Uniform Polycarbonate Nanofibers Produced By Electrospinning

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ABSTRACT

Electrospinning is a process of generating very fine fibers in the sub micron to nanorange by applying a voltage to a polymer in solution. The high electrostatic potential overcomes the surface tension of the polymer and makes it stretch into fibers. In the present work electrospinning of polycarbonate has been attempted to generate uniform nanofibers with minimal bead densities. Electrospinning was performed at various concentrations ranging from 14 to 18%, voltages of 25-30 kV, flow rates of 0.01 to 0.5 ml/min and distances 4 to 10 inches. The ambient parameters like temperature and humidity were monitored throughout the experiment. After imaging the spun fibers with SEM, image processing was done to find the fiber thickness and bead densities. The Design of experiment was performed. It was concluded that a 16% PC with 0.01ml/min, distance of 10 inches, voltage of 30 kV, temperature of 28°C and humidity around 32% could generate uniform PC nanofibers with minimal bead densities.

Keywords: Electrospinning, Polycarbonate, Nanofibers, Design of Experiment

1. INTRODUCTION

Electrospinning is an emerging technology being used for the production of fibers in the nano diameter size. Fibers of such small size have large surface area to volume ratios and very small pore sizes. Due to these advantages, the nanofibers are being used in many commercial applications like manufacture of filtration membranes, fabrication of protective clothing, nanotubes etc. However the process itself is not as complicated. A polymer is chosen and is dissolved by means of a suitable solvent. The complete dissolution is done through an ultrasonicator. The dissolved solution is taken in a syringe attached to a syringe pump. The pumping of the flow meter ejects a drop of liquid from the tip of the syringe. A voltage is supplied to the polymer from a voltmeter via an electrode. The surface tension of the polymer is overcome because of this electric potential. The polymer undergoes a whipping process and gets stretched into fibers which collected as a mat on an aluminum target placed opposite to the syringe.

2. EXPERIMENTAL CONDITIONS

The polymer polycarbonate of bisphenol A of molecular weight 28,000 Daltons was purchased from Aldrich Chemical Company Inc. The solvents used were Tetrahydrofuran (THF) and Dimethylformamide (DMF) which were also purchased from Aldrich. A solvent mixture ratio of THF: DMF = 60:40 was used throughout the experiment. The experimental set-up of electrospinning is shown in Figure1. At the beginning of the work a design of experiment was planned with suitable parameters with Minitab software. Experiment was conducted for these combinations of parameters to get nanofibers. The spun fibers were then imaged with an Amray 1400 Scanning Electron Microscope and Philips EM 400 Transmission Electron Microscope.

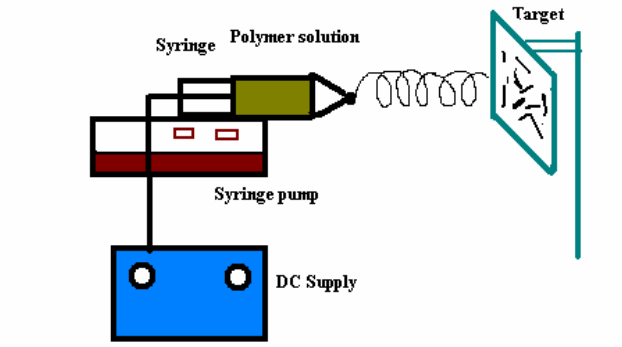
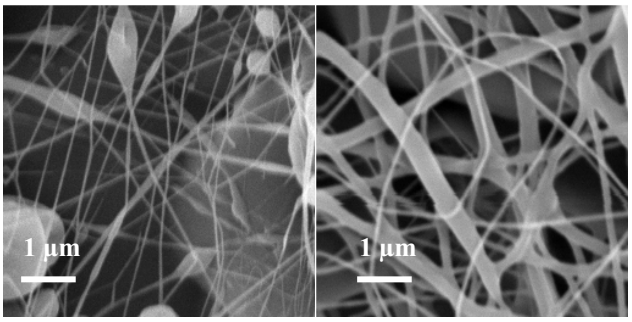


Figure 1: Experimental set-up of electrospinning

3. RESULTS AND DISCUSSION

3.1 Effect of concentration

Electrospinning was performed for polycarbonate concentrations varying from 14% to 18%. It was found that as the concentration increased the fiber thickness also increased, thereby making the fibers at 18% the thickest. It can be observed from the SEM micrographs of Figure 2 that there was an increase of fiber thickness from 75.4 nm at 14% concentration to 179.6 nm at 18% concentration. The reason for increased fiber thickness was that the increased solution viscosity made it difficult for the polymer to be whipped into fibers.



14% 18%

Figure 2: Increase of fiber thickness with concentration

During electrospinning, fibers may not be formed at all times. Due to poor processing parameters, sometimes the polymer might not spin properly and form beads instead of fibers. Our aim was to try to optimize parameters and reduce the beads to a minimal value. It was also found that as the concentration increased there was a decrease in bead density [2]. This is attributed to the increase in viscosity of the solution.

Figure 3 shows the decrease of bead density from 29% at 14% concentration to 9% at 18% concentration. But, since the aim of the present work was to obtain nanofibers with minimal bead density a optimized concentration had to be chosen which had thin fibers and yet very few beads.

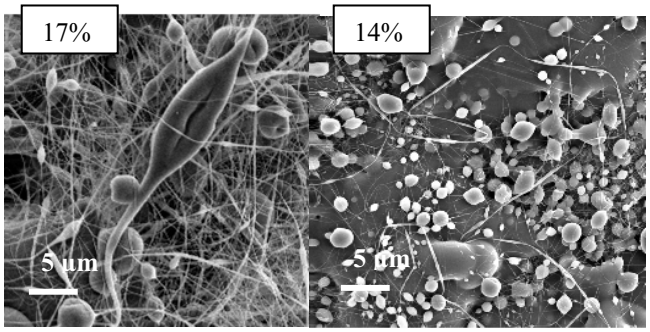
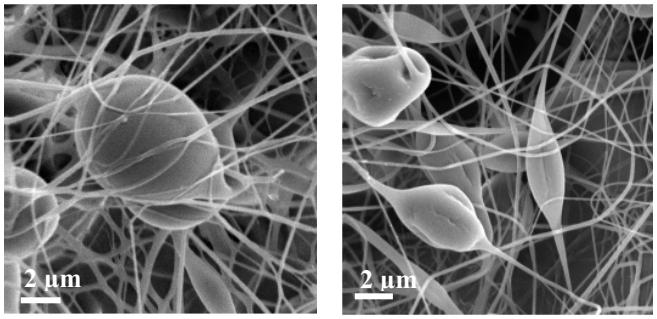


Figure 3: Effect of concentration on bead density

3.2 Effect of flow rate

The rate at which the polymer was being ejected from the tip of the syringe was controlled with the help of a syringe pump. Flow rates from 0.01 to 0.5 ml/min were applied to study the effect of changing flow rates on fiber morphology. It was found that too high flow rates did not yield fibers as the polymer shot out of the syringe so fast that it did not have enough time for whipping. However a very low flow rate was also not preferable due to the time taken to eject the polymer. So, an optimized value between the two extremes had to be found out.

It was found that as the flow rate increased, the fiber thickness and bead density also increased. It can be seen from the SEM micrographs of Figure 4 that smaller beads were obtained at 0.05 ml/min but very large beads were obtained at 0.09 ml/min



0.09 ml/min 0.05 ml/min

Figure 4: Effect of flow rate on bead density

4. IMAGE ANALYSIS

4.1 Measurement of bead density

Bead density measurement was performed with the help of Scion imaging software. A high contrast SEM image was taken. The software recognized the difference in contrast in the image after following a series of steps of inverting and thresholding. The beads were counted and the area of each bead measured with the help of the software. The bed density was then calculated by the formula,

Bead density = [Area of beads in image/Area of image]*100.

The image in Figure 5 shows the image processed image for bead density measurement

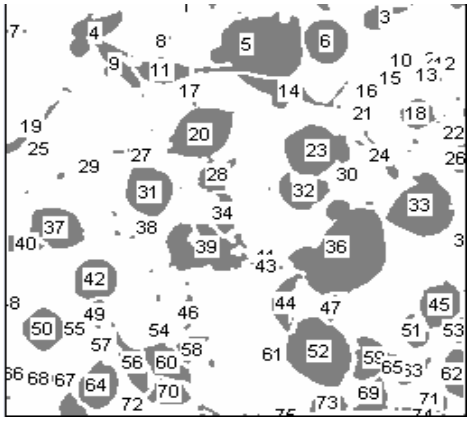


Figure 5: Bead density measurement

4.2 Fiber thickness Measurement

Fiber thickness was measured with the help of GAIA Blue software. Lines were drawn on each fiber in the image and the software gave the thickness of the fiber according to the pre-calibrated scale. Approximately 60 fibers were marked on each fiber and three images were image processed to generate an average fiber thickness value for good approximation.

5 DESIGN OF EXPERIMENT

The design of experiment (DOE) was performed by using Minitab software to find the most significant parameter out of all the parameters involved in the experiment. After the image processing the fiber thickness and bead density values were applied into the worksheet given by Minitab. The software then analyzed the data and produced Pareto charts which showed the most significant parameters for this system. From the Pareto chart in Figure 6, concentration was found to be the most significant parameter to reach the goals of fiber thickness and bead density.

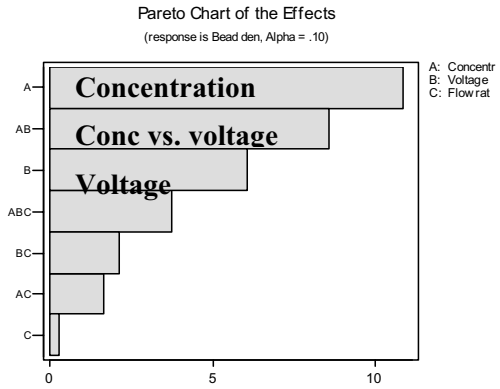


Figure 6: Pareto charts of effects for fiber thickness

The software also gave the main effects plot shown in Figure 7 which interprets that as the concentration increases the fiber thickness increases. From the cube plot shown in Figure 8 we were able to optimize the concentration at a value of 16%. The plot served as a map to show the direction to follow for the rest of the experiment. So, in order to reach the value of 54.2 nm it showed that the voltage and flow rate have to be increased and a concentration of 16% has to be used.
The DOE also helped to predict a theoretical model to the experiment. This is useful because we are able to develop some form of model to a completely unknown system.

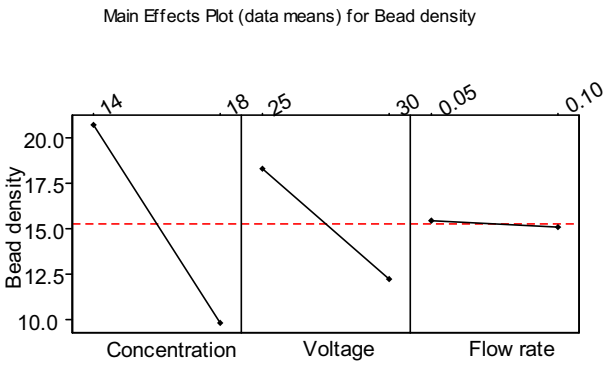


Figure 7: Main effects plot

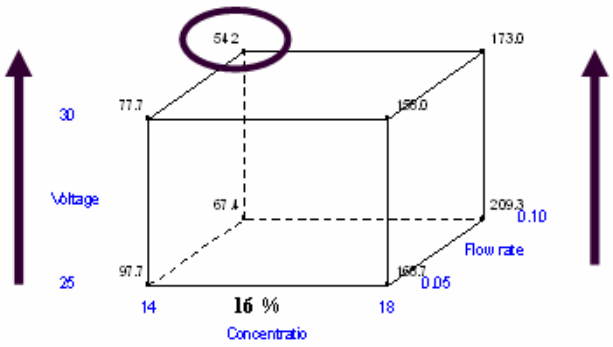


Figure 8: Cube plot

6 EFFECT OF DISTANCE

Since concentration had been optimized at 16%, in the next part of the experiment the flow rate and the distance were varied to see the effect on the fiber morphology. Distance was varied from 6 to 10 inches and flow rate was varied from 0.01 to 0.1 ml/min. It was found that uniform nanofibers were obtained for 10 inches and not for 6 and 8 inches. The reason was that the 6 and 8 inches were studied during the winter time when the temperature was less, about 20.1°C and humidity was about 26%. But when the spinning was done for 10 inches, the temperature had risen considerably to 28.2°C and humidity was 34%. Since all other parameters were constant, we suspect that the humidity and temperature have a major effect on the solvent evaporation rate. It can be seen from the SEM micrographs of Figure 9 that the fibers obtained at 6 inches have a lot of beads and are non-uniform. But the fibers obtained at 10 inches are more or less uniform and have very few beads.

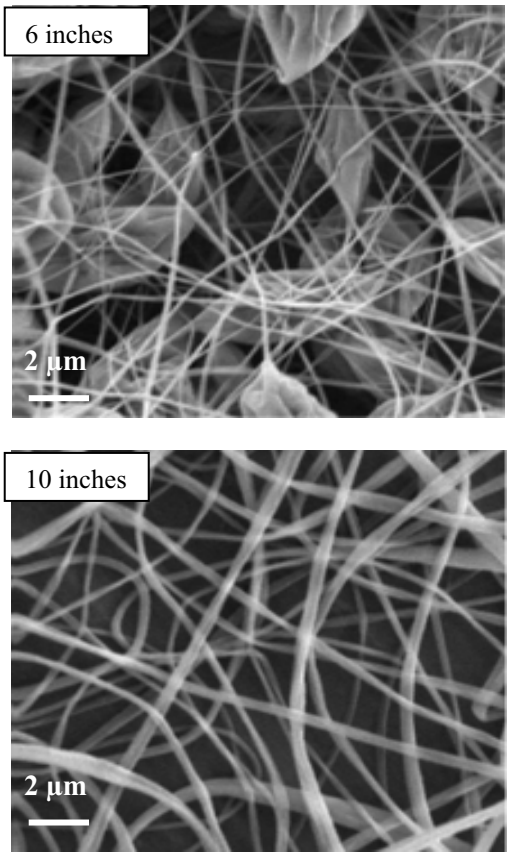


Figure 9: Fibers formed at 6 and 10 inches target distance

On comparing the fibers that were obtained from previous studies we found that smoother and more uniform fibers were obtained now. Previously due to the high solvent mixture ratio of THF: DMF, the DMF evaporated slowly from the fibers after they were formed and caused pores on them. But in the present study, since a right solvent mixture ratio has been used we obtained uniform and smooth nanofibers as seen in the TEM micrograph of Figure 10

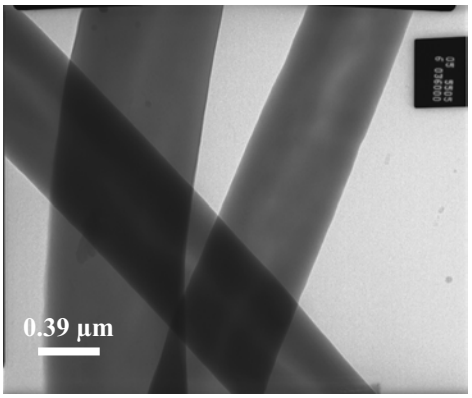


Figure 10: TEM micrograph of smooth polycarbonate nanofibers

7 CONCLUSIONS

From the present work it has been shown that nanofibers of polycarbonate can be produced with minimal bead densities at a concentration of 16%, voltage of 30 kV, flow rate of 0.01 ml/min, distance of 10 inches, solvent mixture ratio of THF:DMF = 60:40, temperature of 30°C and humidity of around 35%. From the statistical analysis of the data it has been concluded that concentration is the most important parameter to reach our goals.

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