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OPTIMIZATION OF ELECROSPINNING OF PVDF SCAFFOLDS FABRICATION USING RESPONSE SURFACE METHOD

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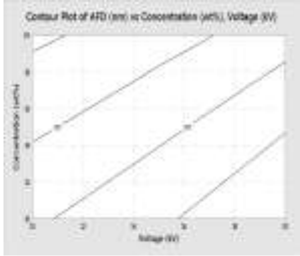
Madana Leela Nallappan[a], Mohamad Mahmoud Nasef[b]*

[a]Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Malaysia Japan International Institute of Technology, International Campus, Universiti Teknologi Malaysia, Jalan Semarak, 54000 Kuala Lumpur, Malaysia.

*Corresponding author
mahmoudeithar@chem
e.utm.my

Graphical abstract



Abstract

Poly(vinylidene fluoride) (PVDF) scaffolds were prepared via electrospinning. The response surface methodology (RSM) was used to optimize the parameters that influence the average fibre diameter. The objective is to produce fibres with small diameters. The factors considered for experimental design were the applied electric voltage, the PVDF solution concentration, and the distance between the needle tip and the collecting drum. The Central Composite Design (CCD) was used to generate the experimental design whilst the analysis of variance (ANOVA) was performed to obtain statistical validation of regression models and to study the interaction between input parameters. The optimum operating conditions that guaranteed PVDF scaffolds with small nanofibre diameter were in the voltage and concentration range of 16-20 kV and 10-14wt%.

Keywords: Poly(vinylidene fluoride), electrospinning, optimization, response surface methodology, central composite design

Abstrak

Gentian poli(vinilidin florida) (PVDF) telah disediakan melalui teknik elektrospinning. Gerak balas permukaan telah digunakan untuk pengoptimuman parameter yang mempengaruhi diameter gentian purata. Objektifnya adalah untuk menghasilkan gentian berdiameter kecil. Faktor yang dipertimbangkan untuk reka bentuk eksperimen adalah voltan elektrik, kepekatan larutan PVDF, dan jarak antara hujung jarum dan drum pengumpulan. Mod reka bentuk komposit pusat telah digunakan untuk menjana reka bentuk eksperimen manakala analisis varians (ANOVA) dilaksanakan untuk mendapat pengesahan statistik model regresi dan mengkaji kaitan antara parameter. Parameter optimum yang diperolehi adalah voltan 16-20kV dan kepekatan 10-14wt%.

Kata kunci: Poli(vinilidin florida), elektrospinning, pengoptimuman, gerak balas permukaan, reka bentuk komposit pusat

1.0 INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is a polymer that possesses high mechanical strength and high acidic, chemical and thermal resistances. It is mainly utilized in various industrial application polymeric membrane electrolyte fuel cell (PEMFC)[1-3] and filtration.[4-6] PVDF is vastly being used for preparation of microfibers, nanofibers and hollow fibers as this material is ideal for applications involving harsh environments. Its high solubility in many common organic solvents enables the electrospinning of PVDF to be performed with ease.[7-9]

Electrospinning has been recognized as an efficient method to synthesize nano- to micro-sized continuous fibers from solutions. It is used to generate nanofibrous scaffolds from synthetic or natural polymers such as collagen, gelatin, chitosan, silk, and elastin.[10-12] Intense research has been focused on nanofibrous materials mainly due to their large surface area to volume ratios, flexibility in surface functionalities and superior mechanical performances when compared with any other known form of materials.[7,13-15] These properties provide nanofibrous materials an edge to be used in various industrial applications such as in filtration processes[16] and biomedical applications.[12,15]

In electrospinning a high voltage source is used to inject charge of a certain polarity into a polymer solution which enables the solution to accelerate towards a collector of opposite polarity. Eventually when the electrical force surpasses the surface tension of the polymeric solution, the Taylor's cone is formed and a fibre jet is ejected from the head of the syringe. Once the jet flows away from the droplet in a nearly straight line, it bends into a complex path, which electrical forces stretch and thin. The solvent also evaporates leading to the deposition of solid polymer fibres on the collector.[16-17]

Generally there are a number of parameters that can influence fibre formation and its structure in the electrospinning process. A few of the most important parameters to be governed are 1- Systemic parameters such as molecular weight of polymer and its distribution, type of solvent and solution properties. 2- Processing parameters such as electric potential, flow rate and distance between syringe and collector (or interval). 3- Ambient parameters such as temperature, humidity and air velocity in the chamber. By studying the effect of these parameters on the nanofibrous scaffolds formed, they can be suitably manipulated to obtain the desired properties such as small and uniform diameter.[18-20]

The classical method of optimization, wherein one independent variable is changed while the others are fixed at given values, has vastly been employed for electrospinning of nanofibrous materials. However, this conventional method involves too many experiments deeming it time consuming. The classical method also does not take into consideration the interaction between operating parameters.[20-23]The design of experiments (DOE) is an effective statistical technique for optimizing performance of systems with known input variables. DOE plays an important role in maximizing the amount of information gained while minimizing the number of experimental runs.[24]

Response surface methodology (RSM) is used to analyze the significance of operating parameters onto the responses. It is a statistical method that has been proven to be an effective investigation tool for optimization of processes containing several input variables. This approach uses polynomials in place of local approximations to the true input or output relationship as a practical modeling method. Using the RSM, the optimized response that is influenced by several independent variables can be improved. Instead of a one factor at-a-time approach, this method allows the experimental investigation of individual factors and interactions of factors simultaneously.[25-28]

The purpose of this paper is to 1- Study the effects of the electrospinning variables (applied voltage, distance between needle tip and the collector and PVDF solution concentration) on the PVDF nanofiber diameter 2- find the optimum conditions for the electrospinning of nanofibrous scaffolds.

2.0 EXPERIMENTAL

2.1 Materials

The spinning solutions were prepared from PVDF powder supplied by Aldrich (M_w=534,000, d=1.74g/cm^3, m_p= 165°C). N,N-dimethylformamide (DMF, 99.5%) and acetone (99.7%) purchased from Merck were used as solvents. All of these materials were used without further purification.

2.2 Preparation of Electrospun PVDF Scaffolds

The process of electrospinning starts with the preparation of PVDF solution. Three solutions of PVDF with concentrations ranging from 10-20 wt% were prepared. The solvent used was a mixture of pure DMF and acetone at 8:2 v/v ratio. Solubilization was performed under continuous stirring, for an hour at a temperature of 70°C.

The electrospinning set-up is shown in Figure 1 and consists of a syringe to hold the polymeric solution, which is connected to a steel needle with an internal diameter of 0.7mm, a syringe pump (TERUMO, TE-331), a high voltage power supply in the kV range (Gamma, ES3OP-20W/DDPM) and a grounded aluminium plate as collector. PVDF nanofibres were prepared based on the experimental design in Table 1. Three electrospinning parameters were taken into consideration when performing the experimental design, process parameters i.e. voltage (kV) and needle tip to collector distance (cm) and the solution parameter i.e. PVDF solution concentration. The process was carried out at a constant flow rate of 0.3 ml/h and temperature of 25°C.

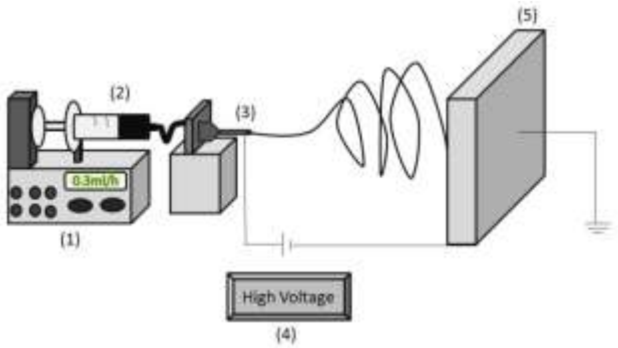


Figure 1 Schematic diagram of electrospinning set-up. (1) Syringe pump, (2) syringe containing PVDF solution, (3) steel needle (4) high voltage supply, (5) grounded collector

In this study the average fibre diameter (AFD) of the PVDF nanofibres is the response of the system. The Minitab 17 software was used to conduct the statistical design of experiment and data analysis. A total of 15 runs were obtained, by using the face centered, central composite design (CCD), with 1 centre point. Table 1 provides the operating ranges and levels of considered variables given in actual and coded values, whereas, the experimental design is shown in Table 2. The AFD was obtained by examining the surface of the non-woven electrospun PVDF scaffolds by a scanning electron microscope. The fibre diameter was measured at three different places of the SEM image for each of the fifteen samples, to determine the AFDs. Figure 2 indicates some randomly selected SEM images from 15 sets of experiments showing the morphology of electrospun PVDF scaffolds.

Table 1 Coded and actual values of variables used in design

Design variable	**Symbol**	**Actual values of coded levels**		
		-1	0	1
Voltage (kV)	a_1	10	15	20
Distance (cm)	a_2	3	9	15
Concentration (wt%)	a_3	10	15	20

Table 2 Central Composite Design (CCD) for electrospinning experiments

Run	**a_1 (kV)**	**a_1 (cm)**	**a_1 (wt%)**	**Response AFD (nm)**
E1	-1	-1	-1	303
E2	1	-1	-1	200
E3	-1	1	-1	312
E4	1	1	-1	240
E5	-1	-1	1	423
E6	1	-1	1	354
E7	-1	1	1	476
E8	1	1	1	317
E9	-1	0	0	348
E10	1	0	0	258
E11	0	-1	0	370
E12	0	1	0	315
E13	0	0	-1	257
E14	0	0	1	402
E15	0	0	0	315

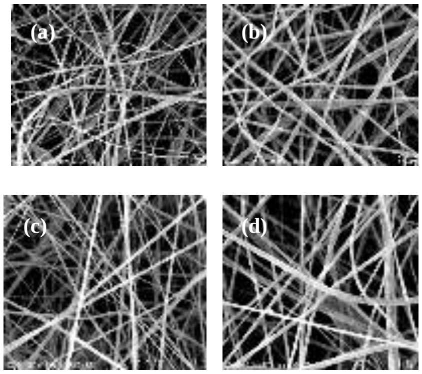


Figure 2 SEM images showing the morphology of electrospun PVDF nanofibres for experimental runs: (a) E3 (b) E4 (c) E12 (d) E14.

3.0 RESULTS AND DISCUSSIONS

By multiple regression analysis, the coefficients of the parameters (voltage, distance and PVDF solution concentration), significance probability (P-value) and correlation coefficient were obtained and are presented in Table 3. The significance test was conducted at 95% confidence interval. The P-value determines the effect that each variable has on the average fibre diameter obtained. A P-value of less than 0.05 proves that the variable has a significant effect on the average fibre diameter and vice versa. Therefore based on the calculated coefficients and P-values, it can be inferred that the average fibre diameter is most significantly influenced by the concentration of PVDF solution, followed by voltage and lastly by distance. In such a scenario, response surface plots could be used to further determine the coefficients that play a dominant role. Equation (1) shows the relationship between the dependent variable (average fibre diameter) and independent variables (process and solution parameters). It can be observed from the following contour plots in Figures 3, 4 and 5 that the correlation between voltage and distance and the correlation between concentration and distance are not significant. Since interaction between the different process parameters (voltage and distance) is not significant, the response surface equation for the average fibre diameter is given by:

$$y = C_0 + C_1 a_1 + C_2 a_2 + C_3 a_3 \qquad (1)$$

Table 3 Analysis of variance for process variables, significance probability (P-value) and correlation coefficient

Term	Coefficient	P-value*
Constant	310.13	0.000
Voltage: a_1	-49.40	<0.001
Distance: a_2	2.7	0.021
Concentration: a_3	55.40	<0.001

*R^2 = 0.946

The calculated equation is:

$$y = 310.13 - 49.40\, a_1 + 2.70\, a_2 + 55.40 a_3 \tag{2}$$

where, y is the average fibre diameter, and a_1, a_2 and a_3 are the coded values of voltage, tip-collector distance and solution concentration respectively. The co-efficient of determination (R^2) between the experimental and calculated values obtained from the response surface equation is 0.946. This value indicates a good correlation between the process and solution parameters in obtaining fibrous PVDF scaffolds with small average fibre diameter. The desirable quality being sought after in this study is small average fibre diameters, below 250nm. The following contour plots have been generated from RSM to show the interaction between different combinations of input parameters and how they correlate to affect the average fibre diameters obtained.

Figure 3 shows the interaction effect of PVDF solution concentration and voltage on the average fibre diameter produced. With an increase of voltage and a decrease in solution concentration a gradual decrease is observed in the average fibre diameter. The smallest diameter, < 250nm, is obtained in the region where the PVDF solution concentration range is 10-14 wt% and the voltage range is 16-20 kV. Whereas the largest fiber diameter, > 400nmn, is found in the region where PVDF solution concentration range is 17-20 wt% and the voltage range is 10-12 kV. The contour plot shows that in order to get small diameters at higher concentrations voltage needs to be increased. This is because PVDF solutions with higher concentration have higher viscosities giving it enough strength to lower the bending instability of the jet causing the solution to become resistant to stretching by the electrical charges on the electrospinning jet.

Figure 4 shows the interaction between PVDF solution concentration and tip-collector distance on the average fibre diameter formed. With an increase in tip-collector distance there is no change in fibre diameter. Although an increase in fibre diameter can be observed when the concentration is increased, it is apparent that solution concentration and diameter do not interact at all to affect the average fibre diameter. This is attributed to the lack of significance in the interaction between the variables involved i.e. concentration and tip-collector distance. Similarly in Figure 5 it can be observed that there is no significant interaction between the tip-collector distance and voltage. This is contrary to what was observed in Figure 4 where the variables significantly interacted to affect the average fibre diameter. This proves that it is fundamentally important to optimize the process by simultaneously studying the interaction of variables instead of investigating the parameters individually to arrive at a conclusion.

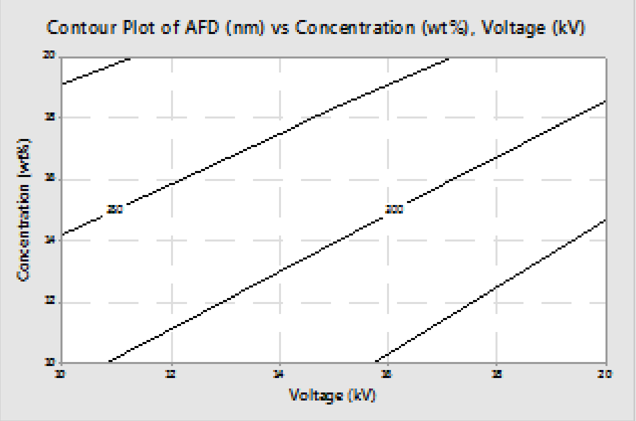


Figure 3 Contour plot of interaction effect of solution concentration and voltage on average fibre diameter

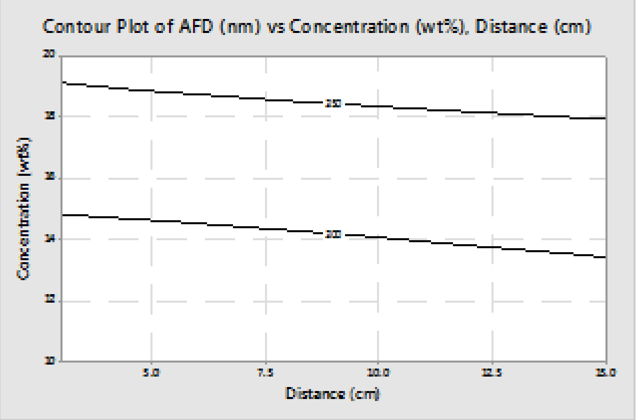


Figure 4 Contour plot of interaction effect of solution concentration and distance on average fibre diameter

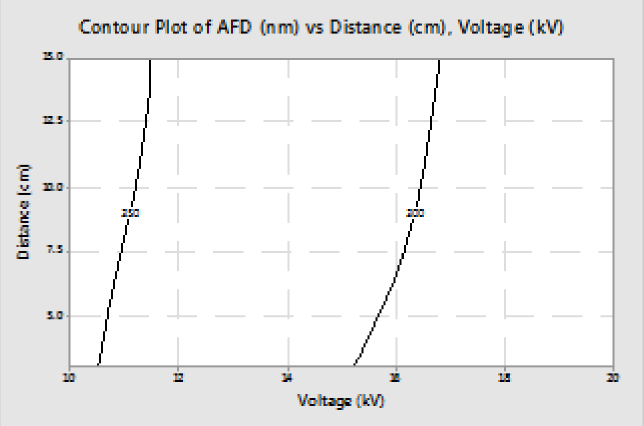


Figure 5 Contour plot of interaction effect of distance and voltage on average fibre diameter

4.0 CONCLUSION

In this paper, RSM was applied to optimize the input parameters conditioned to produce electrospun nanofibrous PVDF scaffolds with diameter lower than 250nm. The parameters varied were the polymer voltage (10–20 kV), tip-to-collector distance (3–15 cm) and concentration (10–20 wt%). The current research was conducted to understand the behavior of the factors towards the PVDF nanofiber diameter, thereby proposing a mathematical formulation using the RSM. The results obtained indicate that the voltage and PVDF solution concentration had a significant influence on the average fibre diameter. It was also found that distance does not significantly affect fibre diameter and that interaction between voltage and concentration with tip-to-collector distance is insignificant. It can be concluded that the smallest average fibre diameters (<250nm) were obtained in the region where the voltage and concentration ranges are 16-20kV and 10-14wt%.

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