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ORIGINAL PAPER

Experimental design as a tool for the manufacturing of filtering media based on electrospun polyacrylonitrile/β-cyclodextrin fibers

D. Noreña-Caro · M. Alvarez-Láinez

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Abstract The aim of this work is the manufacturing of non-woven fabrics to be used as Filtering media. These fabrics were produced from polyacrilonitrile (PAN) and β-cyclodextrin (β-CD) solutions in dimethylsulfoxide using a horizontal electrospinning system with a flat collecting screen. The information from the experiments was statistically analyzed in order to define the process parameters (PAN concentration in solution, volumetric flow and applied voltage) needed for obtaining fibers with the smallest average diameters. First, PAN fibers were produced following a full factorial 3^3 experimental design and this information was used for preparing the corresponding Response Surfaces needed to define the best conditions for the production of PAN/β-CD nonwoven fabrics. The viscosity of the polymer solutions was analyzed using a rotational rheometer and a pseudoplastic behavior was observed, the diameter of the obtained nanofibers was determined using scanning electron microscopy. At the end, the polymer concentration (viscosity) and the volumetric flow rate were selected as the most statistically significant factors affecting the fiber diameter. Besides, uniform PAN and PAN/β-CD nanofibers with average fiber diameters between 200 and 500 nm were obtained.

Keywords Polyacrylonitrile · β-cyclodextrin · Electrospinning · Filtering media · Response surface

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1 Introduction

During the last years, the electrostatic spinning technique, commonly known as Electrospinning, has been gaining interest for the production of polymer fibers with average diameters under 500 nm. Polymer fibers of this size have promising applications in different areas such as biomedical engineering, environmental engineering and composite materials manufacturing [1]. Regarding the environmental protection applications, electrospun polymer fibers may be used in filtration operations as very thin non-woven fabrics with sheet caliper under 1 μm and average fiber diameters of 250 nm [2]. Generally, non-woven fabrics with these characteristics are able to capture very small particles with sizes under 0.5 μm (such as smog, diesel soot, tobacco smoke, viruses and small bacteria) due to their high surface to volume ratio and high surface cohesion they present [1,2].

For manufacturing electrospun fibers, the raw polymeric material should be able to flow through a capillary. This can be done by dissolving the polymer in an adequate solvent or by melting the polymer. Although melt electrsopinning is preferred when it is difficult to dissolve the polymer, and if it is desirable to avoid the use of toxic solvents [3–5], the most common way for manufacturing electrospun polymer fibers is by preparing a polymer-solvent solution.

The most basic electrospinning array is composed by a capillary (commonly a syringe needle or spinneret) containing the polymer solution, a flat collecting metallic screen and a direct current (DC) voltage supply. With these components, an electrostatic field can be generated between the needle tip and the grounded screen. When a droplet of polymer solution is located at the tip of the needle and the electric field overcomes the surface tension and viscosity forces of

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the solution, the polymer fiber is formed from an electrically charged jet coming out of an elongated conic droplet of fluid (known as Taylor cone) generated by the electrostatic attraction between the surface charges of the polymer solution molecules and the collector. The recently formed fiber then travels to the screen, and during its path, the jet is looped, the fiber is stretched while its diameter is reduced, and the solvent is evaporated. At the end of the process, the fiber reaches the grounded target and a circular non-woven fabric is formed on the aluminum foil wrapped collecting screen [6,7].

As it may be inferred from the aforementioned information, the electrospinning process is affected by several factors. These factors are classified as polymer solution variables (polymer concentration and molecular weight, viscosity, conductivity and surface tension), process variables (applied voltage, tip to collector distance, flow rate and shape of collector) and environmental variables (temperature and relative humidity) [8]. Because a successful electrospinning process requires a delicate balance of forces for stable fiber formation regime, and due to the complex interrelationships among factors affecting the process, experimental design is a common method used for the optimization of variables affecting the fiber manufacturing process [9].

To define the appropriate levels for the factors or variables to be evaluated in the design of experiments, an interaction between the operator (human) and the electrospinning setup is necessary. In other words, if a well formed electrospun fiber fabric (product) is desired for evaluating its morphology (fiber diameter and appearance), a region of stable electrospinning should be defined. Therefore, it is necessary to establish the values or intervals of the solution, process and environmental variables under observation for which the fiber formation process is conducted with minor failures and interruptions. To manufacture well defined fibers, an interaction between the product (polymer fiber fabric) and its environment (variables) are needed. Therefore, experimental design method involves an Interactive Design approach [10].

The experimental design has been used as a tool for the manufacturing of PAN [11,12] and polyvinyl alcohol (PVA) fibers [13]. The aforementioned works present the statistical analysis of the information and the response surfaces or contours for the average diameter of fibers depending on different factors. Regarding PAN fibers, solutions of PAN in dimethylformamide (DMF) are used for the electrostatic spinning process and the effects of polymer concentration, applied voltage and tip to collector distance on the average fiber diameter are evaluated (flow rate is fixed) [11,12]. The results of both works are very similar, and while one of them presents that PAN electrospun fibers with diameters under 100 nm may be produced with low concentration polymer solutions (8–10 % w/v), applied voltages between 10 and 20 kV ant tip to collector distances between 10 and 12 cm [11], the other one shows that PAN fibers with diameters around 120 nm may be produced with 10 % w/v polymer solutions, 12 kV of applied voltage and tip to collector distance of 12 cm [12].

In the case of PVA fibers, it was accomplished a complete statistical analysis of the electrospinning process considering the effects of polymer concentration, applied voltage, tip to collector distance and flow rate on fiber diameter [13]. The number of treatments presented is very large (96) and diverse conclusions about the effects of factors on fiber diameter are presented. This provided a more complete understanding of the manufacturing parameters of PVA fibers.

Most of the published articles regarding PAN electrospinning describe the use of DMF as solvent for the polymer solution. However this solvent is generally recognized as toxic and carcinogenic [14]. For this reason, it is desirable to evaluate the manufacturing process of electrospun fibers using a safer solvent such as dimethylsulfoxide (DMSO) which has successfully been used for the electrospinning of PAN in some other works [15–19].

With regard to the manufacturing materials, polyacrylonitrile (PAN) is a well-known polymer with good mechanical and stability properties. Even though acrylic fibers are more brittle and less flexible than commonly used polyethylene and polypropylene fibers, they have better temperature resistance properties (high crystalline melting of 317 °C), good chemical resistance to acids and soft bases, and particularly good resistance to outdoor exposure, sunlight and microorganisms. Because of this, PAN fibers are commonly used materials for the manufacturing of filtering media designed for corrosive environments [2,20].

On the other hand, β-cyclodextrin (β-CD) is a toroid shape cyclic oligosaccharide consisting of seven units of 1,4-linked glucopyranosides (see Fig. 1) which can form host-guest complexes with organic molecules (e.g. aromatic pollutants) due to its internal hydrophobic cavity [21]. Even though the β-CD molecule has traditionally been used in pharmaceuticals, foods, cosmetics and chemical products, it has gained special attention as functional additive that can trap molecules and improve the efficiency of filtering media based on electrospun fibers with high surface area [22–24].

The objective of the work described in this paper is using an experimental design approach for establishing the conditions to manufacture PAN and PAN/β-CD electrospun fibers with the lowest possible average diameters using DMSO as polymer solvent. In that vein, the design of experiments is proposed to identify the effects of polymer concentration, flow rate and applied voltage on average fiber diameter.

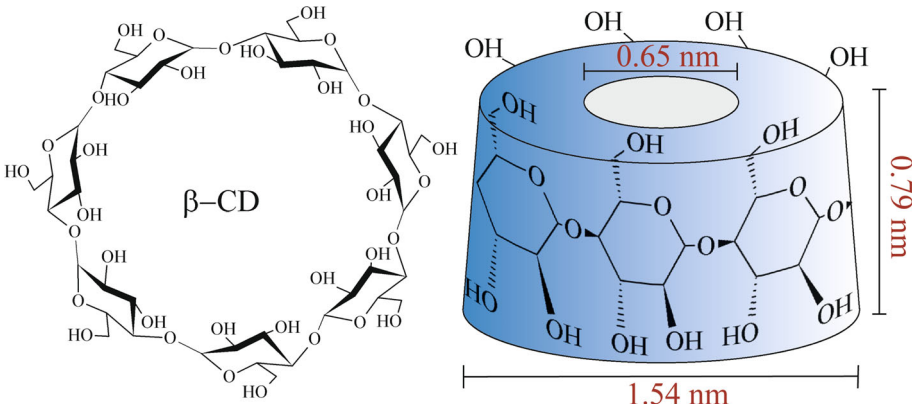

Fig. 1 Molecular structure and dimensions of β-cyclodextrin

2 Materials and methods

2.1 Materials

Polyacrylonitrile (PAN) powder with a molecular weight of 150.000 g/mole was purchased from Scientific Polymer Products Inc. (Ontario, NY, United States) and β-cyclodextrin powder (Cavamax W7-β-CD) was kindly provided by Wacker Chemie AG (Munich, Germany). For the preparation of polymer solutions, it was used Dimethylsolfoxide (DMSO) 99.9 % pure manufactured by Carlo Erba Reagents (Rodano, MI, Italy). The materials were used as received without further purification.

2.2 Solution preparation

PAN/DMSO and PAN/β-CD/DMSO polymer solutions were prepared in glass flasks by adding measured amounts of the mentioned materials to the DMSO solvent. After manual mixing, solutions were subjected to magnetic stirring at 500 rpm during 15 h for obtaining homogeneous mixtures. In order to enhance the dissolution of polymer and cyclodextrin in DMSO, the medium was heated for 1 h at 50 °C at the beginning of the mixing process. The flasks were sealed with polyethylene and aluminum foil during the time they were under agitation. After the mixture preparation time, the solutions were used immediately for Electrospinning.

2.3 Polymer solutions characterization

2.3.1 Conductivity of polymer solutions

Solution conductivity of PAN/DMSO and PAN/β-CD/DMSO polymer solutions was measured using a PC700 Oakton electrical conductivitymeter (Vernon Hills, Illinois, USA). Measurements were carried out <2 h after finishing the solution preparation stage. Registered conductivity data were the average of two measurements per solution.

2.3.2 Rheometry of polymer solutions

In order to observe the rheological behavior of PAN/DMSO and PAN/β-CD/DMSO polymer solutions, samples of these materials were subjected to rotational rheometry (Discovery Hybrid Rheometer, TA Instruments, New Castle, DE, United States). The assembly used consisted of a Peltier plate and a plane circular geometry. The rheological analysis was carried out at 25 °C and the flow sweeps were conducted at shear rates between 0.1 and 700 s^{-1}. In order to predict fluid viscosities at different shear rates between the range of the flow sweeps, the rheometry results for each polymer solution were fitted to the modified Carreau model proposed by Menges, Wortberg and Michaeli [24] (Eq. 1) where shear rate (γ) dependent viscosity (η) is described by the coefficients A (null viscosity), B (Inverse of the shear rate in the transition zone) and n (log–log slope of the pseudoplastic zone).

$$\eta(\dot{\gamma}) = \frac{A}{(1 + B\dot{\gamma})^{1-n}} \tag{1}$$

2.4 Electrospinning setup

The production of electrospun PAN and PAN/β-CD nonwoven fabrics was conducted in a horizontal electrospinning array consisting of a controlled flow syringe pump (Cole Parmer, Venon Hills, IL, United States), a 20 ml glass syringe connected to a stainless steel needle (0.603 mm nominal ID - 20G), a high voltage DC supply model EQ-30P1 (Matsusada Precision Inc, Kusatsu, Shiga, Japan) and a flat rectangular collecting screen wrapped with aluminum foil. In order to generate the electrical field for the fiber formation, the positive pole of the high voltage DC supply was connected to the tip of the metallic needle and the negative (ground) electrode was connected to the rectangular flat screen (21 cm × 21 cm). A schematic draw of the Electrospinning setup is presented on Fig. 2.

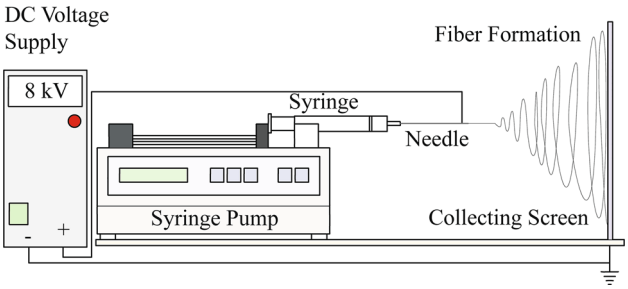

Fig. 2 Diagram of horizontal electrospinning setup

2.5 Fiber fabrication methodology

The PAN and PAN/β-CD solutions were electrospun at room temperature (22 °C) and humidity (55 %). Because the fiber manufacturing process by electrospinning is affected by several factors, the factorial experimental design is ideal for evaluating all the possible combinations among levels of selected factors [26]. Considering this, the manufacturing of fibers was conducted following full factorial experimental designs (3^3 factorial designs for PAN/DMSO solutions and 3^2 factorial designs for PAN/β-CD/DMSO), and the effects of the different factors on the average fiber diameter were evaluated at the same time. The experimental approach was divided in two stages. In the first stage, only PAN/DMSO solutions were electrospun and the process conditions needed for a stable production of PAN fiber with the smallest mean fiber diameter were defined. In a second stage, PAN/β-CD/DMSO solution was electrospun. During the experiments, the tip to collector distance was kept fixed at 10 cm. For the 3^3 factorial design (27 treatments), PAN concentration in solution (5, 7, 9 % w/w), volumetric flow rate (0.5, 0.7, 1.0 ml/h) and applied voltage (7.5, 8.0 and 8.5 kV) were evaluated as independent variables. For the 3^2 factorial design (9 treatments), the concentration of the PAN/β-CD/DMSO solution was fixed at 5 %, the amount of β-CD was kept constant (20 % w/w based on PAN concentration) and volumetric flow rate (0.5, 0.7, 1.0 ml/h) and applied voltage (7.5, 8.0 and 8.5 kV) were varied. Table 1 summarizes coded variables for the Electrospinning of PAN/DMSO and PAN/β-CD/DMSO solutions.

2.6 Fiber characterization methodology

PAN and PAN/β-CD fibers morphology was analyzed using Scanning Electron Microscopy (SEM) in a Phenom World G2 PRO Model Microscope (PhenomWorld, Eindhoven, Netherlands). Samples were observed after gold metallization and three pictures of each treatment were taken for further image analysis. Using the Image J software, the diameter of thirty fibers per picture was measured in order to obtain ninety fiber diameter data per treatment.

Diameter data for each treatment were used to calculate the average fiber diameter and the standard deviation (See Table 2). This information was also used for preparing fiber diameter distribution histograms and fiber diameter box-plots.

2.7 Statistical modelling

The full factorial 3^3 and 3^2 experimental designs considered in this work allow the adjustment of results to a second order polynomial model which was analyzed using the R Project software. Considering the main effects and interactions among factors (two and three factors) the polynomial equations of the empiric model for the Average Fiber Diameter of electrospun fibers from PAN/DMSO (Y1) and PAN/β-CD/DMSO (Y2) solutions may be written as shown in Eqs. 2 and 3. Note that coefficients β and γ correspond to empirical values obtained from the regression.

$$Y_1 = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3 \quad (2)$$

$$Y_2 = \gamma_o + \gamma_2 X_2 + \gamma_3 X_3 + \gamma_{22} X_2^2 + \gamma_{33} X_3^2 + \gamma_{23} X_2 X_3 \quad (3)$$

In order to have a good regression fit to the equation, it was necessary to assure that all the obtained non-woven fabrics were composed by fibers. For that reason, the levels of the three evaluated factors (PAN concentration, flow rate and applied voltage) were carefully chosen by testing operating conditions for a stable and reliable process.

Besides the construction of the ANOVA table and the Pareto charts for the selection of statistically significant fac-

Table 1 Coded variables for the electrospinning of PAN/DMSO and PAN/β-CD/DMSO solutions

Tip to collector distance 10 cm
5 % w/w PAN, 1 % w/w β-CD (20 % β-CD based on PAN)

Variable	Description	Coded variable level		
		Low	Center	High
X_1	PAN concent. (% w/w)	5 % (−1)	7 % (0)	9 % (+1)
X_2	Flow rate (ml/h)	0.5 (−1)	0.7 (−0.2)	0.9 (+1)
X_3	Applied voltage (kV)	7.5 (−1)	8.0 (0)	8.5 (+1)

Table 2 Observation table for the electrospinning of PAN/DMSO and PAN/β-CD/DMSO solutions

Treatment	X_1	X_2	X_3	AFD (nm)	SD (nm)
PAN/DMSO solutions					
1	−1	+1	−1	182.59	31.21
2	−1	+1	0	193.59	31.98
3	−1	+1	+1	193.10	37.04
4	−1	−0.2	−1	196.89	35.59
5	−1	−0.2	0	203.01	35.82
6	−1	−0.2	+1	256.36	43.08
7	−1	−1	−1	222.76	37.69
8	−1	−1	0	202.15	32.69
9	−1	−1	+1	253.21	40.72
10	0	+1	−1	304.42	55.01
11	0	+1	0	372.35	48.45
12	0	+1	+1	321.24	47.16
13	0	−0.2	−1	294.37	51.21
14	0	−0.2	0	320.51	41.70
15	0	−0.2	+1	349.00	59.41
16	0	−1	−1	351.20	99.40
17	0	−1	0	331.52	43.53
18	0	−1	+1	344.42	43.62
19	+1	+1	−1	410.49	57.86
20	+1	+1	0	408.75	42.81
21	+1	+1	+1	418.18	62.94
22	+1	−0.2	−1	436.33	72.18
23	+1	−0.2	0	456.56	48.67
24	+1	−0.2	+1	438.23	50.52
25	+1	−1	−1	479.42	53.37
26	+1	−1	0	475.65	44.29
27	+1	−1	+1	479.80	45.31
PAN/β-CD/DMSO solution					
1	−1	+1	−1	213.67	39.64
2	−1	+1	0	231.76	32.39
3	−1	+1	+1	267.48	44.72
4	−1	−0.2	−1	232.12	30.79
5	−1	−0.2	0	229.18	36.64
6	−1	−0.2	+1	253.85	40.32
7	−1	−1	−1	270.99	38.39
8	−1	−1	0	261.54	39.03
9	−1	−1	+1	264.45	53.79

AFD Average fiber diameter, *SD* standard deviation

tors and interactions, the experimental information for the model was tested for the basic three assumptions for reliable multivariable regression.

1. Normality of the data, which analysis was done by Normal probability plots of residuals.
2. Independence of the data, which could be analyzed by comparing Residuals versus Run Order.
3. Constant variance of the data, which could be analyzed by comparing Residuals versus Fitted Values.

3 Results and discussion

3.1 Polymer solutions characterization

3.1.1 Conductivity of PAN/DMSO and PAN/β-CD/ DMSO solutions

Table 3 shows how polymer solution conductivity increases when higher amounts of PAN are added. Although the conductivity of more concentrated PAN solutions is higher, the difference between PAN 9 % and PAN 7 % conductivity is smaller than the conductivity difference between PAN 7 % and PAN 5 % solutions. This indicates that the charges in the mixtures are interacting and saturating the system. Therefore, adding more polymer will not necessarily increase the conductivity of the medium. The addition of β-CD to the PAN/DMSO solution did not increase the conductivity and this is contrary to what was expected.

3.1.2 Rheometry of PAN/DMSO and PAN/β-CD/DMSO solutions

Flow sweeps of the four different solutions used for Electrospinning are presented in Fig. 3 and Table 3, which summarizes the results of the fitting process to the modified Carreau model. It can be seen how viscosity changes when PAN concentration and shear rate are increased. For all the solutions, the flat viscosity region can be seen between 0.1 and 70 s^{-1} shear rates.

Considering the B coefficients of the Carreau model presented in Table 3, transition to pseudoplastic zone occurs at 70.64 s^{-1} for the PAN/DMSO 5 % (w/w) solution, while this change appears at 164.84, 397.95 and 85.08 s^{-1} shear rates for PAN/β-CD/DMSO 5 % (w/w), PAN/DMSO 7 % (w/w) and PAN/DMSO 9 % (w/w) solutions respectively. Taking into account the inner diameter of the needle and the different flow rates evaluated during the experiments, the apparent shear rates applied to polymer solutions during the electrospinning process vary between 6.44 s^{-1} (0.5 ml/h) and 12.88 s^{-1} (1.0 ml/h). The effect of the addition of β-CD on the viscosity of 5 % (w/w) PAN polymer solution can also be seen by comparing the information on Table 3 (Null Viscosity and estimated viscosities at different apparent shear rates). As it is expected when adding more solids to the DMSO solvent, the solution viscosity is 8 % more viscous compared to the solution without β-CD, and this change may be significant for the average fiber diameter of the electrospun fibers

Table 3 Properties of PAN/DMSO and PAN/β-CD/DMSO solutions

Polymer solution	Conductivity (μS/cm)	Carreau model coefficients[a]			Estimated solution viscosities[b]		
		A (Pa.s)	B (s)	*n*	η (6.44 s^{-1})	η (9.02 s^{-1})	η (12.88 s^{-1})
PAN/DMSO 5 % (w/w)	42.3	0.2179	0.0142	0.8938	0.2159	0.2151	0.2141
PAN/DMSO 5 % (w/w)–(20 %β-CD)	40.7	0.2343	0.0061	0.8907	0.2333	0.2330	0.2324
PAN/DMSO 7 % (w/w)	51.4	0.7739	0.0025	0.5979	0.7689	0.7660	0.7641
PAN/DMSO 9 % (w/w)	56.5	1.3206	0.0118	0.7405	1.2958	1.2865	1.2731

[a] A: nule viscosity, B: inverse of transition shear rate, n: power law index (pseudoplastic region)
[b] Estimated viscosities at 25 °C and apparent shear rates for 0.5, 0.7 and 1.0 ml/h flow rates

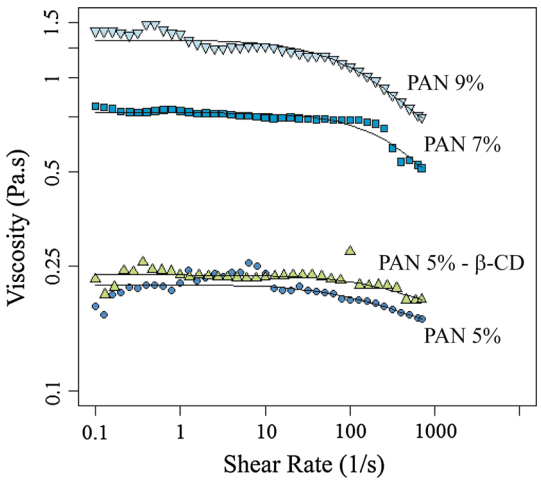

Fig. 3 Flow sweeps for PAN/DMSO and PAN/β-CD/DMSO solutions

even when the addition of β-CD in the solution did not show any increase in conductivity. As it is shown in Table 3, polymer solution viscosity decreases with an increasing apparent shear rate. Although, the viscosity change is small and it can be said that the fiber manufacturing process is carried out with chiefly Newtonian solutions of PAN and PAN/β-CD in DMSO, the power law index (n) indicates that this newtonian behavior is more pronounced for the less concentrated (5 % (w/w) PAN) polymer solutions which n index is closer to 1. For 7 % (w/w) PAN and 9 % (w/w) PAN solutions in DMSO, the pseudoplastic behavior is more pronounced and the n index is decreased.

3.2 Electrospinning of PAN fibers

The analysis of variance (ANOVA) for the 3^3 experimental design considered for the manufacturing of PAN fibers is summarized in Table 4. The information from this table is complemented by the pareto chart on Fig. 4. Considering the *p* values and the standardized effects from Table 4, it can be said that PAN concentration and flow rate are the most statistically significant factors affecting the average fiber diameter of electrospun PAN fibers. While the mean diameter increases with the polymer concentration, it is decreased when the flow rate increases.

The polymer concentration is by far the most important variable affecting the fiber diameter in the Electrospinning process of PAN fibers under the tested conditions. In this case, the *p* value of this factor is very small and its standardized effect on the pareto chart (*t* value) is very high with respect to the other factors and interactions. The diameter increasing effect of concentration is coherent with the results from reference works ([11,12]) and it can be explained taking into account that the droplets of more concentrated solutions contain a higher amount of polymer and the electrospun fibers originated from the Taylor cone at the droplet are thicker.

The flow rate presented the second most significant effect on fiber diameter as shown in the pareto chart on Fig. 4 (the flow rate standardized effect is higher than the critic *t* value for 95 % confidence but much lower than the standardized effect of polymer concentration). In this case, it can be said that the average fiber diameter is reduced while the volumetric flow rate is increased. The inverse relationship between flow rate and fiber diameter is opposite to what it was expected and it is also contrary to the results presented by other authors [13,27]. In this case, the small reduction on fiber diameter observed with increasing flow rate may be related to the slight viscosity reduction of the solutions at higher shear rates levels (see Table 3). When the solutions have lower viscosity, the polymer molecules are less entangled and they are more susceptible to be stretched by the charges on the jet [28].

The third most important factor affecting the Electrospinning process is voltage. Despite this variable is not as significant as concentration and flow rate for the evaluated levels (7.5–8.5 kV) and its standardized effect on the pareto chart is slightly lower than the critic *t* value for a 95 % confidence, it could be mentioned that the average fiber diameter increases with increasing voltage. This could be related to the generation of additional surface charge on polymer, making it more susceptible to acceleration under electrical forces, leaving

Table 4 ANOVA table

Source	Sum of squares	Deg. of freedom	Mean square	*t* value	*p* value	
Intercept	254,409.89	10	25,440.99	27.943	5.24E-15	Significant
X_1-concentration	244,940.40	1	244,940.40	21.906	2.34E-13	Significant
X_2-flow rate	6,065.46	1	6,065.46	−3.525	0.0028	Significant
X_3-app. voltage	1,702.71	1	1,702.71	1.833	0.0855	
X_1^2	93.33	1	93.33	0.431	0.6724	
X_2^2	218.73	1	218.73	0.659	0.5191	
X_3^2	0.28	1	0.28	0.023	0.9816	
X_1X_2	574.94	1	574.94	−1.069	0.3009	
X_1X_3	681.91	1	681.91	−1.119	0.2797	
X_2X_3	0.24	1	0.24	−0.007	0.9945	
$X_1X_2X_3$	132.09	1	132.09	0.512	0.6154	
Residual	8,050.12	16	503.13			
Total	262,460.01	26				

Response surface quadratic model for AFD of electrospun PAN fibers
Multiple R^2: 0.9693. Adjusted R^2: 0.9502
AFD Average fiber diameter

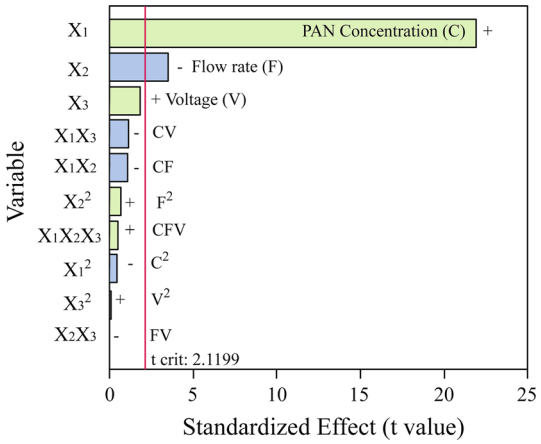

Fig. 4 Pareto chart. Statistically significant variables from the quadratic model for the electrospinning of PAN fibers in DMSO

less remaining time for fiber elongation and diameter reduction.

In order to prove the reliability of the quadratic model describing the electrospinning process, the normality, independence and constant variance tests for the multivariable regression were conducted (plots not shown). In the first place, regarding the normal probability plot, it could be seen how the experimental data were approximately normally distributed as needed. Secondly, the independent of experimental data was checked because model residuals for each run were randomly distributed. For the constant variance test, it was verified how standardized residuals compared to fitted values and distributed randomly.

After reviewing the Analysis of Variance results and checking the reliability of the empirical quadratic model for average fiber diameter of electrospun PAN fibers (Y_1), the polynomial presented by Eq. 4 was used to prepare the response surfaces and contours displayed on Fig. 5. It is worth mentioning that the circles shown on the response surfaces correspond to experimental data and they are located this way in order to indicate graphically how the regression equation (Eq. 4) fits the empirical observations.

$$\begin{aligned} Y_1 = {} & 326.42 + 116.19X_1 - 18.64X_2 + 9.72X_3 \\ & -3.94X_1^2 + 6.33X_2^2 + 0.21X_3^2 - 6.88X_1X_2 \\ & -7.27X_1X_3 - 0.04X_2X_3 + 4.04X_1X_2X_3 \end{aligned} \quad (4)$$

Response surfaces and contours presented on Fig. 5 summarize the results obtained during the manufacturing of PAN and PAN/β-CD fibers. Fig. 5a (response surface) and b (contour plot) show the change in fiber diameter when 5 % w/w PAN/DMSO solution is electrospun at different flow rates and voltages. Based on the analysis of variance and the pareto chart previously described, in order to obtain the thinnest PAN fibers, solutions with the lowest possible polymer concentration should be electrospun. Considering the information from Fig. 5a and b, the Electrospinning of PAN/DMSO solutions should be conducted with applied voltages between 7.5 and 8.0 kV and programmed flow rates from 0.7 to 1.0 ml/h, so that PAN fibers with average diameters from 180 to 200 nm are obtained.

Figure 5e and f display the average fiber diameter change when solutions of PAN/DMSO with polymer concentrations between 5 and 9 % w/w are subjected to Electrospinning at 8.0 kV with volumetric flow rates from 0.5 to 1.0 ml/h. In the same way, Fig. 5g and h present how the average fiber diameter is modified when PAN/DMSO solutions (5–9 % w/w) are

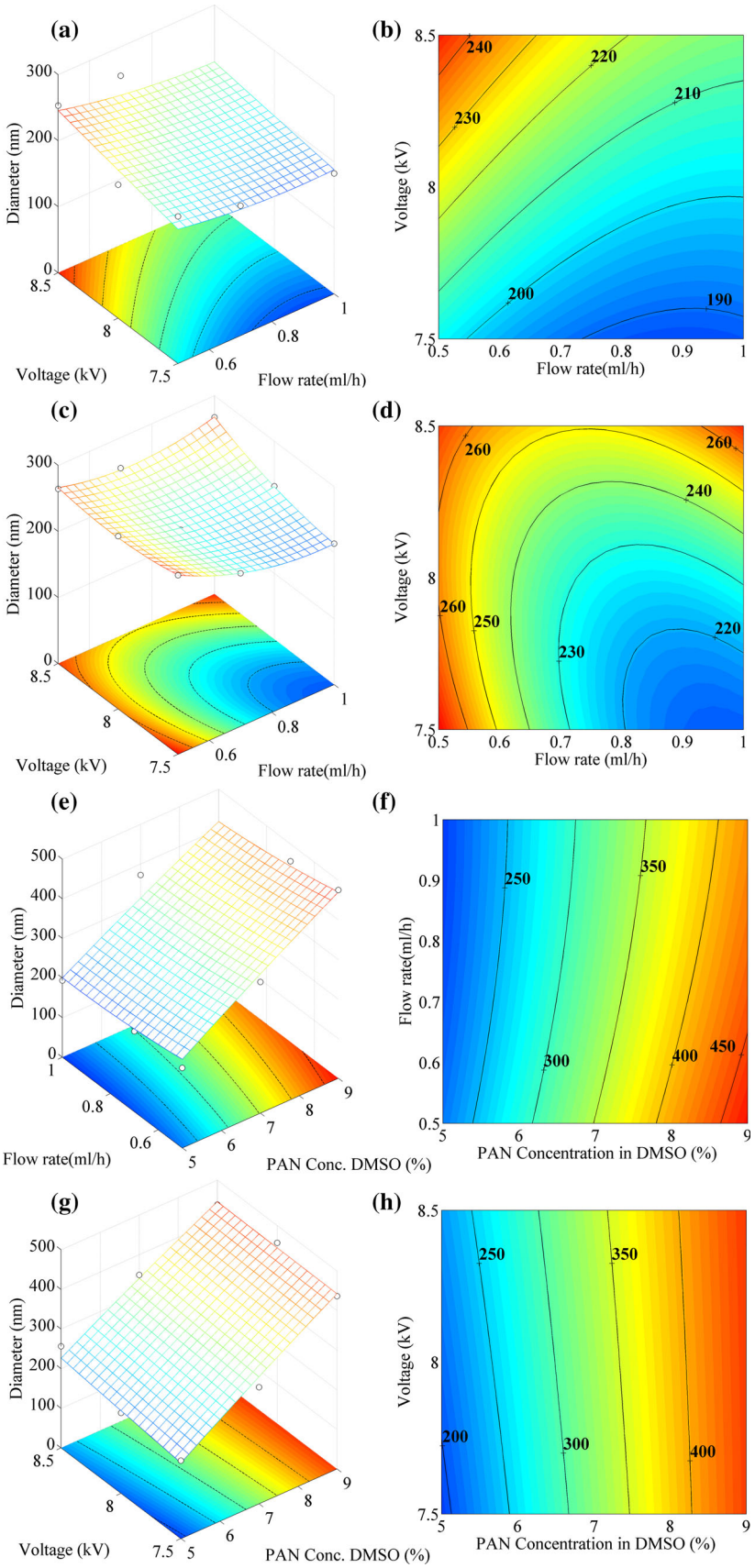

Fig. 5 Response surfaces and contours for polymer fiber manufacturing: **a**, **b** electrospinning of PAN fibers from 5 % (w/w) solutions in DMSO; **c**, **d** electrospinning of PAN/β-CD fibers from 5 % (w/w) solutions in DMSO; **e**, **f** electrospinning of PAN fibers at an applied Voltage of 8 kV; **g**, **h** electrospinning of PAN fibers at a flow rate of 0.7 ml/h

Table 5 ANOVA table

Source	Sum of squares	Deg. of freedom	Mean square	*t* value	*p* value	
Intercept	3,413.51	5	682.70	101.743	2.09E-6	Significant
X_2-flow rate	1,020.40	1	1,020.40	−11.752	0.0013	Significant
X_3-app. voltage	793.44	1	793.44	10.447	0.0019	Significant
X_2^2	509.34	1	509.34	7.728	0.0020	Significant
X_3^2	184.40	1	184.40	4.650	0.0045	Significant
X_2X_3	905.94	1	905.94	10.306	0.0188	Significant
Residual	25.59	3	8.53			
Total	3,439.10	8				

Response surface quadratic model for AFD of electrospun PAN/β-CD fibers
Multiple R^2: 0.9926. Adjusted R^2: 0.9802
AFD Average fiber diameter

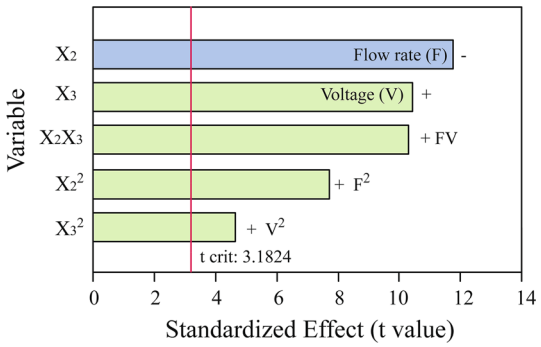

Fig. 6 Pareto chart. Statistically significant variables from the quadratic model for the electrospinning of PAN/β-CD fibers

electrospun applying voltages between 7.5 and 8.5 kV with a programmed flow rate of 0.7 ml/h in the syringe needle. The graphical information from this figures indicates that the average fiber diameter is raised almost linearly with increasing concentration, increasing applied voltage and decreasing flow rate. Even though it can be inferred that manufacturing fibers with less concentrated solutions would lead to obtain thinner fibers, it is worth mentioning that the Electrospinning process with PAN/DMSO solutions under 5 % w/w polymer concentration was not possible during the experiments because the low viscosity and low surface tension of the solution inhibited the formation of a stable Taylor cone which would break when increasing the applied voltage over 7.5 kV.

3.3 Electrospinning of PAN/β-CD fibers

The analysis of variance (ANOVA) for the 3^2 experimental design considered for the manufacturing of PAN/β-CD fibers is summarized by Table 5 and the Pareto chart on Fig. 6. Based on the *p* value and the length of the standardized effect bar on the pareto chart, the most important factor affecting the average diameter of PAN/β-CD fibers is the flow rate because the concentration factor has been fixed. In this case, it can be seen that the average fiber diameter of PAN/β-CD fibers is reduced when the flow rate is increased. The fiber diameter decreasing effect with increasing flow rate was also mentioned in Sect. 3.2 when describing the electrical spinning of PAN/DMSO solutions and this confirms our observations related to a result that is contrary to what has been published in other Electrospinning related works [13,27].

The second most important factor affecting fiber diameter of PAN/β-CD fibers was the applied voltage. In this experiments, it was observed that fiber diameter increased while increasing the applied voltage. From the Pareto chart on Fig. 6, it is clear that the standardized effect bar of voltage is closer to the standardized effect of flow rate when compared with the Pareto chart for the experimental design without β-CD (see Fig. 4). Although no effect was expected with the addition of β-CD to the polymer solution because it did not increase the conductivity of the medium, the significant increasing diameter effect of applied voltage observed after cyclodextrin addition could be attributed to the presence of extra hydroxil groups from β-CD increasing the surface charge on polymer fibers. Because of this additional charge, fiber formation could be even more susceptible to the electric field generated by the electric potential difference. Moreover, because the surface of PAN/β-CD fibers would be more charged than PAN fibers, the applied electric field could accelerate even more the fiber travel between the needle tip to the collector. As explained in Sect. 3.2, more accelerated fibers would be bigger.

The third most important factor affecting the average fiber diameter is the interaction between flow rate and applied voltage. The interaction of both variables could be interpreted as a stronger electric field per quantity of polymer flowing through the needle. A stronger electric field acting at the droplet would accelerate the forming fiber and this would make it thicker. In other words, the importance of this interaction supports the hypothesis that the addition of β-CD to

the PAN/DMSO solution enhances the susceptibility of the fiber Electrospinning process to changes in applied voltage.

Looking at the remaining significant factors with p values lower than 0.05 (Table 5) and the standardized effects higher than the critic t value for a confidence of 95 % (Fig. 6), it is worth mentioning that the average fiber diameter of PAN/β-CD fibers increases quadratically with increasing flow rate and applied voltage. This is different from the effects of the quadratic terms of voltage and flow rate when Electrospinning PAN solutions without β-CD. In that case the fiber diameter raising effect was almost linear and less pronounced. The significant effects of the quadratic terms of voltage and flow rate also support the hypothesis of a higher electrical susceptibility of PAN/DMSO solutions when β-CD is added.

In order to prove the reliability of the regression, normality, independence and constant variable tests were also conducted (not shown). Based on the results of these tests, and despite the normal probability plot for the 3^2 experimental design showed some points far from the normal distribution line (maybe due to the lower quantity of data), it can be said that the multivariable regression describes well the behavior observed and the polynomial regression equation with coefficients for average fiber diameter of electrospun PAN/β-CD fibers (Y_2) is displayed in Eq. 5.

$$Y_2 = 228.51 - 14.01X_1 + 12.50X_2 + 16.73X_1^2 + 9.60X_2^2 + 14.95X_1X_2 \quad (5)$$

Using this empirical model, the response surface and contour plot for the manufacturing of PAN/β-CD fibers is presented on Fig. 5c and d. Note that the surface on these figures represent the electrospinning of 5 % w/w PAN/β -CD/DMSO solution at different flow rates and voltages between 0.5 and 1.0 ml/h and 7.5 and 8.5 kV respectively. By comparing the surfaces on Fig. 5a (without β-CD) and c (with 20 % β-CD based on PAN) and the corresponding contour plots on Fig. 5b and d, it is possible to see graphically that the addition of β-CD to the system increases the average fiber diameter and this could happen because the solution is more susceptible to the electrical effects associated to the changes in applied voltage and the fiber formation process is accelerated.

3.4 Fiber morphology

As it was mentioned earlier, the levels of concentration, flow rate and applied voltage used in this experimental design were selected, the obtained non-woven fabrics were composed by fibers without beads. In that vein, Fig. 7 shows scanning electron microscopy (SEM) images of reference samples of PAN and PAN/β-CD with the corresponding fiber diameter distribution histograms.

This SEM images are related to electrospun fibers manufactured from different concentration solutions using a flowrate of 0.7 ml/h at the syringe needle and applying a voltage of 8.0 kV. Because all obtained fibers were bead-free, multivariable regressions with high multiple and adjusted

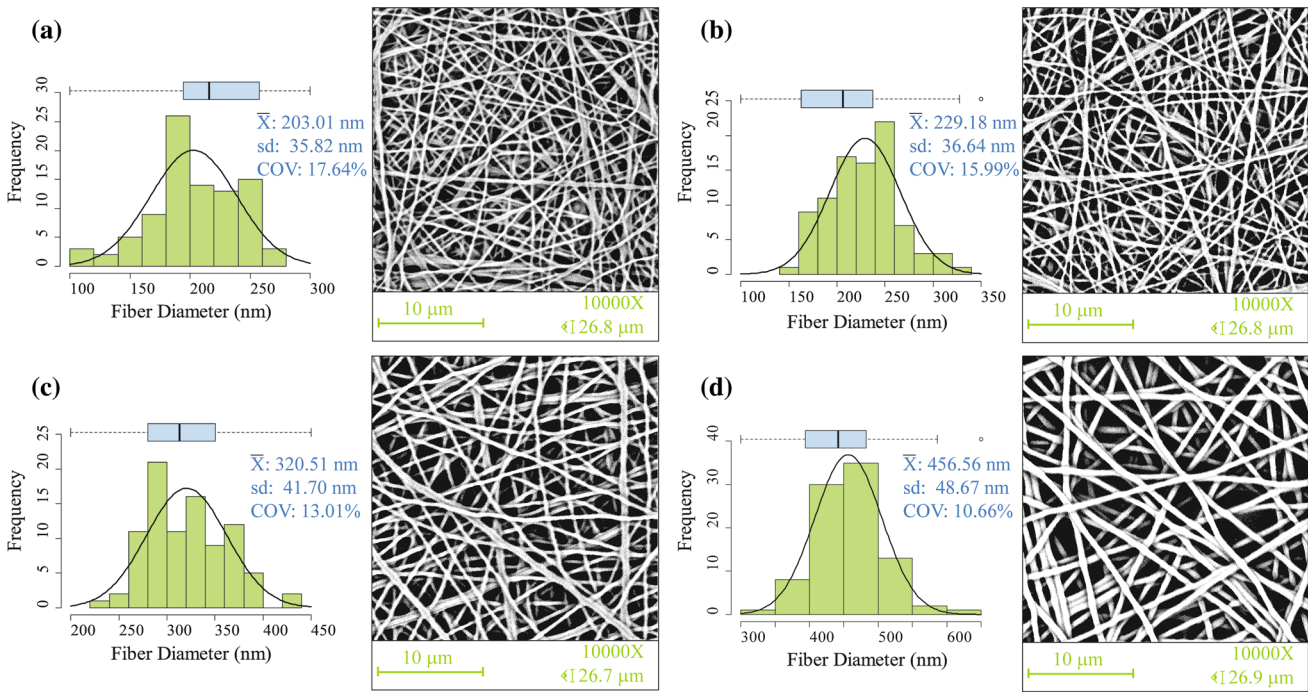

Fig. 7 SEM pictures of PAN fibers with corresponding fiber diameter distribution histograms: **a** PAN fibers (5 % w/w, 0.7 ml/h, 8.0 kV), **b** PAN/β-CD fibers (5 % w/w, 0.7 ml/h, 8.0 kV), **c** PAN fibers (7 % w/w, 0.7 ml/h, 8.0 kV), **d** PAN fibers (9 % w/w, 0.7 ml/h, 8.0 kV)

correlation coefficients (R^2) were obtained. The SEM images present how average fiber diameter increases with concentration as mentioned during the statistical analysis. In the same way, it can be seen how fibers become thicker with the addition of β-CD to the polymer solution of PAN in DMSO.

Although the thinnest fibers were produced from polymer solutions with low PAN concentrations (5 % w/w), they are not as homogeneous as the fibers produced form higher concentration solutions. Regarding this, the set of SEM images also illustrates how fiber uniformity increases with polymer concentration. The change in uniformity can be observed by looking at the coefficient of variation (COV). This coefficient represents the ratio between the standard distribution and the mean value of fibers diameter. As the coefficients of variation are reduced when the concentration of the polymer solution increases, it can be noted that more homogeneous electrospun fibers are manufactured from solutions with higher polymer concentration. This observation is similar to what it is described by other authors [16].

4 Conclusion

An experimental approach was used for the manufacturing of electrospun PAN and PAN/β-CD fibers with average fiber diameters between 200 and 500 nm approximately. In order to observe their effect on the average fiber diameter, different levels of polymer concentration (w/w), flow rate and applied voltage were simultaneously evaluated following full factorial 3^3 and 3^2 experimental designs. The levels of the evaluated factors were selected from preliminary laboratory tests taking into consideration that the forces acting on the Electrospinning process should be equilibrated for having a stable spinning regime. The information from the experiments was statistically analyzed and quadratic multivariable models describing the observations with high adjusted coefficients of correlation were generated (R^2: 0.9502 and R^2: 0.9802). This models were used to prepare response surfaces and contours showing the relationships between the dependent and independent variables involved in the Electrospinning process within the observation window. Based on the information from the surfaces and the SEM images of electrospun fibers, the following remarks can be mentioned:

Polymer concentration was the most important factor affecting the fiber diameter and thicker fibers were obtained from higher PAN concentration solutions as expected. This means that the lowest possible polymer solution concentration should be used if the main objective is to obtain the thinnest fibers. However, this concentration should be high enough for the droplet formation at the tip of the needle. During the experiments, it was observed that the PAN/DMSO 5 % solution is close to the lower limit of surface tension and viscosity needed for the Electrospinning process.

The second most important factor affecting the electrospun PAN fibers diameter was the flow rate and the average fiber diameter decreased while increasing this variable. This is contrary to what it was expected but the observation could be explained if the slight viscosity reduction with increasing shear rates at the needle generates lower resistance to stretching and fiber diameter reduction while the fibers travel between the tip and the collector.

Although polymer concentration and flow rate were the most statistically significant factors affecting the average fiber diameter of PAN fibers at the evaluated applied voltages, when β-CD is included in the polymer solution with 5 % PAN w/w, the fiber formation process is more susceptible to the electrical field, voltage becomes a statistically important factor and a fiber diameter increasing effect is observed with increasing voltage. This could happen because of additional charges on the surface of fibers that enhance the acceleration of the fiber formation process. This effect may also be linked to the significant effect of the interaction between the flow rate and the applied voltage on the fiber diameter when the cyclodextrin is added.

Finally, according to the observations and generated empirical models, PAN electrospun fibers with average fiber diameters around 200 nm may be manufactured using 5 % w/w PAN solutions in DMSO, with flow rates at the needle between 0.7 and 1.0 ml/h and applying a difference of electric potential between 7.5 and 8.0 kV when the tip to collector distance is fixed at 10 cm. If more uniform fibers are desirable, higher viscosity and concentration solutions may be used (at the same flow rates and voltages) in order to reduce the coefficient of variation. These process parameters may be the starting point when additional molecules such as β-CD are to be added for improving the entrapping properties of the filter media manufactured with electrospun fibers. It should be realized, however, that the inclusion of additional materials could lead to an increase in average fiber diameter.

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