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Investigation on the Effect of Process Variables on Polyurethane Nanofibre Diameter Using a Factorial Design

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Abstract
In this study, a factorial experimental design was used to study the effects of process parameters on nanofibre diameters, the voltage applied and the distance from the tip to collector. Nanofibres were produced using 10% concentration solution of polyurethane-tetrahydrofuran. The effects of solution parameters on the diameters of nanofibres are known. However, there has not been common agreement on the effect of the voltage applied on the diameter of nanofibres. A 32 factorial design was applied to identify the main and two-factor interaction effects. Analysis of the results from the design show that the distance and voltage applied had significant effects on polyurethane nanofibre diameter. It was found that for the main effect the distance from the tip to collector exhibits a great influence on the fibre diameter. The results also showed that the two-factor interaction effect significantly influenced the fibre diameter.

Key words: *nanofibers, polyurethane, electrospinning, process parameters, experiment design.*

Introduction

Polymer nanofibres exhibit superior properties that make them an ideal material for the development of tissue engineering scaffolds, filtration devices, sensors, and high strength lightweight materials. Electrospinning produces polymer fibres of a diameter in the range of nanometers to micrometers in size [1, 2]. In the literature there are studies that reported on the successful electrospinning of polyurethane solutions [1, 3].

Having information about the relative effects of process parameters on fibre diameter should be useful for process control and the prediction of electrospun fibre production. Many variables that influence the process, including the polymer type, molecular weight, solvent systems, additives, polymer concentration, solution properties, electric field , solution feed rate, nozzle diameter, distance from the nozzle to collector, and ambient conditions, may effect nanofibre diameter. Beachley et al. explored the effect of different electrospinning parameters on maximum fibre length [2]. Thompson et al. investigated the effects of 13 material and operating parameters on electrospun fibre diameters [4]. Chowdhury et al. produced nylon 6 nanofibres with a diameter ranging from 150 nm to 1300 nm by the electrospinning process [5, 6]. Liu et al. studied the effect of molecular weight, flow rate, voltage, and composition on the properties of PLGA nanofibres [7]. Gemci et al. reported that voltage had an important effect on fibre diameter [8]. Kilic et al. investigated the effect of polarity on nanofibre production efficiency [9]. Heikkila et al. evaluated the importance of different parameters in the multi-nozzle electrospinning of polyamide-6 [10]. Theron et al. measured the physical parameters for a number of polymer solutions [11].

Because of interaction between parameters, investigating of the effect thereof on nanofibres is really important and difficult [12]. The factorial design can be used to analyse the data and determine the significant interactions and their effect [13]. Processing variables involved in the process have a great effect on the properties of electrospun nanofibre.

It is known that the type of polymer solution is of great significance, the effect of which on the morphologies of nanofibres is reported by Cengiz et al. [14]. However there are conflicting results about the effect of voltage on electrospun fibre morphology [15]. Thus we obtained nanofibres by using the same solution concentration and investigated the effects of process parameters on the fibre morphologies. The aims of this study were to obtain polyurethane nanofibres and investigate the effects of process parameters on the nanofibre diameter using factorial design.

Experimental

Materials and methods

The thermoplastic polyurethane (PU, 270000 g/mol) was supplied from Coim Co. It was chosen due to its superior mechanical properties for future applications. Tetrahydrofuran (THF, Aldrich, analytical) was used as a solvent. For preparing electrospinning solutions, polyurethane was dissolved in THF. The PU:THF was 10:100 (w/w). The electrospinning apparatus consisted of a syringe pump, a high-voltage direct current (DC) power supplier generating positive DC voltage up to 30 kV and a grounded collector that was covered with aluminum foil (Gamma power supply). The solution was loaded into a syringe and a positive

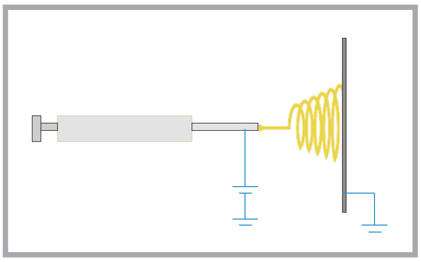

Figure 1. Electrospinning setup.

Table 1. Factors and factor levels.

Factor	Level		
	1	2	3
Applied voltage, kV	10	15	20
Distance, cm	5	7.5	10

electrode was clipped onto the syringe metal needle, having an outer diameter of 1.2 mm. The feeding rate of the polymer solution was controlled by a syringe pump (Goldman) and the solutions were electrospun onto the collector (***Figure 1***). The syringe pump was set at a volume flow rate of 2 ml/h. All solution preparations and electrospinning were carried out at room temperature. A SEN-3000M model Mini-SEM was used to take nanofibre images. Adobe Acrobat X Pro was used for measuring nanofibre diameters, and 20 measurements were made to evaluate the mean diameters. Minitab 15 Statistical software was used for statistical analysis.

Experimental design

The multiple independent variables involved in electrospinning suggest factorial design experiments. In this work two prosess variables, which are expected to have a significant effect on the nanofibre diameter, were considered. These variables are the applied voltage and the distance from the tip to the collector. Process variables were varied according to a 3^2 design. For each variable, a lower (1), a medium (2) and higher level (3) were chosen in the range to be studied (***Table 1***). The design was generated and the results were evaluated using Minitab 15 software.

Results and discussion

Table 2 shows the design matrix of experimental design and effect of the applied voltage and the tip to collector distance on nanofibre diameter. The experiments of a 3^2 factorial experimental design with two replicates (a total of 18 runs) are listed in the ***Table 2***. From these results, it can be seen that the diameter of fibres ranged from 538.4 to 1063 nm depending on the process conditions. ***Figures 2*** and ***3*** show the thinnest and the thickest fibres for the given PU solution and process parameters. The thinnest fibres are obtained at 15 kV and 10 cm of the distance. The thickest fibres are obtained at 10 kV and 7.5 cm of the distance.

Within this framework, the effect of the applied voltage, the distance and the interaction of these factors were investigated. Statistical analysis was used to study the influence of each prosess variable irrespective of/in combination with the other process variables on the diameter of nanofibre. A statistical method based on analysis of the variance was used to determine the statistical significance of effects and interactions comparing the mean square with an estimation of experimental error. ***Table 3*** shows the ANOVA analysis of the variables on the diameter of fibre. The data of the diameters of the nanofibres were used to do the ANOVA analysis. In the table, DF represent the degree of freedom of each factor and Seq SS is the sum of squares, f is the f-value of the f distribution, respectively.

Table 2. Design matrix of experimental design.

Exp.	Applied voltage	Distance	Diameter	St. Dev.
1	3	3	585.8	162,360
2	1	1	825.9	95,960
3	1	1	831.0	95,572
4	3	1	647.6	128,000
5	1	3	608.4	120,674
6	1	2	1023.3	151,542
7	2	3	541.2	116,866
8	3	2	780.4	128,146
9	3	2	823.9	113,966
10	1	2	1063.0	109,925
11	3	1	614.8	187,709
12	3	3	604.4	226,460
13	2	2	845.6	172,393
14	2	2	896.0	169,091
15	2	1	917.2	109,247
16	2	3	538.4	119,280
17	2	1	874.6	116,759
18	1	3	590.9	170,405

In this work, the effects and interactions with p-values (0.000) less than 0.05 indicate that they are significantly different from zero at the 95.0% confidence interval. R^2 is 98.99%, indicating that the fitting was excellent.

Based on the data collected in ***Table 2*** and ***3***, plots for the main effects of applied voltage and the distance on the diameter of nanofibres are presented in ***Figure 3***. ***Figure 3*** shows that the distance has greater impact on diameter than the voltage applied (Seq SS is 328.684 for distance and 66.784 for voltage). It is also illustrated in the figure that, when the distance changes from 5 cm to 10 cm, the effect of distance on diameter shows a positive trend in the beginning and reaches a peak at around 7.5 cm. After the second level of the distance the effect shows an opposite trend. The diameter of fibres firstly increases then decreases with increasing distance. Similar behavior was previously observed in the literature [2, 8].

Table 3. Analysis of variance (ANOVA) on the diameter of fibre.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Applied voltage	2	66784	66784	33392	62.71	0.000
Distance	2	328684	328684	164342	308.62	0.000
Applied voltage×Distance	4	75005	75005	18751	35.21	0.000
Error	9	4793	4793	533		
Total	17	475265				
S = 23.0762 R-Sq = 98.99% R-Sq(adj) = 98.10%						

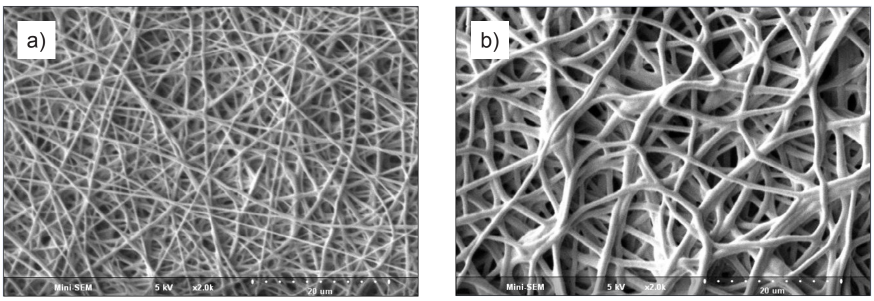

Figure 2. SEM images for the nanofibres of the minimum (a) and maximum (b) diameter (2000×).

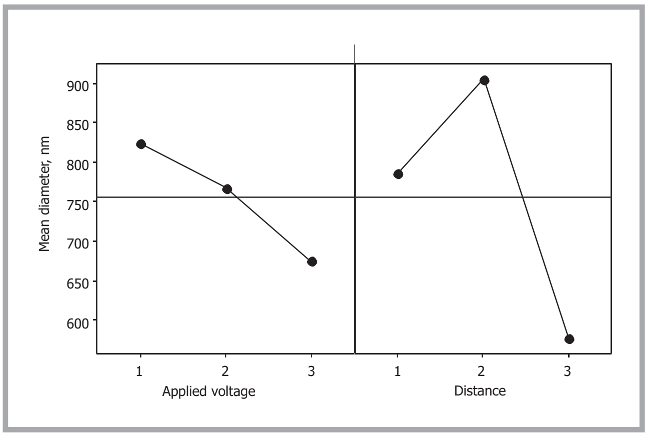

Figure 3. Main effects plot for fibres diameter.

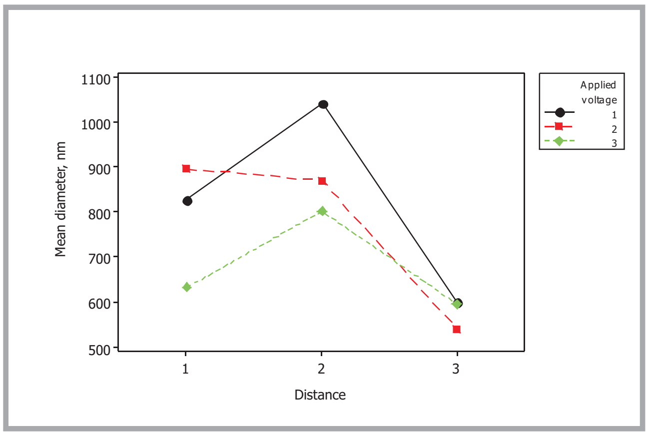

Figure 4. Interaction plot for fibre diameter.

When the voltage increases from 10 kV to 20 kV, the diameter decreases as shown in ***Figure 3*** and it can be observed from ***Table 2***. For example, for the first distance level the mean diameter is about 827 nm (Exp 2, 3) at the lowest voltage level and 632 nm (Exp 4, 11) at the highest voltage level.

This can be explained in that the higher voltage caused an increase in an electric field and electrical forces resulting in a thinner fibre. Voltage is considered the most essential parameter in electrospinning, because of the fact that it initiates the jetting and causes instabilities, which stretch the jet. The voltage determines the average strength of the electric field together with the distance between the nozzle and the collector. The distance affects on deposition time, evaporation rate of solvent and instability interval. An increase in voltage and thus, in electric field, was found mainly to decrease, but also increase the fibre diameter . In previous works, an increase in distance (decrease in field) has found to both increase and decrease the fibre diameters [10].

Significant interaction between the voltage and diameter can be seen from ***Figure 4***. The interaction plot suggests interactions as the lines are not parallel. It means the effect of distance on the fibre diameter is dependant on the applied voltage.

Conclusion

The type of polymer solution on the morphologies of the nanofibres is known. However there are conflicting results about the effect of voltage on electrospun fibre morphology. In this paper, a study of the effects of /selected processing variables, the applied voltage and the distance, on the diameter of polyurethane nanofibreis presented for the given polymer solution. These conclusions concern only polyurethane nanofibres produced from the solution in THF and the concentration of 10% wt for the given polymer. A 3^2 factorial experimental design is applied. From the design, it is proved that the distance and applied voltage have significant effects on the fibre diameter. An experimental and statistical studies show that fibre diameter depends on the applied voltage and distance, furthermore, the interaction of these factors affects fibre diameter significantly.

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