

Predicting Poly(vinyl pyrrolidone)'s Solubility Parameter and Systematic Investigation of the Parameters of Electrospinning with Response Surface Methodology

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ABSTRACT: The solubility parameters were used to choose the solvent for poly(vinyl pyrrolidone) (PVP) in electrospinning. In this study, a novel method for predicting the contribution value of the pyrrolidone group (a typical part of the PVP molecular structure) was proposed. The solubility parameters of PVP were calculated by this method, and accordingly, ethanol was chosen as the solvent for PVP. What is more, response surface methodology was used to facilitate a systematic investigation on the influence of the PVP solution concentration, feed rate, distance between the tip and collector, and operating voltage on the fiber diameter and morphology in electrospinning. The predicted fiber diameters by the response regression model, and the experimental values were in close proximity. The solution concentration and feed rate both had significant effects on the PVP fiber diameter, and there was some interaction between the solution concentration and the feed rate in this system. In addition, this study provided a train of thought for the electrospinning of polymer fibers with controllable and predictable fiber diameters. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40304.

KEYWORDS: electrospinning; fibers; manufacturing; molding; nanostructured polymers

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INTRODUCTION

Electrospinning is a simple and versatile technique for producing fibers on the microscale or nanoscale. It is popular with researchers because of its versatility in spinning various kinds of polymer fibers, ability to control the diameter and morphology of fibers, simple device, and ease of operation.^{1–3} In the electrospinning process, the tensile force that is generated by a high-voltage electric field forces the polymer solution to jet out from the needle. As the charged polymer jet moves toward a counter electrode, it is elongated by the electric force to form polymer fibers that deposit on oppositely charged collecting plates by means of solvent evaporation.^{4–7} Electrospinning is a complicated process that involves solvent diffusion/evaporation/cooling, heat transfer, water condensing, and polymer diffusion in addition to operation variables.⁸ Different outcomes of single-factor analysis on electrospinning parameters and solution properties have been reported in the published literature. Megelski et al.⁹ proposed that the polystyrene (PS) fiber size decreased from about 20 to 10 μm because of the increase in applied voltage from 5 to 12 kV. On the other hand, Yuan et al.¹⁰ suggested that increasing the voltage caused a slight change in the fiber diameter in the electrospinning polysulfone

solution. However, Demir et al.¹¹ reported that the fiber diameter increased in a sigmoidal manner with increasing voltage.

For this reason, response surface methodology (RSM) provides a more systematic investigation of the processing parameters, including the interaction of the parameters, and modeling of the fiber diameter simultaneously. RSM is a combination of statistical and mathematical techniques that are useful for the development, modeling, and optimizing processes.¹² It reduces the number of experimental runs and still provides sufficient and acceptable results.¹³ Agarwal et al.¹⁴ used RSM to define a quantitative relationship between electrospinning parameters and average fiber diameters and its distribution for each chitosan–polylactide ratio. In addition, Lou et al.¹⁵ facilitated a systematic understanding on the parameters of solution-blown electrospinning; this indicated that the interaction between the air pressure and injection rate had a significant effect on the average fiber diameter. Until now, RSM has been widely used in the investigation of the electrospinning of various polymers, such as polyacrylonitrile,¹⁶ poly(D,L-lactide),¹⁷ Bombyx mori silk,¹⁸ and chitosan/poly(vinyl alcohol).¹⁹ It, thus, appears that RSM is an effective technique for designing, analyzing, modeling, and optimizing electrospinning, which is a process with several influence variables.

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The choice of a suitable solvent for a given polymer is fundamental and important to the electrospinning process. However, the search for solvents has been based on experience from similar polymer systems, trial and error, and solubility models limited by a physicochemical database.²⁰ Solubility parameters have been widely used to identify suitable solvents and solvent systems for polymers in electrospinning. It has been reported that the group contribution method is widely applied in determining the solubility parameters of polymers.^{21–26} Haas et al.²⁰ and Ghorani et al.²⁷ both used Hansen solubility parameters calculated by the group contribution method to select individual and binary solvent systems suitable for cellulose acetate. Fiber mats with different morphologies were obtained by changes in the solvent and electrospinning parameters. Lubasova and Martinova²⁸ evaluated the solubility parameters of solvents for poly(vinyl butyral) (PVB) by the application of a group contribution method. Specifically, it was found that a mixture of good and poor solvents for electrospinning PVB led to the generation of a pore structure on the fibers. Similarly, PVB fibers with surface porosity were manufactured with a solution in binary solvent mixing high- and poor-solubility solvents by Luo et al.²⁹ It was demonstrated that the phase separation induced by solubility differences in the electrospun PVB solution and relative humidity contributed to pore formation on the fibers. In coaxial electrospinning, the degree of miscibility of core and shell solutions decided the morphologies of the resulting fibers.³⁰ Kurban et al.³¹ developed a solvent selection system by Hansen solubility parameters, which facilitated the choice of compatible solvents for the core and shell. It was demonstrated that fibers electrospun from a semimiscible core-shell (PS–ammonia borane) solution were highly porous, but fibers obtained from a miscible PS–ammonia borane solution had a classic coaxial structure.

The limited data available on structural groups is a practical problem of using a group contribution method to calculate the Hansen solubility parameters, especially for complex molecules.^{21,32} For example, poly(vinyl pyrrolidone) (PVP). PVP is a hydrophilic polymer with excellent solubility, biocompatibility,^{33,34} and spinnability, which has been electrospun to fibers and fiber composites by numerous researchers.^{35–38} However, there has been no literature on the calculation of the solubility parameters of PVP directly by a group contribution method. The reason may be the complex molecular structure of PVP, which has a five-membered ring with a nitrogen atom, called a *pyrrolidone group*, as shown in Figure 1(a,b). There is no available information about the pyrrolidone group's contribution to the solubility parameter in the literature yet.

In this study, we proposed a novel method of calculating the contribution values for the pyrrolidone group, which contributes to the solubility parameter of PVP. Accordingly, ethanol was chosen as the solvent for PVP in electrospinning. Although the PVP/ethanol system has been electrospun before, a more systematic investigation of its processing parameters, including the interaction of the parameters and the modeling of the fiber diameter was conducted by RSM. The effect of the applied voltage, solution concentration (mass fraction of the solution), feed rate, and tip-to-collector distance (TCD) on the diameters of

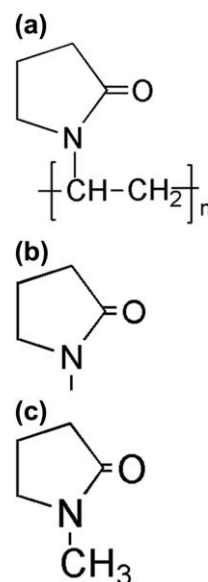


Figure 1. Molecular structural formula of (a) PVP, (b) pyrrolidone group, and (c) *N*-methyl-2-pyrrolidone.

the PVP fibers was evaluated by the Box–Behnken design (BBD) of RSM. The main effect and interaction of the parameters on the PVP fiber diameter were studied. The objective of this study was to estimate the contribution value of the pyrrolidone group, which could then be used to calculate the solubility parameter for the materials with the group. Another objective of this study was to construct a mathematical model of the electrospun fiber and investigate the individual factors and the interactions of the processing parameters of electrospinning.

CALCULATING THE SOLUBILITY PARAMETER OF PVP

The one-dimensional solubility parameter (δ) developed by Scatchard and extended by Hildebrand and coworkers has been applied to nonpolar materials.^{22,39} There must be some modification of the solubility parameter to polar materials. In Hansen's approach,⁴⁰ δ was given by a simple sum of three partial parameters, the dispersion force component (δ_d), the polar force component (δ_p), and the hydrogen-bonding component (δ_h), according to eq. (1). The three partial parameters were calculated by method of Hoftyzer and van Krevelen (VKH) with eq. (2), in which F_d , F_p , and E_h are the contributions of the dispersion force component, the polar force component, and the hydrogen-bonding component, respectively, to the cohesive energy; i is the contributing group; and V is the molar volume.⁴¹ However, F_d , F_p , and E_h of the pyrrolidone group have not been reported in the literature yet. Thus, a new method to predict the contribution values of the pyrrolidone group based on the solubility parameters of *N*-methyl-2-pyrrolidone [Figure 1(c)] was presented. The solubility parameters of *N*-methyl-2-pyrrolidone were $\delta_d = 18 \text{ MPa}^{0.5}$, $\delta_p = 12.3 \text{ MPa}^{0.5}$, $\delta_h = 7.2 \text{ MPa}^{0.5}$, and $V = 96.5 \text{ cm}^3/\text{mol}$.⁴² According to eq. (2), the contribution of the pyrrolidone group could be obtained with the F_d , F_p , and E_h values of methyl [the total contribution values ($\sum F_{di}$, $\sum F_{di}^2$ and $\sum E_{hi}$) subtracted from the value of methyl], as listed in Table I.

Table I. F_{di} , F_{pi} , and E_{hi} Calculations for the Pyrrolidone Group

Structural group	F_{di} ($J^{0.5} \cdot cm^{1.5}/mol$)	F_{pi} ($J^{0.5} \cdot cm^{1.5}/mol$)	E_{hi} (J/mol)
Pyrrolidone group	1320	1190	5000

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

$$\delta_d = \frac{\sum F_{di}}{V}, \delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V}, \delta_h = \sqrt{\frac{\sum E_{hi}}{V}} \quad (2)$$

$$V_{PVP} = M/\rho = 88.8 \text{ cm}^3/\text{mol} \quad (3)$$

The solubility parameter of PVP (K90, average molecular weight = 1,300,000 g/mol) was predicted with eq. (2), as shown in Table II. In addition, V of PVP was calculated by eq. (3), in which M is the relative molecular weight of PVP's repeating unit and ρ is PVP's density (1.25 g/cm^3).⁴³ The solubility parameter of PVP calculated by this method was $24.3 \text{ MPa}^{0.5}$; this was consistent with the experiment value of $25.6 \text{ MPa}^{0.5}$.⁴⁴ Analogously, Huang et al.⁴⁵ estimated the F_{di} , F_{pi} , and E_{hi} values of the sulfonyl group and 1,2,4-phenyl; these were in good accordance with the experimental results of Barton⁴⁶ and Kirk and Othmer.⁴⁷ In addition, Yang et al.⁴⁸ obtained the Hansen solubility parameters of poly(ether sulfone) with the calculated value of the sulfonyl group; this was in good agreement with the experimental data of Tam et al.⁴⁹ It was implied that a mathematical model for calculating the groups' F_{di} , F_{pi} , and E_{hi} is advisable.

What is more, the solubility parameter of ethanol was $25.2 \text{ MPa}^{0.5}$ with the method of VKH. It was recorded in literature that if the difference in the solubility parameters of the materials is less than $5.0 \text{ MPa}^{0.5}$, the materials are miscible.⁴¹ Hence, ethanol and PVP are theoretically miscible.

EXPERIMENTAL

Materials

PVP K90 (average molecular weight = 1,300,000 g/mol) was purchased from Sigma Aldrich Chemical Co. Ethanol (absolute, $\geq 99.5\%$) was purchased from Fuyu Chemical Co., Ltd. (Tianjin).

Electrospinning Processes

A PVP solution was prepared by the dissolution of PVP powder in ethanol and mixing under magnetic stirring for 6 h at room temperature. To discharge the bubbles, the PVP solution was set out under ambient conditions for 1 h. The electrospinning apparatus was self-assembled. The PVP solution was held in a glass syringe, and the solution injection rate was controlled by a constant-flow syringe pump. A foil plate was used to collect the fibers. All of the electrospinning process was done under 296 kV and a relative humidity of $55 \pm 3\%$.


Characterization

The morphology of the electrospun PVP fibers was analyzed with scanning electron microscopy (SEM; model JSM-6390). The sample was coated with gold for 90 s before observation under the SEM. The average diameter of the PVP fibers was determined by analysis of the SEM images by Image Pro Plus 6.0 (Media Cybernetics), and the diameters of 20 fibers were measured in every sample. A Student's t test of statistical analysis was performed with SPSS version 16 (SPSS, Inc., Chicago, IL). A p value of less than 0.05 was considered to be statistically significant. In addition, the standard deviation (SD) error bars were obtained from Origin 8.0 (OriginLab).

Experimental Design

A standard RSM design named BBD was used to investigate the relationship between the fiber diameter and the processing parameters. The applied voltage (A ; kV), solution concentration (B ; %), TCD (C ; cm), and feed rate (D ; mL/h) were selected as the four independent variables. The average fiber diameter of the fibers obtained from the experiments was the response value. The ranges of the variables were selected from preliminary one-factor experiments. The experiment points (27 points) and analysis of variance (ANOVA) were designed and analyzed by Design-Expert 8.05b software.

Table II. Hansen Solubility Parameter Calculations for PVP with the Method of VKH

		$-\text{CH}_2-$	$-\text{CH}<$	Sum	Solubility parameter component ($\text{MPa}^{0.5}$)	Solubility parameter ($\text{MPa}^{0.5}$)
Number of groups	1	1	1			24.3
$N \times F_{di}$ ($J^{0.5} \cdot cm^{1.5}/mol$)	1,320	270	80	1,670	δ_d	18.8
$N \times F_{pi}^2$ ($J \cdot cm^3/mol^2$)	1,416,100	0	0	1,416,100	δ_p	13.4
$N \times E_{hi}$ (J/mol)	5,000	0	0	5,000	δ_h	7.5

*N, number of groups.

Table III. Response of the Experimental Data Designed by BBD

Experiment number	A (kV)	B (%)	C (cm)	D (mL/h)	Average fiber diameter/(nm)
1	8	8	6	1.0	731
2	13	8	10	1.0	522
3	13	8	6	1.5	706
4	8	8	14	1.0	681
5	8	5	10	1.0	307
6	13	11	10	1.5	1220
7	13	8	6	0.5	486
8	18	8	6	1.0	833
9	8	8	10	0.5	568
10	13	8	10	1.0	572
11	18	5	10	1.0	329
12	13	5	10	0.5	275
13	13	5	14	1.0	248
14	18	8	10	0.5	518
15	18	8	10	1.5	739
16	8	8	10	1.5	607
17	13	8	10	1.0	546
18	13	5	10	1.5	242
19	13	11	10	0.5	864
20	13	8	14	0.5	468
21	13	11	6	1.0	1114
22	13	5	6	1.0	419
23	18	11	10	1.0	1198
24	13	11	14	1.0	1084
25	18	8	14	1.0	718
26	8	11	10	1.0	1052
27	13	8	14	1.5	573

RESULTS AND DISCUSSION

Response Surface Model

All 27 experimental data and the response were analyzed to fit a second-order polynomial equation, listed in Table III. By regression analysis, the significance probability (p) and the coefficient of the electrospinning parameters were obtained. The p value was used to examine the significance of each term. A p value of the terms of less than 0.05 indicated that it was significant in model terms.⁵⁰ The 0.05 significance level is conventionally used as the maximum for determining the model. In this case, A , B , C , D , BD , A^2 , B^2 , and C^2 were significant model terms. The refined response model without the nonsignificant terms is as follows:

$$\begin{aligned} \text{Average fiber diameter} = & 1892.22 - 104.03A - 138.64B - 109.23C \\ & - 367.33D + 64.83BD + 4.25A^2 + 12.79B^2 + 4.92C^2 \end{aligned} \quad (4)$$

The fitness of the model was evaluated by the coefficient of determination (R^2). For an acceptable p , it is desirable when R^2 is larger than 0.9. The R^2 value of this model was 0.9800, which suggested that 98% of the variation could be explained by this model. The ANOVA data of this model are listed in Table IV.

The model F value of 110.32 implied that the model was significant. There was only a 0.01% chance that a model F value this large could occur due to noise. The lack-of-fit F value of 4.19 implied that the lack of fit was not significant relative to the pure error. There was a 20.95% chance that a lack-of-fit F value this large could occur due to noise. The comparison diagram of the experimental value of the average fiber diameter and predicted value is shown in Figure 2. The agreement between the experimental and model predicted values was decided by the computation of the linear correlation coefficient. Adequate precision measured the signal-to-noise ratio. A ratio greater than 4 was desirable. In this case, the ratio was 34.686, and this indicated an adequate signal. Therefore, this model could be used to navigate the design space.

Response Surface Analysis

Influence of the Applied Voltage on the Fiber Diameter. The effect of altering the applied voltage on the fiber diameter is revealed in Figure 3(a–c). It was suggested that the PVP fiber diameter did not vary significantly with a change in voltage. The increasing applied voltage showed a trend of diminishing the average fiber diameter and then slightly increased the fiber diameter at high voltage. As the applied voltage in

Table IV. ANOVA of the Regression Model

Source	Sum of squares	Degrees of freedom	Mean square	F	p
Model	2.1118×10^6	8	2.647E+003	110.32	<0.0001
A	12,610.08	1	12,610.08	5.26	0.0341
B	1.850×10^6	1	1.850E+006	771.17	<0.0001
C	22,274.08	1	22,274.08	9.28	0.0069
D	68,705.33	1	68,705.33	28.64	<0.0001
BD	37,830.25	1	37,830.25	15.77	0.0009
A ²	67,752.08	1	67,752.08	28.24	<0.0001
B ²	79,541.78	1	79,541.78	33.15	<0.0001
C ²	37,222.50	1	37,222.50	15.51	0.0010
Residual	43,186.98	18	2399.28		
Lack of fit	41,936.31	16	2621.02	4.19	0.2095
Pure error	1250.67	2	625.33		

electrospinning was raised, the charge on the solution jets increased. Hence, the stretching of the electric field force went up correspondingly; this caused a decrease in the fiber diameter. However, the enlargement of the applied voltage raised the acceleration of the solution jets in the normal course. More solution suspended at the tip of the nozzle and sprayed out from the needle. Meanwhile, the fly time of the solution jet in the electric field diminished. As a result, thicker PVP fibers were obtained. In this study, the effect of the applied voltage on the fiber diameter resulted from the competition of the two previous reasons. For instance, in the research on the electrospinning of a poly(vinyl chloride)/tetrahydrofuran/dimethylformamide solution, Lee et al.⁵¹ observed a monotonous decrease in the fiber diameter with an increase in the applied voltage. It was shown that the first reason, higher voltage, led to more stretching, and the smaller fiber diameter played the dominant role. Figure 3(b,c) clearly shows that there was no significant change with different applied voltages coupled with the TCD and feed rate. Also, no relevant interactive terms between the applied voltage and TCD and the applied voltage and feed rate were in the fitted model.

Influence of the Solution Concentration on the Fiber Diameter. The influence of the solution concentration on the fiber diameter is illustrated in Figure 3(a,d,e). It is worth noting that the average fiber diameter apparently increased with increasing solution concentration. This observation was consistent with early research on electrospinning.^{9,52,53} When the solution was electrospun at 14 kV [as shown in Figure 3(d)], the average fiber diameter

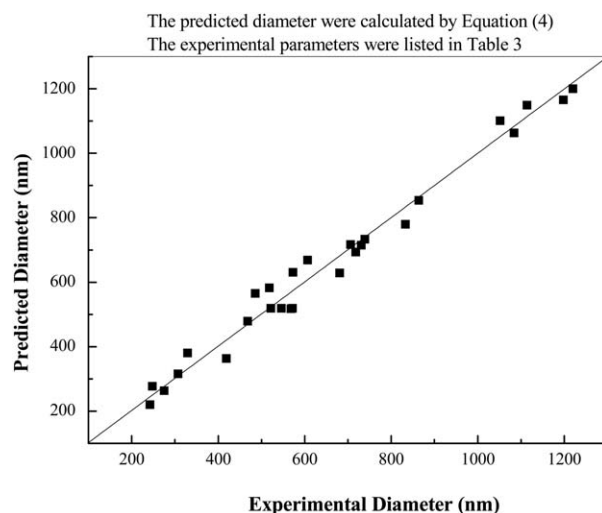
Table V. Statistical Assessment of the Effect of the Solution Concentration on the Fiber Diameter

Solution concentration (%)	Mean (nm)	SD	p value of the paired-sample t test
5	309.45	43.058	5% versus 7% 0.000
7	511.11	52.596	7% versus 9% 0.000
9	694.53	67.272	5% versus 9% 0.000

was lower than 300 nm with a solution concentration of 5%, whereas an average fiber diameter of more than 1000 nm could be produced at a solution concentration of 11%. An enlargement of the solution concentration led to an increase in the solution's viscosity and surface tension because of greater molecular chain entanglement; this indicated that the higher viscoelastic force suppressed the electric field force. Hence, the fiber diameter increased. It was also theoretically indicated that thinner fibers were

Table VI. Statistical Assessment of the Effect of the Feed Rate on the Fiber Diameter

Feed rate (mL/h)	Mean (nm)	SD	p value of the paired-sample t test
0.3	558.98	65.347	0.3 versus 0.9 0.000
0.9	695.87	55.319	0.9 versus 1.2 0.000
1.2	916.54	71.897	0.3 versus 1.2 0.000

**Figure 2.** Plot of the model predicted response versus the experimentally obtained response.

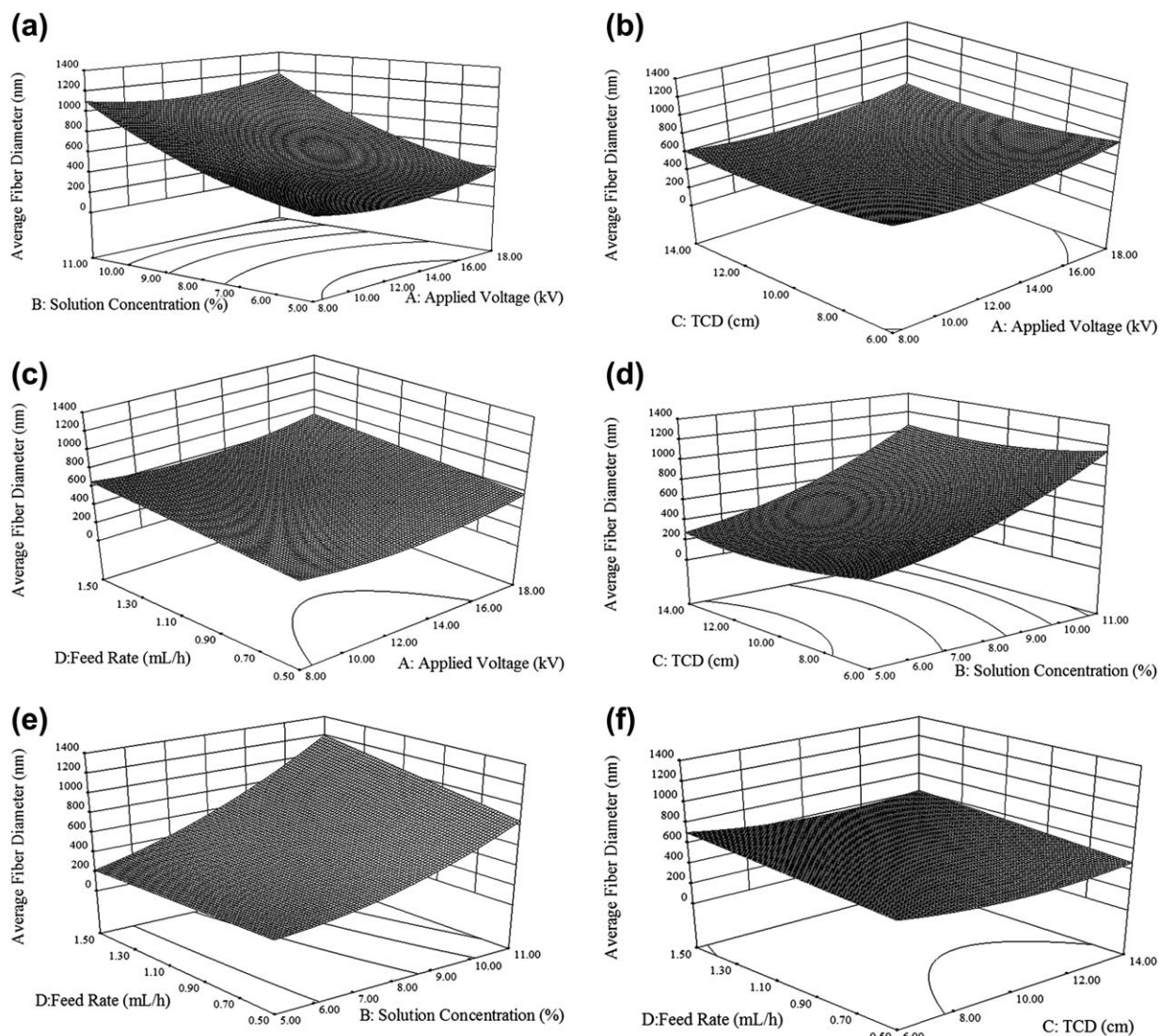


Figure 3. Response surface of the response as a function of the following factors: (a) applied voltage and solution concentration (TCD = 10 cm and feed rate = 1.0 mL/h), (b) applied voltage and TCD (solution concentration = 8% and feed rate = 1.0 mL/h), (c) applied voltage and feed rate (TCD = 10 cm and solution concentration = 8%), (d) solution concentration and TCD (applied voltage = 13 kV and feed rate = 1.0 mL/h), (e) solution concentration and feed rate (applied voltage = 13 kV and TCD = 10 cm), and (f) TCD and feed rate (applied voltage = 13 kV and solution concentration = 8%).

produced when the solution concentration was lower than 5%, as shown in Figure 3(e). However, it was not viable to produce continuous fibers by the electrospinning of the PVP/ethanol solution with concentrations below 5%.

Influence of TCD on the Fiber Diameter. Figure 3(b,d,f) shows the impact of TCD on the average fiber diameter. There were no significant changes in the fiber diameter when TCD was varied. As demonstrated in Figure 3(f), the range of fiber diameter was from 600 to 700 nm. However, this result was different than that of the investigation of TCD on cellulose acetate fibers, which indicated that increasing the TCD led to a decrease in the fiber diameter.⁵⁴ TCD of electrospinning had a dual influence on the fiber diameter. An increase in TCD made the electric field intensity decrease, but the flying time increased. The higher TCD was, the weaker the electric field stretching was, and this led to thicker fibers. On the other hand, a longer

flying time of the solution jets was prone to more stretching and the evaporation of solvent, and this produced thinner fibers. Therefore, the influence of TCD on the fiber diameters was complex and depended on the competition and the electric field intensity and the flying time.

Influence of the Feed Rate on the Fiber Diameter. The effect of the feed rate on the fiber diameter is shown in Figure 3(c,e,f). Given the other processing parameters at a certain value, the fiber diameter increased monotonously with increasing feed rate. The feed rate of the solution played a decisive role in fiber formation.¹⁵ To keep the dynamic balance of the Taylor cone, there had to be a certain amount of polymer solution suspended at the tip of the nozzle.¹⁵ It was not feasible to form a Taylor cone when the feed rate is too low. An increase in the feed rate enlarged the solution amount spraying from the nozzle and reduced the electric force per unit volume. Consequently,

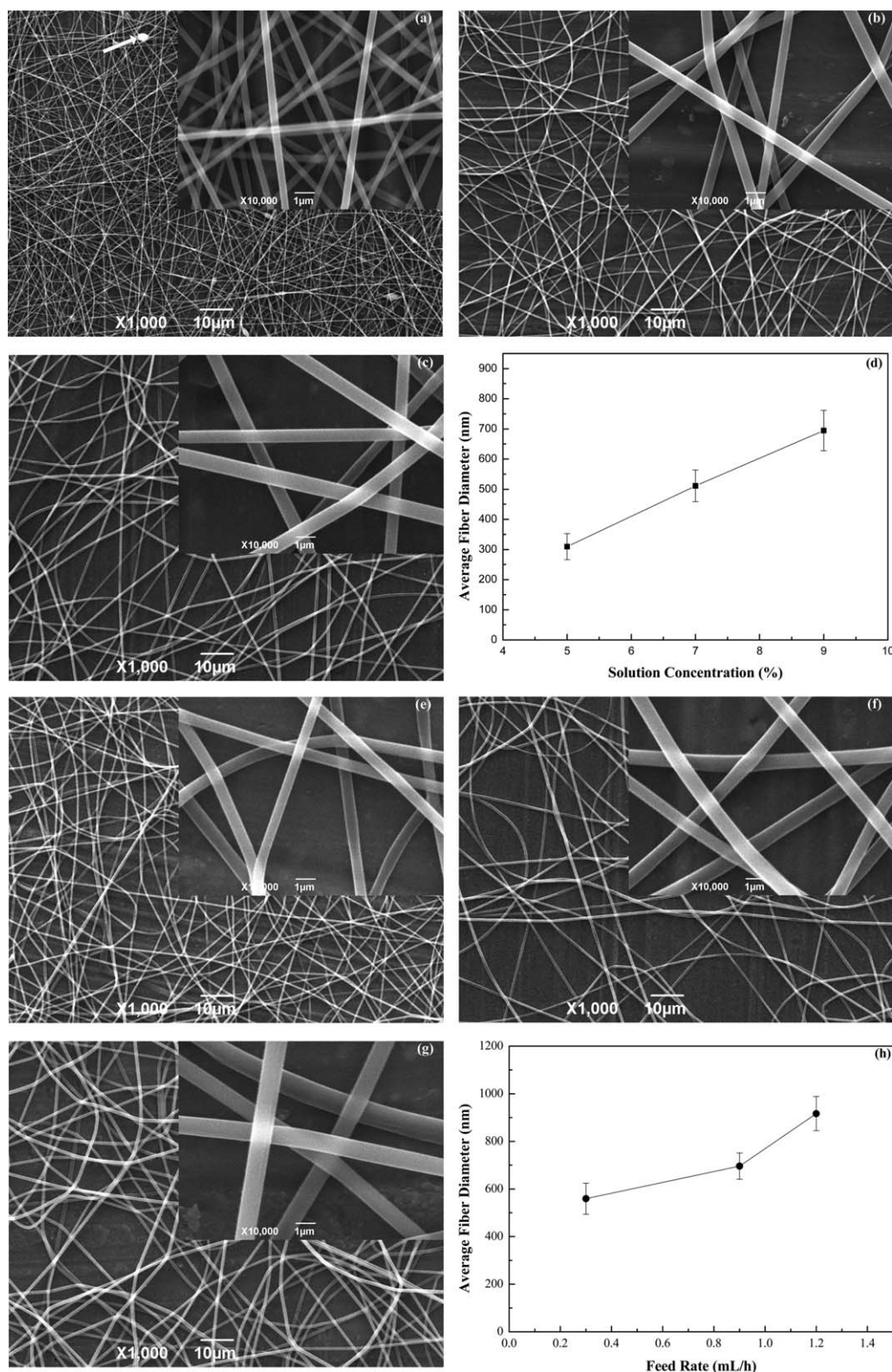


Figure 4. Morphologies of the fibers with solution concentrations of (a) 5, (b) 7, and (c) 9%. (d) Main effect of the solution concentration on the average fiber diameter (TCD = 9 cm, feed rate = 0.6 mL/h, and applied voltage = 12 kV). Morphologies of the fibers with feed rates of (e) 0.3, (f) 0.9, and (g) 1.2 mL/h. (h) Main effect of the feed rate on the average fiber diameter (TCD = 6 cm, solution concentration = 9%, and applied voltage = 14 kV).

the fiber became thicker with when the feed rate of the solution was improved. At a high solution concentration, increasing the feed rate had a visible impact on increasing the fiber diameter, whereas at a concentration of 5%, the fiber diameter was not remarkably changed when the feed rate was varied, as shown in Figure 3(e). Compared to the applied voltage and TCD, the fiber diameter was more responsive to the solution concentration and feed rate. It was demonstrated that there was only a relevant interactive term between the solution concentration and the feed rate in the fitted model [eq. (4)].

Main Effect Plots and Interaction Plot of the Factors on the Average Fiber Diameter

The p value (Table IV) suggested that the p value for terms related to the solution concentration ($p < 0.0001$) and the feed rate ($p < 0.0001$) had significant impacts on the average fiber diameter. It was shown that the only relevant interactive term existed in the regression model of the fiber diameter. Furthermore, the effects of these two factors on the average fiber diameter are shown in Figure 4. The paired-sample t test of variable solution concentration were performed ($p < 0.001$), and the values are shown in Table V; these values indicated that there were statistically significant differences in the variable solution concentration. The results of the paired-sample t test of different feed rates ($p < 0.001$ of all) are shown in Table VI; these results indicated that there were statistically significant differences in the variable feed rates. Notably, the average fiber diameter of PVP showed a remarkable elevation with increasing solution concentration and feed rate, as shown in Figure 4(d,h). In addition, continuous and uniform fibers with cylindrical structures and smooth surfaces were obtained in this study, as shown in Figure 4. However, few beads appeared when the solution was electrospun at a concentration of 5% [as marked by the white arrow in Figure 4(a)]. The uneven loading on the polymer jets from the electric field and inconsistencies in the molecular chain orientation explained this phenomenon. With a higher concentration, the entanglement of the molecular chain was enhanced, and the jets were uniformly stretched. Thus, fibers with no beads were obtained when the solution concentration was increased.

To this end, the interaction between the solution concentration and feed rate is illustrated in Figure 5. Notably, there was some

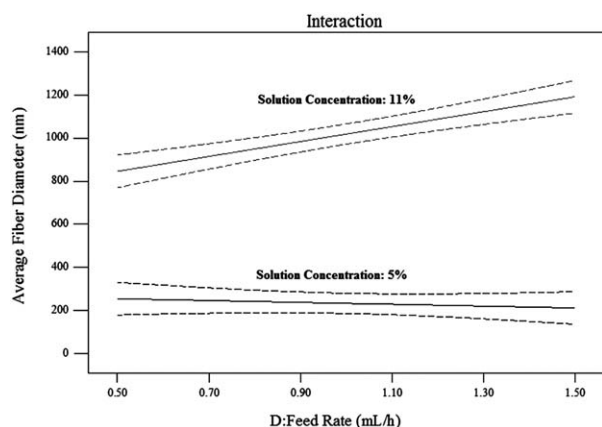


Figure 5. Interaction plots between the solution concentration and feed rate on the average fiber diameter.

interaction between these two factors. At a lower concentration of 5%, the feed rate had less influence on the average fiber diameter, although at a higher concentration of 11%, the average fiber diameter increased significantly when the feed rate was raised. It was reported that average fiber diameter is related to the solution concentration according to a power law relationship with an exponent of 3.^{11,52} Hartman et al.⁵⁵ discovered that the drop-jet diameter was proportional to the feed rate with power exponents of 0.48 or 0.33. This may explain why the average fiber diameter varied remarkably with the changing of feed rate at high solution concentrations. This result was similar to previous research on poly(D,L-lactide) solution¹⁷ and poly(vinyl chloride) solution,⁵¹ which suggested that when the solution concentration is higher, the effect of the applied voltage on the fiber diameter is greater.

CONCLUSIONS

The solubility parameter is especially important for the application of PVP. In this study, a novel method was proposed for predicting the solubility parameters of PVP, and it proved to be simple and useful. With the help of the group contribution method, the solubility parameters of PVP calculated were $\delta_d = 18.8 \text{ MPa}^{0.5}$, $\delta_h = 13.4 \text{ MPa}^{0.5}$, $\delta_p = 7.5 \text{ MPa}^{0.5}$, and $\delta = 24.3 \text{ MPa}^{0.5}$. Ethanol was chosen as the solvent for PVP in electrospinning because its solubility parameter was close to that of PVP. RSM was introduced to investigate the relationship between the processing parameters coupled with the solution concentration and fiber diameter. The response of RSM showed that the solution concentration and feed rate had significant impacts on the fiber diameter. The solution concentration and feed rate both enlarged the fiber diameter. The predicted fiber diameters of the regression model were in good agreement with the experimental values. The response regression model was proven to be an effective way to obtain fibers with predictable diameters. In summary, a new method was established for calculating the solubility parameter of PVP, and a systematic investigation on the electrospinning parameters was conducted with RSM.

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