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Formation of Poly(vinylidenefluoride) Nanofibers: Part I Optimization by Using of Central Composite Design

A. Akbari*[,a], A. Yunessnia Lehi[b], M. Bojaran[b]

[a] *Department of Carpet, Faculty of Architecture & Art, University of Kashan, Kashan, Iran*

[b] *Institute of Nanoscience and Nanotechnology, University of Kashan, Kashan, Iran*

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**Corresponding author:*
E-mail address:
akbari@kashanu.ac.ir
Phone: +98 361 5913154
Fax: +98 361 5913131
P.O. Box: 87317-51167

Abstract

Poly(vinylidene fluoride) (PVDF) nanofibers were prepared via electrospinning process. Several different factors influence on this process and application of experimental design for its optimization is of great importance. The central composite design (CCD) was used for planning and optimizing of the experiments and also, the analysis of variance (ANOVA) was employed for the statistical validation of regression models. In this research, we found optimal condition for the effects of four factors, i.e. PVDF concentration, flow rate, voltage and interval on the fiber diameter. The model indicated that the flow rate (negatively) and solution concentration (positively) influence extremely on the fiber diameter, whereas the voltage and interval influence equally together on the response (negatively).

1. Introduction

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymeric material that mainly is utilized for preparation of microfibers, nanofibers and hollow fibers in various industrial applications e.g. polymeric membrane electrolyte fuel cell (PEMFC) [1-3] and filtration [4-6]. Moreover, PVDF is characterized by high mechanical strength, high acidic, chemical and thermal resistances. Therefore, this material is ideal for applications involving harsh environments [7-9]. PVDF has a high solubility in many common organic solvents [10-12]. The solvents completely penetrate and dissolve PVDF when it is in its crystalline state at 60 °C [10]. Therefore, these solvents can be used for the preparation of fibers by electrospinning process with different morphologies and diameters [13-18].

One process which has attracted much attention in recent years to prepare polymeric fibers is electrospinning [13]. The electrospinning allows the simple preparation of 3D highly porous polymeric fibers composed of nanofibers [15]. This process utilizes a high voltage source to inject charge of a certain polarity into a polymer solution, which then causes to accelerate this solution toward a collector of opposite polarity. Eventually in this process, a fiber jet is ejected from head of syringe (i.e. from Taylor cone) as electric field strength exceeds surface tension of liquid. The fiber jet travels through atmosphere that allows evaporating the solvent, thus leads to deposition of solid polymer fibers on the collector [15, 16]. The produced fibers by using of this process typically have diameters in the order of a few micrometers down to tens of nanometers [15].

In order to control the diameter or properties of fibers, we require understanding how this process transforms a millimeter-diameter fluid stream into solid fibers with four orders of smaller magnitude in diameter. The most parameters and processing variables influence on the electrospinning process to consist of 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 careful manipulation of these parameters, a wide variety of fiber diameters can be obtained [4, 17-21].

The classical approach of optimization is time-consuming and complicated for a multi-variable system such as electrospinning process. Recently, response surface methodology (RSM) has been proven to be effective tools for the investigation, modeling and optimization of these multi-variable processes [22-24]. This approach enables the experimental investigation of individual factors and interactions of factors simultaneously as opposed to one factor at-a-time approach. The central composite design (CCD) is one of designs in this approach that can be very useful in the optimization process, since estimated major effects and interactions can be used to predict an optimum combination of factors by suggested model [22, 24]. Additionally, statistical design had been proven to be useful in the electrospinning process [25-28].

To date, the electrospinning studies of PVDF were mostly focused on its applications, however, fundamental understanding and optimization of the formation process has been limited. Moreover, PVDF concentration influences more significantly on the fiber formation. And, this effect changes the diameter of fibers in the electrospinning. In order to control this process for PVDF fibers, we applied an expert design for the first time. The central composite design is one of these expert designs that were applied. In this research, a homemade apparatus was used to obtain efficient and accurate experimental data. The purpose of this research is to efficiently determine optimal parameters to achieve smaller diameters in the formation of PVDF nanofibers under varying four parameters, i.e. PVDF concentration, flow rate, applied voltage and interval and provides prediction capability for the process. The result of experiments in this research was average fiber diameter (AFD).

2. Experimental procedure

PVDF granules was supplied by Aldrich (M_w = 275,000, M_n = 107,000 g/mol, d = 1.74 g/cm^3, m_p=165°C) and was used as polymer for the preparation of solutions. Also, N, N-

dimethylformamide (DMF, reagent grade) was purchased from Merck and was used as solvent. All of these materials were used without further purification. The used electrospinning system in this research was a homemade system (Fanavaran Nano-Meghyas Co., Tehran: Iran Polymer and Petrochemical Institute) composed of a variable high voltage power supply, a syringe pump suitable for different controlled flow rates, a syringe as the solution reservoir with a metal syringe needle and aluminum tulle used as collector (Fig. 1).

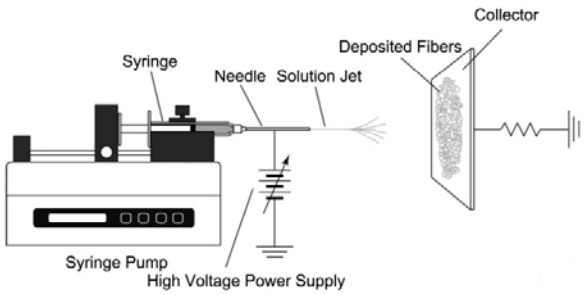

Fig. 1. Used electrospinning setup for PVDF nanofiber preparation.

As received PVDF granules was first dissolved in DMF at various concentration, ranging from 20 to 25% wt., and solution temperature of 75±2°C. The solutions were magnetically stirred for at least one day to guarantee complete dissolution of the polymer. After that, the prepared homogeneous solutions were loaded into syringe. A positive high voltage supply was attached to syringe needle, making it the cathode. The syringe was connected to a metering pump to maintain a constant flow rate and solution at the syringe tip. The fibers were spun at flow rates ranging from 0.1±0.05 to 0.7±0.05 mL/h, with an applied voltage between 10±0.1 and 20±0.1 kV and were collected on a grounded aluminum tulle. The distance between syringe tip and collector (or interval) was maintained from 10±3 to 20±3 cm. The temperature of electrospinning environment was 38±2°C in all of the experiments. The range of parameters was selected from trial experiments and represented the attainable limits for the nanofiber formation and/or equipment operation. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to extraneous factors [26, 29].

The diameter and morphology of electrospun fibers were examined by using of scanning electron microscopy (SEM, LEO 1455VP, England). All samples were sputter-coated with platinum before analysis. The diameters of electrospun fibers were measured with an image analyzer (Microstructure Measurement software, Nahamin Pardazan Asia Co.). The average fiber diameter was determined from about 26 measurements of the random fibers in 3 SEM images taken from different areas of the mat [26].

3. Results and discussion

The optimization of significant factors in the electrospinning process via conventional method of investigation involves changing of one variable in time while all other variables have fixed at constant levels, and studying of the effect of single variable on the response. This classical approach of optimization is time-consuming and complicated for a multi-variable system. In order to overcome such difficulty, the statistical technique of central composite design (CCD) for the study of PVDF nanofiber formation process was applied. We utilized Design-Expert 8.0.2.0 program (Stat-Ease Inc., USA) for this research.

The central composite design consists of three distinct sectors: 1- Full factorial design in which factor levels were coded to usual low (-1) and high (+1) values; 2- Axial points localized on the axis of

each variable at a distance α from the designed center; and 3- Center points that can be replicated to provide an estimation of experimental error variance. The type of used central composite design was face centered type with α=1 [24].

The operating ranges and levels of considered variables are given in actual and coded values in Table 1. Also, the expert design for planning of the experiments is shown in Table 2. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to extraneous factors. The response of this experimental design, i.e. average fiber diameter (AFD) was determined experimentally according to designed runs in order to ascertain the effects of parameters on the electrospinning process.

Table 1: Design variables, their coded and actual values used for experimental design.

Design variable	Symbol	Actual values of coded levels				
		-1	**-α**	**0**	**+α**	**+1**
Flow rate (mL/h)	F	0.1	0.22	0.4	0.58	0.7
Voltage (kV)	V	10	12.03	15	17.97	20
Interval (cm)	I	10	12.03	15	17.97	20
Concentration (%	C	20	21.01	22.5	23.99	25

Table 2. Central composite design and experimental response.

Run	Design variable				Response
	Flow rate (mL/h)	Voltage (kV)	Interval (cm)	Concentration (% wt.)	AFD (nm)
1	-1	0	0	0	1063.4
2	+α	-α	-α	+α	1141.7
3	0	0	-1	0	865.8
4	0	0	0	0	903.9
5	+α	+α	+α	-α	589.5
6	0	0	0	-1	1348.7
7	0	1	0	0	926.9
8	-α	+α	+α	+α	1545.5
9	0	0	1	0	840.7
10	0	0	0	0	786.3
11	-α	-α	+α	-α	692.6
12	+α	-α	+α	+α	1123.9
13	0	-1	0	0	754
14	0	0	0	0	798.8
15	0	0	0	1	3583.5
16	1	0	0	0	729.1
17	0	0	0	0	992.3
18	+α	+α	-α	-α	608.6
19	0	0	0	0	1002.6
20	-α	-α	-α	-α	662.05
21	-α	+α	-α	+α	2139.6

Generally, a second-order polynomial model with main, quadratic and interaction terms can be developed to fit the experimental data obtained from experimental runs [24]. Based on the obtained experimental results, regression is constructed by central composite design method to figure out the functional relationship for approximation and prediction of fiber diameter. Thus, the functional relationship with actual variables is shown in equation (1). The

significance of regression coefficients in the functional relationship with actual variables has been tested by using of the statistical Student's t-test. Thus, in equation (1) only significant terms were retained. Also, the significance of coefficients has been tested by means of analysis of variance (ANOVA) (Table 3). In this respect, F-value is determined which is a measure of the variance of data about the mean, based on ratio of the mean square of group variance due to error [22-24].

$$\frac{1}{\sqrt{D}} = -0.582 - 0.086F + 0.067C + 0.025F^2 - 0.0066I + 0.006FV - 0.006V \qquad (1)$$

Table 3. Analysis of variance (ANOVA) for diameter of PVDF fibers.

Source	DF	SS	MS	F-value	P-Value	R^2
Model	14	7.012E-4	5.008E-5	8.22	<0.0001	0.9505
Residual	6	3.655E-5	6.091E-6			
Lack of Fit	2	2.152E-5	1.076E-5	2.86	0.1691	
Pure Error	4	1.503E-5	3.757E-6			
Total	20	7.377E-4				

If F-value is departed significantly from unity, then it is more certain that design variables adequately explain variation in the mean of data. Having F-value and degree of freedoms, P-value is then calculated. If P-value is low, one may concludes that functional relationship is statistically validated for the prediction of response. Most investigators accept central composite design for the prediction, if P-value is less than 0.05. In Table 3, ANOVA results are presented for central composite design developed.

According to ANOVA results, F-value is high and P-value is smaller than 0.0001. In addition, R^2 value for the fiber diameter is 0.9505 which is desirable (Fig. 2A). All these statistical estimators reveal that developed central composite design for the prediction of fiber diameter is statistically validated for the approximation of response over the range of experimentation considered (valid region). The goodness-of-fit of central composite design is illustrated in Fig. 2 which is desirable. On the basis of this figure, the values of errors are low in the experimental design (Fig. 2B) and are distributed randomly (Fig. 2C). The samples of these fibrous mats are shown in Fig. 3.

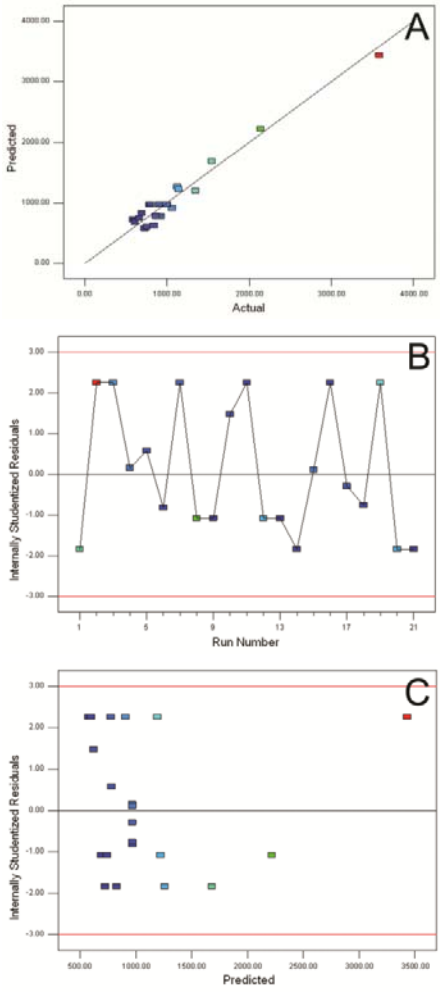

Fig. 2. Goodness-of-fit of central composite design for diameter of PVDF fibers.

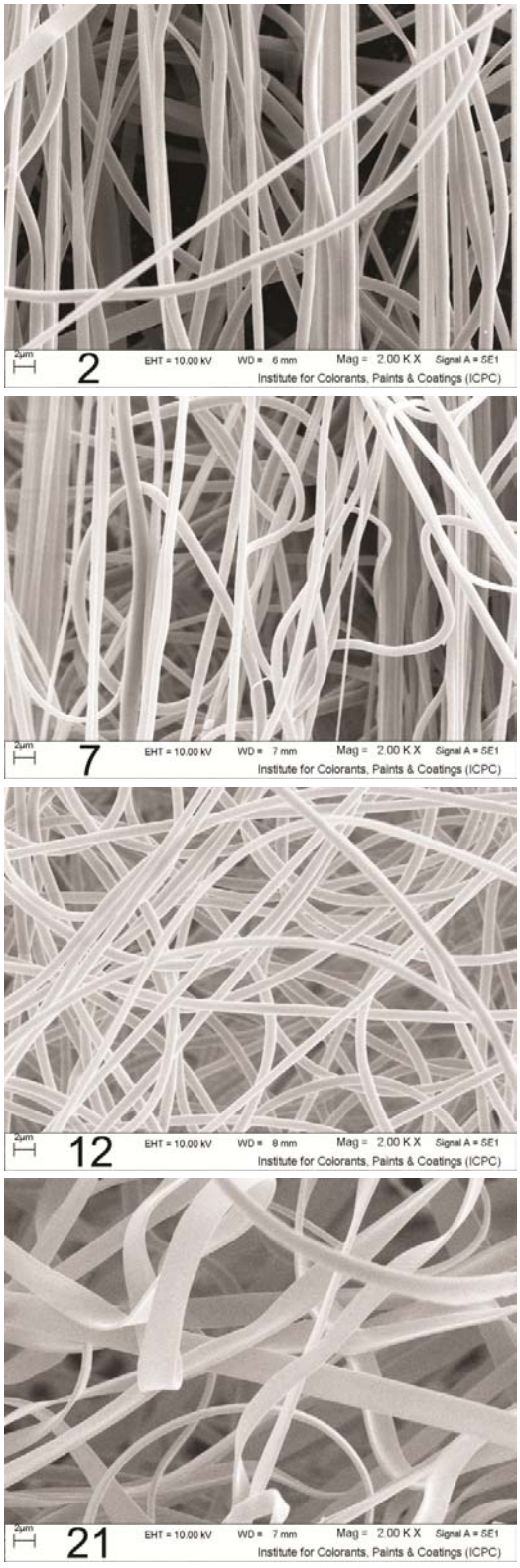

Fig. 3. Samples of prepared fibrous mats on the basis of experimental design.

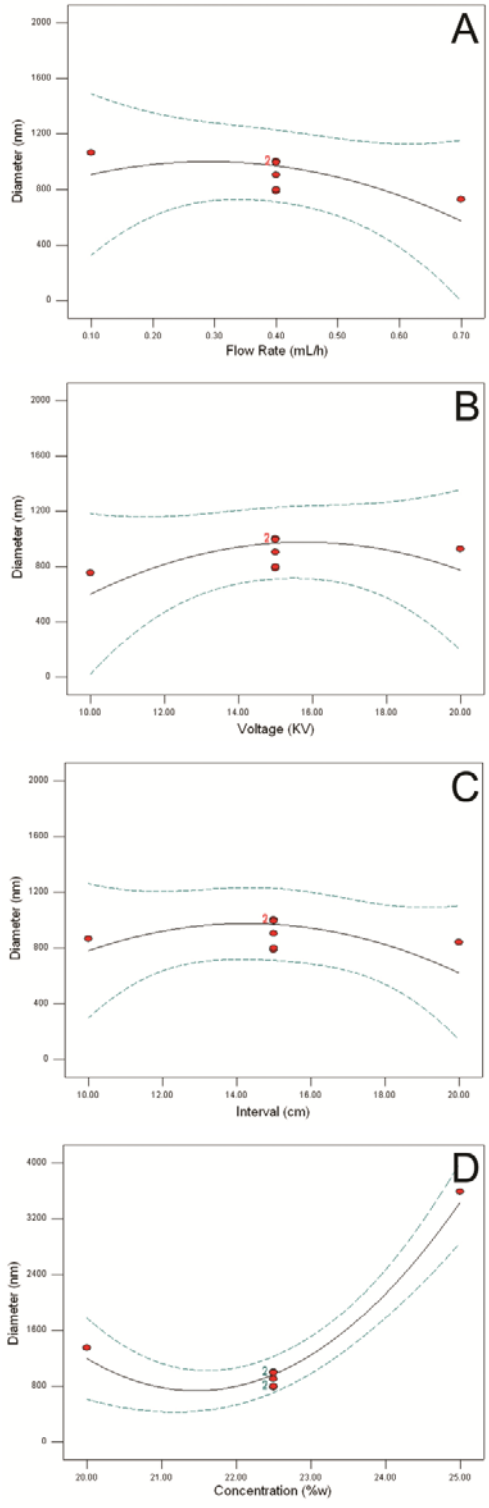

Fig. 4. Effect of parameters on the diameter of PVDF fibers, A: flow rate, B: voltage, C: interval and D: concentration.

Also in Fig. 4, the effects of four parameters (main effect) have been presented for the response function. The quadratic effects in the model are similar for all factors giving the contribution to response surface curvature. Based on the above analysis, the flow rate (negatively) and solution concentration (positively) are the most significant factors that influenced on the fiber diameter. But, the main effects of voltage and interval are equally together on the response (negatively). The effect of PVDF concentration on the fiber diameter efficiency becomes more important at higher values. PVDF solution must be optimized to have a high enough concentration to cause PVDF entanglements yet not so high that achieved smaller fibers.

For the optimization, Montgomery described a multiple response method called desirability [24]. The method makes the use of an objective function, D(X), called desirability function (Equation 2). It reflects the desirable ranges for each response (d_i). The desirable ranges are from zero to one (least to most desirable, respectively). The simultaneous objective function is a geometric mean of all transformed responses. In this equation, n is the number of responses in the measure. If any of the responses or factors falls outside their desirability range, the overall function will become zero.

$$D(X) = (d_1 \times d_2 \times ... \times d_n)^{\frac{1}{n}} = (\prod_{i=1}^{n} d_i)^{\frac{1}{n}} \qquad (2)$$

The optimization module in the Design-Expert 8.0.2.0 searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. The goals are combined into an overall desirability function. The program seeks to maximize this function. Seeking the goal begins at a random starting point and proceeds up the steepest slope to a maximum. There may be two or more maximums because of curvature in the response surfaces and their combinations into desirability function. By starting from several points in the design space chances improve for finding best local maximum. The default is in 30 starting points. The goal of optimization is to find the good set of conditions that will meet all the goals, not to get the desirability value of 1.0. Desirability is simply a mathematical method to find the optimum.

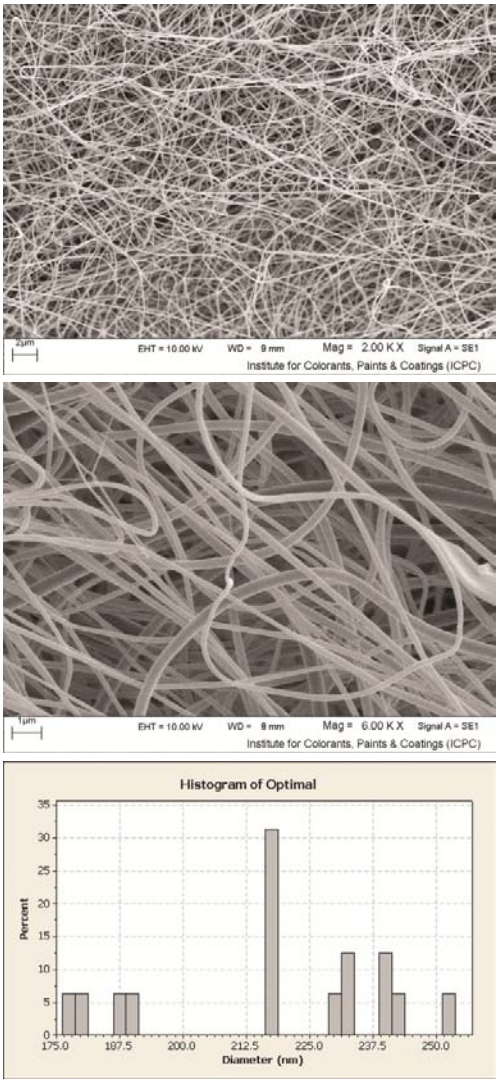

Fig. 5. SEM image of PVDF nanofibers and its distribution in the optimal condition (F=0.67 mL/h, V=12.7 kV, I=18.5 cm, and C=21.7% wt.).

On the basis of achieved computations and this multiple response method, the optimal condition for PVDF fiber formation is F=0.67 mL/h, V=12.7 kV, I=18.5 cm, and C=21.7% wt. The experimental value of response in this optimal point (D=218.2 nm) is lower than any fiber diameter value achieved in the initial experiments conducted according to experimental design (Table 2). Additionally, a set of experiments were carried out for the optimal condition of fiber formation process in order to figure out the reproducibility of diameter that were desirable. Fig. 5 indicates the formed PVDF mat in the optimal condition.

4. Conclusion

In this research, an attempt had been made to predict and optimize the effects of four parameters on PVDF fiber formation. The experiments were carried out based on central composite design with PVDF concentration, flow rate, voltage and interval as process parameters. In this research, we understand that flow rate (negatively) and solution concentrations (positively) are the most important factors and effects of voltage and interval are equally together on the response (negatively). The optimal condition for PVDF fiber formation is F=0.67 mL/h, V=12.7 kV, I=18.5 cm, C=21.7% wt. and experimental value of response in this optimal point is D=218.2 nm.

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