

Electrospun fibers of poly (vinylidene fluoride-trifluoroethylene)/(P (NDI2OD-T2)) composites

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Abstract

Poly (vinylidene fluoride-trifluoroethylene)-PVDF-TrFE and poly{[N, N'bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)}-P(NDI2OD-T2) are electroactive polymers that are compatible with flexible electronics. PVDF-TrFE is a ferroelectric copolymer and P(NDI2OD-T2) is a *n*-type semiconducting polymer. Devices based on these polymers are typically fabricated using thin films. Using the electrospinning technique we have successfully fabricated *for the first time* composite fibers of these polymers. The solutions used in the preparation of composite fibers consisted of a mixture of PVDF-TrFE dissolved in tetrahydrofuran (THF) at various concentrations, and P(NDI2OD-T2) dissolved in dichlorobenzene in a 2wt% concentration. UV/Vis spectroscopy showed that the P(NDI2OD-T2) was uniformly incorporated into the PVDF-TrFE solution with no polymer segregation. The presence of semiconducting [P(NDI2OD-T2)] increased the quantity of PVDF-TrFE fibers as seen using a Scanning Electron Microscope (SEM). SEM images of the composite fibers also show that P(NDI2OD-T2) reduces the beading effect on the fibers making them good candidates for use in devices. The ability to produce these fibers opens up the possibility of fabricating miniaturized low power consumption ferroelectric field effect transistors that possess the memory effect of PVDF-TrFE and the semiconducting property of P(NDI2OD-T2).

Keywords: PVDF-TrFE, P(NDI2OD-T2), Electrospinning

1. Introduction

Poly (vinylidene fluoride-trifluoroethylene), also called (PVDF-TrFE), is an electrically insulating co-polymer that exhibits ferroelectric (FE) behavior. This co-polymer can exist in several phases but it is polar (FE) only for TrFE content in the range 20-50% at room temperature and is labelled the β phase[1]. The co-polymer PVDF-TrFE has ferroelectric characteristics induced by the dipole moments pointing perpendicularly to the main chain polymer backbone. This ferroelectric characteristic and the capability to control the polarization, permits use of this co-polymer in nonvolatile organic memory devices[2]. The applications of PVDF-TrFE are abundant because of its flexibility, charge storage capability, low thermal conductivity, high chemical corrosive resistivity, heat resistance and low water absorption. Some of the applications are: insulator of electrical wires, sensors, batteries and capacitors. The fabrication of ferroelectric (FE) based devices typically use thin films of this co-polymer. We focus our attention on the fabrication of nanofibers of PVDF-TrFE. In the past, fibers of PVDF-TrFE using the electrospinning technique usually required the preparation of a high concentration solution (~20wt%)[3]. In this paper we add a small amount of a *n*-doped semiconducting polymer P(NDI2OD-T2) to the electrospinning solution and obtain nanofibers of PVDF-TrFE composites at a lower PVDF-TrFE concentration (~7wt%). This is due to the fact that charge on the conducting polymer lowers the surface tension of the electrospinning solution[4]. The addition of P(NDI2OD-T2) to the solution also promotes an increase in the quantity and quality of the composite nanofibers

fabricated via electrospinning. Our method thus opens up the possibility of fabricating one dimensional (1-D) multifunctional devices based on these nanofibers that are smaller in size and have low power requirements.

2. Experimental

PVDF-TrFE (75/25) was purchased from Kureha, Japan and used as received. Solutions of PVDF-TrFE in tetrahydrofuran (THF) were prepared and kept aside. This co-polymer was soluble in THF at a temperature of approximately 60°C and dissolved in about an hour. The weight percent concentrations of PVDF-TrFE dissolved in THF and used in this experiment were: 1wt%, 3wt%, 5wt%, 7wt%, 9wt%, 11wt%, 13wt% and 15wt%. A second solution containing a concentration of 2wt% of the *n*-doped polymer P(NDI2OD-T2) dissolved in dichlorobenzene was also prepared and kept aside. Then 0.85g of the PVDF-TrFE solution and one drop (0.11g) of the P(NDI2OD-T2) solutions were mixed together; this mixture was then stirred to obtain a homogenous solution and was then used to fabricate fibers, henceforth labeled as the composite solution.

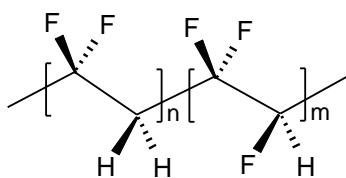


Figure 1. PVDF-TrFE chemical structure

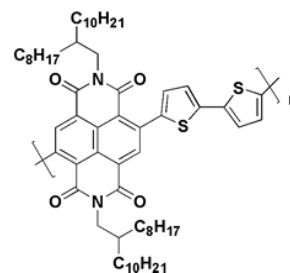


Figure 2. P(NDI2OD-T2) chemical structure

Figure 1 shows the chemical structure of PVDF-TrFE and Figure 2 shows the chemical structure of the *n*-type polymer P(NDI2OD-T2) and were purchased from commercial sources. Figure 3 shows the basic elements of the electrospinning apparatus. The electrospinning setup consists of a syringe pump, a hypodermic syringe connected to a high-voltage DC power supply and a grounded collector (in our case aluminum foil) [5][6]. The syringe containing 0.5 mL of the composite solution as prepared above was placed on the syringe pump and the flow out of the syringe controlled to ~2mL/hr. Then a voltage was applied to the needle. As the voltage was increased, there came a time when the electric force on the drop formed at the needle tip was greater than the surface tension of the drop and a fine jet in the form of a spiral was seen to emerge from the needle and head toward the grounded cathode. In the process there is a rapid expansion of the drop and subsequent evaporation of the solvent, hence several fine fibers were seen to adhere to the Al foil in the form of a non-woven fiber mat. The fiber samples were then dried at 80°C in air before further analysis.

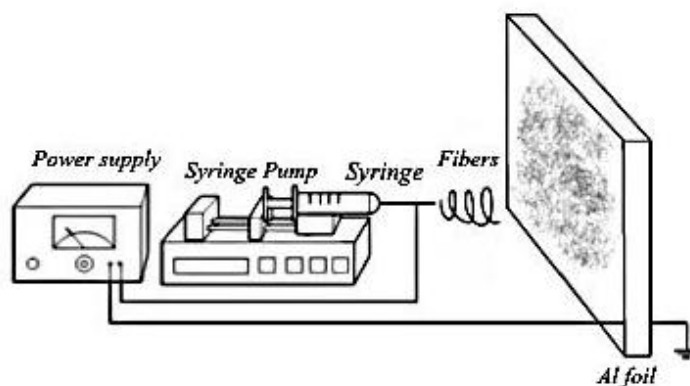


Figure 3. Electrospinning Apparatus

3. Results

Figure 4 shows the UV/VIS spectra of the various composite solutions of PVDF-TrFE and P(NDI2OD-T2) as mentioned above. There is a broad peak centered around 490 nm and represents the π - π^* transition of the electronic absorption spectra. The spectra of pure PVDF-TrFE is featureless as it is transparent in solution and the spectra shown in Figure 4 are similar to that of pure P(NDI2OD-T2)[7]. The fact that the spectra of the composite solution is similar to that of pure P(NDI2OD-T2) implies that P(NDI2OD-T2) is uniformly incorporated as a blend in the solution and is not chemically affected by the ferroelectric polymer. Further observations show that the solutions once mixed and stored in glass vials, stayed homogeneous for several weeks with no indication of phase separation of the PVDF-TrFE/THF and P(NDI2OD-T2)/dichlorobenzene components and strengthens the claim that the P(NDI2OD-T2) is well dispersed in the PVDF-TrFE/THF solution. The fibers obtained from this solution are hence true composites of the two polymers.

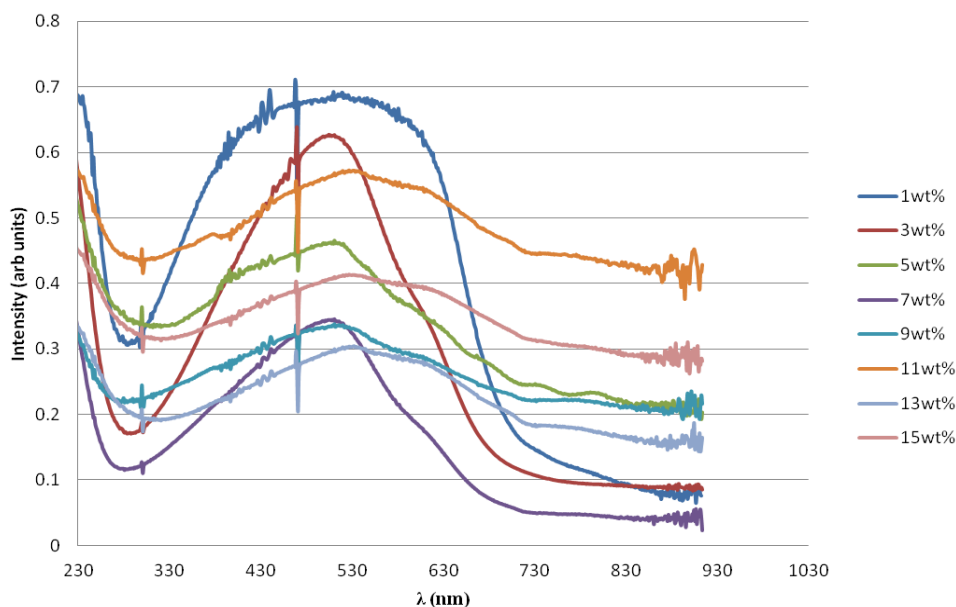


Figure 4. UV/VIS spectra of the composite solutions prepared from various PVDF-TrFE concentrations with P(NDI2OD-T2).

Figures 5(a)-5(h) shows the Scanning Electron Microscope (SEM) images of the electrospun solutions of PVDF-TrFE/P(NDI2OD-T2) composites. The images on the left are those of electrospun pure PVDF-TrFE in THF, while the images on the right are for the electrospun composite solutions. As seen in the images, there are no fibers formed for the 1wt%, 3wt% and 5wt% solutions with or without P(NDI2OD-T2). This is because the solution is not viscous enough and during the electrospinning process we see a spraying effect. This is a consequence of the small amount of polymer in the solution. At 1wt%, the PVDF-TrFE content is so small that we see the formation of thin films. This is because the deposit left on the Al foil after the electrospinning process is wet and subsequent drying in the oven leads to the formation of the films seen in Figure 5(a) and (b). As the polymer concentration is increased to 3wt% or 5wt%, we see the presence of beads on the Al foil. In this case too, the deposit left on the Al foil after the electrospinning process was still wet, however, now there is enough polymer in the solution to lead to a coalescence of the polymer during the drying process leading to the formation of beads. Increasing the concentration of the PVDF-TrFE co-polymer to 7wt% now leads to the formation of fibers as seen in Figures 5(g) and (h). The number of beads are now reduced and are connected with fibers. The solution viscosity is now high enough so that polymer chains get entangled as the solution is being electrospun and this leads to fiber formation. As seen in Figure 5(h),

there are more fibers formed and the beads have a more elongated shape as compared to Figure 5(g). This is due to the presence of P(NDI2OD-T2) which increases the charge in the solution and reduced its surface tension. The addition of charge into a polymer solution to improve the quality of electrospun fibers is therefore an easy method of preparing fibers of a polymer that are insulators.

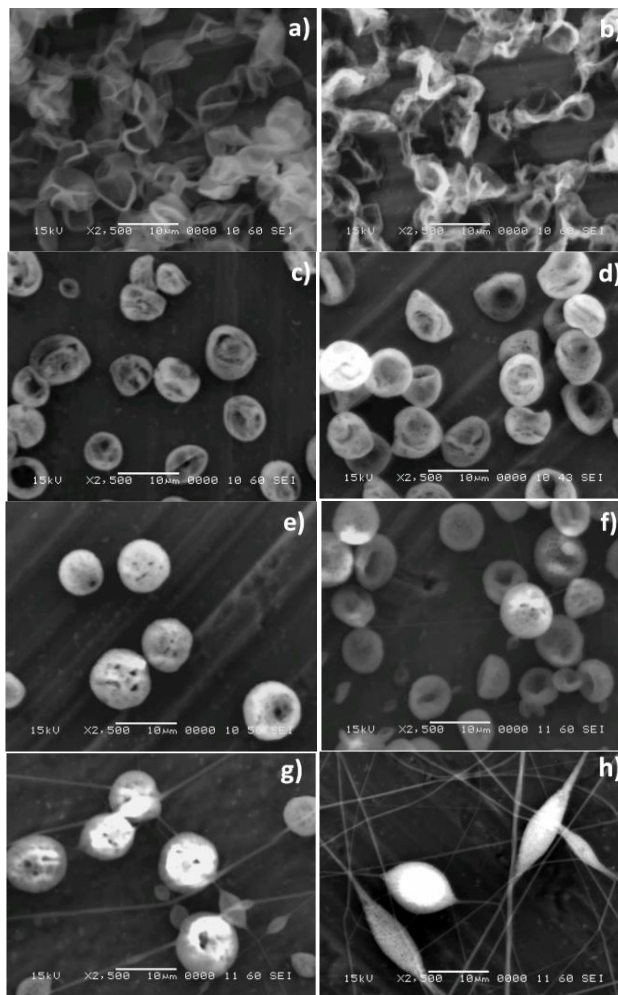


Figure 5. SEM images of electrospun fibers of: a) 1wt% PVDF-TrFE, b) 1wt% PVDF-TrFE and one drop P(NDI2OD-T2), c) 3wt% PVDF-TrFE, d) 3wt% PVDF-TrFE and one drop P(NDI2OD-T2), e) 5wt% PVDF-TrFE, f) 5wt% PVDF-TrFE and one drop P(NDI2OD-T2), g) 7wt% PVDF-TrFE, h) 7wt% PVDF-TrFE and one drop P(NDI2OD-T2). All the images have the same magnification and the scale bar represents 10 μ m.

Figures 6(a) – (h) shows the SEM images of fibers electrospun from polymer concentrations of 9wt%, 11wt%, 13wt% and 15wt% respectively. As in Figure 5, the images on the left are those of electrospun pure PVDF-TrFE in THF, while the images on the right are for the electrospun composite solution. When the concentration was increased to 9wt% and 11wt% (Figure 6(a) and (c)) the beads were reduced and more fibers were formed. After the addition of P(NDI2OD-T2) the beads decreased and the number of fibers increased (Figure 6 (b) and 6(d)). At 13wt% and 15wt% as seen in Figure 6(e) and (g) the fibers were increased and the elongated beads disappeared, they are also thicker in diameter and are more abundant compared to those in Figure 5. In Figure 6(f) and (h), the presence of P(NDI2OD-T2) reduces the surface tension of the composite solution and the fibers now are smoother (higher quality) and more abundant compared to the pure counterparts (6(e) and (g)). From these images, we see

that the addition of a conducting polymer assists in fiber formation. Being a conducting polymer that exhibits *n*-type behavior also increases the versatility of these fibers in devices that could potentially exhibit the charge storage capability of PVDF-TrFE combined with the semiconducting *n*-type property of P(NDI2OD-T2). Such devices that are based on polymers and that are multifunctional represent the future of plastic electronics that are cheap and easy to fabricate.

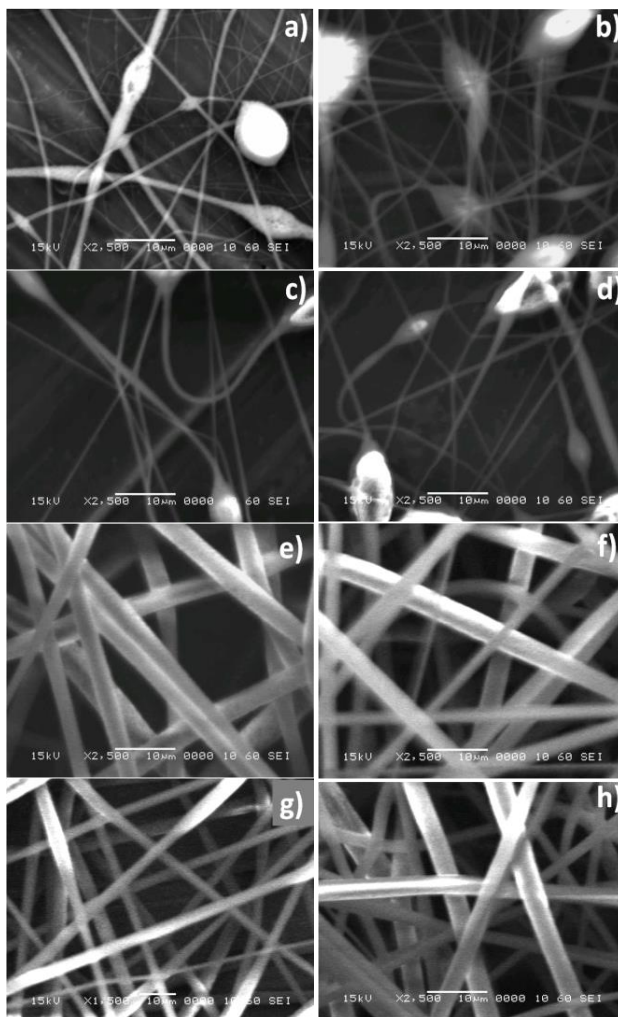


Figure 6. SEM images of electrospun fibers of: a) 9wt% PVDF-TrFE, b) 9wt% PVDF-TrFE and one drop P(NDI2OD-T2), c) 11wt% PVDF-TrFE, d) 11wt% PVDF-TrFE and one drop P(NDI2OD-T2), e) 13wt% PVDF-TrFE, f) 13wt% PVDF-TrFE and one drop P(NDI2OD-T2), g) 15wt% PVDF-TrFE, h) 15wt% PVDF-TrFE and one drop P(NDI2OD-T2). All the images have the same magnification and the scale bar represents 10 μ m.

4. Conclusions

Nanofibers of the co-polymer PVDF-TrFE have been successfully electrospun for polymer concentrations > 7wt% with the assistance of a charge carrying *n*-type semiconducting polymer P(NDI2OD-T2). UV-VIS spectra of the composite solutions show that the two polymers are blended uniformly with no phase separation. The presence of

P(NDI2OD-T2) increases the charge in the electrospun solutions reducing its surface tension. This results in the formation of a greater quantity of fibers with fewer beads. Since the composite fibers have the capability of charge storage and are semiconducting, it opens up the possibility of fabricating ferroelectric field effect transistors that represent the next generation of polymer electronics suitable for use in flexible displays.

5. Acknowledgements

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6. References

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