

Electrospun Composite Nanofibers of Poly (Vinylidene Fluoride-Trifluoroethylene)/Polyaniline-Polystyrene Sulfonic Acid

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ABSTRACT: Nanofibers of poly(vinylidene fluoride-trifluoroethylene)/polyaniline-polystyrene sulfonic acid (PVDF-TrFE/PANi-PSSA) were fabricated in air at room temperature using electrospinning, with the thinnest fiber having a diameter of ~ 6 nm. This is a cheap, fast, and reliable process for generating PVDF-TrFE/PANi-PSSA composite nanofibers. The presence of conducting PANi-PSSA increased the charge density of the solution and assisted in the fabrication of PVDF-TrFE nanofibers at low polymer concentrations in dimethylformamide without the

beading effect. Ultraviolet and visible spectroscopy showed that PANi-PSSA was well incorporated into the PVDF-TrFE solution with no polymer segregation or degradation. A scanning electron microscope was used for morphological characterization of the fibers and a profilometer used to determine the fiber diameter. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3640–3644, 2011

Key words: composites; conducting polymer; ferroelectricity; nanofiber

INTRODUCTION

The copolymer poly(vinylidene fluoride-trifluoroethylene) $[(-CF_2-CH_2)_n-(CF_2-CHF-)_m]$ (PVDF-TrFE) is an electrically insulating ferroelectric (FE) polymer at room temperature for TrFE content in the range 20–50%.^{1–5} The FE nature of this polymer arises from the permanent dipole moments that point in a direction perpendicular to the polymer backbone, and the ability to control the material polarization has been exploited in the use of nonvolatile organic memory devices.^{6–9} Capacitors that use this material as the dielectric, form the basic storage element in such FE-based devices and have been fabricated using low cost spin coating techniques, typically leading to two-dimensional devices. Recently, there have also been field effect transistors (FET's) fabricated that use PVDF-TrFE as the gate dielectric, where the polarization of this material via a gate voltage can affect charge transport across a semiconducting channel in intimate contact with the dielectric.^{10–12} Preparing true nanofibers of PVDF-based polymer have proven difficult due to the high concentrations of the polymer needed in solution to make them.¹³ Using a well-

known electrospinning technique, we were able to fabricate true PVDF-TrFE nanofibers by incorporating a small fraction of the conducting polymer (CP) poly(3,4-ethylenedioxythiophene) (PEDOT) into the solution.¹⁴ The composite fibers have the additional property of being able to retain the FE and the conducting property of the individual components. The main advantage of being able to fabricate nanofibers is that one can potentially fabricate quasi 1-D devices that make use of the FE or the electrical conducting properties or both, and simultaneously have a large surface to volume ratio that can be used in the fabrication of low power consumption devices and supersensitive sensors. In this article, we report on the fabrication of PVDF-TrFE nanofibers incorporating water soluble polyaniline doped with polystyrene sulfonic acid (PANi-PSSA) using the electrospinning technique. Our results show the formation of nanofibers at lower concentrations of PVDF-TrFE/PANi-PSSA compared with the PVDF-TrFE/PEDOT-PSSA blends and the resulting electrospun fibers also have a much smaller diameter. The linear and less bulkier repeat unit in PANi compared with PEDOT is proposed as being responsible for these morphological differences.

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EXPERIMENTAL

Chemicals

PVDF-TrFE (75/25) was purchased from Kureha, Japan (KF W# 2200) with a purity level of 99.0% and with a molecular weight of 350,000 and used as

received. *N,N*-dimethylformamide (DMF) was used as the solvent and the following concentrations of PVDF-TrFE in DMF were prepared: 1, 3, 5, 7, 9, 11, 13, and 15 wt%. The viscosities of these solutions fall in the range 0.92 cp for DMF to ~ 5000 cp for the 15 wt% solution. In a separate synthesis, polyaniline (PANi) was prepared and doped with polystyrene-sulfonic acid (PSSA) as follows: 10 mL of 0.02M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 1.0M PSSA (aq.) was quickly poured into a beaker containing 10 mL of 0.02M aniline in 1.0M PSSA (aq.) at room temperature under magnetic stirring for 5 min after which the stirring was stopped and the reaction allowed to proceed for 2 h. The reaction mixture was then transferred to a dialysis tubing (Spectra/Por, 12-14,000 MW cutoff) and dialyzed against 4 L deionized water for 20 h. The dialysis bath was changed six times during the course of the 20 h dialysis.¹⁵ The resulting aqueous polymer solution was dark green in color.

Electrospinning

To electrospin nanofibers of PVDF-TrFE, 0.06 g of PANi-PSSA aqueous solution was mixed with 0.85 g of the pure PVDF-TrFE solution in DMF at the various concentrations mentioned above. These were stirred gradually until they appeared homogenous and were green in color. For example, the sample labeled as 3 wt% PVDF-TrFE/PANi-PSSA was prepared by mixing 0.85 g of the 3 wt% PVDF-TrFE/DMF solution with 0.06 g of the PANi-PSSA solution. Although the concentration of PANi-PSSA was kept fixed in all the samples, that of PVDF-TrFE was changed from 1 wt% to 15 wt%, thus the final solution that was electrospun would have a slightly smaller PVDF-TrFE concentration than that stated. Once the solutions were prepared, a small part was transferred into a ultraviolet and visible (UV/VIS) cell for optical spectroscopy and the rest used for electrospinning to prepare nanofibers. Figure 1 shows the main elements of the electrospinning apparatus that consists of a hypodermic needle, a high voltage power supply and a syringe pump. About 0.5 mL of the solution was filled in a hypodermic needle and placed in a syringe pump calibrated to yield a flow of about one drop every 15–20 s. As the voltage applied to the needle was increased, the electric field force on the droplet overcomes the surface tension and a jet is issued forward toward the cathode. As the solvent evaporates, fine fibers of the polymer deposit themselves on the grounded Al foil and could be peeled off as a free standing nonwoven fiber mat. Electrospinning was carried out at a voltage of ~ 10 kV and the distance between the needle tip and grounded Al foil was about 15 cm.

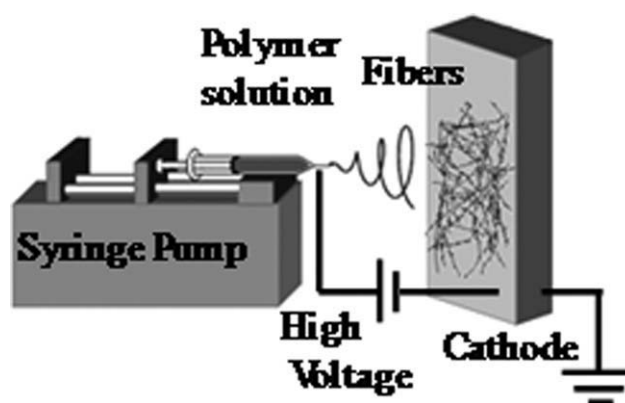


Figure 1 Basic electrospinning apparatus used in the fabrication of PVDF-TrFE/PANi-PSSA nanofibers. The voltage was kept fixed at ~ 10 kV and the cathode distance ~ 15 cm.

Characterization

A JEOL JSM-6360 scanning electron microscope (SEM) was used to observe the morphology of the fibers after drying them in air at 70°C for several hours. A Perkin-Elmer Lambda 35 spectrometer was used to measure the UV/VIS spectra in solution and a Alpha Step 500 surface profiler (KLA Tencor) was used for diameter measurements on individual fibers captured on Si/SiO₂ wafers.

RESULTS AND DISCUSSION

The UV/VIS spectra of the PVDF-TrFE/PANi-PSSA solutions were measured before electrospinning and are shown in Figure 2 for different PVDF-TrFE concentrations. UV/VIS spectra of pure PVDF-TrFE and pure PANi-PSSA in DMF were also measured and included in Figure 2. Regardless of the PVDF-TrFE concentration, the spectra of the composite PVDF-TrFE/PANi-PSSA solutions are very similar to that of pure PANi-PSSA, and include a broad absorption in the range 450–650 nm that is usually assigned to the π - π^* transition and a relatively sharp absorption peak at ~ 780 nm which is typically due to the localized polaron band in doped PANi. This peak appears to blue shift with increasing PVDF-TrFE concentrations suggesting a more compact coil configuration of the PANi-PSSA chains due to the confining effect of the high wt % PVDF-TrFE. Similar results were observed in PANi-HCSA with increasing polyethylene oxide concentrations.¹⁶ The UV-VIS spectra of PVDF-TrFE by contrast is flat and featureless in this energy range and is consistent with the transparent nature of the solution. All of these results show that the PANi-PSSA is uniformly incorporated as a composite in the solution and does not degrade. Visual inspection of the solution after several days did not show any polymer segregation or

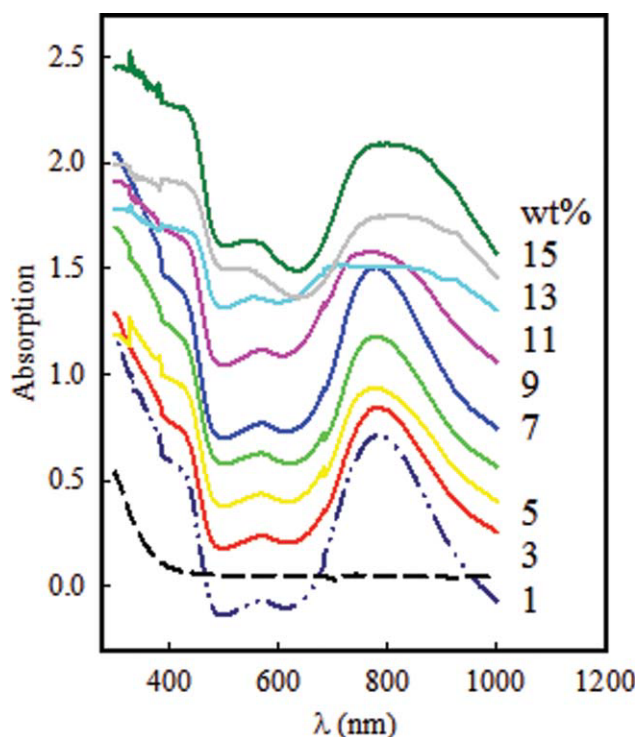


Figure 2 UV/VIS spectra of the various PVDF-TrFE/PANi-PSSA solutions in DMF. The spectra of pure PVDF-TrFE (dashed) and pure PANi-PSSA (dashed-dots) in DMF is also included. Individual traces have been shifted to avoid overlap. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)]

precipitation. For PVDF-TrFE concentrations above 11 wt%, the absorption peak due to the localized polaron band gets broader. This could be due to the inability of the polymer chains to deaggregate in solution as the PANi-PSSA chains become more and more entangled with that of PVDF-TrFE and are less mobile. A small absorption at 576 nm in pure PANi-PSSA and PANi-PSSA containing samples may be due to the benzene ring along the PSSA chain or an indication of incomplete doping to the emeraldine salt form of polyaniline. This feature is not seen as being important to the fabrication of PVDF-TrFE nanofibers reported here.

Figure 3(a–h) shows the SEM images of electrospun fibers of PVDF-TrFE/PANi-PSSA composites at various concentrations of PVDF-TrFE (1, 3, 5, and 7 wt% respectively). As seen in Figure 3(a and b), at 1 wt% without and with PANi-PSSA, there were no fibers formed as the solution was not viscous enough and there was a very small amount of the polymer in solution to cause chain entanglement as the solvent evaporated while electrospinning. The SEM images show that of the resulting residue after droplet evaporation. Without PSSA, as one increases the PVDF-TrFE concentration, while the solution gets progressively more viscous, there are still no visible signs of fiber formation, although at 5 wt%

and higher [Fig. 3(e)], one begins to notice a few scattered fibers emerging as protrusions from the polymer beads and this is enhanced in the 7 wt% sample. These results are reasonable, since at such low concentrations, the polymer jet breaks up during electrospinning due to reduced extensional viscosity.¹⁷ The high boiling point of DMF also decreases the possibility of solvent evaporation in the electrospun jet and thus necessitates the use of higher polymer concentrations for fiber formation. Typically, what was observed at such low concentrations (<5 wt%) was a spraying effect that covered the grounded Al foil in the electrospinning apparatus with DMF droplets inter dispersed with polymer beads. Figure 4(a–h) shows the SEM images of electrospun fibers of PVDF-TrFE/PANi-PSSA composites at higher concentrations of PVDF-TrFE (9, 11, 13, and 15 wt%, respectively). Here, we notice a

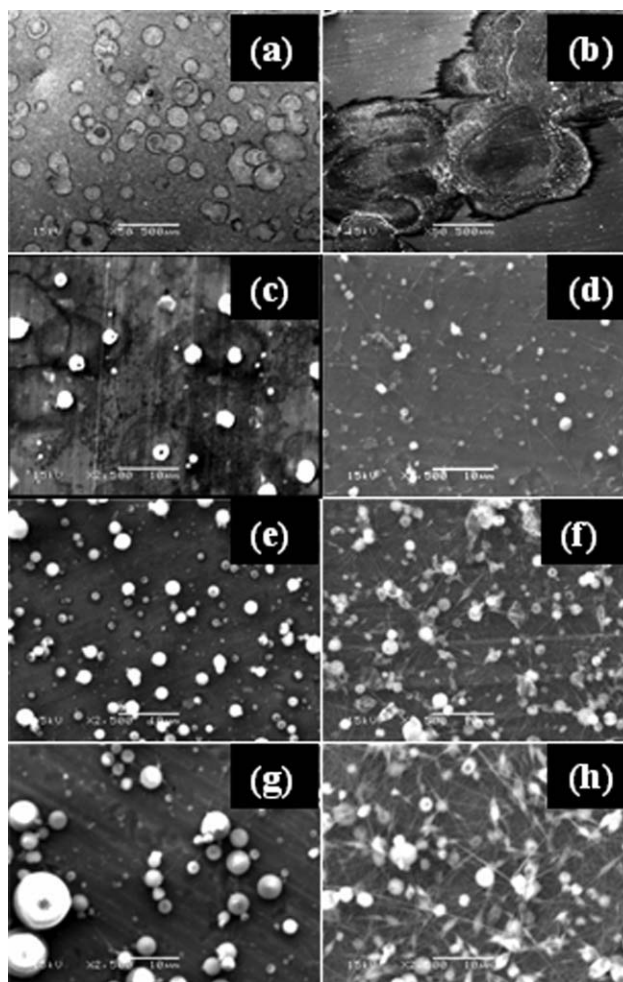


Figure 3 SEM images of electrospun fibers of (a) 1 wt% PVDF-TrFE; (b) 1 wt% PVDF-TrFE/PANi-PSSA; (c) 3 wt% PVDF-TrFE; (d) 3 wt% PVDF-TrFE/PANi-PSSA; (e) 5 wt% PVDF-TrFE; (f) 5 wt% PVDF-TrFE/PANi-PSSA; (g) 7 wt% PVDF-TrFE; and (h) 7 wt% PVDF-TrFE/PANi-PSSA. All images except (a) and (b)] have the same magnification and the scale bar in each represents 10 μm .

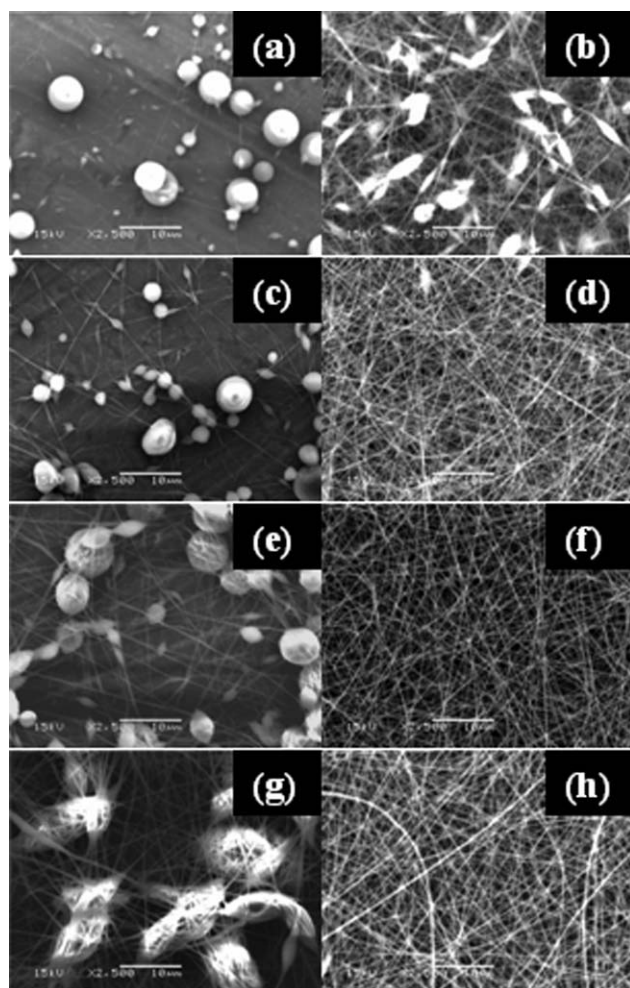


Figure 4 SEM images of electrospun fibers of (a) 9 wt% PVDF-TrFE; (b) 9 wt% PVDF-TrFE/PANi-PSSA; (c) 11 wt% PVDF-TrFE; (d) 11 wt% PVDF-TrFE/PANi-PSSA; (e) 13 wt% PVDF-TrFE; (f) 13 wt% PVDF-TrFE/PANi-PSSA; (g) 15 wt% PVDF-TrFE; (h) 15 wt% PVDF-TrFE/PANi-PSSA. All images have the same magnification and the scale bar in each represents 10 μm .

clear difference in the formation of fibers compared with Figure 3 in the absence of PANi-PSSA. The addition of PVDF-TrFE in DMF increases the viscosity of the solution and fibers are easily formed although one notices the formation of beads along the fiber lengths, whose shape seem to change from spherical to oval as the PVDF-TrFE concentration is increased. From the left hand side images in Figures 3 and 4, we see that when pure PVDF-TrFE fibers are formed at polymer concentrations >7 wt% the fibers are few and are indiscriminately interrupted by the presence of polymer beads. Such polymer morphologies are impractical for use in any device and sensor applications where the large surface to volume ratio of the fibers is to be exploited. To overcome this deficiency, we have added a small amount of a water soluble CP PANi-PSSA, in an effort to increase the net charge density in the electrospin-

ning solutions. Such an addition has been known to reduce the surface tension of the solution leading to more uniform fibers without the beading effect.^{18,14} The right hand side SEM images in Figures 3 and 4 show the result of increasing charge density very clearly compared with the corresponding left hand side image without PANi-PSSA. As the PVDF-TrFE concentrations increase, the presence of small quantities of PANi-PSSA allows for the formation of uniform fibers with decreasing beading effects due to the increase in the net charge density carried by the jet.¹⁹ The fibers are also seen to be longer in length and are more abundant. Several of these fibers were seen to bridge the gap between the needle and the cathode and had to be physically removed to allow for a continuous collection of fibers. Reducing the amount of PANi-PSSA in solution led to the reappearance of beads along the fibers consistent with reduced charge density.

To quantitatively characterize the fiber size, individual fibers of PVDF-TrFE/PANi-PSSA were captured on polished Si/SiO₂ wafers and placed on the profilometer stage for fiber diameter measurements. Figure 5 shows the plot of diameters of the PVDF-TrFE/PANi-PSSA fibers as a function of PVDF-TrFE wt%. The fiber diameters increase linearly as the PVDF-TrFE wt% increases from 3 wt% to 9 wt%, due to the increase in solution viscosity (while the applied voltage was held fixed), with the smallest diameter measuring ~ 6 nm for the 3 wt% sample. Above 9 wt% there is a noticeable increase in the fiber diameters that could be related to the relative reduction in

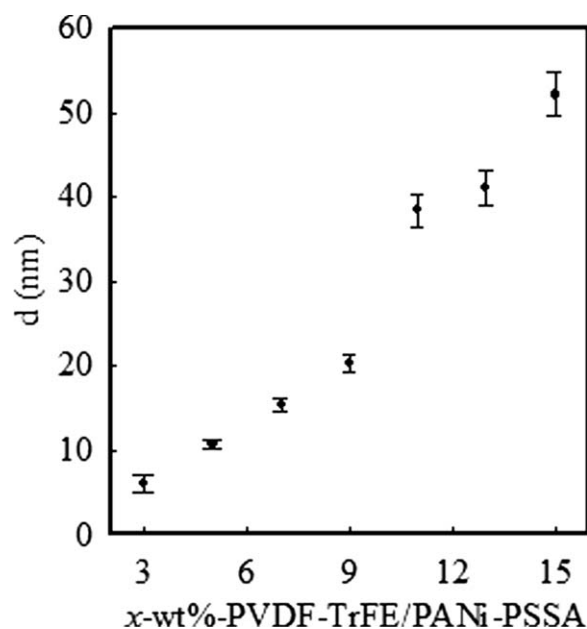


Figure 5 Plot of the electrospun fiber diameters (d) taken using a profilometer as a function of wt% of PVDF-TrFE/PANi-PSSA. The diameters were extracted from the vertical step height of the profilometer scan.

charge density due to the increased amount of PVDF-TrFE in the more viscous solutions. These results are consistent with qualitative observations of the right hand side images of Figures 3 and 4 where a gradual increase in fiber diameter is observed as the PVDF-TrFE content is increased. The difference in this study compared to our previous results on PVDF-TrFE/PEDOT-PSSA fibers is that PANi-PSSA assisted fibers are comparatively thinner for similar PVDF-TrFE wt % in DMF. One possible explanation we propose is that PANi is a linear chain polymer and is less bulky than PEDOT. This implies that PANi would be more flexible than PEDOT and could lead to easier stretching during the electrospinning process leading to thinner diameter fibers. The advantage of these fibers is then the expected rapid response compared to the PEDOT based fibers when they are used as gas and light sensors due to their enhanced surface to volume ratio. Efforts are currently underway to utilize the FE and/or the conducting properties of these fibers for device and sensor fabrication and testing.

CONCLUSIONS

Composite nanofibers of PVDF-TrFE/PANi-PSSA were fabricated using the electrospinning method for various concentrations of PVDF-TrFE in DMF. The addition of the CP PANi-PSSA increased the charge density of the solution and assisted in the fabrication of nanofibers at lower than normal PVDF-TrFE concentrations in DMF without the beading effect that commonly occurs when electrospinning this polymer. The fiber diameters increased as the wt % of PVDF-TrFE increased, nevertheless, all of the fibers had diameters <100 nm and were hundreds of microns long, giving them a large aspect ratio. UV-VIS spectroscopy showed that the PANi-PSSA was uniformly incorporated into the composite PVDF-TrFE/PANi-PSSA solution with lit-

tle change in the localized polaron band, implying that the CP was not chemically altered in solution.

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