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ORIGINAL ARTICLES

Optimization Of Electrospinning Parameters Using Response Surface Methods To Enhance Fiber Diameter, Mechanical Properties And Orientation Of Nanofibers

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ABSTRACT

Electrospinning is a direct process that produces continuous fibers with nano-sized diameters and high specific surface area ratios. The process is capable of producing nano-sized fibers at a lower manufacturing cost compared with the conventional melt spinning process. In the present study, optimization of electrospinning parameters (supplied voltage, polymer concentration in solvents, and flow rate) was conducted through the response surface methodology (RSM) to reduce diameter size, enhance mechanical properties, and improve orientation (alignment) of the fibers. Polyacrilonitrile (PAN) dissolved in dimethylformamide (DMF) was used as a precursor. Fiber diameters and orientation were measured through Scanning Electron Microscope analysis. Tensile test on the fiber bundles was carried out using INSTRON Universal Tester. Fibers with diameters of ~150 - 350 nm were successfully collected. For diameter analysis, voltage is found to be the most significant parameter in determining fiber diameter. Flow rate of syringe pump is the non-significant factor. The optimum parameter combination is voltage of 15kV, weight percentage PAN of 10wt%, and flow rate of 4ml/hr. The fibers exhibited fine surfaces and were homogenous in terms of cylindricality. In tensile test analysis, voltage and weight percentage are found to be the most significant parameter in determining ultimate tensile load of fibers. The optimum parameter combination consists of voltage of 25 kV, weight percentage PAN of 10wt%, and flow rate of 6 ml/h. Approximately 60% of the fibers were oriented in the range of -30^{o} to +30^{o} from its principal axis. For orientation analysis, flow rate of syringe pump is found to be the most significant parameter in determining fiber alignment. The optimum parameter combination to gain aligned fiber is voltage of 15kV, weight percentage of 12wt%, and flow rate of 6ml/hr. Model equations were constructed for each analysis through Response Surface Methodology (RSM). RSM was successfully used to find collaborations between the parameters with the required outputs.

Key words: Electrospinning, Response Surface Methodology (RSM), fiber diameter, Orientation

Introduction

The fabrication of polymer nanofibers by electrospinning has received significant attention in recent years (Beachley & Wen, 2008). In recent works, a greater understanding of processing parameters has resulted in the formation of fibers with diameters in the range of ~ 100 - 500 nm, typically referred to as nanofibers (Sill & Recum, 2008). In electrospinning, polymer nanofibers are formed through the creation and elongation of an electrified fluid jet (Reneker & Yarin, 2008). Polymer nanofibers have diameters ranging from a few nanometers to greater than 1µm. Moreover, the nanofibers possess unique characteristics, such as, extraordinary high surface area per unit mass (for instance, nanofibers with ~100nm diameters have a specific surface of ~1000m^2/g), excellent structural mechanical properties, extreme flexibility, low basis weight, and cost effectiveness, among others (Chronakis, 2005). It has been proven that the smaller the diameter and the higher the strength is, the more interesting the applications of these fibers are, particularly in textile and filtration.

Polyacrylonitrile (PAN) is the precursor of approximately 90% of carbon fibers manufactured at present (Zhang & Hsieh, 2008). This is due to their potential application as heat-management materials, composite reinforcement, high-temperature catalysis, membrane-based separation, and as components for nanoelectronics and photonics (Zussman *et al*., 2005). As long as a polymer can be electrospun into nanofibers, diameters of the fibers will be consistent and controllable, fiber surface will be defect-free or defect-controllable, and continuous single nanofibers will be collectable. However, researchers have found that these objectives are not easily achievable (Huang *et al*., 2003). Courtney *et al*. (2006) stated that the alignment of fibers is determined by the linear velocity of the mandrel. Scaffolds below 1.5 m/s show very slight fiber orientation. An aligned fiber

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J. Appl. Sci. Res., 8(5): 2510-2517, 2012

network is evident in mandrel speeds above 2.0 m/s scaffold, with progressively more anisotropy and increasing mandrel velocity.

The summary of the findings from other researchers is presented in Table 1. Based on this, the objective of the present study is to optimize the electrospinning parameters by studying effect of electrospinning parameters on the diameter size, mechanical properties and orientation of the electrospun fibers.

Table 1: Highlight of electrospinning parameters for polymer fibers.

Materials	Parameter	Physical Properties	Mechanical Properties	Fiber orientation	References
PCL, NaCl, Methanol	Concentration: 8-20% w/v PCL & 0.06% w/v NaCl Voltage: 10-20 kV Feedrate : 0.6-1.5 ml/hr Spin length : 2-50cm	SEM Hitachi-TM 1000 : 10000 times magnification			Beachley& Wen 2008.
PAN in DMF	Molecular Weight: 121000 & 73400 Concentration : 8-16% w/w Syringe : 1.13mm Voltage: 10-30kV Collector distance: 8-16cm	Measurement of 50 fibers, through multiple sampling			Yordem *et al.* 2008.
Polyester urethane (PEUU) in HFP	Concentration: 5 wt% Voltage PEUU: +12kV Voltage Collector: -7kV			Linear velocity of collector : 0.3-14m/s	Courtney *et al.* 2006.
Polymer gelatin type A in TFE	Syringe inner diameter : 0.85mm Concentration: 2.5% -15% w/v Feed rate: 0.8ml/h Voltage: 10-16kV Distance: 12cm		Tabletop Instron Tester Model 3345 Load cell of 10kN Crosshead speed : 10mm/min Tensile Speciment width: 10mm Gauge length: 30mm		Huang *et al.* 2004.

Materials and Methods

The electrospinning experiment was initiated by diluting PAN powder into the DMF solvent with an appropriate concentration (~ 10 - 14 wt %). The solution was stirred with a magnetic stirrer at 450 rpm for 2 hour before feeding it into a syringe. Figure 1 shows the electrospinning set-up which consists of a DC voltage, syringe pump, collector, and polymer solution. The distance between the syringe end and collector was adjusted to 9 cm. The positively charged clamp of the voltage supply was connected to the syringe needle while the grounded clamp was connected to the collector.

The experiment parameters are shown in Table 2. The orientation and physical properties of the nanofibers were studied. The parameters were selected based on previous research. Measurements of the fibers and the fiber orientation were carried out using the scanning electron microscope (SEM) Carl Zeiss EVO MA10 (Beachley & Wen, 2008). The optimization plot was generated to determine the optimum parameter combination.

Table 2: Experiment parameters generated through the Box Behnken Design in RSM

Run	Voltage (kV)	Weight percentage (wt %)	Flow rate (ml/hr)
1	15	10	5
2	25	10	5
3	15	14	5
4	25	14	5
5	15	12	4
6	25	12	4
7	15	12	6
8	25	12	6
9	20	10	4
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11	20	10	6
12	20	14	6
13	20	12	5
14	20	12	5
15	20	12	5

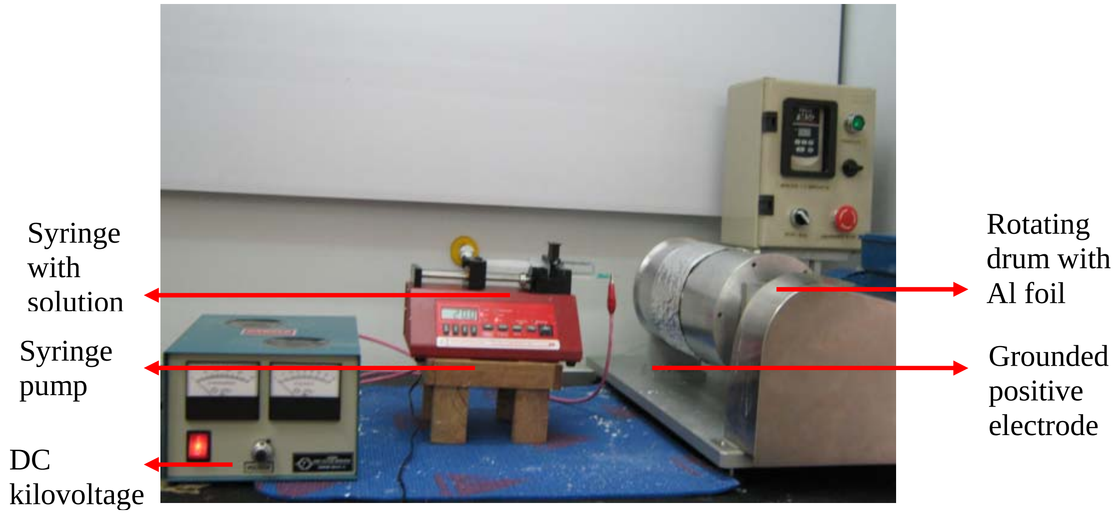

Fig. 1: Assembly of electrospining system

Tensile test on the fiber bundles was carried out using the INSTRON Universal Tester 4381L machine. Three samples were tested for each run to obtain an average result. Speed for the tensile test was fixed at 1 mm/min. Average of the results was calculated to obtain the mean of the ultimate tensile load per weight and mean of the strain.

To determine the fiber orientation, the SEM figure which consists of a minimum of 100 fibers was classified into six orientation groups (0^o to - 30^o, - 30^o to - 60^o, - 60^o to - 90^o, 0^o to 30^o, 30^o to 60^o, and 60^o to 90^o) in directions of the base line that refers to the alignment of the rotating direction of the collector as shown in Figure 2.

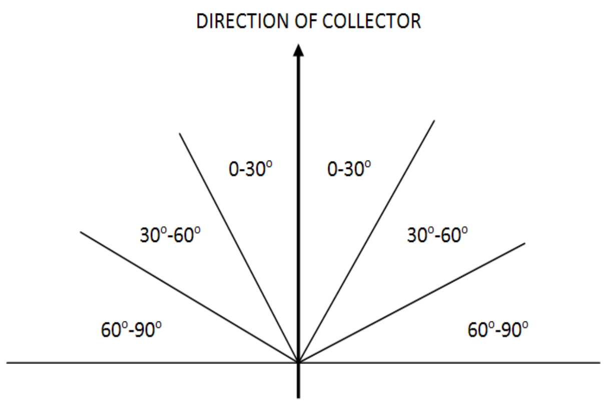

Fig. 2: Classification of fiber orientation based on collector direction

Results and Discussion

1   Fiber Diameter:

ANOVA analysis performed according to the target to reduces the fiber diameter to enhance the aspect ratio. Figure 3 presents variations of the fiber diameter determined in the present study.

Results of the ANOVA analysis of the fiber diameter show that voltage is the most significant parameter in determining the fiber diameter while flow rate of the syringe pump is the least significant factor. Kidoaki *et al*. (2006) once reported that increasing syringe pump where voltage is not a limiting factor results in average fiber diameter increasing. The optimum parameter combination is composed of a voltage of 15 kV, weight percentage PAN of 10wt%, and flow rate of 4 ml/h. From this combination, the fiber PAN diameter of 49 nm can be obtained. The equation (1) used to derive the aimed diameter, which is

Diameter, D (nm)= $- 4414.49 + 101.49X_1 + 274.45X_2 + 741.30X_3 - 2.30(X_1)^2 - 5.47\ (X_2)^2$ –

$$35.26\,(X_3)^2 + 0.90X_1\,X_2 - 2.33\,X_1\,X_3 - 28.36\,X_2\,X_3 \qquad (1)$$

where X_1 = voltage (kV), X_2 = weight percentage (wt %), and X_3= flow rate (ml/h).

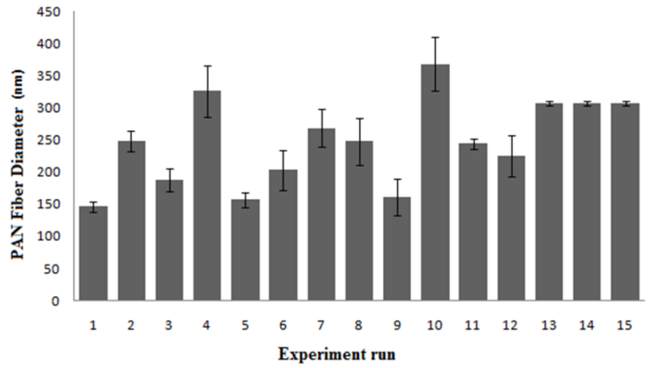

Fig. 3: Variation of PAN fiber diameters

The equation (1) can be applied, as results obtained for Run 1, the parameters combination of the 15 kV, 10wt%, and flow rate of 5 ml/h, give an average diameter of 150 nm as in Figure 4.

Diameter, D (nm)= $- 4414.49 + 101.49\,(15) + 274.45(10) + 741.30\,(5) - 2.30(15)^2 - 5.47\,(10)^2 - 35.26\,(5)^2 + 0.90(15X10) - 2.33\,(15X5) - 28.36\,(10X\,5) = 155.11$ nm

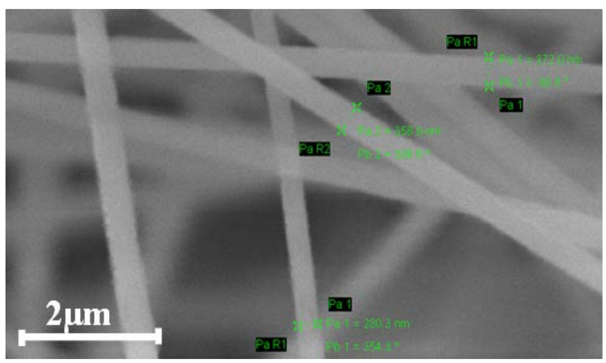

Fig. 4: SEM images of fiber diameter of Run 1 (average diameter ~150 nm)

Mechanical Properties:

PAN is commonly used in the textile field; therefore, good mechanical properties are required. Figure 5 shows that the variations of failure strength of the ANOVA can be performed according to the target.

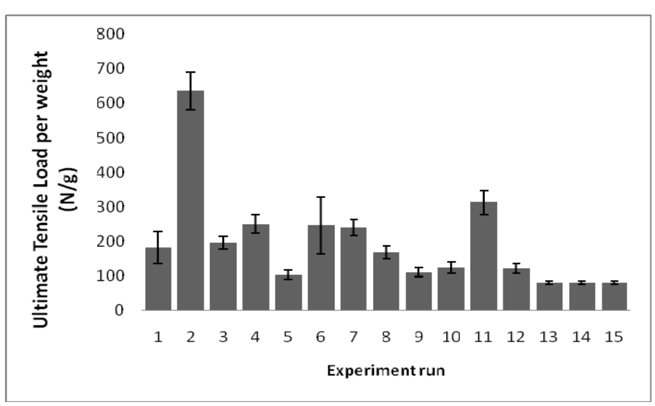

Fig. 5: Variation of ultimate tensile load for PAN fibers at different electrospinning parameters

J. Appl. Sci. Res., 8(5): 2510-2517, 2012

During the process of drawing, certain samples clearly exhibited brittle and ductile characteristics. Ductile characteristics can be ascertained by the presence of necking as illustrated in Figure 6 (a), such occurred on the sample Run 2. On the other hand, brittle characteristics are shown in Figure 6 (b), that clearly be seen on sample Run 13.

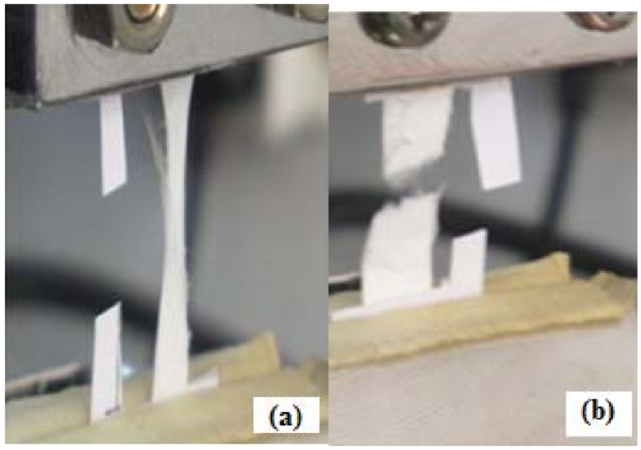

Fig. 6: Failure behaviour of (a) ductile sample:Run 2, and (b) brittle sample: Run 13

During the determination of the ultimate tensile load per weight, voltage and weight percentages were the most significant parameters. The flow rate of the syringe pump was the insignificant factor as revealed by the ANOVA analysis. The optimum parameter combination consists of the following: voltage of 25 kV, weight percentage PAN of 10wt%, and flow rate of 6 ml/h. Consequently, the ultimate tensile load per weight of 512 N/g was obtained. The equation of the ultimate tensile load per weight is

Ultimate tensile load per weight (N/g) = $632.07 - 39.83X_1 - 263X_2 + 551.45X_3 + 4.95(X_1)^2 + 21.23(X_2)^2 + 1.27(X_3)^2 - 7.34X_1X_2 - 11.36X_1X_3 - 25.49X_2 X_3$

where X_1 = voltage (kV), X_2 = weight percentage (wt %), and X_3= flow rate (ml/h).

As shown in Figure 7, the surface plot generated through the ANOVA of the ultimate tensile load is obtained through the weight percentage vs. flow rate at 25 kV. This indicates that to produce fiber with high failure strength, the higher weight percentage of the solution should be used with higher flow rate during the electrospinning process at a power supply of 25 kV.

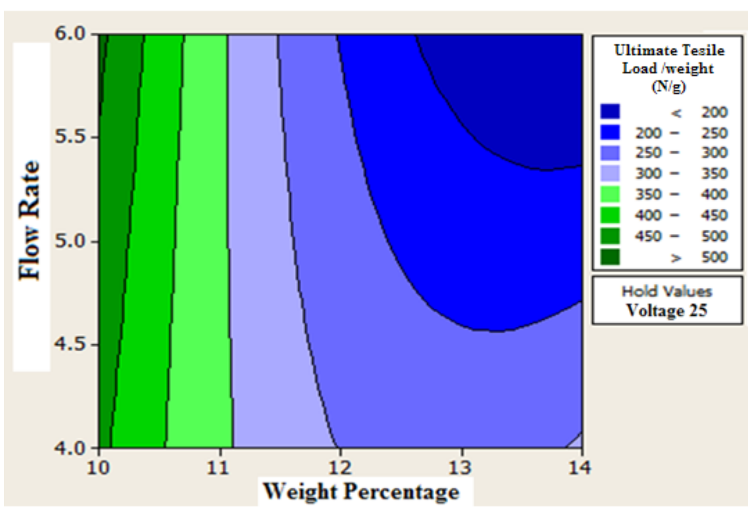

Fig. 7: Variation of ultimate tensile load at different weight percentages and flow rate of 25 kV

Fiber Orientation:

A hundred fibers were studied for each experiment run. The directions of the fibers were categorized into six orientation groups (0° to - 30°, - 30° to - 60°, - 60° to - 90°, 0° to 30°, 30° to 60°, and 60° to 90°) in directions

J. Appl. Sci. Res., 8(5): 2510-2517, 2012

of the base line that refers to the alignment of the rotating direction of the collector. The results of the overall fiber orientation are summarized in Figure 8. Cumulatively, 60% of the fibers are in the 0 - 30^{o} direction, which filled half of the desired fiber orientation.

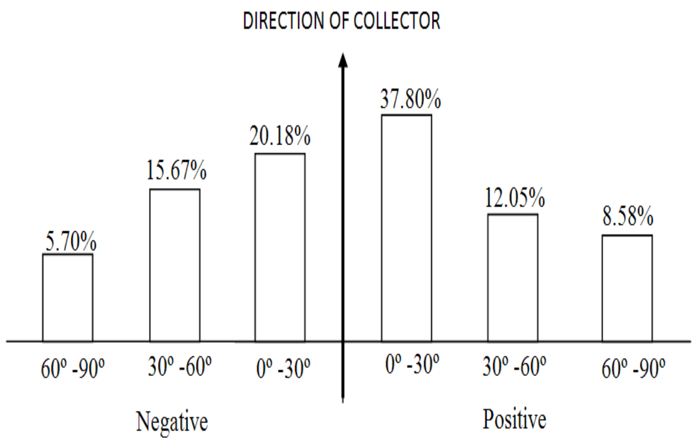

Fig. 8: Percentage of fiber orientation based on collector direction axis

In the analysis of fiber orientation, the result segment for each experiment run was dominated by the percentage of the 0º - 30^{o} group. The flow rate of the syringe pump was the most significant parameter in determining the percentage of fibers in the 0º - 30º group orientation. The weight percentage was the insignificant factor as found by the ANOVA analysis. However, Matsuda *et al*. (2005) reported that high rotation speed contributes to the alignment of the fibers. This argument was countered by Courtney *et al*. (2006) who reported that the better factor to consider in determining the fiber alignment is the linear velocity of the mandrel.

To ensure the success of the response surface optimization, the maximum goals were selected to maximize fiber orientation of the first group in the 0^{o}- 30^{o} direction. The target value was 100%. The optimum parameter combination comprised a voltage of 15 kV, weight percentage PAN of 12wt%, and flow rate of 6 ml/h. Hence, 33% of the fibers obtained were in the 0º - 30º direction, as shown in Figures 9 and 10.

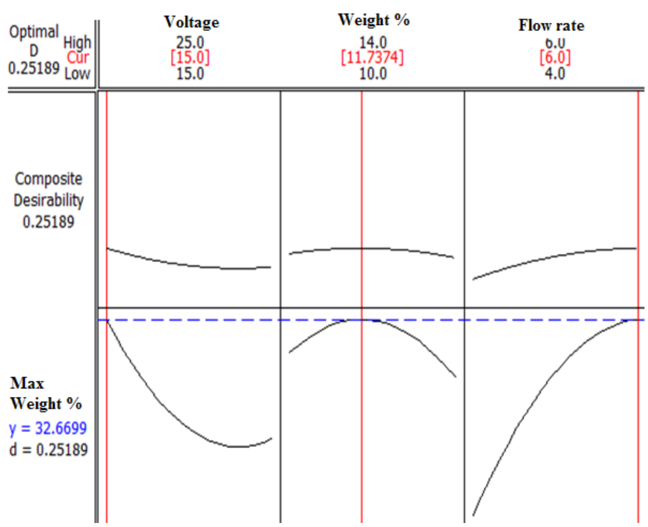

Fig. 9: Optimized parameters based on RSM by targeting 100% oriented fibers at 0^{o} - 30^{o}

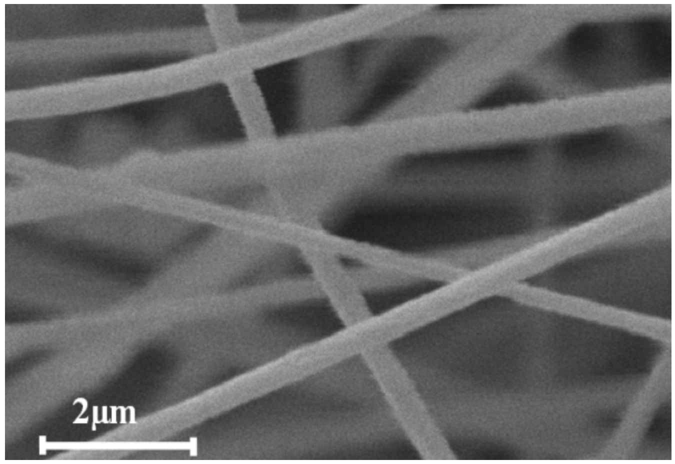

Fig. 10: SEM image fibers at optimized electrospinning parameters (15kV, 12 wt%, and 6 ml/hr)

Conclusion:

Objectives have been achieved in this study. Analysis for diameter, mechanical properties, and orientation has been carried out by using MINITAB software. Model equations were constructed for each analysis through Response Surface Methodology (RSM). To gain fiber with lower diameter size, then increase the voltage supply for electrospinning process. To get fiber with higher mechanical properties, then the voltage and weight percentage of polymer solution need to be increased. To obtain aligned fiber, then increase the syringe pump.

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J. Appl. Sci. Res., 8(5): 2510-2517, 2012

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