2004

Microscale polymeric helical structures produced by electrospinning

Royal Kessick
Sentor Technologies Incorporated

Gary C. Tepper
Virginia Commonwealth University, gctepper@vcu.edu

Kessick, R. and Tepper, G.C. Microscale polymeric helical structures produced by electrospinning. Applied Physics Letters, 84, 4807 (2004). Copyright © 2004 AIP Publishing LLC.

Microscale polymeric helical structures produced by electrospinning

Royal Kessick
Sentor Technologies Incorporated, Glen Allen, Virginia 23060

Gary Tepper[a)]
Department of Mechanical Engineering, Virginia Commonwealth University, Richmond Virginia 23284

(Received 19 January 2004; accepted 13 April 2004; published online 21 May 2004)

Microscale helical coils consisting of a composite of one conducting and one nonconducting polymer were produced using electrospinning. The nonconducting polymer was poly(ethylene oxide) and the conducting polymer was poly(aniline sulfonic acid). The coil structures were studied over a range of processing conditions and fiber composition. The data suggest that the helical structures are formed due to viscoelastic contraction upon partial neutralization of the charged fibers. Polymeric microcoils may find applications in microelectromechanical systems, advanced optical components, and drug delivery systems. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1762704]

Micro- and nanoscale helical structures have been of increasing interest and have potential applications in areas, such as structural or inductive components in microelectromechanical systems devices, advanced optical components, and drug delivery systems. However, in order to generate helical structures at the micro- or nanoscale, synthesis or processing strategies must be employed. For example, stable helices of porous manganese oxide materials have been produced from the contraction of a sol-gel upon solvent evaporation.[1,2] In other recent studies, vapor processing methods were used to produce nanoscale helical structures of zinc oxide and silicon dioxide.[3,4]

In this letter, we report on the development of microscale polymeric helical structures using electrostatic spinning. Electrostatic fiber spinning or electrospinning has gained renewed attention due to the potential to form nanoscale fibers from a wide range of materials.[5–7] In the typical electrospinning process, a solvent containing a dissolved polymer is placed at a high potential with respect to a counterelectrode (or vice versa). A hypodermic syringe is often employed to produce very high electric-field magnitudes at the syringe tip. The strong electric field exerts an electrostatic force on the solution, distorting the solution interface into a conical structure known as a Taylor cone. In steady state, the Taylor cone represents a balance between electrostatic forces and surface tension. If the electric field is sufficiently large, an electrified fluid jet emerges from the tip of the Taylor cone and travels a short distance before the onset of a mechanical instability characterized by a rapid whipping motion. If the solution concentration is high enough for chain entanglement to occur, solid polymeric fibers are produced upon solvent evaporation and can be collected on a substrate in the form of a nonwoven mat.

The formation of large loops and ribbons is prevalent in the electrospinning process and can normally be attributed to the structure and motion of the electrified fluid jet.[8] However, uniform microscale helical structures have not been reported in the electrospinning literature. Here, we report on the development of highly uniform microscale polymeric helical structures produced by electrospinning from a solution containing two dissolved polymers. The first polymer, poly(ethylene oxide) (PEO) is electrically insulating, while the second polymer, poly(aniline sulfonic acid) (PASA), is conductive. The data suggest that the helical microcoils are spontaneously produced on a conducting substrate due to viscoelastic contraction of a linear fiber upon partial charge neutralization.

PEO and PASA were chosen for the electrospinning work and were obtained commercially from Aldrich Chemical Co. (Milwaukee, WI) with an average molecular weight of 400 000 and 50 000 amu, respectively. Stock solutions of 10% by weight of PEO in water and in water/methanol (90/10) were prepared and, from this solution, a variety of PEO and PEO/PASA solutions were produced. The methanol was added in the second stock solution to reduce the surface tension of the solvent. All of the solutions, after preparation, were gently placed under a vacuum overnight before use.

The experimental configuration for the electrospinning setup was conventional and the electrospinning source consisted of an 18-gauge needle fit into a 1 ml plastic syringe. The counterelectrode was a grounded metal plate supporting a glass substrate coated with gold. The dc voltage between the tip and counterelectrode was 6000 V at a distance of approximately 10 cm. A Fluke high-voltage power supply, providing a maximum output of 10 kV, provided the dc potential, and the typical output current was measured to be between 100–150 nA during the electrospinning. The flow rate was controlled using a Harvard PHD 2000 Infusion syringe pump and was set at 20 ml per minute for all samples. Characterization of the fibers and structures was performed using an Olympus Light Microscope.

For all data reported here, the PASA concentration was fixed at 0.75% while the PEO concentration was varied from 4% to 10% by weight. Figure 1 shows two dark-field optical microscope images illustrating several different helical structures deposited onto a gold substrate. For the data of Fig. 1, the PEO concentration was 8% and the solvent was water/

[a)]Author to whom correspondence should be addressed; electronic mail: gtepper@vcu.edu

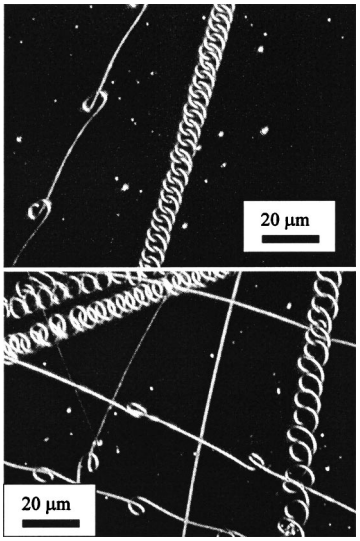

FIG. 1. Dark-field microscope images of an electrospun mixture of 8 wt % PEO and 0.75 wt % PASA in water/methanol.

methanol (90/10). It is interesting to note that, while the coil density (number of loops per unit length) varies significantly from structure to structure, the coil diameter is relatively consistent and falls between 10 μm and 20 μm for all of the structures shown in Fig. 1. Analysis of the helical structures produced under various processing conditions confirmed this trend.

Figure 2(a) is an optical microscope image showing three helical structures produced on a gold substrate from a water solution containing 6% PEO and 0.75% PASA and Fig. 2(b) is a dark-field image of a single coil produced from a water solution containing 8.5% PEO and 0.75% PASA. The three coils in Fig. 2(a) are similar with an average coil diameter between 5 and 10 μm, while the coil of Fig. 2(b), produced at the higher PEO concentration, exhibits a larger diameter.

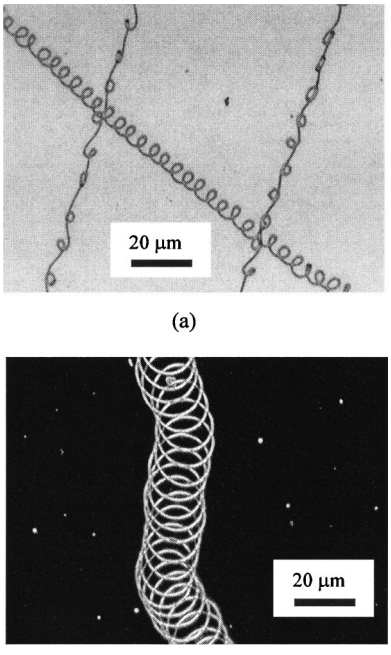

FIG. 2. Fibers produced from (a) 6 wt % PEO and 0.75 wt % PASA in water, (b) 8.5% PEO and 0.75% PASA in water.

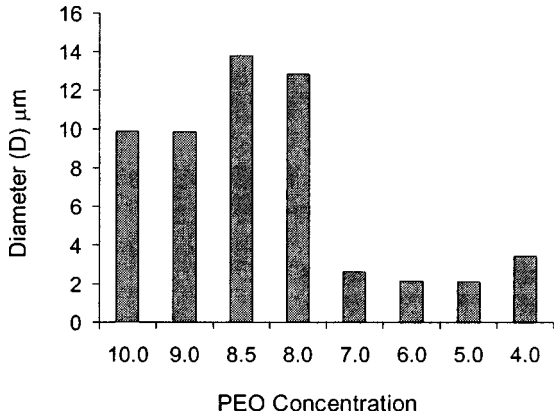

FIG. 3. Histogram of the "loop diameter" vs PEO wt % concentration with a constant PASA concentration of 0.75 wt % in water.

The effect of solution concentration on the resulting helical structures was investigated by measuring the average coil diameter as a function of PEO concentration in the water solution. The diameter of each coil within a given region on the gold substrate was tabulated and an average diameter was calculated for PEO concentrations ranging from 4% to 10% in water. The PASA concentration was fixed at 0.75%. Figure 3 is a histogram of the average coil diameter as a function of PEO concentration.

The histogram of Fig. 3 reveals two distinct regions, separated by a critical PEO concentration between 7% and 8% at a PASA concentration of .75%. At PEO concentrations above the critical concentration, the average coil diameter is between 10 and 14 μm, while below the critical concentration, the average coil diameter abruptly decreases to between 2 and 4 μm. This bimodal dependence was unexpected and, at this time, we do not have a satisfactory explanation for this result.

The experimental conditions were varied to investigate possible mechanisms for the formation of the observed helical structures. The helical structures could not be produced from a single component system (e.g., pure PEO) and we, therefore, surmise that the spontaneous formation of the microscale helical structures is due to the composite nature of the fibers. In addition, helical structures could not be formed on an insulating substrate mounted onto the surface of a grounded support. Fibers were collected on an insulating polycarbonate sheet backed by a grounded electrode and coils were not observed under any of the processing conditions described above. Fibers were also collected on an interdigitated electrode consisting of gold strips separated by insulating gaps and the results were most interesting. Figure 4 is an optical microscope image of an electrospun structure deposited onto the surface of the interdigitated electrode. The gold strips (the dark regions in the image) are approximately 20 μm wide with a center-to-center spacing of 40 μm and were deposited onto the surface of a glass substrate. As can be seen in Fig. 4, the helical structures are only present on the gold strips and the fiber is linear on the glass regions. In fact, the structure of the single fiber shown in Fig. 4 alternates between a helical geometry and a linear geometry at a frequency governed by the underlying metal electrode.

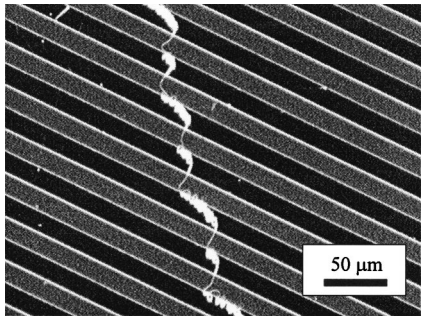

FIG. 4. Microscope image of a single fiber deposited onto the surface of an interdigitated microelectrode.

These results suggest a possible mechanism for the production of microscale helical polymers on a metal substrate. The polymer fibers produced from electrospinning are electrically charged. The sign of the charge depends on the polarity of the applied voltage and can be either positive or negative. The like charges on the polymer fiber repel each other resulting in a net Coulombic elongational force acting along the length of the fiber. In equilibrium, the electrostatic repulsive force is balanced by the viscoelastic restoring force of the polymer fiber. When the polymer fiber lands on a conductive surface, a fraction of the charge (primarily that from the conductive PASA regions) is transferred to the surface resulting in a force imbalance when the contracting viscoelastic force exceeds the repulsive Coulombic force. In order to restore equilibrium, the fiber undergoes a structural rearrangement and spontaneously contracts into the observed helical structures. This explanation for the formation of the observed helical structures is consistent with the results of Fig. 3 because, at lower PEO solution concentrations, the polymer fiber will contain a larger percentage of PASA and will lose more charge to the surface resulting in a larger force imbalance and a tighter helical contraction.

In conclusion, microscale helical structures were produced on a conductive substrate by electrospinning from a two-component solution. The two-component solution consists of one conductive and one nonconductive polymer. A mechanism, based on partial charge neutralization followed by viscoelastic contraction, is proposed and appears to be consistent with the observed data.

This work was supported by Contract No. FA9550-04-C-0007 from the Air Force Office of Scientific Research.

[1] O. Giraldo, S. Brock, M. Marquez, and S. Suib, Nature (London) **405**, 38 (2000).
[2] M. Marquez, I. Veretennikov, and C. Chang, Langmuir **18**, 8792 (2002).
[3] X. Y. Kong and Z. L. Wang, Nano Lett. **3**, 1625 (2003).
[4] H. Zhang, C. Wang, E. C. Buck, and L. Wang, Nano Lett. **3**, 577 (2003).
[5] Y. Shin, M. Hohman, M. Brenner, and G. Rutledge, Polymer **42**, 9955 (2001).
[6] M. Bergshoef and G. Vansco, Adv. Mater. (Weinheim, Ger.) **11**, 1362 (1999).
[7] E. Boland, G. Bowlin, D. Simpson, and G. Wnek, Polym. Mater. Sci. Eng. **85**, 51 (2001).
[8] S. Koombhongse, W. Liu, and D. Reneker, J. Polym. Sci., Part B: Polym. Phys. **39**, 2606 (2001).