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Mathematical Modeling of the Relation between Electrospun Nanofibers Characteristics and the Process Parameters

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Additional information is available at the end of the chapter

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Abstract

Electrospinning, the most favorable process of obtaining nanofibers, is capable of processing solution or melt polymers, ceramic materials or metals in many morphological variants, thus providing diverse functionalities. The chapter reviews the main ways in which nanofibers' characteristics can be influenced by solution parameters, process parameters and ambient conditions, afterwards focusing on the role of some of the most significant electrospinning parameters (applied voltage, flow rate, nozzle to collector distance) on the diameter of the nanofibers. Experimental studies to model the influence of process parameters in the case of electrospinning polyetherimide solutions are presented. Response surface methodology and MATLAB simulation software have been used to obtain the mathematical models that indicate the most favorable parameters.

Keywords: electrospinning, polyetherimide, process parameters, nanofiber diameter, mathematical model

1. Introduction

Electrospinning is an extremely flexible technique, being applicable to both polymer solutions and melts, which can be converted into nanometer-grade fiber. This method offers access to completely new materials, which may have complex chemical structures and a very wide range of usage areas.

Electrospun nanofibers have many applications in filtration processes, bio-medicine (tissue engineering, drug delivery, scaffolds and wound healing), in energy devices and sensors, depending on their morphological characteristics. The morphology of the fibers obtained through electrospinning is governed by many factors. These factors are related to the polymer solution characteristics, process and ambient parameters.

2. Main electrospinning parameters affecting nanofibers morphology

The morphology of the nanofibers obtained through electrospinning is influenced by many factors. These factors can be grouped into three categories: polymer solution characteristics, process parameters and ambient parameters. Knowing the way these factors influence the electrospinning process, it becomes easier to obtain nanofibers with controlled structure and required functions [1, 2].

2.1. Polymer solution

2.1.1. Viscosity

Some of the key parameters of the electrospinning process are the surface tension and the viscoelastic properties of the polymer solution [3–5]. The correct choice of the concentration of the polymer solution has a decisive effect on these processes, respectively, on the characteristics of the obtained nanofibers (diameter and morphology) [6, 7].

It is generally accepted that the viscosity of the polymer solution is the decisive parameter of the process, including the possibility of electrospinning and the characteristics of the nanofibers. In order to make electrospinning possible, the viscosity must be in a relatively narrow range. At very low viscosity values, the polymer filaments break and polymer droplets are produced, while at very high viscosity values, the polymer solution cannot pass through the nozzles and electrospinning does not take place. The area of optimum viscosity depends essentially on three parameters: the nature of the polymer, the nature of the solvent and the concentration of the polymer solution.

Figure 1 shows the great significance of the polymer solution viscosity for electrospinning.

Usually, a solution having a viscosity of 1–20 poise and whose surface tension is in the range of 35–55 dyn/cm² is considered to be suitable for electrospinning. If the viscosity values exceed the upper limit of the abovementioned range, the cohesion of the solution greatly increases in order to achieve stable polymer flow. Large beads are formed, with great distance between them, which generates larger fiber diameters. For polymeric solutions with a viscosity of less than 1 poise, the breaking of the polymer flow is recorded, with the formation of frequent beads [9]. With the increase in the solution concentration, there is a change in the shape of the beads, which passes from spherical to spindle-like [10].

There is a direct proportionality relationship between the concentration of the electrospun polymer solution and the diameter of the obtained nanofibers, but the value of the ratio of proportionality varies within relatively large limits.

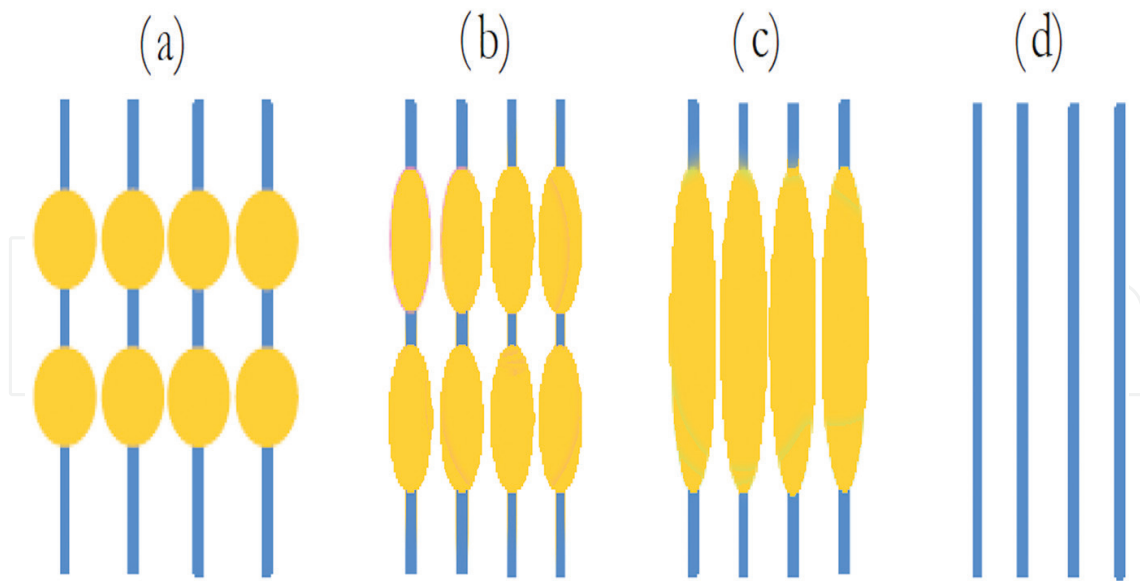


Figure 1. The viscosity increases from (a) to (d): (a) drops; (b) slightly extended drops; (c) extended drops; (d) nanofibers.

However, the use of decreasing the concentration of the polymer solution to reduce the diameter of the fibers is limited by inherent difficulties in electrospinning or even the impossibility of electrospinning, as well as by problems in diminishing the diameter by subsequent treatments [11]. It is worth mentioning the possibility of increasing the surface of the fibers by further modification of their morphology either by changing the shape of their cross-section or by forming pores, pits or bumps on their surface [12].

The close relationship between the viscosity and the concentration of the polymer solution to be electrospun has been studied for polymers such as poly (lactic-co-glycolic acid) (PLGA) [13], poly (ethylene oxide) (PEO) [14, 15], poly (vinyl alcohol) (PVA) [16–18], poly (methyl methacrylate) (PMMA) [19], polystyrene (PS) [20], poly (L-lactic acid) (PLLA) [8], gelatin [21] and dextran [22]). A study on the relationship between viscosity and concentration on electrospinning of seven solutions of linear homopolymers of poly (methyl methacrylate) with diverse molecular weights (dimethylformamide—DMF—was the solvent) demonstrated that when electrospinning solutions with concentrations below the value obtained by multiplying the overlap concentration by six (the overlap concentration is the concentration of the polymer solution for which there is a sudden change in viscosity) no filaments are obtained, but only beads, while high molecular weight PMMA at concentrations in this range produces fibers having a relatively limited number of beads. [18].

A new method of reducing the viscosity of the polymer solution is the application of low-frequency vibrations during electrospinning, when the polymer chains are untangled as a result of the breakage of the interchain van der Waals bonds. In the case of a PMMA solution to which a vibration of 300 rad/sec was applied, the viscosity diminution was achieved by an order of magnitude [23, 24]. The application of vibrations with a frequency of about 400 Hz on the tip of the capillary when electrospinning a solution of poly (butylene succinate) (PBS)/CHCl₃ led to a significant reduction in the diameter of the obtained nanofibers [25]. The use of vibrations may make possible the electrospinning of more concentrated polymer solutions that would otherwise not be electrospun, as well as suspensions or coagulated materials [12].

2.1.2. Conductivity

Since electrospinning is essentially based on the process of passing electrical charges from the electrode to the polymer solution at the tip of the injection needle, it is imperative that the polymer solution exhibits a certain level of electrical conductivity without which the process cannot be realized.

The conductivity of the polymer solution means the number of electrical charges found on the surface of the solution, the presence of which determines the formation of nanofibers rather than nanoparticles.

Upon dissolution of a polymer, an increase in the conductivity of the solution is recorded because the various polymeric ionic species (mostly impurities or additives) are available in this way. It has been found that a decrease in conductivity can be observed if increasing the concentration of the polymer solution [26]. In the particular case when the polymer is a polyelectrolyte, its solution will exhibit high conductivity, its value depending largely on the concentration of the solution [21].

The addition of electrolytes leads to an increased number of electrical charges, thus improving the conductivity, which leads to the increase of the elongation capacity of the polymer solution, the fibers obtained in this case being smoother and finer [13].

For conductivity enhancement, inorganic salts such as NaCl (0.01 M) [6, 14, 15] or ionic organic compounds such as pyridinium formate [26], palladium diacetate [16], chloride trialkylbenzyl ammonium can be added to the solution [17, 18].

The morphology of the nanofibers thus obtained is influenced by the dimensions of the ions introduced into the electrospinning solution, there being a relationship of inverse proportionality between the ion size and the uniformity of the nanofibers. In addition, for small dimensions of the added ions, the number of defects decreases [19].

2.1.3. Surface tension

The surface tension is a property of liquids that makes them take a geometric shape of minimum area in the absence of external forces, due to the cohesion forces between molecules [20].

The surface tension has an important significance in the electrospinning process. For example, lower surface tension will allow electrospinning to be achieved at an inferior electric field [28, 30–34]. Because it depends on the characteristics of the solvent, its correct choice is of the utmost importance, both for a homogeneous solution and for a consistent surface tension.

As a rule, it is considered that, for a given situation, surface tension determines the limits of the range in which electrospinning can be achieved [23–25, 27–29].

When an electric field is not applied, the surface tension of the solution causes the solution to be retained at the tip of the capillary. When applying an electric field, the electric charges exceed the forces of superficial tension and the polymer jet forms. Decreasing the surface tension of the polymer solution can cause the instability of the polymer jet, whose tendency to break and form droplets increases [1, 35–39].

Proper adjustment of the surface tension can be achieved by choosing the correct polymer solution concentration [40–44] or by adding a surfactant; in this second case, the uniformity of the electrospun fibers increases. However, the mere presence of a low superficial tension of a polymer solution does not guarantee the possibility of electrospinning it [20, 45].

2.2. Process parameters

Process variables, such as fluid flow rate, spinneret to collector distance and electric field strength have a significant influence on the properties of the electrospun nanofibers.

2.2.1. Fluid flow rate

Many of the elements of the electrospinning process, such as the initial shape of the droplet, the persistence of the Taylor cone, the trajectory of the extruded jet, the area in which the nanofibers are deposited and their essential characteristics, such as the size and uniformity of the diameter, are controlled by the flow rate of the polymer solution into the syringe.

As a rule, lower flow rate allows longer polarization times; if this speed exceeds a certain threshold value, a value that depends on the nature of the polymer and the solvent, the feed rate of the polymer solution exceeds the rate at which it is pulled from the tip due to the applied electrical forces. In this situation, since the solidification time of the polymer filament until it reaches the collector is too low, the obtained fibers have a high density of beads and an increased number of large droplets.

The way the shape of the polymer cone changes with increasing flow rate is shown in **Figure 2**.

When electrospinning a polystyrene solution, it was found that the formation of beads occurs when the flow rate exceeds 0.1 mL/min, conditions in which fiber diameter and pore size increase [47]. When electrospinning a solution of 20% polysulfone in N, N-dimethylacetamide at 10 kV, it was observed that at a feed rate of 0.66 mL/h, smaller diameters of fiber were obtained [48], while when electrospinning a nylon 6 solution, bead fiber formation occurred when the flow rate surpassed 4 mL/min [49].

The flow rate can be increased, in association with increased applied stress, to improve the productivity of the process, obtaining thinner nanofibers. If the flow rate is very much increased webs may be obtained instead of fibers, as the solution ejected from the tip does not have enough time to dry until reaching the collector [46].

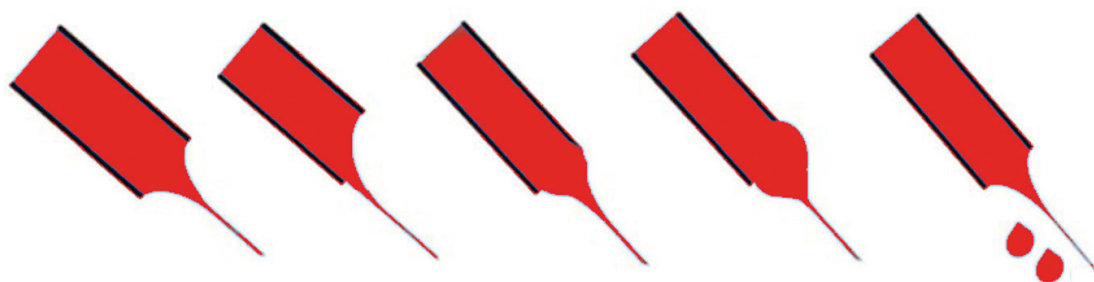


Figure 2. Development of various jets when flow rate increases.

In addition to this, if the flow rate is increased, a broader fiber diameter distribution is obtained. Because too high or too low flow rates influence the electrospinning process and the diameter of the resulted nanofibers, it is better to keep a flow rate as low as to ensure the equilibrium between the extruded polymer solution and the fresh replacing solution during the formation of the jet [2].

Choosing an appropriate flow rate leads to a limitation of the formation of defects such as blobs, splitting and branched fibers. In addition, a stable and constant flow rate is required [50].

2.2.2. Distance between the spinneret and the collector

The morphology and the diameter of the electrospun fibers can be controlled by proper setting of the distance between the spinneret and the collector.

If this distance is too small, the fibers will not solidify before reaching the collector, while if the distance is too long, droplets may appear on the surface of the fibers [1, 21]. The distance between the syringe tip and the collector has to be judiciously set, as the speed of the solvent removal is very important in order to produce quality nanofibers. Even the smallest modification of this distance can have serious effects on fiber characteristics.

Additionally, if the distance between the nozzle and the collector is increased, the level of the electric field between the two decreases, forming fewer charged ions, boosting bending instability and elongation tendency and decreasing the diameter of the polymer jet [50, 51].

Many papers show that a small spinneret to collector distance leads to faulty and large-diameter nanofibers, while the nanofibers diameter decreases as the distance is increased [52]. In the case of poly (vinylidene fluoride) nanofibers obtained through electrospinning from a 28 wt% solution at 12 kV, a decrease in diameter from 397 nm to 314 nm was observed when the distance between the nozzle and the collector increased from 15 cm to 16 cm, associated with better uniformity [53].

A study on the influence of the distance between the spinneret and the collector on the diameter of nanofibers electrospun from 12% polyetherimide solution, obtained using a mixture of dimethylacetamide /tetrahydrofuran 1:1 as solvent, led to the conclusion that the smallest values of the diameter are obtained for a distance of 45 mm [44].

Usually the appropriate distance between the spinneret and the collector differs from one polymer system to another, but there were cases when no effect on the morphology of the nanofiber occurred when altering the distance between the needle and collector [54].

2.2.3. Applied voltage

The applied electrical voltage is considered to be one of the most significant parameters of the electrospinning process, as it drastically affects both the dynamics of the fluid flow and the morphology of the electrospun fibers. Its impact depends upon the concentration of the polymer solution and the distance between the spinneret and the collector [55].

The applied voltage is important because the charged polymer jets leave the Taylor cone only if the applied voltage exceeds a specific threshold value, which depends on both the type of polymer and the type of solvent [2, 38].

The way the applied stress influences the morphology of the electrospun nanofibers is subject to controversy.

Some studies identify a relationship of inverse proportionality between the applied voltage and the diameter of the electrospun nanofibers. The argument for this behavior is the more prolonged elongation of the extruded polymer filament when the rejection forces are greater [56, 57]. There are also studies that did not find a correlation between the two parameters when electrospinning a poly (ethylene oxide) solution [49, 58]. Moreover, in case of aqueous poly (vinyl alcohol) solution electrospinning, the increase in the applied voltage leads to an increase in the diameter of the nanofibers [54]. It can be concluded that the applied voltage value frequently affects the diameter of the obtained nanofibers, but the type of influence depends on the nature of the polymer / solvent system and the distance between the electrode and the collector [59].

Expert opinions are far less divergent as to the relationship between the value of the applied voltage and the probability of defect formation. It has been found that an increase in the applied tension leads to an increase in the deposition rate, which explains the augmentation of the number of defects [56, 60]. The length of electrospun nanofibers decreases when the applied voltage increases, without affecting the pore size [34, 61]. It was found that in most cases a lower applied voltage will cause the production of nanofibers with uniform morphology and with low number of defects [62].

The study on a mixture of polyaniline-camphor sulfonic acid/poly (ethylene oxide) highlighted the fact that higher voltage leads to thinner nanofibers, but also a greater diversity of diameters and a wider distribution of diameters [64].

2.3. Ambient conditions

Any interaction between the environment and the polymer solution may affect the electrospun fibers' morphology, with the greatest impact given by humidity, temperature and atmospheric pressure.

2.3.1. Humidity

The role of the humidity of the electrospinning environment is manifested in terms of fiber morphology, deposition orientation and solvent evaporation rate. When the humidity is very low, a volatile solvent can dry very quickly. It also has been suggested that high humidity helps discharging static electricity from electrospun fibers.

At high humidity, condensation may occur at the fiber surface due to the cooling of the jet surface, caused by the rapid evaporation of the volatile solvent, and the air flow may interrupt the formation of the fibers, causing fiber breaking [34].

An experiment on polysulfide electrospun nanofibers [63] revealed that at a moisture content of less than 25%, the fibers are smooth, glossy, with non-porous surface; at a humidity of

31–38% there is a visible difference in fiber morphology, with a relatively small number of randomly distributed circular pores; at 31–45% humidity the pores move toward the surface of the fiber; at a humidity of 50–59% the pores are numerous at the fiber surface; while at a moisture content of 60–72% the pores are larger and more uneven because of the incomplete drying of the electrospun fibers and their entanglement on the surface of the collector.

When electrospinning a polyaniline-camphor sulfonic acid/poly (ethylene oxide) mixture, it was found that only low ambient humidity allowed the formation of defect-free nanofibers over the entire range of applicable voltages. When the humidity reaches 25%, fibers start to break forming uneven and irregular surfaces, while at relative humidity higher than 40%, electrospinning is no longer possible [64].

2.3.2. Temperature

The temperature of the electrospinning ambient significantly influences the process. A first effect is manifested on the evaporation rate of the solvent, which exponentially decreases with decreasing temperature; the evaporation process of the solvent becomes slower, the jet takes a longer time to solidify, which can lead to defects in fiber formation [35].

Temperature has an important influence on the rigidity of the polymeric chains, which decreases as the ambient temperature increases. Under these conditions, associated with a low viscosity of the polymer solution, it is possible to obtain a better stretch of the polymer filament under the action of Coulombic forces, resulting in smaller diameter fibers.

2.3.3. Atmospheric pressure

At low atmospheric pressure, the polymer solution in the syringe tends to flow, causing unstable jet initiation, and at very low pressures electrospinning cannot take place due to direct discharge of electrical charges.

3. Mathematical models of the electrospinning of polyetherimide

Our study investigated the way the distance between electrodes and some of the main technological parameters affect the diameter of the electrospun polyetherimide fibers [39, 44]. A 12% polyetherimide solution, obtained using as solvent a mixture of dimethylacetamide / tetrahydrofuran (1:1 ratio), has been used. The spinning equipment, which worked at normal atmosphere, is of multijet type, with needle and uniaxial delivery.

In earlier experiments [43, 65, 66], the solubility of polyetherimide in the dimethylacetamide/tetrahydrofuran solvent (DMAC/THF) has been tested by computing the Hansen coefficients, and the results proved that the polymer has very good solubility at 12% concentration, unlike other tested concentrations (8–14%).

The properties of the 12% polyetherimide solution in the DMAC/THF mix [44, 67] are conductivity 1.18 mS/cm, surface tension 30.3 mN/m, zero shear viscosity 0.191 Pas.

In order to obtain the polymer solution, the polymer was dried for 2 hours at 100°C in vacuum. The polymer dissolution in the solvent mix was made by magnetic stirring for 24 h at 500°C.

The experimental equipment that has been used has three 3 mL syringes with 0.2 mm inner needle diameter and an inter-nozzle distance of 2.5 mm and a rotating cylinder type collecting mechanism, with cylinder rotation speed $v = 1000$ rpm. The displacement range along the Ox axis was 100 and 80 mm along the Oz axis.

The parameters that have been varied in the experiment were the distance between the needles and the collector (45, 70, 100, 120, 120 mm) and the technological parameters: flow rate (0.05, 0.075, 0.1, 0.15 mL/min) and the voltage (15, 20, 25, 30 and 35 kV).

Scanning electron microscopy (SEM) was used to characterize the obtained polyetherimide electrospun nanofibers; the nanofibers have been previously gold plated using a Phenom G2 equipment [39, 66]. To determine the diameter of the electrospun fibers, a Lucia image analysis software was used. For each technological variant, 100 measurements of the diameter of the electrospun fiber have been carried out [44, 66].

To analyze the experimental data, the Response Surface Methodology (RSM) was used as a mathematical and statistical technique. RSM was used to find the dependence between d_{med} , the mean fibers diameter, and D , the distance between needles and collector, in conjunction with the flow rate Q and the voltage U . The notations for the variable parameters are x_1 for D , x_2 for Q and x_3 for U . These are the predictors of the model, which were varied together in accordance with the experimental plan, in order to determine the most favorable combinations of Q and U which gives the desired fiber diameters resulting from the electrospinning process.

The experiments were performed under the following environmental conditions: 20°C, RH = 40%, normal atmospheric pressure. Under these specified conditions, the values for spinning distance, applied voltage and volume flow rate have been selected to determine the influence of these parameters on the polyetherimide nanofiber electrospinning process.

In order to study the dependence between the average fibers diameter d_{med} and the distance between the needles and the collector, (D) correlated with the flow rate (Q) and the applied voltage (U), response surface methodology (RSM) has been used. All the three explanatory variables were varied at the same time, in compliance with the experimental design.

The relationship between the response variable d_{med} and the explanatory variables can be written as $d_{med} = f(x_1, x_2, x_3)$, where the function f is to be found. The multiple regression method has been applied to approximate f with a second order polynomial $P(x_1, x_2, x_3)$, but after applying the statistical tests it was found that the complexity of the model does not require such a high-accuracy approach. In this case, the research plan was focused on using RSM to investigate three partial dependencies: a) $d_{med} = u(x_1, x_2)$, for all the five values of $x_3 = U$ considered in the experiment, b) $d_{med} = v(x_2, x_3)$, for three values of $x_1 = D$ which are expected to be favorable for the aim of obtaining very small fiber diameters, according to the results obtained at (a) and (c) $d_{med} = w(x_1, x_3)$, for two values of $x_2 = Q$.

In addition to the generation of the quadratic models for u , v and w , RSM supplies three-dimensional charts of the response surfaces, which are useful in the visualization of the relationship

between the response and the predictors (independent variables) and allow us to observe the influence of each predictor.

The experiment was conducted for five levels of D , four levels of Q and five levels of U . Therefore, there are $5 \times 4 \times 5 = 100$ treatment combinations of parameters. **Table 1** presents the regression equations for $d_{\text{med}} = u(x_1, x_2)$ for each of the five considered values of U .

The adjusted R-squared has been used, as this statistic is the most significant in selecting the right regression model. This value is designed to avoid the problem with the regular R-squared value. When a new term is added in the model, R-squared increases, which can be misleading and can lead to choosing a too complex model, which is not necessarily the right choice. Usually, it has been chosen from the models with greater adjusted R-squared values, which means that a high fraction of data is fitted by the model. In contrast to the regular R-squared, the adjusted R-squared increases only if the new term improves the model more than would be expected under random conditions. The adjusted R^2 always has a lower value than regular R^2 .

Figure 3(a)–(e) shows the diagrams of the response surfaces for $d_{\text{med}} = u(x_1, x_2)$, for the five values of U . The charts display the correlation between D and Q and their influence on d_{med} .

Moreover, to give an overview on the behavior of d_{med} for the five values of the parameter $x_3 = U$, we have represented the five response surfaces within the same coordinates system in **Figure 3(f)**.

It appears that d_{med} increases as both $x_1 = D$ and $x_2 = Q$ increase. It is obvious that higher values of U ($U = 25$ kV, $U = 30$ kV and $U = 35$ kV) are the most favorable.

We have further determined the approximation models for the dependency $d_{\text{med}} = v(x_2, x_3)$, for $D = 45$ mm, $D = 70$ mm and $D = 100$ mm. The results are shown in **Figure 4**, where the chart displays a simultaneous representation of the three models. The charts indicate that d_{med} increases as D increases.

Finally, the approximation models for the dependency $d_{\text{med}} = w(x_1, x_3)$ have been determined. A chart with all the response surfaces, for the five values of Q , is given in **Figure 5**.

The statistical analysis has been performed using Matlab 7.5.0 (R2007b) and the technical interpretation of the results provided by the data analysis is given further.

No.	U (kV)	Regression equation	R^2_{adj}
(1)	15	$d_{\text{med}} = 356.7 - 1.55D + 5553.6Q + 14.59DQ - 0.02 D^2 - 18834.5Q^2$	94.42%
(2)	20	$d_{\text{med}} = 480.1 + 0.44D - 522.4Q - 25.8DQ + 0.0055 D^2 - 5535.3Q^2$	97.03%
(3)	24	$d_{\text{med}} = 411.6 - 0.81D + 348.7Q - 30.66DQ + 0.0087 D^2 - 2018.1Q^2$	93.72%
(4)	30	$d_{\text{med}} = 349.7 - 1.2D + 186.3Q + 25.77DQ + 0.0125 D^2 - 206.9Q^2$	93.34%
(5)	35	$d_{\text{med}} = 283.2 - 1.05D + 2759.6Q + 21.3DQ + 0.018 D^2 - 17259.6Q^2$	89.72%

Table 1. Mathematical models for mean fibers diameter as function of D and Q .

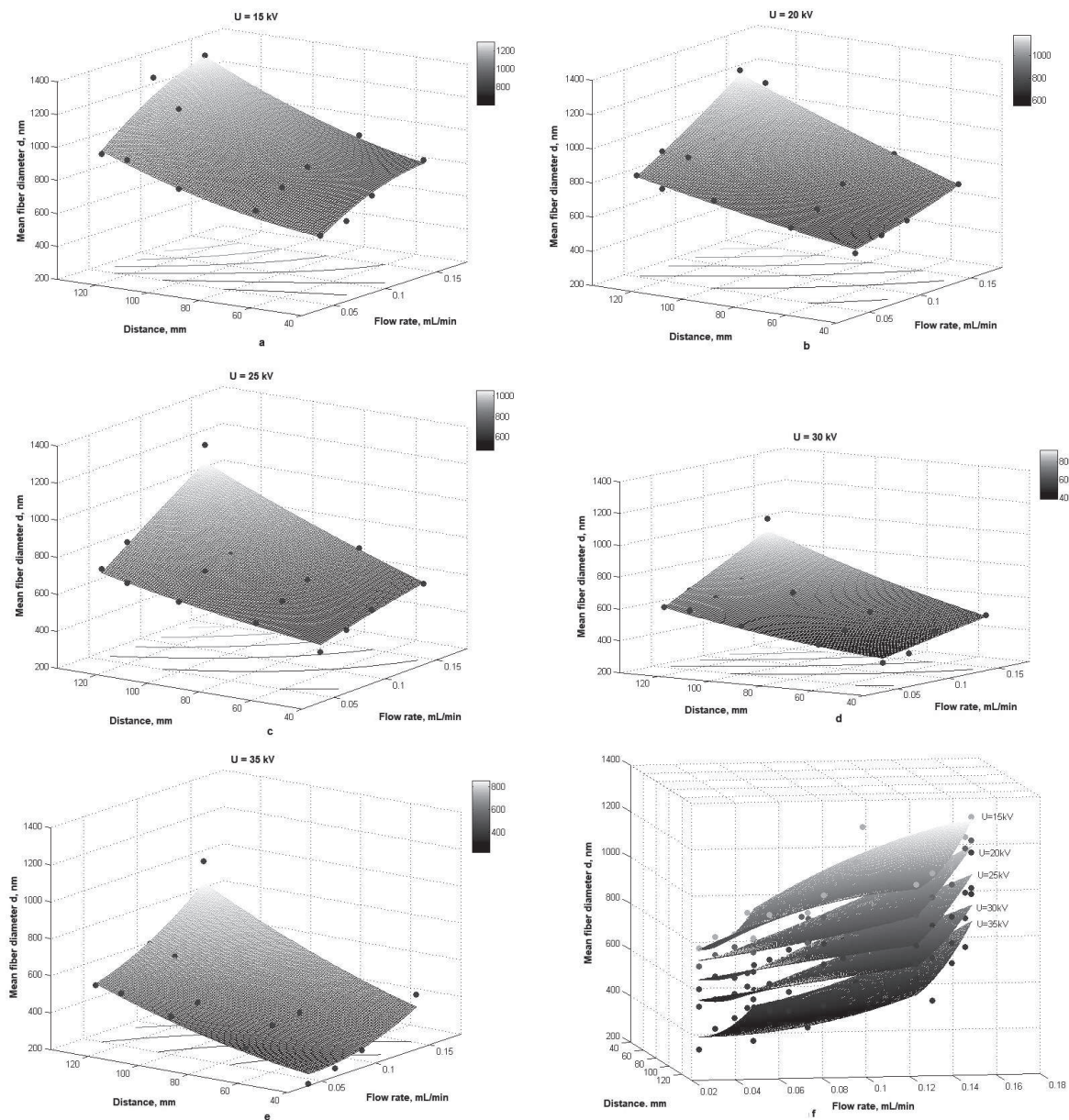


Figure 3. Response surfaces for mean fiber diameter in terms of spinning distance (D) and flow rate (Q) for the five values of U : (a) $U = 15$ kV, (b) $U = 20$ kV, (c) $U = 25$ kV, (d) $U = 30$ kV, (e) $U = 35$ kV, (f) Simultaneous representation for the five response surfaces.

As the presented charts display, longer spinning distance induces an increase in the fiber diameter. In Eqs. (1), (3)–(5) from **Table 1**, the coefficient of D is negative. In Eq. (2), the coefficient is positive, but very small. The literature reports both increase in fiber diameter and decrease in fiber diameter [45, 60, 65, 66] depending on D , due to different ratio between D and the electric field strength E (KV/cm), polymer solution concentration and solvent evaporation rate. In order to observe the influence of each term, the test for the individual coefficients was performed for the five models. The results of the stepwise regression show that the significant terms are those related to Q , D^2 and Q^2 for Eq. (1) and those related to DQ and D^2 in Eqs. (2)–(5).

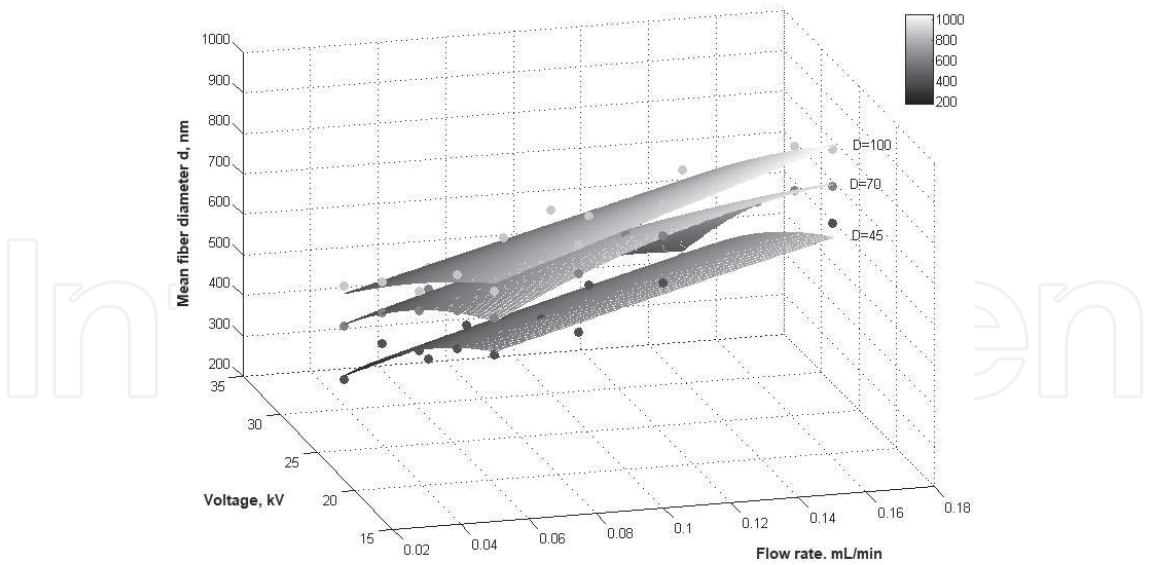


Figure 4. Response surfaces for mean fiber diameter in terms of voltage (U) and flow rate (Q) for three values of D. Simultaneous representation.

It can be concluded that the mathematical models as well as the observations on the response surfaces plotted for the partial dependencies (d_{med} as function of D (mm) and Q (mL/min), Q (mL/min) and U (kV), and as function of D (mm) and U (kV)) show that the optimum technological domain is defined by small values of the spinning distance ($D = 45\text{--}70$ mm). As we previously concluded, appropriate values of the mean fiber diameters are obtained for the smallest values of D (mm). The minimum value of fiber diameter is obtained for $D = 45$ mm, $Q = 0.05$ mL/min and $U = 35$ kV.

Next, our attention was focused on the results provided by RSM for $d_{med} = v(x_2, x_3)$, for three values of $x_1 = D$ which are the most favorable for obtaining very small diameter fibers and for $d_{med} = w(x_1, x_3)$, for two values of $x_2 = Q$.

The model $u(x_1, x_2)$ revealed that d_{med} decreases as x_1 decreases. Therefore, in representing the response surfaces for the dependency $d_{med} = v(x_2, x_3)$, we have considered for $x_1 = D$ only the three smallest values: $D = 45$ mm, $D = 70$ mm and $D = 100$ mm. The surfaces are represented in **Figure 6(a)–(c)**.

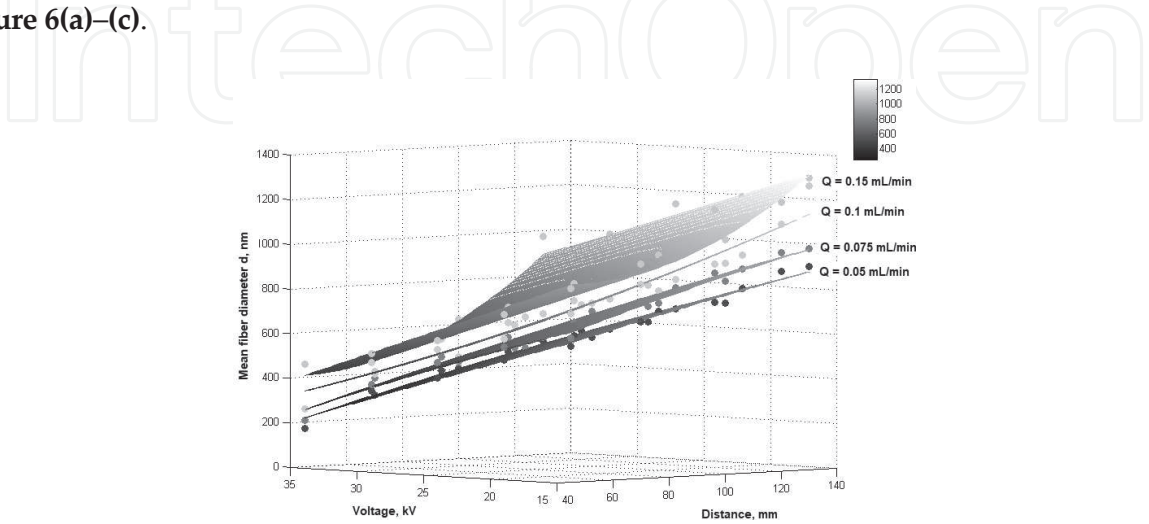


Figure 5. Response surfaces for mean fiber diameter in terms of spinning distance (D) and voltage (U). Simultaneous representation for the four values of Q.

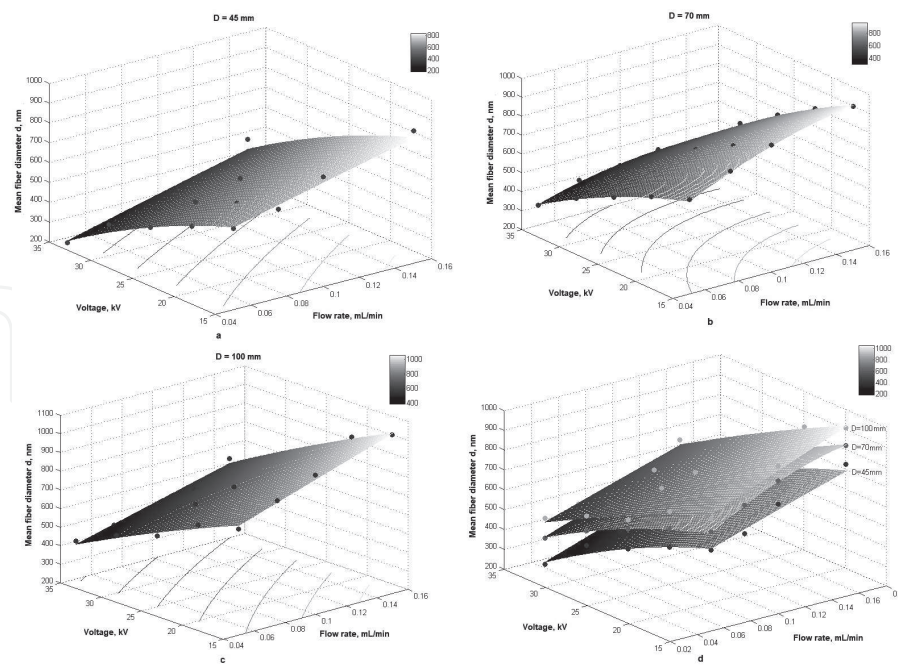


Figure 6. Response surfaces for mean fiber diameter in terms of voltage (U) and flow rate (Q) for three values of D : (a) $D = 45$ mm, (b) $D = 70$ mm, (c) $D = 100$ mm, (d) simultaneous representation for the three response surfaces.

It appears that small values of the flow rate entail small mean fiber diameters: d_{med} decreases as Q decreases. Therefore, the approximation models for the third partial dependency $d_{med} = w(x_1, x_3)$ has been analyzed only for $Q = 0.05$ mL/min and $Q = 0.075$ mL/min (the lowest values of the flow rate). The graphic representation of this dependences (the response surfaces) are shown in **Figure 2(a)–(c)** and demonstrate that d_{med} decreases as $x_3 = U$ increases. In addition, it can be seen that d_{med} also increases with $x_1 = D$ as demonstrated previously by the model $d_{med} = u(x_1, x_2)$.

Further the three models $u(x_1, x_2)$, $v(x_2, x_3)$, $w(x_1, x_3)$ have been integrated, providing the technical interpretation of the results. This interpretation considers the behaviors and facts communicated on this topic, derived by other researchers [39, 55, 66] from similar experiments.

The response surfaces previously shown allow the visualization of the relationship between the response variables (the flow rate Q and voltage U) and the explanatory variables (the average fibers diameter in correlation with the distance between the needles and the collector). The influence of the nozzle to collector distance D (symbolized by x_1) on the fibers diameter has been previously analyzed. Numerous scientific articles dealing with this topic state that the fiber diameter may sometimes increase, but in other situations it decreases [39, 53, 55, 66] upon D . The main factors that influence this dependency are the ratio between nozzle to collector distance D and the electric field strength E , the concentration of the polymer solution and solvent evaporation rate. When electrospinning a polyetherimide solution, a mathematical model was found indicating that longer nozzle to collector distance induces an increase in the fibers diameter.

With respect to the influence of the flow rate $Q = x_2$ (mL/min) on the mean fibers diameter, the experiments showed that d_{med} increased with the volume flow rate, as depicted in **Figure 3(a)–(f)** and also in **Figure 6(a)–(c)**. The Eqs. (3)–(5) in **Table 1** support this conclusion, as the coefficient of DQ is positive and the corresponding terms are significant. Our findings are consistent with previous research [28, 65].

Studying the influence of the voltage $U = x_3$ (kV) on the mean fibers diameter, it was found that the diameter decreases when the voltage increases. The chart (a)–(c) in **Figure 6** and (a)–(b) in **Figure 7** also display this behavior. It can be observed that the minimum value of the fibers diameter is obtained for $U = 35$ kV, meaning that experimental data comply with the previous conclusion.

Figure 8 presents the projection of the response surface in **Figure 3(e)**, for the most favorable value of U , which leads to small fibers diameter, namely 35 kV. The dark-gray lines are displayed in the favorable zone of the parameters (while the light-gray ones are higher).

This study proved that the optimal technological domain is determined by small values of the nozzle to collector distance ($D = 45\text{--}70$ mm), small flow rate values ($Q = 0.05\text{--}0.075$ mL/min) and high applied voltage values ($U = 30\text{--}35$ kV). The desired characteristics for the fibers diameter are obtained when D (mm) and Q (mL/min) are minimal and U (kV) is maximum.

It can be concluded that the ability to control the diameter of electrospun nanofibers is of utmost importance as it affects the majority of the properties of the final product. The diameter of the electrospun nanofibers is dependent on a series of parameters, and in order to correctly assess the role of each parameter, the one-variable-at-a-time technique is not very eloquent. That is why addressing the problem by using experimental design can provide a more accurate picture of these dependences.

Based on our studies and many other scientific approaches in this area of research, it can be stated that an accurate choice of environmental and technological parameters for each

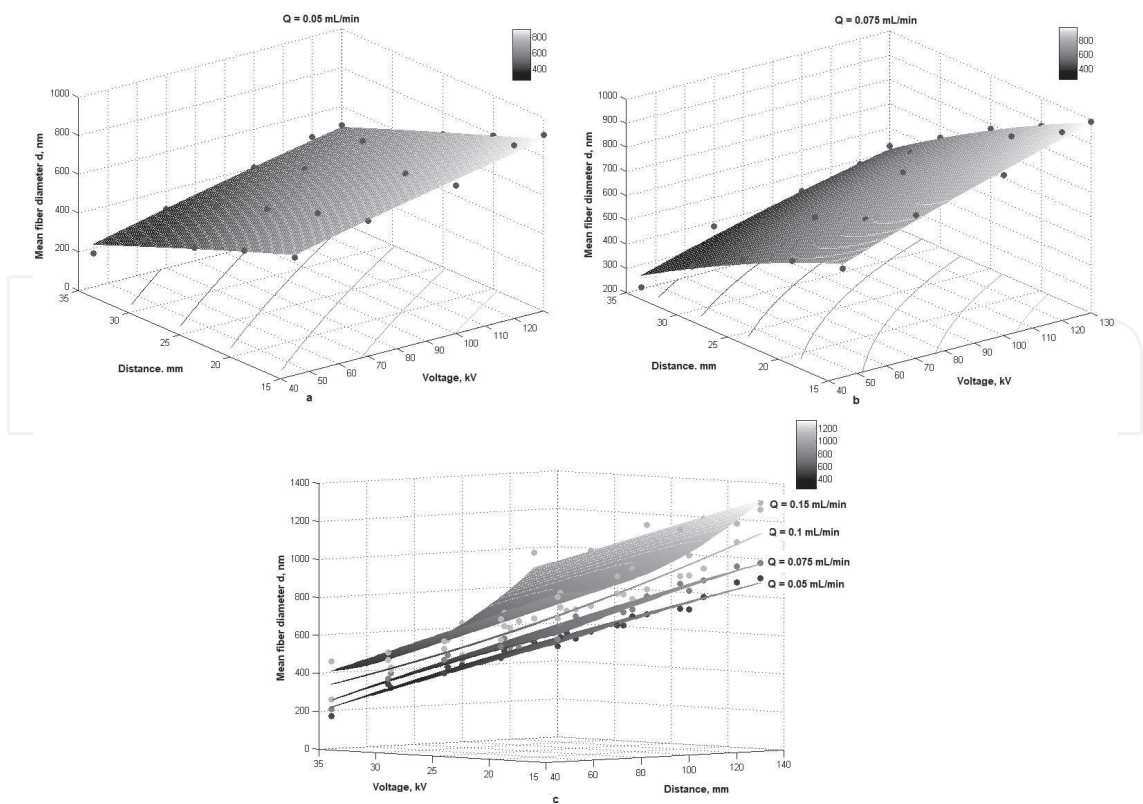


Figure 7. Response surfaces for mean fiber diameter in terms of distance (D) and voltage (U) for two values of Q : (a) $Q = 0.05$ mL/min, (b) $Q = 0.075$ mL/min, (c) simultaneous representation for all the values of Q .

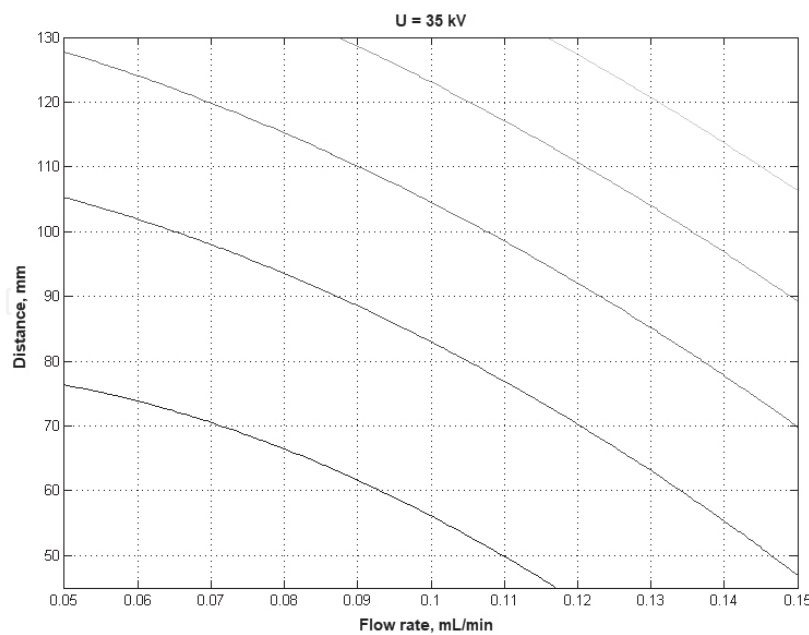


Figure 8. The projection of the response surface for $U = 35$ kV.

polymer solution (with optimal values of concentration, viscosity, molecular weight, solution conductivity) and a proper correlation of these parameters lead to obtaining flawless fibers with predetermined diameter.

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