DOE Optimization and Phase Morphology of Electrospun Nanofibers of PANI/PMMA Blends

K. Desai, C.Sung

Center for Advanced Materials,
Department of Chemical & Nuclear Engineering,
University of Massachusetts, Lowell, MA, Changmo_Sung@uml.edu

ABSTRACT

Electrospinning derived from electro spraying is a process by which sub-micron polymer fibers can be produced using an electrostatically driven jet of polymer solution. The fibers are collected as non-woven mat and offer a high surface to volume ratio. Polyaniline (PANI) is an organic conducting polymer and can be used to fabricate conducting nano fibers by blending with suitable polymers like poly methyl methacrylate (PMMA). In this present work we have explored the effects of electrospinning parameters on the formation of PANI/PMMA fibers using design of experiments (DOE) and the phase morphology of the electrospun fibers using transmission electron microscopy (TEM) and electrostatic force microscopy techniques (EFM).

Keywords: Electrospinning, Polyaniline, TEM Staining, Electrostatic Force Microscopy, Design of Experiments.

1 INTRODUCTION

Electrically conducting organic polymers are a novel class of 'synthetic metals' that combine the chemical and mechanical properties of polymers with the electronic properties of metals and semiconductors. Electronically conducting polymers have been studied extensively owing to their applications in energy conversion devices, sensors, electro chromic devices, electromagnetic interference shielding (EMI), electronic circuits etc. Polyaniline is an organic polymer, but is totally unmoldable and insoluble. It is a conducting polymer and exists in three oxidation states [1]. It has varied applications; its first applications were to make conducting coating of plastic materials i.e. printed circuit board production and also corrosion protection.

Electrospinning is a process by which sub-micron polymer fibers can be produced using an electrostatically driven jet of polymer solution [2]. The fibers are collected as a non-woven mat or membrane with high surface area to volume ratio. Since polyaniline is insoluble in most organic solvents it cannot be spun by itself, as for electrospinning a polymer solution is required. Therefore it has to be blended with other polymers to form a polymer solution for spinning. In this study we have blended polyaniline (PANI) with poly methyl methacrylate (PMMA) to form electrospun fibers.

2 EXPERIMENTAL

2.1 Materials

Polyaniline (PANI) with molecular weight 65,000, Campor Sulphonic Acid (CSA), and poly methyl methacrylate (PMMA) with molecular weight 120,000 were purchased from Aldrich and used. The solvent chloroform was also purchased from Aldrich. Solution of polyaniline / poly methyl methacrylate at varying compositions were prepared and electrospun at various conditions to obtain nanofibers.

2.2 Electrospinning Set-Up

The electrospinning apparatus consisted of a DC power source (Gamma High Voltage Research, Inc. Model HV ES 30P/100), where the charged electrode wires were connected to the polymer solution containing syringe. The polymer solution was fed into a syringe pump so that the flow rate of the solution could be controlled. Electrospun fibers were collected on an electrically grounded target. Spinning potentials ranged from 15 to 25 kV. **Figure 1** shows the basic layout of the electrospinning apparatus.

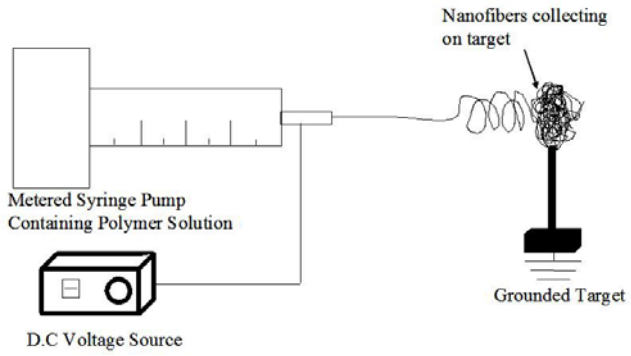

Figure 1: Electrospinning Set-Up

2.3 Design of Experiments (DOE)

Electrospinning is a process by which sub-micron sized polymeric fibers can be easily obtained as a non-woven mat when the polymer solution is sufficiently charged such that the polymeric molecules overcome their surface tension and viscous forces become dominant such that fibers are formed.

The formation of fibers depends on the concentration of the polymers, voltage applied to polymeric solution, the distance between tip and target and the flowrate of the solution.

With so many processing parameters involved in electrospinning to study the effects of individual parameters and the interplay between the key parameters a design of experiments on our process was performed using the Minitab DOE software. A full factorial two level design was used wherein the factors were the polymer concentrations, spinning voltage, tip-target distance and solution flow rates. The responses were characterized in terms of fiber thickness and bead density.

2.4 Phase Characterization

The electrospun fibers were characterized using Scanning electron microscope (SEM, Amray 1400 LaB6) to study fiber morphology, Transmission electron microscope (TEM, Philips EM 400 T) to study phase morphology by staining and Electrostatic force microscopy (EFM, PSIA model XE-100) to study phase morphology of the electrospun fibers. The photomicrographs obtained were then image processed by image processing software (GAIA Blue) to calculate fiber thickness, bead density.

For phase characterization by TEM, the fibers were spun onto a 3mm copper grid which was stained using OsO_4 (Osmium tetroxide), the stain attacks the amide bond in polyaniline giving it a darker contrast compared to the PMMA region.

Electrostatic force microscopy was also used for the phase characterization of the fibers. Since, polyaniline is a conducting polymer when a charged EFM tip is brought in contact with the PANI rich phase it will exhibit a repulsive or attractive force depending on the charge carried by the tip and the material. Polyaniline is positively charged so when a positively charged EFM tip comes in contact with the PANI rich phase would appear darker and if the EFM tip is negatively charged then the PANI rich phase would have a brighter contrast.

3 RESULTS AND DISCUSSION

When a polymeric solution is sufficiently charged it starts spinning into fibers, as the goal was to make nanofibers we have studied the influence of processing parameters in terms of the fiber thickness and bead density. Beads are formed either when the solution is not sufficiently charged or the viscosity of the solution is not sufficient, they should kept minimal.

3.1 Design of Experiments

The experimental runs were generated using Minitab design of experiments software. A two level full factorial design was created involving the four basic electrospinning parameters, the polymer concentrations, the spinning voltage, tip-target distance and solution flow rate. The experiments were performed according to the runs generated and the response values namely the fiber thickness and the bead density were input into the software so as to perform the statistical analysis.

The software generated a set of graphs showing the importance of individual processing parameters on the response values known as the pareto chart. The pareto chart of effects for fiber thickness is shown in Figure 2.

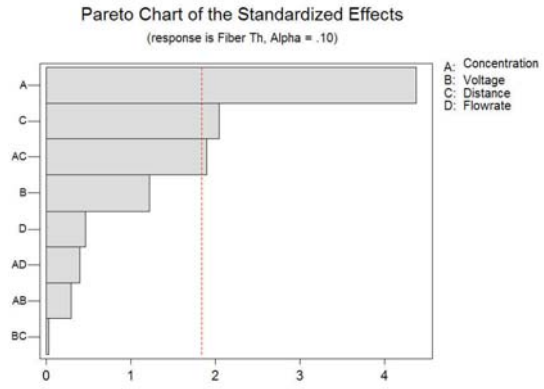

Figure 2: Pareto chart of effects for fiber thickness.

As can be seen from figure 2 concentration and voltage have the most effect on the fiber thickness as we increase the concentration of the polymers in the solution thicker fibers but at the same time a minimal concentration of polymers is needed to generate electrospun fibers otherwise only polymer spraying occurs. [3]. As the spinning voltage is increased thinner fibers are formed as more charge is applied to polymer molecules and they electrospun jet is stretched. Figure 3 shows the plot of effect of processing parameters on the bead density.

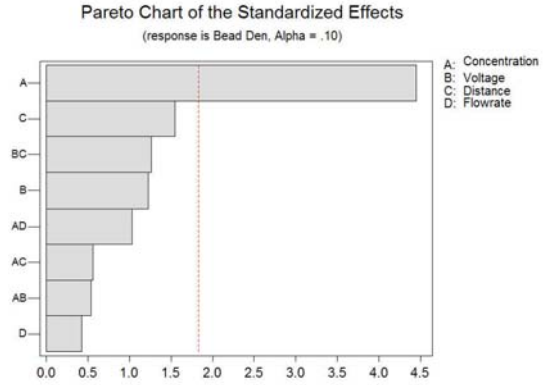

Figure 3: Pareto chart of effects for bead density.

It can be seen from figure 3 that controlling the bead density also polymer concentration and distance between the tip and target are the most important parameters. With increasing polymer concentrations the viscosity of the

solution increases and overcomes the surface tension effects and beads are stretched into fibers [3]. It can also be observed that interaction of two parameters also has a significant effect on the response like for fiber thickness interaction of the polymer concentration and the tip-target distance has a significant effect on the fiber thickness thus emphasizing the complexity in understanding the electrospinning process.

Thus by performing a design of experiments we can understand the importance of the effects of the individual processing parameters and further optimize our process to get the desired output. From our experimental and statistical analysis we found for electrospinning of polyaniline/poly methyl methacrylate blends a polymer concentration of 4 wt% PANI-CSA and 16 wt% PMMA and 8 wt% PANI-CSA and 12 wt % PMMA, spinning voltage of 25 kV, tip-target distance of 5 inches and flowrate of 0.3 ml/min is suitable for fabricating of fibers with thickness ranging in the sub-micron range (120 – 800 nm) and bead density of 8% - 28 %.

3.2 Phase Characterization

To understand the phase morphology of the electrospun fibers of PANI/PMMA blends we used staining of polymers technique and electrostatic force microscopy (EFM).

The PANI/PMMA fibers were stained using OsO_4 wherein the stain attacked the amide bond in polyaniline to give it a darker contrast in the TEM images. Figure 4 shows the TEM image of unstained fibers of 8 wt% PANI-CSA and 12 wt% PMMA. Figure 5 shows the TEM image of stained 8 wt% PANI-CSA -12 wt% PMMA fibers showing the presence of polyaniline particles in the PMMA matrix. From TEM images we can see that polyaniline does not form a homogenous mixture with PMMA but aggregates along length of PMMA fibers.

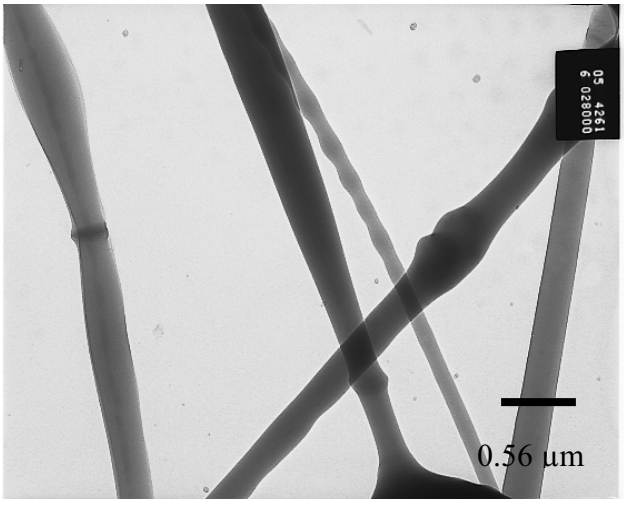

Figure 4: Unstained TEM image of 8 wt% PANI-CSA and 12 wt % PMMA.

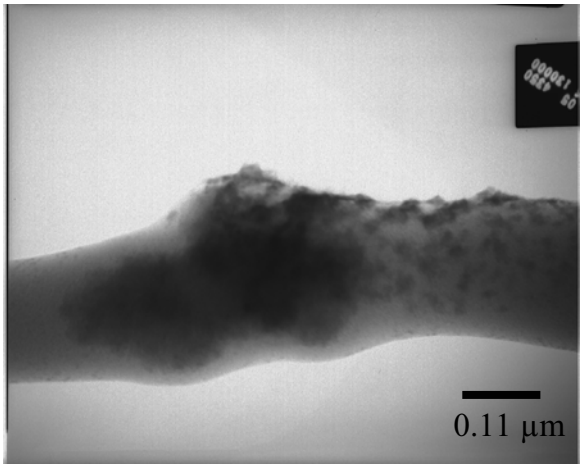

Figure 4: Stained TEM image of 8 wt% PANI-CSA and 12 wt % PMMA.

Polyaniline is a conducting polymer therefore to validate the phase information obtained by TEM we also tried electrostatic force microscopy on the formed fibers and PANI/PMMA thin films. In EFM the AFM cantilever is given a positive or negative bias such that when it scans over a conductive area of the sample the tip will vibrate differently depending on the electrostatic force between the charged tip and conducting surface. If the tip and the sample are of the same bias then the conducting area would appear dark in the EFM image and if both are oppositely charged then it would appear bright. Polyaniline is positively doped with CSA thus giving it a positive charge, therefore when a negatively biased AFM cantilever is brought in contact with the PANI region a brighter contrast is observed in the EFM image.

The difficulty in obtaining a good EFM image of the formed fibers initially propelled us to study the phase morphology of the PANI/ PMMA thin films by EFM. Figure 5 shows the EFM image of the PANI/PMMA thin films it can be seen from them that PANI forms aggregates in the PMMA matrix with some interconnectivity observed within the distinct PANI domains. This is consistent with phase morphology of PANI/PMMA thin films reported earlier [4]. The EFM images of the PANI/PMMA fibers as shown in figure 6 also shows similar information wherein PANI is present as aggregates in the PMMA region and some interconnectivity observed between the distinct PANI domains.

Thus from the phase characterization of the PANI/PMMA fibers by both EFM and TEM staining we can conclude that PANI forms aggregates along the length of the PMMA fibers. However, to obtain conducting nanofibers out of these blends we would have to obtain inter connected network of PANI particles in the PMMA matrix and this could be achieved using a higher molecular weight of PANI.

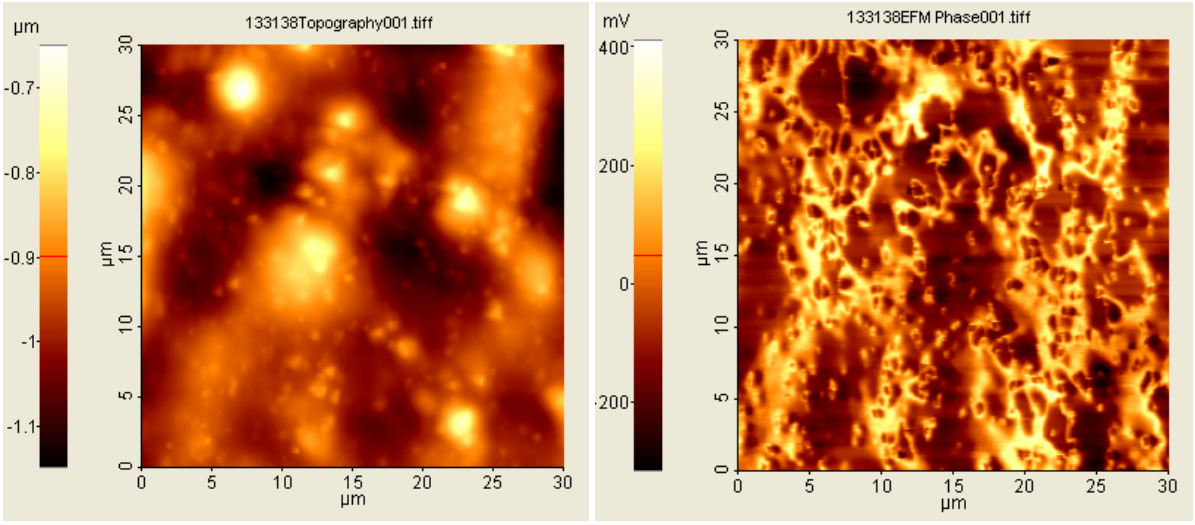

Figure 5: EFM image of 8 wt% PANI-CSA and 12 wt% PMMA thin films (bright area is PANI phase).

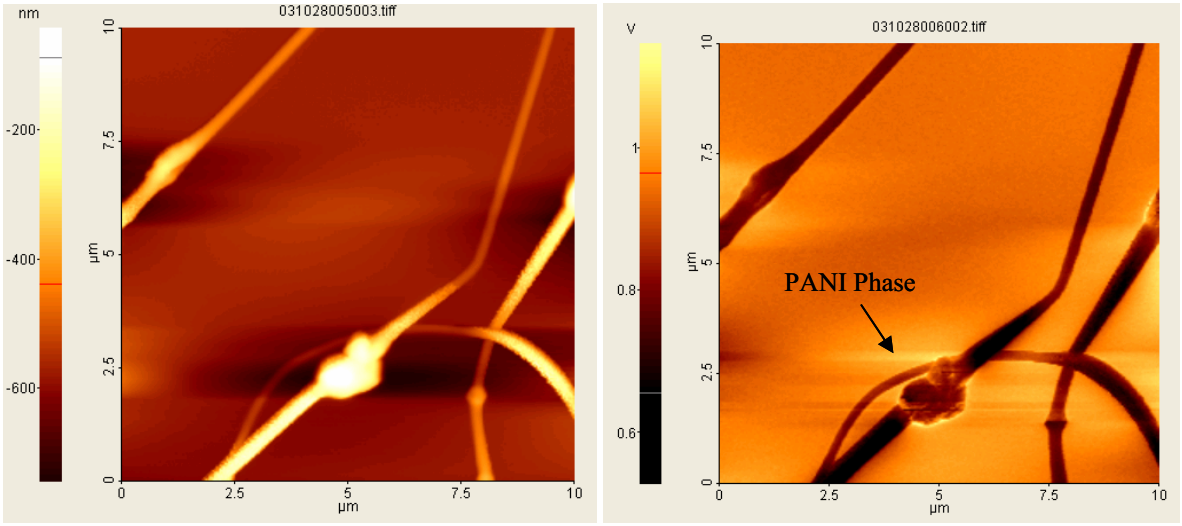

Figure 6: EFM image of 8 wt% PANI-CSA and 12 wt% PMMA fibers.

4 CONCLUSIONS

Electrospinning is a relatively easy method of fabricating nanofibers of polyaniline blends. There is a strong dependence of the processing parameters on the obtained fiber morphology and the desired fiber size can be obtained by controlling the processing parameters as has been observed by design of experiments. The phase characterization of the fibers reveals the presence of PANI aggregates along the length of the fibers, thereby to form conducting nanofibers the process needs to be further optimized so as to get more dispersion of PANI in PMMA perhaps by using a higher molecular weight of PANI in the blend.

REFERENCES

[1] B.Wessling, Synthetic Metals, 85,1313-1318, (1997).
[2] J. M. Deitzel, J. Kleinmeyer, D. Harris and N.C. Beck Tan, Polymer **42**, 261-272 (2001).
[3] K.Desai and C.Sung, Mater.Res.Soc.Proc., 736, 121-126,2002.
[4] C. Y. Yang, Y. Cao, Paul Smith and A. J. Heeger, Synthetic Metals 53, 293-301 (1993).