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Electrospinning Of Nanofibers Solutions With PVDF, DMF, Acetone And Fe_3O_4 Nanoparticles

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Abstract

This study aims at evaluating the effects of several concentrations of poly (vinylidene fluoride) (PVDF), N,N-dimethylformamide (DMF) and acetone solutions combined with iron oxide nanopowder (Fe_3O_4 particle diameter of 20 nm to 30 nm) on the behavior of formation of nanofibers using electrospinning. In order to get oriented nanofibers, a DC Motor with a speed controller was set up to rotate the sample during the synthesis. The morphology of the nanofibers and solutions was analyzed by Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). Best results were found with the polymeric solutions containing PVDF, DMF and acetone at a concentration of 18 wt % and DMF to acetone ratio of 3 to 1. Nanopowder to PVDF ratios of 1:5, 1:10, and 1:15 were analyzed. Lower concentrations of PVDF resulted in the deposition of drops, characteristic of the electrospray process. The concentration of PVDF ratio at 1:15 resulted in nanofibers with a diameter of 150 nm to 250 nm, as verified by SEM. However, the diameters of the fibers were non-uniform due to the formation of iron oxide agglomerates.

Keywords: Nanofibers, Electrospinning, Nanoparticles

1. Introduction

Nanostructures with one dimensional poly(vinylidene fluoride) (PVDF) is a frequently used material due to its excellent chemical stability, mechanical properties, and ferroelectricity. PVDF is a polymer commonly used as electrical wire insulators due to its properties of heat resistance, low weight, low thermal conductivity, and high resistance to corrosion. Combining a solution of PVDF with different solvents and using the electrospinning process, polymer fibers ranging from nanometers to micrometers can be obtained. The process of fiber formation from the liquid state is entirely physical, either by solvent loss or by freezing of a melt[1]. During electrospinning, the solution forms a droplet at the tip of a needle due to surface tension. By placing the needle at a distance from 1 to 10 cm from the ground metal plate and applying a sufficiently high electrical voltage (1-30 kV) to the solution, electric charges will accumulate in the droplet. When the electrostatic force surpasses the surface tension of the solution droplet, the tip of the droplet extends towards a collection plate forming a conical shape droplet at the tip of the outlet[2-4]. Then, an electrically charged stream of polymer is ejected. This stream is stable near the tip, but it soon undergoes a process of instability and elongation. The solvent evaporates as the stream travels and nanofibers are randomly deposited on the collection plate.

Iron oxide nanopowder is commercially available with particle diameters between 1 to 100 nanometers, and with purity over 95%. The two main forms are magnetite (Fe_3O_4) and its oxidized form (γ-Fe_2O_3), both interesting due to their paramagnetic properties and their potential applications for magnetic storage devices, catalysis, and sensors[5,6].

The main objective of the current research was to determine the optimal solution concentration in order to obtain the finest diameter possible of the nanofiber and synthesize oriented magnetic fibers for future applications.

2. Experimental Methodology

2.1 Materials

The solutes used consisted of PVDF with a density of 1770 Kg/m^3 density by Sigma-Aldrich and Iron Oxide Nanopowder (Fe_3O_4, particle diameter of 20-30 nm) by US Research Nanomaterials, Inc. The solvents used consisted of N,N-dimethylformamide (DMF) with a density of 944 Kg/m^3 and acetone with a density of 791 Kg/m^3, both manufactured by Sigma-Aldrich. All polymeric solutions containing PVDF, DMF and acetone were kept at concentrations of 18 wt % and the ratio of DMF to Acetone at 3 to 1; since it was previously determined that this solution concentration yielded a better viscosity that lead to thinner nanofibers during the electrospinning process. Keeping the other components constant, variable ratios of Nanopowder to PVDF at 1:5, 1:10, and 1:15 were analyzed. The mixture of the solutions was achieved by stirring overnight at a temperature of 55^{o}C.

2.2 Electrospinning

A high voltage power supply (ES30, 0-30KV) was used to create an electrical field, and was previously determined to use an applied voltage of 15KV. The Becton Dickinson syringe used was 0.5cc in size, and the needle was 0.40mm in diameter and 13mm in length. With the intention to acquire oriented nanofibers deposited on a silicon wafer, a DC step motor with a speed controller was setup to rotate the sample and was placed at the midpoint position of the electric current. The DC motor was connected to a 2 cm plastic cylinder with the silicon attached and the speed of rotation during the collection remained at 1 revolution per second. The distance between the needle and the metal collector was set at 10 cm. A diagram depicting this setup just described is shown in Figure 1.

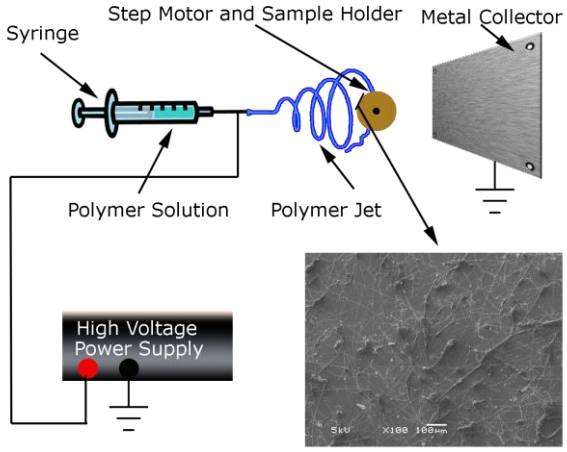

Figure 1. Setup of electrospinning experiment

2.3 Characterizations

The solutions were characterized by transmission Fourier Transform Infrared Spectroscopy (FTIR) using Spectrum 100 by Perkin Elmer within the range of 650 to 4000 cm^{-1}. The morphology of the nanofibers was analyzed using a Scanning Electron Microscope (SEM) model 6480LV, manufactured by JEOL, at 5KV with a magnification of 15,000 and 10,000. The diameters of the fibers and the agglomerates of Iron oxide were determined byusing the software "*image J*" developed by the National Institute of Health.

3. Results and Discussions

Results of the solution analyses with FTIR are shown in Figure 2, depicting all nanopowder to PVDF ratios studied.

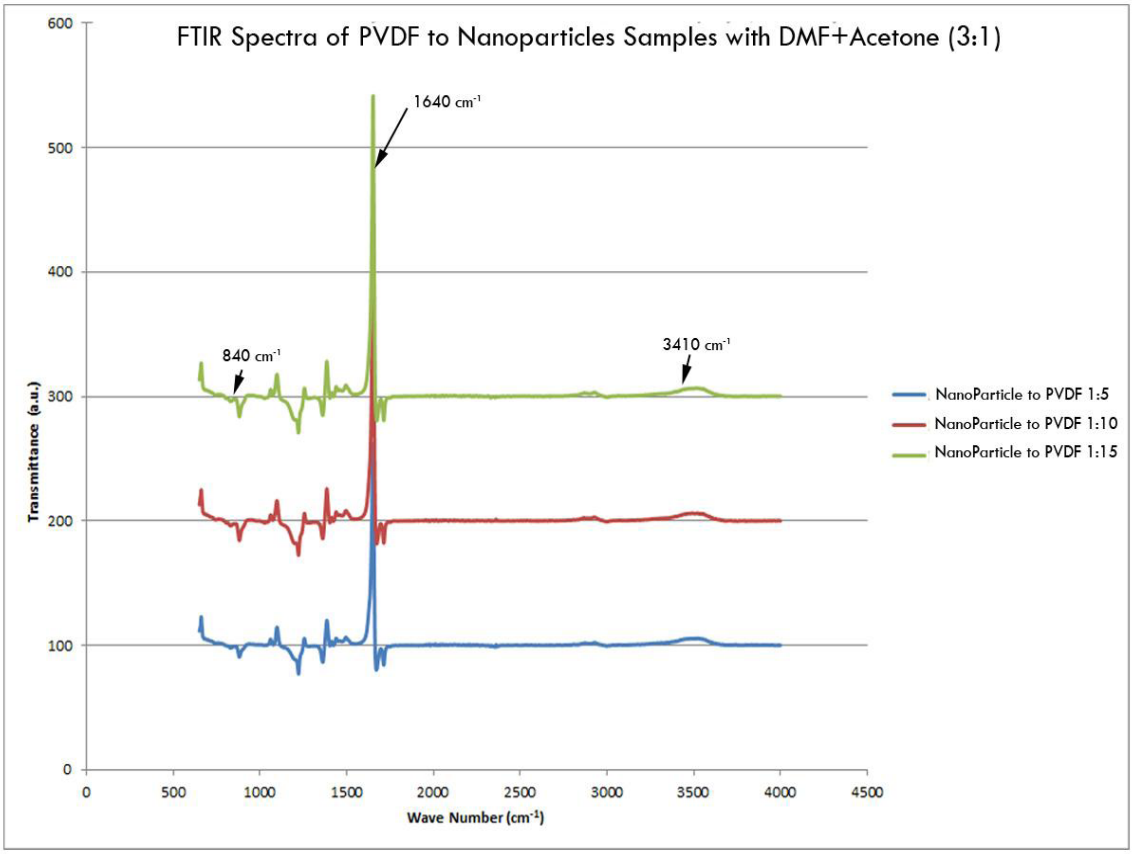

Figure 2. FTIR spectra of solutions studied

All samples presented bands at 840 cm^{-1}, characteristic of the β phase of PVDF[7,8]. The FTIR spectrum of the Fe_3O_4 magnetite nanoparticles has a strong absorption band at 584cm^{-1}, which is associated to the vibrations of the Fe-O bond. This peak was not observable with the FTIR utilized in this study, because of its limitations to only acquire wavelengths starting at 650 cm^{-1}. A broad band observed at 1640 cm^{-1} and a minuscule peak at 3410cm^{-1} are both associated to O-H stretching and bending vibrations present on the surface of the iron oxide nanoparticles[9,10]. Both peaks are clearly depicted in Figure 2. The remaining peaks correspond to the acetone and DMF solvents. These results will be used in further studies for comparison with the spectra obtained from nanofibers using a micro FTIR.

Concerning the electrospinning process, the use of a motor with a controlled speed helped to obtain a more organized fiber deposition on the silicon substrate. Figure 3 shows SEM images of typical nanofibers obtained from samples with different concentrations of nanopowder. As clearly depicted, the nanofibers did not result uniform, and present with agglomerates of nanoparticles. It is speculated that the agglomeration most probably occurred during the electrospinning process, since the fibers are uniformly dispersed in the solution.

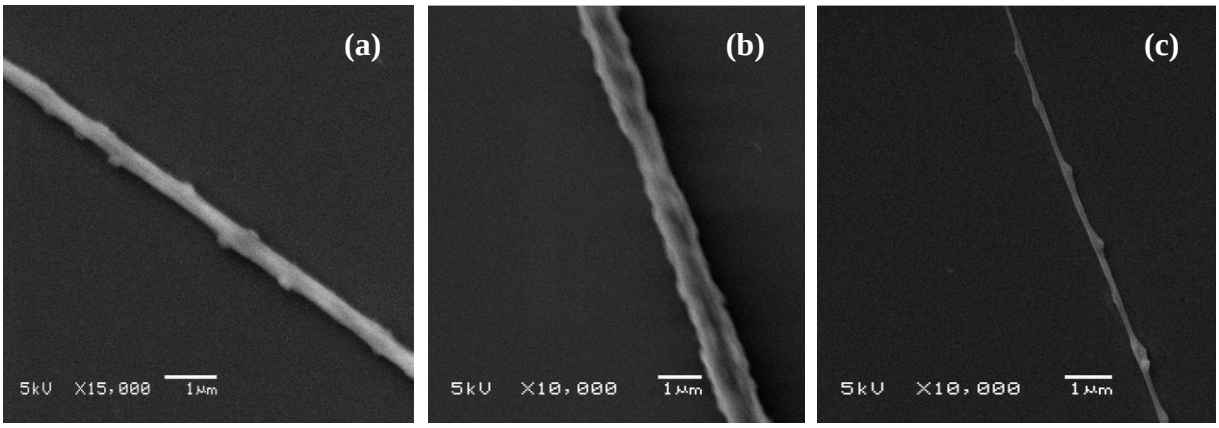

Figure 3. Micrographs of the samples processed from polymeric solutions containing PVDF at 18 wt %, dissolved in DMF and acetone (3 to 1), and nanopowder to PVDF at ratios of: (a) 1:5, (b) 1:10, and (c) 1:15.

Figure 4 presents the average diameter distribution for different nanopowder concentrations. These results demonstrate the influence of the concentration of nanopowder over the obtained diameter of the fiber. Fibers with an intermediate ratio of nanopowder to PVDF ratio (i.e. 1:10) presented a higher average diameter then samples with ratios of 1:5 and 1:15. It is speculated that this effect can be related to the agglomeration of the nanoparticles, which in turn depends of the amount of PVDF in the solution. As seen in Figure 3, the increase of the fiber diameter at nanopowder to PVDF ratio of 1:10 makes the imperfections caused by the agglomerates on the surface less visible; suggesting that the nanoparticles have inserted inside the nanofiber.

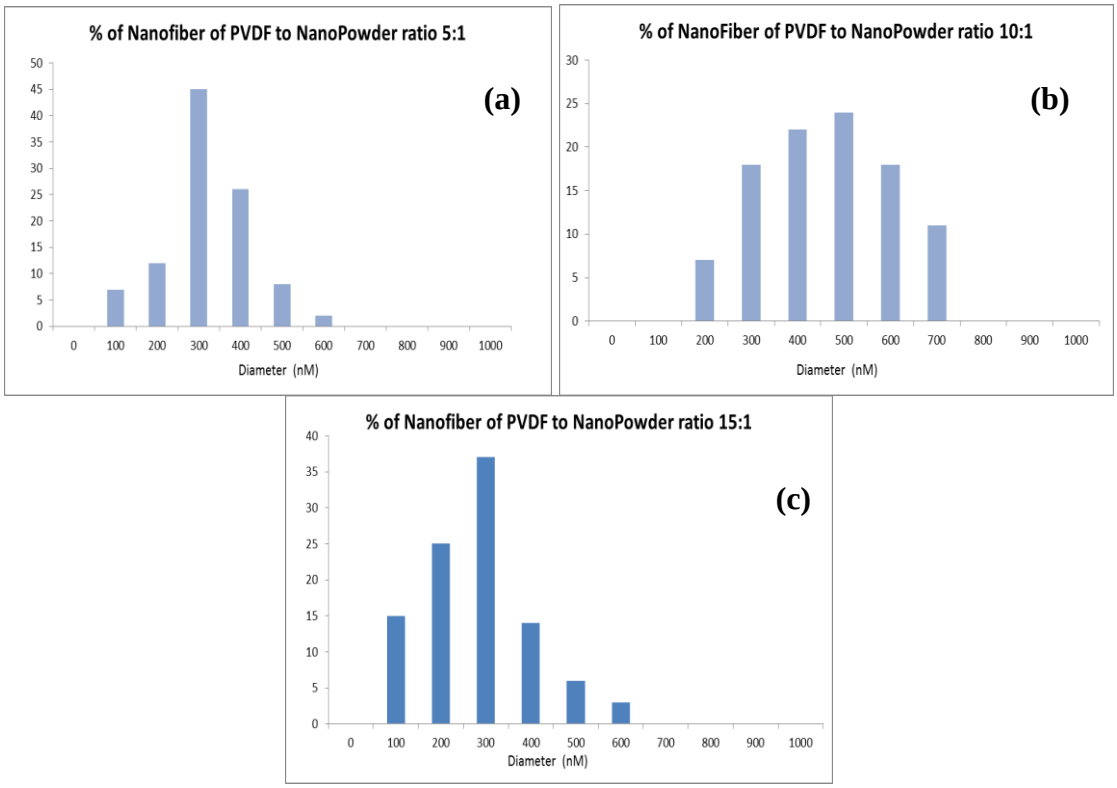

Figure 4. Average diameter of nanofibers from polymeric solutions containing PVDF at 18 wt %, dissolved in DMF and acetone (3 to 1) with nanopowder to PVDF at ratios of: (a) 1:5, (b) 1:10, and (c) 1:15.

Using the software "*image J*", it was possible to estimate the number of iron oxide agglomerates for the samples with nanopowder to PVDF ratios of 1:5 and 1:15. The estimates resulted in 1.3 and 1.0 agglomerates per micron, respectively, indicating a similar tendency due to the proximity of the numbers. A few times, an anomalous nanostructure was observed from the samples. Instead of the nanofibers, the polymer had a uniform pattern of markings that simulated perpendicular "tank tracks", as seen in Figure 5; speculated to be related to fiber stress.

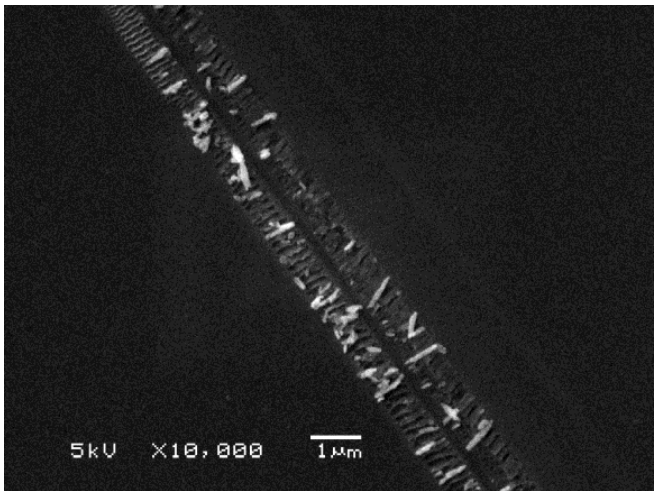

Figure 5. PVDF breaking on the sample forming an array of small lines of 0.8 micron.

4. Conclusions

This work demonstrated that it was possible to obtain fibers at the nanometer scale using the electrospinning process with all the different ratios of nanopowder to PVDF studied. In addition, using a motor with controlled speed helped to obtain a more organized fiber deposition on the silicon substrate. Furthermore, the results demonstrate the influence of the concentration of nanopowder over the obtained diameter and the uniformity of the fiber.

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6. References

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