Formation of Oriented Fibers Using Injection of PEO Solutions inside Electric Fields Defined by Two Parallel Suspended Electrodes

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ABSTRACT

Formation of oriented fibers using injection of polyethylene oxide (PEO) solutions inside electric fields defined by two parallel suspended electrodes is investigated. Images of streams formed with the injection of a large amount of polymeric solution reveal good agreement with electric field distributions obtained with numerical simulation (COMSOL Multiphysics) when appropriate boundary conditions are defined. Oriented fibers with diameters in the range of hundreds of nanometers to micrometers result connected between electrodes (separated by several centimeters) and can be easily collected/transferred keeping their orientation. Fibers with this characteristic find applications in topics such as tissue and sensors engineering. Also, the fibers are flexible and can be shaped with the stylus of a profilometer.

Index Terms: nanofibers, fiber orientation, polyethylene oxide, and polymeric fiber

INTRODUCTION

Electrospinning is a technique that can be used to create nanofibers from a variety of starting materials [1]. At a critical voltage, for the typical electrospinning setup [1-3] depicted in Figure 1, the electrical forces at the surface of the precursor solution (drop at the output of the polarized capillary) overcome the surface tension and cause an electrically charged stream of polymer to be ejected. This stream is stable near to the tip but it soon undergoes an instability and elongation process. The solvent evaporates as the stream travels. A grounded target (aluminum foil) is used to collect the resultant fibers.

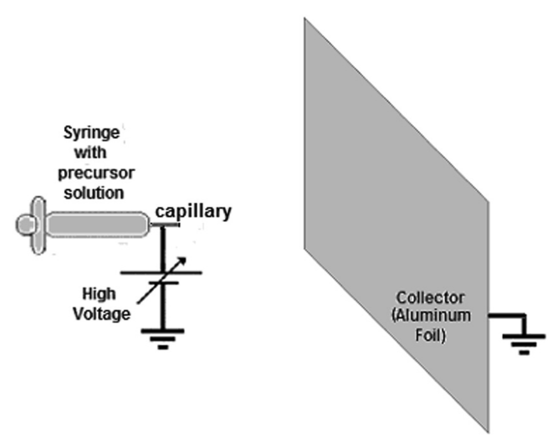

Figure 1. Schematic representation of a typical electrospinning setup.

This approach, which can be categorized as conventional electrospinning, permits to obtain micro- and nanofibers that are randomly deposited. Applications that use these fibers, such as filtration, texturing, composite reinforcement, tissue and sensor engineering, could be improved if the fibers could be oriented/aligned [4, 5].

Several modifications of the typical electrospinning setup have been considered [3, 5, 6] aiming at obtaining: aligned fibers, control of the area covered by the deposited fibers, mixing of fibers of different materials, 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. Thus, they represent the use of more complicated setups.

A simple way of obtaining fiber orientation has been recently proposed by using the injection of polymer inside the electric field defined by two parallel electrodes and keeping the capillary for polymer injection at a floating potential [7]. Here we present a more detailed analysis of this approach.

Aiming at assembling free-standing structures with the fibers, two parallel suspended aluminum blocks were used as electrodes, as depicted in Figure 2, facilitating fiber collection.

EXPERIMENTAL

Polymer solutions were prepared using different amounts of polyethylene oxide (PEO, molecular weight: 2,000,000, Sigma Aldrich) dissolved in 10 ml of chloroform (F.W. 119.36, 1% of ethanol, J. T. Baker) to obtain solutions with 0.25 wt%, 0.5 wt%, 1 wt%, and 2 wt%. The solutions were stirred (1,000 rpm) during 24 hours at room temperature before deposition.

The electrodes, depicted in Figure 2, were made of aluminum with dimensions of 5.0 cm x 2.5 cm x 1.2 cm. Electrodes separation from 5 cm to 20 cm were examined. Polymer was injected inside the electric field by positioning the tip of a tuberculin syringe needle at different heights and distances from the positive electrode. Voltages applied between electrodes were in the range between 10 kV and 30 kV.

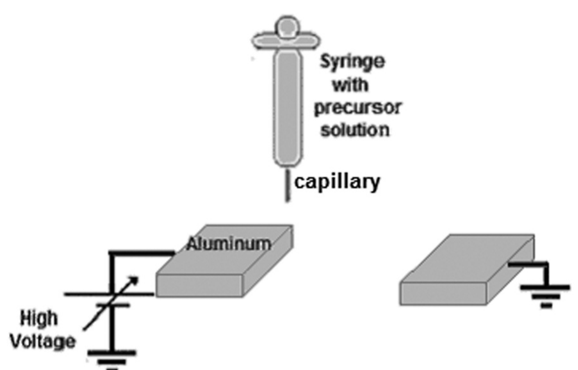

Figure 2. Schematic representation of the experimental setup with parallel macro electrodes.

Images of the deposition process were taken with a Sony DSC-T100 camera. 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.

After deposition, fibers were manually collected on top of a silicon substrate or forming free-standing structures.

Obtained fibers were analyzed using an optical microscope (Nikon ME600) and a Scanning Electron Microscope (Jeol JSM-6360). The stylus of an Alpha Step® 500 surface profiler was used for changing the shape of fibers deposited on silicon substrates.

The COMSOL Multiphysics (COMSOL 3.5a, AC/DC Module) simulation package was used for modeling of electric field distribution. Numerical simulations were performed in a 3D engine. A separation between electrodes of 14 cm was adopted. The needle of the syringe used for polymer injection was kept at a floating potential. The external boundaries were defined by a box with 0.5 m of side (smaller dimensions affected the distribution of the electric field and larger dimensions led to similar results). These boundaries were considered grounded or with a floating potential for comparison. The mesh was generated automatically.

RESULTS AND DISCUSSION

The distinctive behavior obtained with the injection of a large amount of polymer, in order to facilitate visualization, is depicted in Figure 3. Initially, a polymer stream moves towards the positive electrode (Figure 3a). If this stream is not formed, the complete process of fiber formation will not occur. Then, after effective charge rearrangement, polymer streams are ejected from the positive electrode and from the needle of the syringe for polymer injection (Figure 3b). These streams travel towards the grounded electrode (Figures 3c). At the end, oriented fiber(s) (not shown in Figure 3) are formed with the extremities attached to both electrodes.

Figure 4 presents the electric field streamline distributions considering simulation with external boundaries either grounded (Figure 4a) or with floating potential (Figure 4b). These are the most probable conditions to be considered as an approximation of the real case. Comparing Figures 3 and 4, it can be seen that using grounded boundaries a better fitting is obtained, and, therefore, this simulation condition becomes validated. It can be noticed, also, that the electric field distribution plays an important role as the polymeric streams follow quite well the electric field lines. The fibers that result oriented follow the almost straight electric field lines between electrodes, as the one presented in Figure 5.

Using the injection of a small amount of polymeric solution, fibers with a diameter of the order of micrometers are easily observed by eye. After collection, for fibers with a concentration of 1 wt%, diameters in the range of hundreds of nanometers can also be identified using a microscope. The range of average

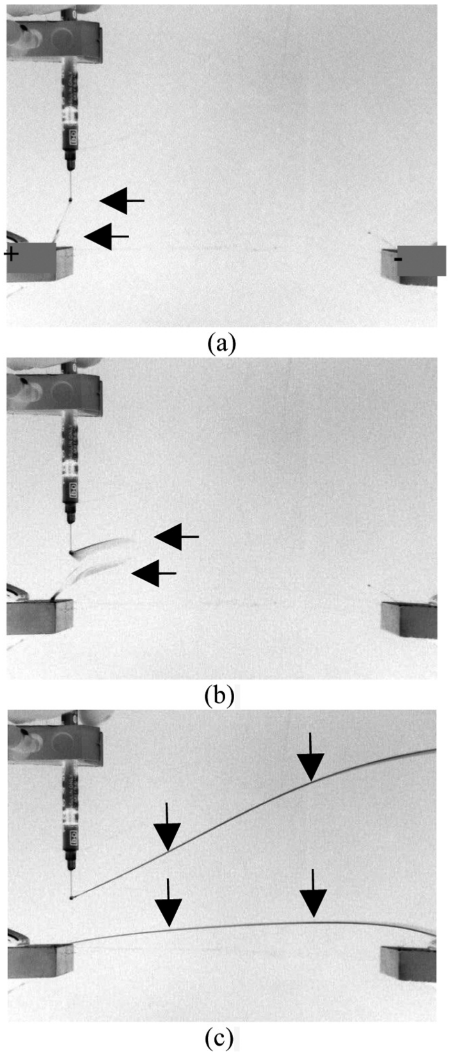

Figure 3. Sequential images for injection of large amounts of solutions with 1 wt%, applied voltage of 20 KV, electrodes separation of 14 cm, and height of the syringe needle of 2 cm. Arrows indicate the position of the polymer streams.

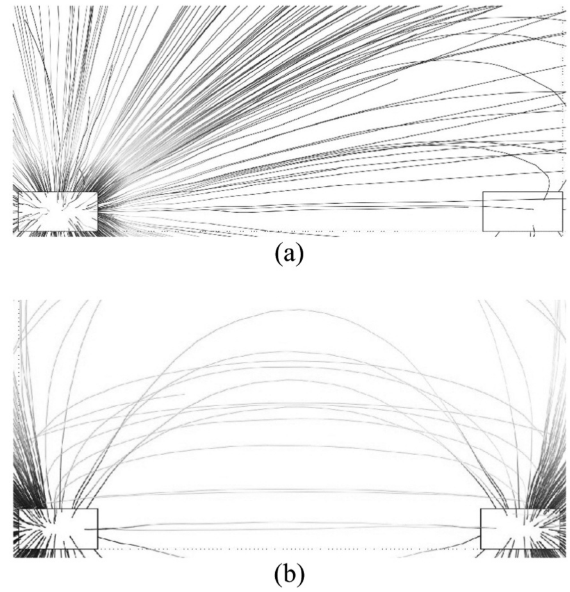

Figure 4. Lateral view of electric field streamlines distribution obtained with numerical simulation: (a) external boundaries grounded and (b) external boundaries with floating potential.

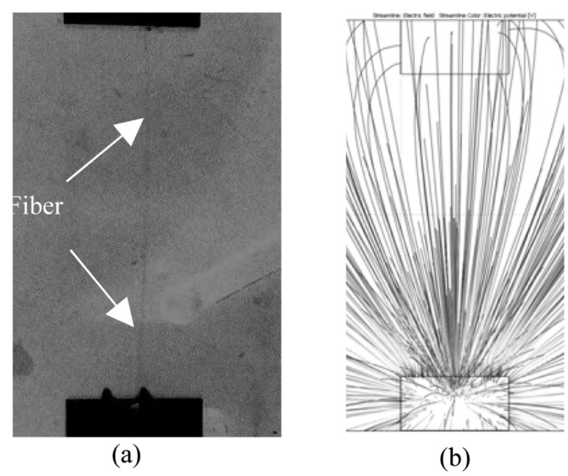

Figure 5. Fiber formed between electrodes: (a) microfiber connected to the electrodes obtained with the injection of a large amount of polymer and (b) electric field streamlines distribution between electrodes obtained with numerical simulation.

diameters is presented in Figure 6. These micro- and nanofibers have lengths of several centimeters what represent an advantage over oriented fibers obtained with the use of conventional electrospinning with additional electrodes [3]. For solutions with a concentration of 0.25 wt% the initial movement of the polymer stream towards the positive electrode is not observed, indicating an insufficiency of effective charge formation. For solutions with concentrations of 0.5 wt% and 2.0 wt% only microfibers were obtained, as observed in Figure 6. Using a concentration of 0.5 wt%, several injections are needed in order to obtain fibers connected between electrodes and in this case the nanofibers are not formed between electrodes. For a concentration of 2 wt%, the higher viscosity favors the formation of fibers with diameters of micrometers.

For voltages lower than 20 kV the behavior presented in Figure 3 is not observed. Values higher than 25 kV resulted in a loss of a practical degree of fiber orientation. For both cases the observed behavior can be associated with the mechanisms of effective charge formation/rearrangement, as the electric field distribution is independent from the applied voltage. For polymeric solution concentrations of 1 wt% and 2 wt%, as seen in Figure 6, the higher applied voltage leads to thinner fibers.

Figure 7 shows the effect of moving the needle for polymer injection towards the grounded electrode with a fixed height (2 cm). Better results in terms of fiber formation were obtained with the syringe positioned close to the border of the positive electrode, as

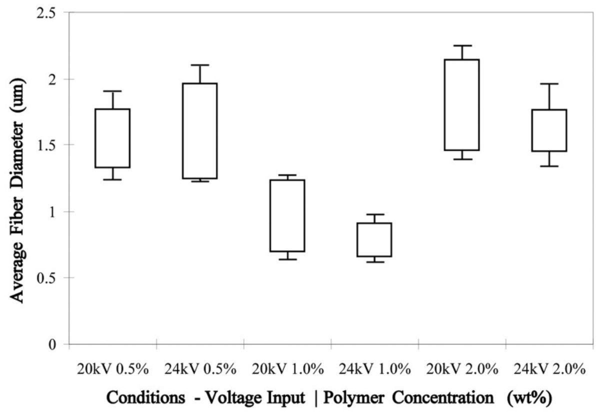

Figure 6. Average fiber diameter as a function of polymeric solution concentration and applied voltage (electrode separation of 14 cm). Twenty fibers were considered for each condition. For each fiber, an average diameter was determined after 10 measurements with Infinity Analyze Software 5.0.2 ©, Lumenera Corporation.

presented in Figure 7a. In this case, as the polymer stream travels towards the positive electrode it encounters a more favorable electric field distribution to be directed to the top of this electrode, as compared to that presented in Figure 7b. As seen in Figure 3, in the process of fiber formation, a stream is ejected from the top of the positive electrode towards the grounded electrode. The electric field intensity is another factor to be considered for positions very far from the positive electrode.

Figure 8 shows nanofibers collected on top of a silicon substrate. Figure 8a shows nanofibers that were collected forming a perpendicular configuration. The magnified image presented in Figure 8b shows that the nanofibers do not have a uniform diameter.

Figure 9 shows an array of free-standing fibers obtained by injecting a single drop multiple times and moving the parallel glass substrates laterally. This approach can be adopted to obtain scaffolds with defined shapes.

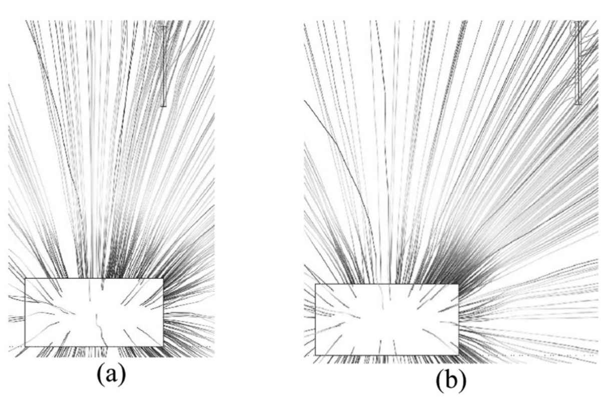

Figure 7. Electric field streamlines distribution for different positions of the needle for polymer injection considering a fixed height of 2 cm: (a) needle positioned on the edge of the positive electrode and (b) needle positioned 2 cm from the edge.

The fibers can be shaped after deposition using the stylus of a profilometer, as shown in Figure 10. In this case a fiber that presented a diameter of 3 μm was used in order to facilitate visualization with an optical microscope. Figure 10a shows that a zigzag shape was defined in the middle of the fiber and Figure 10b shows a magnified image of the region of the fiber that was modified. These results show that the obtained fibers are flexible and can be manipulated without rupture.

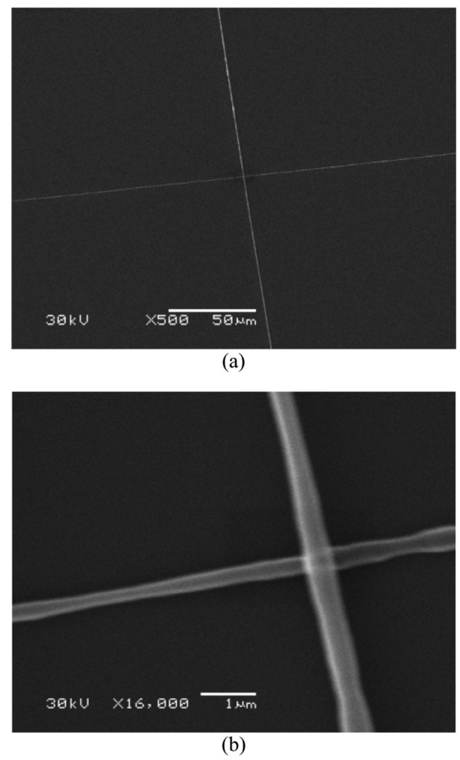

Figure 8. SEM images of nanofibers deposited on a silicon substrate using solutions with 1 wt%, applied voltage of 25 KV, and electrode separation of 14 cm: (a) fibers collected sequentially to obtain a perpendicular configuration and (b) nanofibers detail.

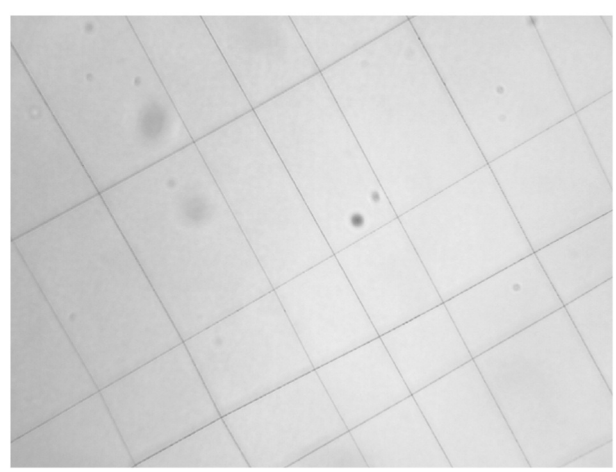

Figure 9. Array of free-standing fibers collected after injecting a single drop of polymeric solution multiple times (1.0 wt%, applied voltage of 20 KV, and electrode separation of 14 cm).

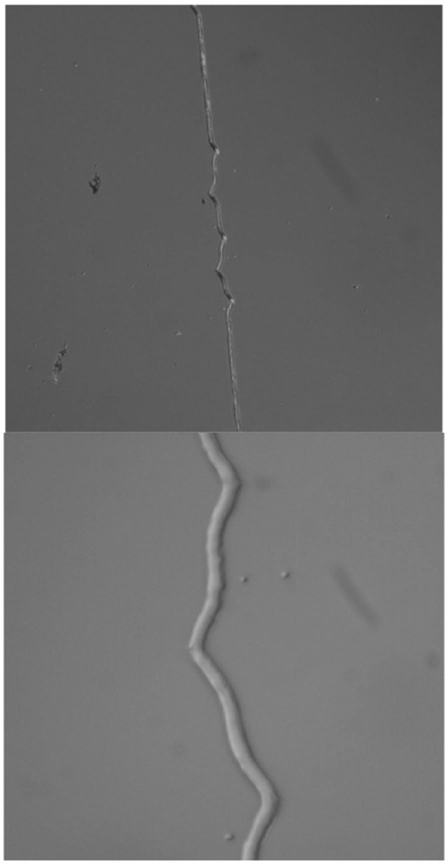

Figure 10. Zigzap shape defined in the middle of a microfiber (3 μm of diameter) using the stylus of a profilometer.

Thus, the injection of polymeric solution containing PEO dissolved in chloroform with a concentration of 1 wt%, applied voltages in the range between 20 kV and 25kV, electrodes distance between 12 cm and 14 cm, and syringe needle with the tip positioned on the edge of the positive electrode with a height of 2 cm allowed obtaining the best results in terms of formation of oriented micro- and nanofibers.

CONCLUSION

The formation of oriented fibers using injection of polymeric solutions (PEO dissolved in chloroform) inside an electric field defined by two parallel electrodes was analyzed experimentally and using numerical simulation of the electric field distribution. Fibers with a typical diameter of the order of hundreds of nanometers to micrometers result with the extremities attached to both electrodes and can be easily collected (transferred) keeping their orientation. They present lengths of several centimeters, what represent an advantage over oriented fibers obtained with the use of electrospinning with additional electrodes. Fibers deposited on a substrate proved to be flexible as they can be shaped using the stylus of a profilometer. The obtained fibers can find applications in tissue engineering what will be explored further. Other polymeric solutions will also be considered. Numerical simulation validated by experimental results helped to explain the behavior of the process of fiber formation. The design of different electrode configurations to improve the process, using numerical simulation, will be explored in future works.

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REFERENCES

1. J. D. Schiffman and C. L. Schauer, *Polymer Reviews*, **48,** 317 (2008).
2. Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, and S. Ramakrishina, *Composites Science and Technology*, **63**, 2223 (2003).
3. W. E. Teo, S. Ramakrishna, *Nanotechnology*, **17**, R89 (2006).
4. C. Chang, K. Limkrailassiri, and L. Lin, *Applied Physics Letters*, **93**, 123111 (2008).
5. Ch. Hellmann, J. Belardi, R. Dersh, A. Greiner, J. H. Wendorff, and S. Bahnmueller, *Polymer*, **50**, 1197 (2009).
6. D. Sun, C. Chang, S. Li, L. Lin, *Nano Letters*, **6**, 4, 839 (2006).
7. R. Furlan, S. V. Arroyo, R. O. F. Torres, J. A. M. Rosado, and A. N. R. da Silva, *Electrochemical Society Transactions*, **23**, 1, 53, (2009).