

Electrospinning Nanofibers of Polyaniline and Polyaniline / (Polystyrene and Polyethylene Oxide) Blends

Manuel J. Díaz-de León
Department of Physics and Electronics
University of Puerto Rico, Humacao, PR 00791-4300

Faculty Advisor: Nicholas J. Pinto

Abstract

Fibers of pure doped polyaniline dissolved in concentrated sulfuric acid and doped polyaniline blended with polystyrene (PS) and polyethylene oxide (PEO) and dissolved in chloroform have been prepared using the electrospinning technique. The conductivity of the pure polyaniline fibers was measured to be 0.76 S/cm similar to the bulk value suggesting that the fiber although it had a diameter of 10 μm was not thin enough to show effects of confinement due the smaller diameter on charge transport. Fibers of doped polyaniline blended with PS had diameters that were < 100 nm as compared to those blended with PEO, suggesting that to obtain thinner diameter fibers of polyaniline blends it is better to use PS perhaps due to the availability of polymer standards for PS with fewer defect structures.

Keywords: Electrospinning, polymers, nanofibers, conductivity.

1.0. Introduction

Polyaniline (PANi) is an organic conducting polymer that was first reported in the literature about 100 years ago. However, recently there has been a surge in research on polyaniline since it was shown that its conductivity could be increased by more than ten orders of magnitude by doping with protonic acids[1]. Depending on the oxidation level, PANi can be synthesized in various insulating forms such as the fully reduced leucoemeraldine base (LEB), the half oxidized emeraldine base (PANiEB) and the fully oxidized pernigraniline base (PNB). Of these three forms PANiEB is the most stable and widely investigated polymer in this family. PANiEB differs substantially from LEB and PNB in the sense that its conductivity can be tuned via doping from 10^{-10} S/cm up to 100 S/cm and more where as the LEB and PNB forms cannot be made conducting. The insulating emeraldine base form of polyaniline (PANiEB) consists of equal numbers of reduced $[-(\text{C}_6\text{H}_4)\text{-N(H)-}(\text{C}_6\text{H}_4)\text{-N(H)-}]$ and oxidized $[-(\text{C}_6\text{H}_4)\text{-N}=(\text{C}_6\text{H}_4)=\text{N-}]$ repeat units as seen in Figure 1(a). The conducting emeraldine salt form (PANiES) is achieved by doping with aqueous protonic or functionalized acids where protons are added to the -N= sites while maintaining the number of electrons in the polymer chain constant and have a structure as shown in Figure 1(b).

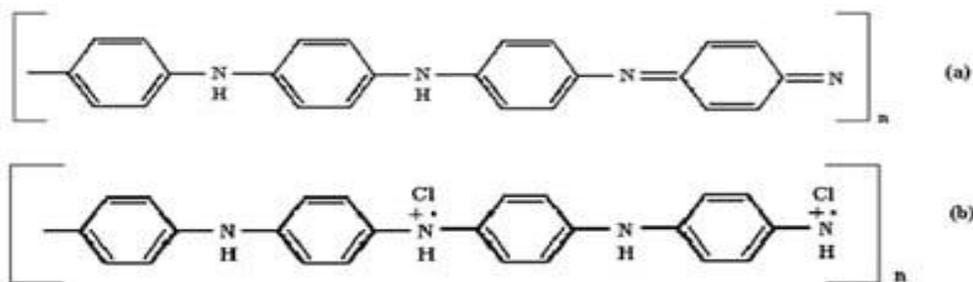


Figure 1: (a) Insulating emeraldine base form of PANi, (b) conducting emeraldine salt form of PANi.

Polymer fibers were obtained using the electrospinning technique. Electrospinning is a straightforward non-mechanical method to produce (meters) long polymer fibers in air discovered in the 1930's [2]. In the electrospinning process, the polymer is dissolved into a low boiling point solvent like chloroform, CHCl_3 , to prepare a viscous solution. The solution is then placed into a pipette and tilted a few degrees below the horizontal depending on the viscosity thus creating a slow flow rate of about one drop per thirty seconds through the pipette. A high voltage (15 kV-25 kV) was then applied to a copper wire inserted into the polymer solution in order to generate an electrical field between the solution and a metallic screen (aluminum foil). As we increase the voltage, the electric field forces overcome the surface tension of the suspended polymer at the end of the pipette tip. Once the voltage reaches a critical value, a single jet is produced. As the jet travels toward the metal cathode the solvent evaporates and the fibers are collected on the metal screen [3]. A schematic drawing of the electrospinning process is shown in Figure 2.

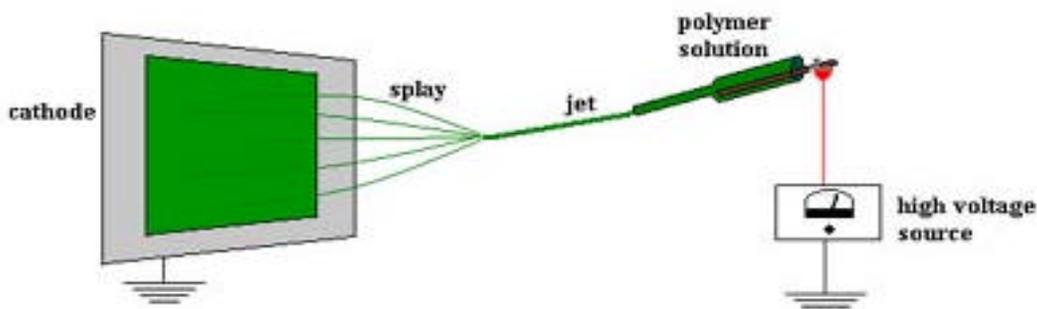


Figure 2: Schematic of the electrospinning process.

Most of the research carried out on polyaniline in the past two decades was done on electrical characterization of bulk films with very few studies on ultrathin fibers [4]. In the present work we prepare fibers of pure PANi and PANi blended with nonconducting polymers. The purpose of this investigation was to prepare fibers of pure PANi or PANi blends having an average diameter < 100 nm and to electrically characterize them at room temperature.

2.0. Experimental

2.1. Materials

Polyethylene oxide (PEO) molecular weight (M_w) 200,000, 10-camphosulfonic acid (HCSA), chloroform (CHCl_3), polystyrene (PS) (M_w 212,400), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), hydrochloric acid (HCl), ammonium hydroxide ($(\text{NH}_4)\text{OH}$), and aniline ($\text{C}_6\text{H}_5\text{NH}_2$) were purchased from Aldrich. These chemicals were used without further purification.

2.2. Sample Preparation

Polyaniline (PANi) was synthesized by the oxidative polymerization of aniline in acidic media. Using a method similar to that reported by MacDiarmid et. al. [1], 5 ml of aniline was dissolved in 300 ml of 1M HCl and kept at 0°C , 11.4 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was dissolved in 200 ml of 1M HCl also at 0°C and added dropwise under constant stirring to the aniline/HCl solution over a period of 20 mins. The resulting dark green solution was maintained under constant stirring for 24 hrs. filtered and washed with water before being added to 500 mL of 1M $(\text{NH}_4)\text{OH}$ solution. After an additional 24 hrs. the solution was filtered and a deep blue emeraldine base form of polyaniline was obtained (PANiEB).

The polyaniline blend solutions were prepared by mixing the exact amount of HCSA (129 mg) with emeraldine base (100 mg) to dope it and dissolving it in 10 mL of chloroform. Two bottles each with 10 mL of chloroform and the doped polymer were prepared. The solutions were stirred constantly for 6 hours and were deep green in color. They were filtered under vacuum using a #40 Whatman Filter Paper to remove any non-dissolved particles. PEO (100 mg) and PS (400 mg) were slowly added to each of the filtered solutions and stirred for 4 hours

to obtain homogeneous solutions of doped PANi/PEO and PANi/PS. These solutions were electrospun as mentioned above.

For the pure PANi fibers we used PANi doped with 2-Acrylamido-2-ethyl-1-propanesulfonic acid (AMPSA) dissolved in concentrated sulfuric acid and this polymer was provided by Dr. MacDiarmid at UPENN. The pure PANi fibers were prepared by dissolving 900 mg of PANiAMPSA in 3 ml of concentrated sulfuric acid using manual stirring with a glass rod for about 30 minutes. The solution was placed in a glass pipette and the pipette was held vertically down with the outlet about 3 cm from a beaker of water that acted as the cathode. The spinning voltage used was 15 kV, this resulted in jets emerging from the end of the pipette (sometimes with sparks) in an erratic manner and depositing itself on the surface of the water in the form of fine fibers. After allowing 12 hours for the sulfuric acid to dissolve in the water the fibers were collected on a degenerately doped Si/SiO₂ wafer.

2.3. Characterization of electrospun fiber

Single and multiple fibers of our samples were captured on degenerately doped Si/SiO₂ wafers by intercepting the jet produced by the electrospinning method for a few seconds. Conductivity measurements were made with a LakeShore constant current source and the voltage was measured using a Keithley model 610C electrometer. The diameter of the fibers and the fiber morphology was made with a Digital Instruments Nanoscope Dimension 3100 Atomic Force Microscope (AFM) in the tapping mode.

3.0. Results and Discussion

Figure 3 shows the IV curve for a pure PANiAMPSA fiber that had an average diameter of 10 μm . The IV curve shows a linear relationship indicating that power dissipation was negligible within the sample and the calculated conductivity of 0.76 S/cm represents the intrinsic conductivity of the fiber. The conductivity of similar fibers was reported to be of the same order of magnitude[5]. The data in Figure 3 were taken with the gate voltage set to 0 V and 10 V. There is no apparent field effect on the conductivity suggesting that perhaps the fiber is not in the semiconducting regime but rather in the metallic regime of charge transport where field effects are negligible.

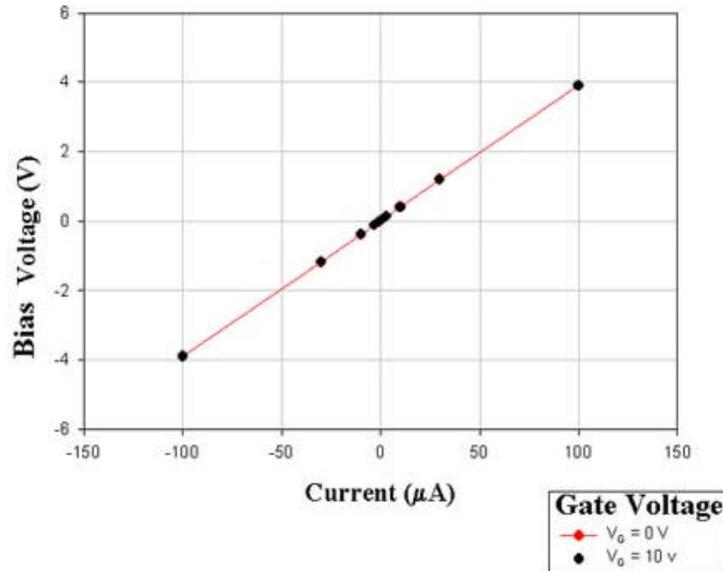


Figure 3: IV curve for a pure PANi single fiber of diameter 10mm.

Figure 4 shows a photographic image of the pure PANi fiber studied above mounted on a degenerately doped Si/SiO₂ wafer with three leads that have been connected with silver paste. These include two leads for the bias voltage and a third lead for the gate voltage. The average diameter of the fiber was 10 μm .

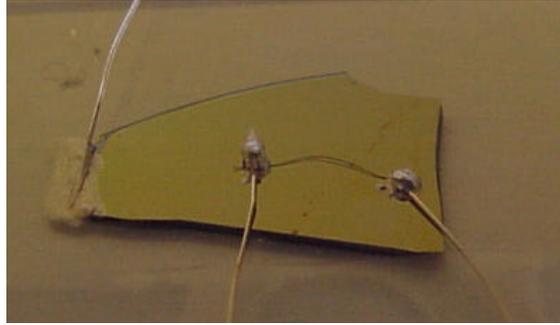


Figure 4: PANiAMPSA single fiber cast on a Si/SiO₂ wafer showing the gate and bias voltage connections.

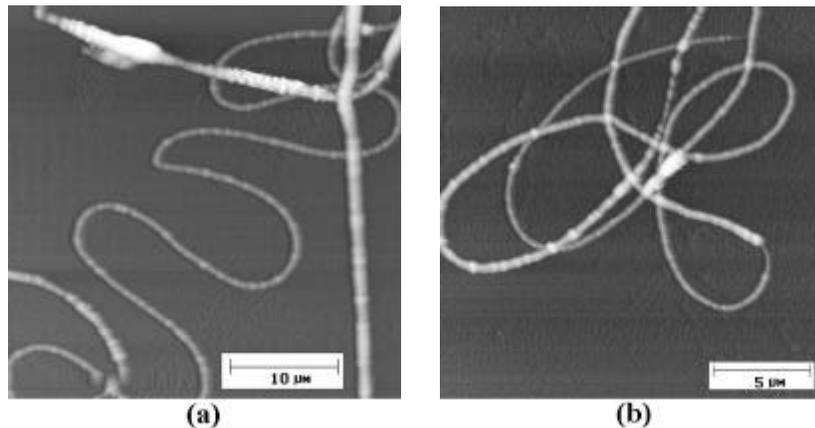


Figure 5: AFM images of PANi/PEO electrospun fibers electrospun at 1kV/cm.

Figures 5(a) and (b) show AFM images of PANi/PEO fibers. As seen in these figures (which are representative of the fibers electrospun) one can obtain meter long fibers with controlled fiber collection techniques. The fibers in this sample have a minimum diameter of 500 nm and a maximum diameter of 3 μm and show some structure. These features appear as beads formed at approximately regular intervals giving the fibers a bamboo stem like feature. One possible reason for this could be that the PEO did not dissolve completely or the solution was not homogenous enough prior to spinning. It could also be due to the effects of surface tension which tries to reduce the surface area per unit mass[3]. One observes from Figure 5(a) that the fibers deposit themselves in a sinusoidal fashion with a branching effect in the upper right hand corner of Figure 5(a). This leads us to conclude that the thick fibers are composed of perhaps a bundle of smaller diameter fibers running parallel to the axis of the thick fiber. Figure 6 (a), (b) and (c) show AFM images of PANi/PS fibers. These fibers clearly have a smaller diameter than the PANi/PEO fibers with the thinnest fiber reported to be 50 nm. One possibility of obtaining thinner diameter fibers of PANi blends with PS is that the PS used was a standard polymer and so had few if any of defects. Fewer defects means fewer branches that could lead to polymer entanglement with PANi and hence thicker fibers of the blends when electrospun as is the case of PANi/PEO. It could also mean that PS form a more uniform blend with PANi in chloroform. The morphology of the PANi/PS fibers as seen in Figures 6(a) and 6(b) are also very uniform supporting this idea and suggesting better chain alignment in the blends. Once again in Figure 6(c) we notice bundles of fibers of smaller diameter bunched together forming a thicker fiber. Since the conductivity in PANi is very sensitive to the amount of defects it is reasonable to suggest that the overall conductivity of the blended fibers will be higher in the PANi/PS blends than in the PANi/PEO blends. Studies to measure these conductivities are in progress and will be reported at a later date. Although not studied in this report we plan to measure the conductivity of these PANi blends and also check to see if any field effect on the conductivity is observed. We also would like to point out the regions in Figures 6(a) and (b) where two polymers cross, this polymer-polymer junction is also of interest to us in making nanoelectronic junction devices. We are also in the process of trying out various other solvents other than chloroform, like tetrahydrofuran and acetonitrile to see which solvent yields thinner and more uniform fibers of PANi blends.

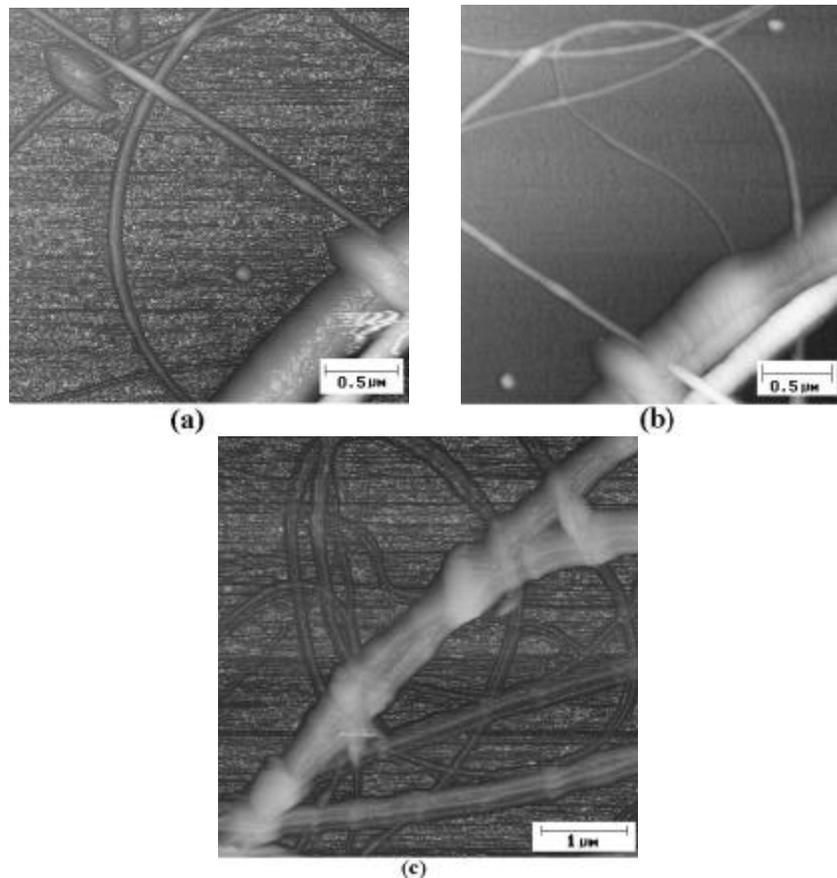


Figure 6: AFM images of PANi/PS electrospun fibers at 1kV/cm.

4.0. Conclusion

Fibers of pure PANi were spun and their room temperature conductivity was measured to be 0.76 S/cm and similar to the bulk value. No field effect was observed on the conductivity of these fibers suggesting that the sample was in the metallic regime rather than in the semiconducting regime where field effects are generally seen. In the case of polyaniline blended with PS and PEO it was found that PS is a better polymer to use in order to get thinner (< 100 nm) diameter fibers. This could be due to the availability of a standard with fewer defects as compared to PEO and better homogeneity of the blend in chloroform.

5.0. Acknowledgements

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6.0. References

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