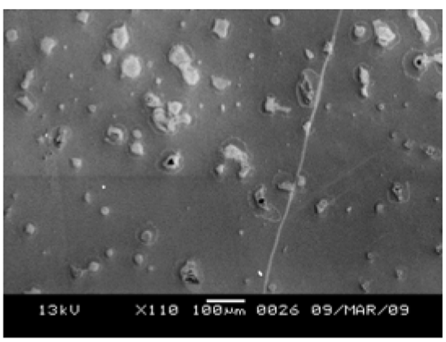


Figure 7. SEM images of nanofibers deposited using the parallel microelectrodes configuration (solutions with PEO and chloroform, 1 wt%, applied voltage of 25 KV, electrodes separation of 14 cm): (a) fibers collected sequentially to obtain a perpendicular configuration and (b) nanofibers detail.

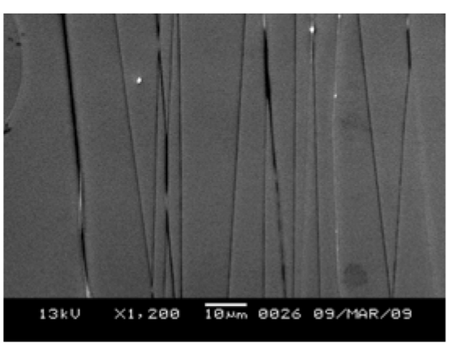
D. Microelectrodes

Using the setup of Figure 2d polymeric streams can be observed, after injection, following the direction of the electric field lines. Polymer is directed to the grounded electrode leading to the formation of fibers. This process has the advantage of using very little precursor solution to obtain fibers that are predominantly placed on top of a substrate, i.e. the deposition is confined to a small area.

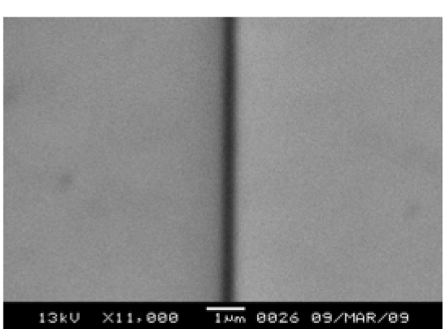
Placing the tip of the needle of the tuberculin syringe very close to the border of the positive microelectrode facilitates the deposition on top of the substrate, as polymer is injected close to a region with concentrated electric field lines that go straight from the positive to the grounded electrode.



(a)



(b)



(c)

Figure 8. Images obtained with SEM for samples prepared using PAN and DMF solutions, microelectrodes separation of 2.5 cm, and applied voltage of 20 kV: **(a)** 2 %wt (formation of beads with some fibers), **(b)** 8 %wt (oriented fibers), and **(c)** 6 %wt (fiber with a diameter of ~500 nm).

The formation of fibers with a good degree of orientation, using aqueous solutions with PEO and solutions with PAN and DMF, was observed for voltages higher than 15 kV. This is a simple way of obtaining fiber orientation, compared to other variations of the electrospinning process that require additional electrodes or a rotating mechanical system.

No influence of the separation of the microelectrodes was noticed, considering the used range (1.5 cm to 3 cm). Thus, this process uses electric field intensity in the range between 5 kV/cm and 13.3 kV/cm that is higher than the intensity typically used for conventional electrospinning (1 kV/cm).

Figure 8 shows the behavior observed using solutions with PAN and DMF. For lower concentrations of PAN fibers can be observed, as in Figure 8a, but there is a predominance of disconnected polymer drops. Increasing the concentration of PAN the formation of fibers is favored and most of then present a certain degree of orientation, as displayed in Figures 8b. A better uniformity in terms of fiber diameters is observed, in comparison with the results obtained for PEO. Fibers with diameters as small as 500 nm can be obtained, as exemplified in Figure 8c.

4. CONCLUSIONS

Modifications of the conventional electrospinning process were analyzed using different setups and conditions. Injecting polymer inside the electric field and using capillary for polymer injection at a floating potential, instead of injecting polymer from the positive electrode (needle of a syringe with positive voltage), in the case of aqueous solutions with PEO, improves polymer flow directionality (polymer flow traveling to the collector). Directionality is obtained with voltages in the range between 25 kV and 30 kV differently from the behavior observed for conventional electrospinning for which directionality is achieved with lower voltages (as low as 2 kV). Image analysis reveals the occurrence of instabilities/oscillations of the polymer flow (caused by redistribution of charges). Also, nanofibers with smaller diameters were obtained with this method, in comparison with conventional electrospinning. The injection of polymer between two parallel macro electrodes, in the case of solutions with PEO and chloroform, led to deposition of oriented fibers with diameters as small as 500 nm. Injecting polymer between micro electrodes with tip to tip alignment led also to a good degree of fiber orientation, for PEO aqueous solutions and solutions with PAN and DMF. Placing the tip of the needle of the tuberculin syringe close to the border of the positive microelectrode facilitates the deposition on top of the substrate, as polymer is injected close to a region with concentrated electric field lines that go straight from the positive to the grounded electrode. A better uniformity in terms of fiber diameters is observed, in comparison with the results obtained for PEO. Fibers with diameters as small as 500 nm can be deposited.

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