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Comparative Study of Electrospinning Parameters for Production of Polylactic Acid and Polycaprolactone Nanofibers Based on Design of Experiment

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Abstract

In terms of applications, the diameter of nanofibers is one of their most important characteristics. This size is influenced by various process parameters, such as: the concentration, the distance between the needle and the collector, volume flow, etc. In this study, we compared the average diameter of nanofibers made from two different polymers, polycaprolactone and polylactic acid.

We investigated the impact of various parameters on the production of nanofibers from polycaprolactone and polylactic acid using the electrospinning technique. We employed a factorial experiment design model to characterize this versatile and efficient fibre fabrication method. By considering the effects of voltage, concentration, distance between the pin and the collector, and flow rate, we established a mathematical model to describe the process. The diameters and morphologies of the resulting fibers were analyzed and compared to each other using SEM analysis. Our findings revealed that, among the studied parameters, concentration had the most significant impact on the diameter of the polymer fibers.

Keywords

electrospinning, response surface method, process parameter

1 Introduction

Electrospinning is a fast, efficient, and inexpensive method for producing micro- and nanometre-range polymer fibers [1–3]. In brief, electrospinning is based on the flow of a polymer solution through a needle in the presence of an electric field on high voltage to produce charged jet by generating mutual repulsive forces between charged polymer molecules to overcome surface tension. Electrospinning involves an electrohydrodynamic process, In brief, electrospinning is based on the flow of a polymer solution through a needle in the presence of an electric field. The electrified polymeric solution is stretched into a continuous jet, and due to the electrohydrodynamic instabilities, after traveling to a short distance in high electric fields, the jet becomes unstable, begins to whip with a high frequency, and formation of the electrospun fibers will be formed [4, 5]. Solution surface tension and viscosity play significant role in establishing the concentration of the polymer solution to obtain continuous fibers after electrospinning. The stable electrospinning jet is composed of four regions: the base, the jet, the splay, and the collection. During the process, solvents with high vapor pressures may begin to evaporate, and the polymer fibre accumulates on the sample collector surface, leading to a two-dimensional network of random fibers [3, 4, 6]. Depending on the type of polymer, the resulting structure can have improved physical properties such as smaller pore size, larger porosity, larger surface-to-volume ratio, and three-dimensional features [1, 7]. Structural properties also depend on experimental conditions such as concentration, applied voltage, needle-collector distance, flow rate, etc. [3, 10]. Different polymers require unique process parameters. Electrospinning can produce a variety of fibers with different diameters and morphologies, which can be used in various applications such as tissue engineering, drug delivery, wound healing, and biosensors [11].

Polymers are macromolecules with versatile structures, compositions, and properties, making them useful in a wide range of applications, including biophysics, medicine, and electronics [12]. Biocompatible polymers, in particular, are notable for their easy processability and

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sterilizability, longer shelf life, light weight, and remarkable properties suitable for various applications in medicine [13]. One of the most popular biopolymers are the polylactic acid (PLA), which is a biodegradable thermoplastic polymer derived from renewable sources like corn starch, cassava, and sugarcane. Its biocompatibility and biodegradability make it useful in a variety of fields such as packaging, agriculture, medical devices, and textile manufacturing [14]. Additionally, the biocompatibility and biodegradability of PLA make it suitable for tissue engineering, drug delivery, surgical implants, mulch films in agriculture, and textile production, including clothing and carpets [15]. Nanoscale fibers made of PLA are one of the most widely used synthetic polymer fibers in medicine and the pharmaceutical industry because they are biocompatible. However, their hydrophobic nature and poor ductility hinder their practical use as a substitute material in tissue regeneration, the issue with it is the hydrophobic nature of the polymer, which is a serious problem in a predominantly hydrophilic biocompatible environment where cells cannot initially attach to the implanted nanofibers [15, 16]. Another important polymer studied for possible medical applications is polycaprolactone (PCL), a biodegradable and biocompatible polyester that has gained significant attention in the field of medical biology due to its unique properties [17]. PCL has a low melting point, making it easy to process into various forms, such as fibers, films, and scaffolds, respectively. It also has good mechanical properties and can be customized to degrade at specific rates, making it suitable for various medical applications such as drug delivery, tissue engineering, and wound healing [17, 18]. Furthermore, PCL has been shown to support cell growth and proliferation, making it an attractive material in regenerative medicine. Several studies have reported successful applications of PCL-based materials in various medical applications, such as the development of nanofibers in tissue engineering and drug delivery systems [12, 17, 18]. PCL nanofibers have demonstrated significant potential in various fields, including tissue engineering, drug delivery, and wound healing, due to their biodegradability, biocompatibility, and tunable mechanical properties. The polymer can be easily electrospun into nanofibrous scaffolds with a high surface-to-volume ratio that can enhance cell attachment, proliferation, and differentiation [12, 18]. Knowing that the average diameter of nanofibers made of the above-mentioned polymers depends on the electrospinning parameters, it is important to optimize these parameters. In order to avoid large number of experiments, the use of desing of experiments can be a good help.

Traditionally, experimental design has involved examining one factor at a time, assuming that factors do not interact. This approach, known as one variable at a time (OVAT), has a number of drawbacks, including the need for numerous experiments, limited data points, and the inability to observe factor interactions, leading to potential misinterpretation of results. Although researchers may find an acceptable response using OVAT, the likelihood of discovering the global optimum is low [7]. To address these limitations, a multivariate statistical approach known as design of experiments (DOE) was introduced. DOE is the most appropriate method for determining the individual and combined effects of factors, as well as their optimal levels. In DOE, the minimum and maximum levels for each factor are defined and expressed on a coded scale (–1 to +1) to facilitate understanding of their significance and interactions [19]. To minimize the impact of unwanted factors, experiments are performed in a randomized order. As the analytical range of a problem typically contains minima, maxima, and saddle points, quadratic terms must be introduced to obtain an appropriate description [7, 19]. To estimate these terms, each factor must be assigned at least three levels. The central composite design (CCD) is one of the most commonly used approaches, which extends the full or fractional factorial design. The CCD involves N experiments and is divided into factorial points, axial points, and centre points, each of which has a specific purpose [7]. Experimental design is the process of conducting research in an objective and controlled manner to maximize accuracy and draw concrete conclusions regarding a hypothesis. Typically, the goal is to determine the effect of an independent variable or factor on a dependent variable. It is particularly useful because it requires relatively few experiments per parameter studied; the interpretation of observations generated by the designs can largely be done using common sense, elementary arithmetic, and computer graphics. When the factors are quantitative but are not capable of fully exploring a large region of the factor space, promising directions for further experimentation can still be determined. Additionally, the designs are easily expandable when examination of another area is needed. In this project, we used experimental design to optimize the diameter of threads with minimal experiments in both polymers. This method also made it possible to compare, in addition to the individual parameters, the combined effect of the

parameters [7, 19]. In our study, we employed electrospinning to investigate the fibre diameters of PLA and PCL nanofibers. The research involved a design of experiment approach to systematically vary parameters such as voltage (*U*), distance (*L*), flow rate (*v*), and concentration (*c*), aiming to research the electrospinning process and characterize the resulting nanofibers by comparing the two.

2 Materials and methods

2.1 Materials, apparatus and software

High purity PLA (with 40 000 Mn) and PCL (with 80 000 Mn) was used purchased from Sigma-Aldrich Co. For the PCL and PLA a 3:2 mixture of dichloromethane (DCM) and chloroform (CLM) was used as a solvent in the preparation steps. Bionicia electrospinning system FLUIDNATEK 2017–F012 was used during the experiments. The fibers were investigated with scanning electron microscope (SEM) and for the interpretation of the images ImageJ software was used. For the regression analysis of experimental data Minitab 19 and Matlab 18 software was used.

2.2 Design of experiment

The process of experimental design can be delineated into three essential phases which comprise of the implementation of statistically designed experiments, calculation of the coefficients of the mathematical model, and validation of the model. The fundamental objective is to develop a mathematical equation that incorporates the influence of the investigated parameters on the thickness and morphology of the fibers. The parameters that were examined encompassed PCL and PLA solution concentration (*c*), applied voltage (*U*), collector distance from needle (*L*), and flow rate (*v*), whereby the levels of these parameters are explicitly specified in Table 1.

The coded and the real values of the factors are presented in Table 2.

The selection of factor levels is based on various factors such as the experimental range size, error in factor fixation, and choice of variation interval. Once the number of factors and the nature and magnitude of their influence are determined, the experimental design is selected. Following this, a mathematical model can be chosen to represent the data. The coefficients in the model indicate the strength of each factor and interaction. The values of these coefficients demonstrate how much the response characteristic is affected when a specific factor change [7, 19, 20].

The response surface method using central composite design was utilized to investigate the impact of the factors mentioned in the "Results and Discussion" and "Conclusion" part. A total of 22 experiments were conducted for each response variable, as illustrated in Table 3.

Table 1 The variables and their levels for the full factorial experimental design

Factor	Name	Units	Min	Max
c	Concentration	%wt	5.00	10.00
U	Voltage	kV	18	24
L	Distance	cm	15	18
v	Flow rate	µL/h	800	1200

Table 2 Explanation of the code system

Factor	Name	Units	–1	0	1
c	Concentration	%wt	5.00	7.50	10.00
U	Voltage	kV	18	21	24
L	Distance	cm	15	16.50	18
v	Flow rate	µL/h	800	100	1200

Table 3 Central composite design and the fibre average diameters (D) for each experimental run

Coded values of the factors					PLA	PCL
Run	*c*(%wt)	*U*(kV)	*L*(cm)	*v*(µL/h)	*D* (µm)	*D* (µm)
1	–1	–1	–1	–1	0.126	0.213
2	–1	–1	–1	1	0.133	0.192
3	–1	–1	1	–1	0.125	0.177
4	–1	–1	1	1	0.124	0.167
5	–1	1	–1	–1	0.128	0.178
6	–1	1	–1	1	0.130	0.175
7	–1	1	1	–1	0.135	0.231
8	–1	1	1	1	0.129	0.162
9	1	–1	–1	–1	0.174	0.423
10	1	–1	–1	1	0.148	0.493
11	1	–1	1	–1	0.453	0.444
12	1	–1	1	1	0.27	0.521
13	1	1	–1	–1	0.28	0.507
14	1	1	–1	1	0.148	0.685
15	1	1	1	–1	0.554	0.7
16	1	1	1	1	0.433	0.631
17	0	0	0	0	0.196	0.378
18	0	0	0	0	0.238	0.332
19	0	0	0	0	0.157	0.29
20	0	0	0	0	0.202	0.274
21	0	0	0	0	0.173	0.304
22	0	0	0	0	0.198	0.327

2.3 Preparation of PLA and PCL solutions and electrospinning process

A solution containing the proper quantity of PCL and PLA was prepared by mixing it with a 3:2 ratio of chloroform and dichloromethane and stirring for six hours with a magnetic stirrer at room temperature, the exact amounts of each components are shown on Table 4. This solution was loaded into the syringe of an electrospinning machine, equipped with a programmable pump that allowed for flow rate control. The collector was placed at the desired distance and covered with baking paper to collect the nanofibers. The voltage was adjusted using a microcontroller within the suitable range for most electrospinning processes. The entire electrospinning process was conducted at room temperature.

2.4 Characterization of prepared PLA and PCL fibre samples

Six scanning electron microscope (SEM, a Hitachi SU8230 –Tokyo, Japan) images were taken for each obtained sample Fig. 1(a). For the analysis of the SEM images, the Fiji program were used, as an image processing tool. The program was used to convert SEM images into segmented images Fig. 1(b). This conversion facilitates the subsequent diameter measurement with the Fiji program by converting each pixel of the SEM images to 1s and 0s. The obtained measurements allow the examination of the distribution of fiber diameters with visually representable histograms Fig. 1(c). In addition, averaging fiber diameters from segmented images allows very accurate diameter thickness determinations.

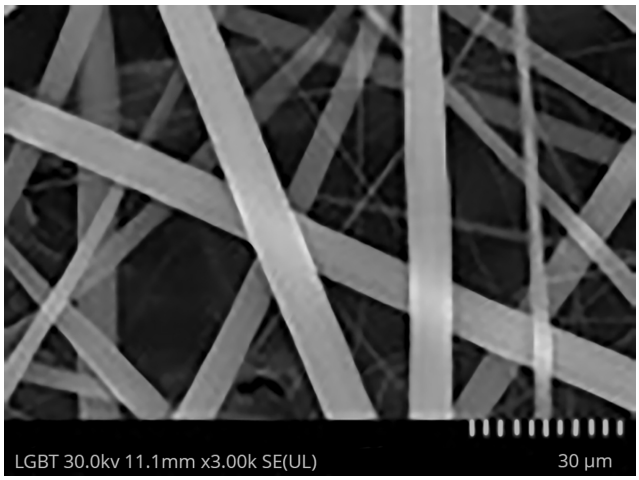
3 Results and Discussion

3.1 Determination of fibre diameter

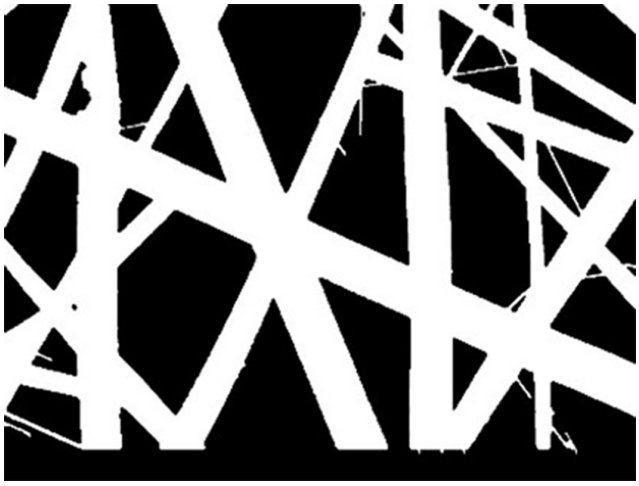
For every sample 5 SEM images were taken, from which around 100 segments were analyzed. It was observed that the fibre diameter of the final product depends on the parameters used in the synthesis procedure. The smallest average diameter was the 4th sample of the PLA 0.124 µm Fig. 2(a) while the largest was the 15th sample of the PCL

Table 4 Amounts of materials used for polymer solutions

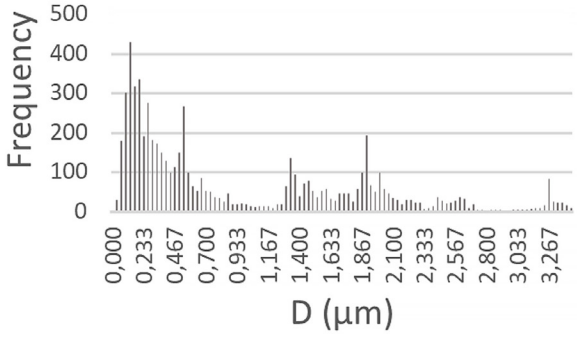
Material	PLA/ PCL	DCM		CLM	
Unit	g	g	mL	g	mL
10 wt%	1.5	8.1	6.09	5.4	3.62
7.5 wt%	1.125	8.325	6.26	5.5	3.69
5 wt%	0.75	8.55	6.43	5.7	3.83



(a)



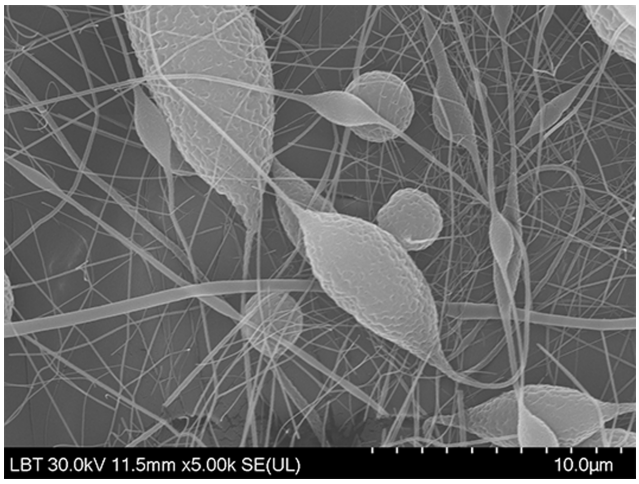
(b)



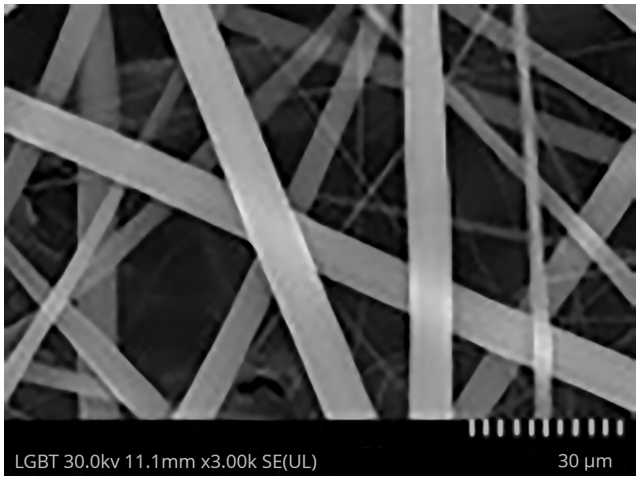
(c)

Fig. 1 Steps to determine fiber diameter: a) SEM image, b) Segmented image, c) Fibre diameter histogram

0.7 µm Fig. 2(b). Our observations were, that the PCL nanofibers were in average 72.7% thicker than the PLA fibers, this can be an effect of the different viscosities of the two solutions. Specifically, a 10 wt% PCL solution in a 3:2 DCM: CLM solvent mixture exhibits a viscosity of



(a)



(b)

Fig. 2 (a) SEM image of the PLA experimental run 4. (10 μm scale) and (b) SEM image of the PCL experimental run 15 (30 μm scale)

1.75 Pas [21], while an equivalent concentration of PLA displays a viscosity of 0.249 Pas [22].

3.2 Estimation of coefficients in a mathematical polynomial function for PLA

After performing the experiments to obtain outputs according to the experimental design, the next step was to consider the vector of variables (*c*, *U*, *L*, *v*) and corresponding respond (diameter). The typical response surface for the PLA function for four inputs is in the form of following equation:

$$\begin{aligned} &Y\left(response\right) = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 \\ &+b_5x_1x_2 + b_6x_1x_3 + b_7x_1x_4 + b_8x_2x_3 + b_9x_2x_4 \\ &+b_{10}x_3x_4 + b_{11}x_1x_2x_3 + b_{12}x_1x_2x_4 + b_{13}x_1x_3x_4 \\ &+b_{14}x_2x_3x_4 + b_{15}x_1x_2x_3x_4, \end{aligned} \tag{1}$$

where x_n is the corresponding factor and b_n is the coefficient, Y is the response in our case the diameter of nanofiber. Using a multiple linear regression analysis on data obtained from experimental results the following model was deduced:

$$\begin{aligned} &D = 8.7 - 1.73c - 0.489L - 0.0084v \\ &-0.407U + 0.0975cL + 0.00168cv + 0.0827cU \\ &+0.000444Lv + 0.0244LU + 0.000414vU \\ &-0.000087cLv - 0.00492cLU - 0.000083cvU \\ &-0.000024LvU + 0.000005cLvU. \end{aligned} \tag{2}$$

The correlation coefficient (R^2) was employed to evaluate the effectiveness of the correlated model. Based on the obtained model, the coefficient value of R^2 is 97.90%, indicating that the model explains 97.90% of the total variations, leaving only 2.10% unexplained. Furthermore, the adjusted R^2 value of 92.66% also confirms the statistical significance of the model, which is considerably high.

Table 5 provides information on the goodness of fit, as assessed by ANOVA analysis. The regression model was found to be highly significant based on the Fisher F-test, which yielded a very low P-value.

3.3 Estimation of coefficients in a mathematical polynomial function for PCL

In case of the PCL, typical response surface function was the following equation:

$$\begin{aligned} &Y\left(response\right) = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 \\ &+b_5x_1x_1 + b_6x_2x_2 + b_7x_3x_3 + b_8x_4x_4 + b_9x_1x_2 \\ &+b_{10}x_1x_3 + b_{11}x_1x_4 + b_{12}x_2x_3 + b_{13}x_2x_4 + b_{14}x_3x_4. \end{aligned} \tag{3}$$

The symbol are the same as for the equation (1).

After using the multiple linear regression analysis on data obtained from the PCL's experimental results we deducted the following model:

$$\begin{aligned} &D = 1.33 - 0.3165c - 0.0718L \\ &-0.000161v + 0.0279U + 0.00819cc \\ &+0.01072cL + 0.000026cv + 0.00302cU \\ &+0.00004Lv - 0.00103LU - 0.00003vU. \end{aligned} \tag{4}$$

The correlation coefficient (R^2) was used to assess the effectiveness of the correlated model. The model produced a coefficient value of 97.22%, indicating only 2.78% of the variations remained unexplained. The adjusted R^2 value of 94.16% is also substantial, just like in the case of the PLA, and provides evidence of the model's significance.

Similarly, to PLA, Table 6 was utilized to determine the quality of the fit for the PCL model, which was further assessed by means of ANOVA analysis. The regression

Table 5 Analysis of variance ANOVA for central composite design

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	15	0.296702	0.019780	18.67	0.001
Linear	4	0.207929	0.051982	49.07	0.000
c (wt%)	1	0.128415	0.128415	121.23	0.000
L (cm)	1	0.009254	0.009254	8.74	0.025
v (µl/h)	1	0.056978	0.056978	53.79	0.000
U (kV)	1	0.013283	0.013283	12.54	0.012
2-Way Interactions	6	0.082799	0.013800	13.03	0.003
cL (wt%cm)	1	0.007894	0.007894	7.45	0.034
cv (wt%µl/h)	1	0.057768	0.057768	54.54	0.000
cU (wt%kV)	1	0.013433	0.013433	12.68	0.012
Lv (cmµl/h)	1	0.001884	0.001884	1.78	0.231
LU (cmkV)	1	0.000176	0.000176	0.17	0.698
v (µl/h)***U* (kV)	1	0.001644	0.001644	1.55	0.259
3-Way Interactions	4	0.004167	0.001042	0.98	0.482
cLv (wt%cmµl/h)	1	0.001250	0.001250	1.18	0.319
cLU (wt%cmkV)	1	0.000081	0.000081	0.08	0.791
cvU (wt%µl/hkV)	1	0.001043	0.001043	0.98	0.359
LvU (cmµl/hkV)	1	0.001794	0.001794	1.69	0.241
4-Way Interactions	1	0.001806	0.001806	1.71	0.239
c (wt%)***L* (cm)***v* (µl/h)***U* (kV)	1	0.001806	0.001806	1.71	0.239
Error	6	0.006356	0.001059		
Lack-of-Fit	1	0.002570	0.002570	3.39	0.125

model was found to be highly significant, as evidenced by the Fisher F-test yielding a P-value with an extremely low probability value.

The Pareto charts (Fig 3.) reproduced from ANOVA results were used to visualize the main effects and their interactions.

The Fig. 3 (a) shows that for PLA, six variables – concentration (*c*), product of concentration and feeding rate (*cv*), feeding rate (*v*), product of concentration and voltage (*cU*), voltage (*U*), and distance (*L*) – are significant at the 93% confidence level. This means that changes in these variables have a strong impact on the outcome of the experiment. In contrast, the Fig. 3 (b) results suggest that there is a strong correlation between the PCL concentration and several factors including concentration multiplied by distance, concentration squared, concentration multiplied by voltage, and feed rate multiplied by voltage. These relationships were found to have a 93% confidence level, indicating a high level of statistical significance.

3.4 Response surface plots

Using the central composite design, response surfaces were generated based on the results obtained. These response surfaces depict the predicted values of fibre diameters calculated from the mathematical model and illustrate the visual relationship between the response and independent variables using a theoretical three-dimensional scheme.

Based on our analysis of the Pareto charts in Fig. 3, we determined that the concentration is the most influential factor affecting both PLA and PCL. To further investigate this relationship, we examined the effects of concentration and other parameters (*U*, *L*, *v*) on diameter using three-dimensional representations, as depicted in Fig. 4. The visualizations allowed us to discern the varying contributions of these parameters to the overall process: a1) The concentration has a much greater impact on fibre diameter compared to voltage, which only causes a negligible change at low concentrations but exhibits a significant diameter-increasing effect at higher concentrations. a2) Increasing the concentration and voltage leads to a larger fibre diameter, with concentration having a more pronounced effect than voltage. b1) The concentration predominantly influences fibre diameter, while the effect of distance is negligible. b2) Elevating both concentration and distance results in an increased fibre diameter, although the impact of distance is minimal compared to concentration. c1) Concentration has

Table 6 Analysis of variance ANOVA for central composite design

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	11	0.612204	0.055655	31.80	0.000
Linear	4	0.035852	0.008963	5.12	0.017
c (wt%)	1	0.030545	0.030545	17.45	0.002
L (cm)	1	0.002212	0.002212	1.26	0.287
v (µl/h)	1	0.000092	0.000092	0.05	0.823
U (kV)	1	0.000719	0.000719	0.41	0.536
Square	1	0.011441	0.011441	6.54	0.029
cc (wt% wt%)	1	0.011441	0.011441	6.54	0.029
2-Way Interaction	6	0.044645	0.007441	4.25	0.022
cL (wt%cm)	1	0.025853	0.025853	14.77	0.003
cv (wt%µl/h)	1	0.002700	0.002700	1.54	0.243
cU (wt%kV)	1	0.008209	0.008209	4.69	0.056
Lv (cmµl/h)	1	0.002257	0.002257	1.29	0.283
LU (cmkV)	1	0.000344	0.000344	0.20	0.667
vU (µl/hkV)	1	0.005283	0.005283	3.02	0.113
Error	10	0.017501	0.001750		
Lack-of-Fit	5	0.010707	0.002141	1.58	0.315
Pure Error	5	0.006794	0.001359		
Total	21	0.629704			

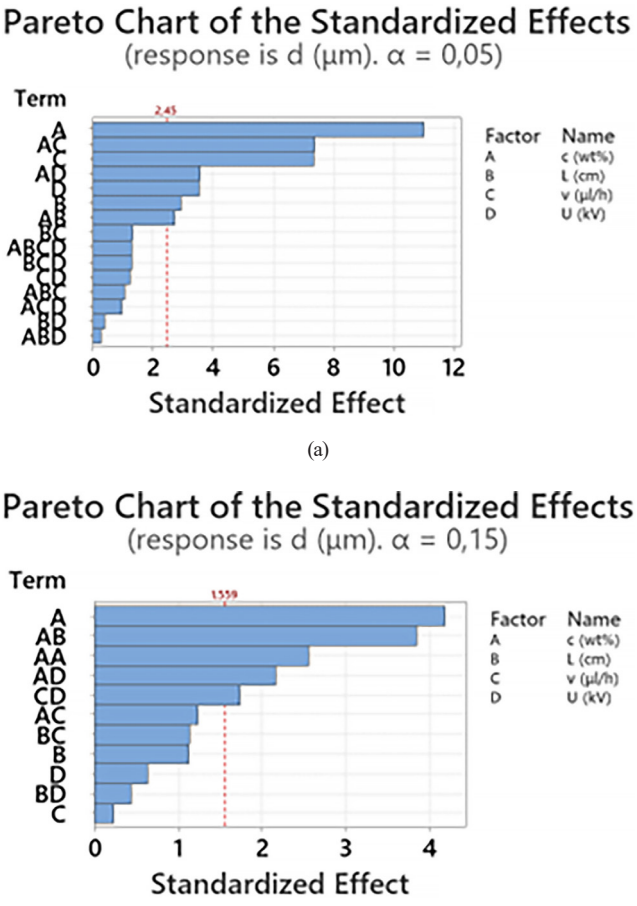


Fig. 3 Pareto chart of the standardized factors, a) for the PLA and b) for the PCL

a significant effect, while the influence of flow rate is negligible. c2) Fibre diameter increases with higher flow rate and concentration, with concentration having the greater effect.

When comparing PCL and PLA using Fig. 4, we observe the following: In the a) row, voltage has an insignificant effect on PLA, while PCL demonstrates better performance at higher concentrations. In the b) row, the diagrams show similar effects, with distance having a greater impact at higher concentrations, although PLA exhibits a higher dependency on distance on average. Conversely, in the c) row, flow rate has low significance for PCL but a notable effect on PLA. In summary, concentration has the highest influence on both PLA and PCL, but at higher concentrations, other parameters and the flow rate become relevant factors for consideration, especially for PLA.

The analysis presented in Fig. 5 depicts the effect of parameters on the diameter when the concentration is held constant. This approach is particularly useful for examining the impact of less significant parameters without the confounding influence of stronger factors such as concentration. The results of this analysis demonstrate the following: a1) At low voltage, the feeding speed significantly increases the fibre diameter, whereas at high voltage (which also increases the fibre diameter), the feeding speed has a smaller effect and reduces the fibre diameter. a2) The fibre diameter increases with an increase in flow rate and voltage, but the feeding rate has a greater effect. b1) The fibre diameter increases with an increase in distance and voltage, but the effect of voltage is negligible compared to distance. b2) Both voltage and distance have a small effect on the fibre diameter. c1) Both distance and feed rate increase the fibre diameter, but increasing distance has a more significant effect. c2) The diameter increases with an increase in distance and feed rate, with the flow rate having a greater effect.

The results of this analysis demonstrate that the parameters in the a) row have a different effect on the two polymers. For PLA, the flow rate has the highest effect, while

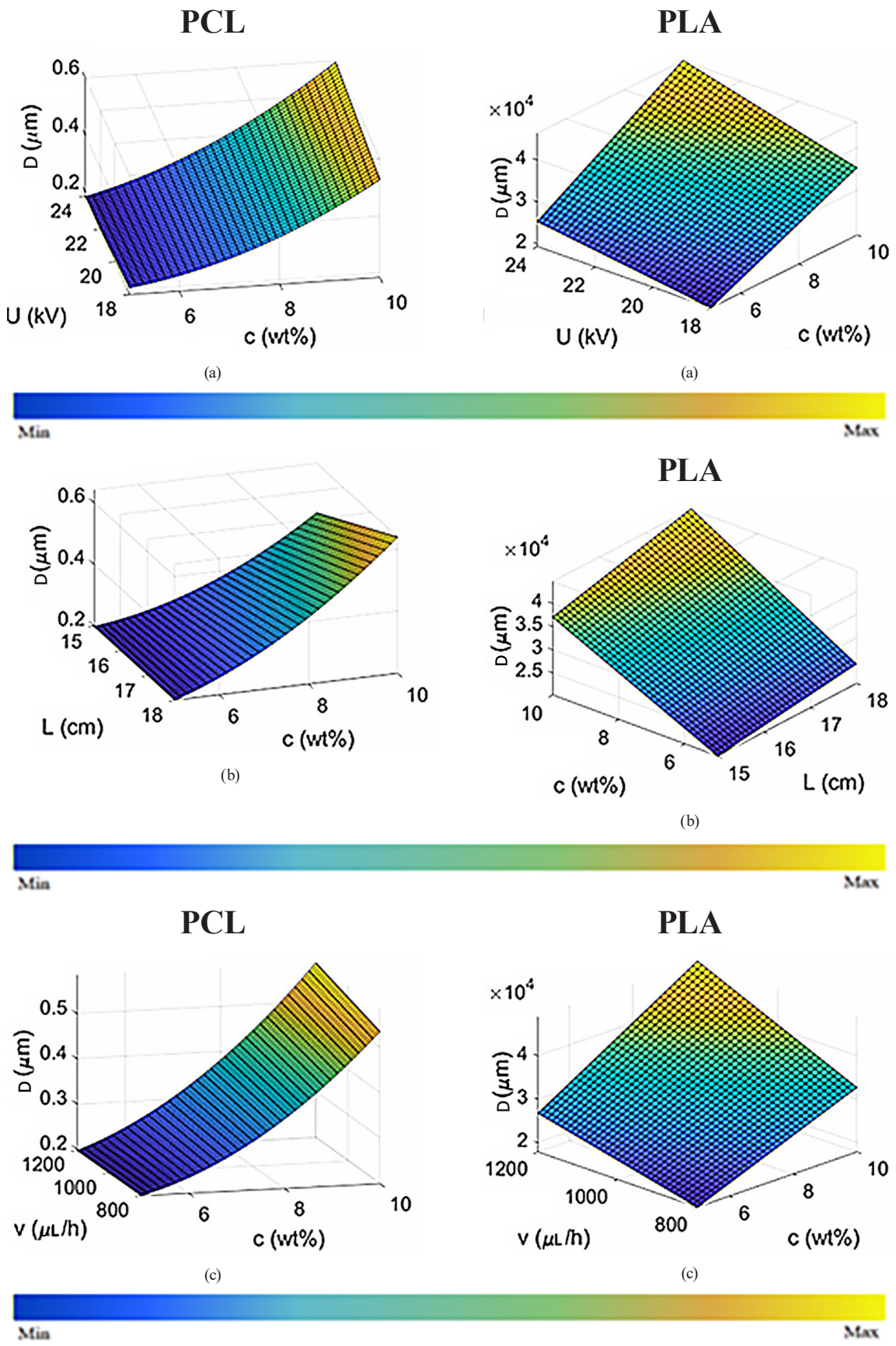


Fig. 4 Investigating the role of concentration and other parameters on PCL and PLA diameter, using three-dimensional representations, a) *D* vs *c*, *U*; *L*=16.5 cm; *v*=1000 µL/h, b) *D* vs *c*, *L*; *U*=21 kV; *v*=1000 µL/h, c) *D* vs *c*, *v*; L=16.5 cm; *U*=21 kV

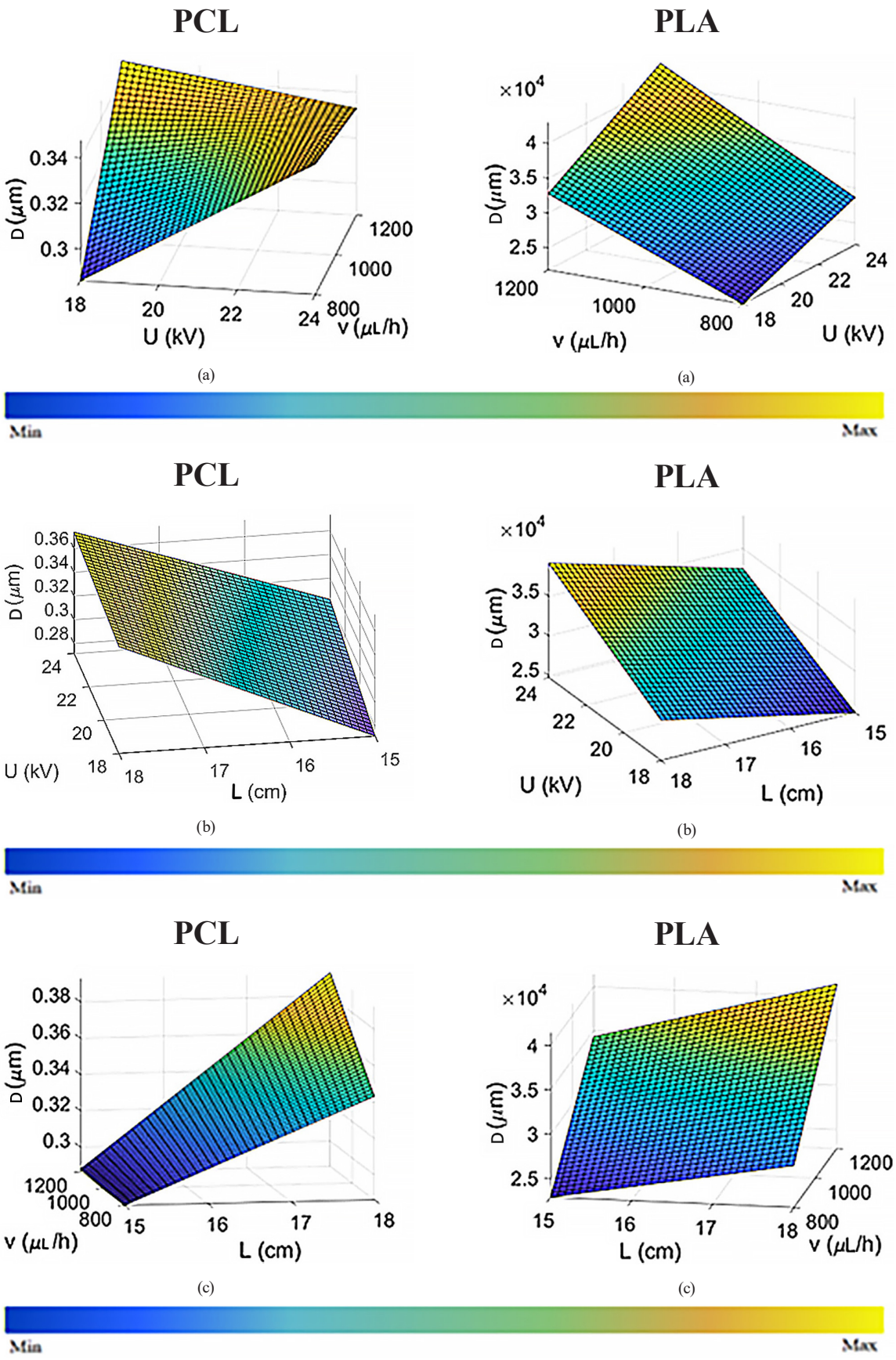


Fig. 5 Investigating the role of the parameters at constant concentration on PCL and PLA diameter, using three-dimensional representations, a) *D* vs *v*, *U*; *c*=7.5 wt%; *L*=16.5 cm, b) *D* vs *U*, *L*; c=7.5 wt%; *v*=1000 μL/h, c) *D* vs *c*, *v*; *c*=7.5 wt%; *U*=21 kV

for PCL, it is the inverse, although in this case, the voltage and flow rate have a strong combined effect. Meanwhile, for the b) row parameters, the distance has a higher effect than the voltage. By increasing both the voltage and distance, the fibre diameter increases, but both have a small effect. For the parameters in the c) row, both the distance and feed rate increase the fibre diameter, but in the case of PCL, the distance has a higher effect, while for PLA, it is the flow rate.

The most influential factor affecting the electrospinnability of both PLA and PCL is the concentration of the polymer solution. At higher concentrations, the solution becomes more viscous, which can lead to the formation of beads and droplets. Additionally, the flow rate and voltage can also affect the fiber diameter, with higher flow rates and voltages generally resulting in thicker fibers. However, the effects of these parameters are not the same for both PLA and PCL. For example, PCL is more sensitive to the voltage than PLA, while PLA is more sensitive to the flow rate. Additionally, the distance between the needle and the collector has a greater effect on the fiber diameter of PLA than PCL.

4 Conclusions

Based on the results, it can be concluded that each 4 parameters (concentration, voltage, flow rate and distance) has an effect on the fibre diameter. Increasing the value of any parameters increases the average fiber diameter. However, the rate of growth varies for the two polymers: for PLA, feed rate and concentration have the greatest effect on fibre diameter, while for PCL, it is concentration. Also, distance and tension have the smallest effect for PLA, while feed rate is negligible for PCL. Overall, it can be clearly seen that the combined effect of parameters and concentration is significant for both PLA and PCL.

Based on the analysis, it can be concluded that the concentration had the most significant impact on both PLA and PCL nanofibers. For PLA, the combined effect of concentration and flow rate, as well as the individual effect of flow rate alone, also had noticeable effects. Similarly, for PCL, the combined effect of other parameters with concentration also had a significant impact. Therefore, the concentration can be identified as the main factor with the most substantial effect, while acknowledging the significant impact of other parameters when combined with concentration.

During the planning phase of our study, we ensured the usage of the same parameters and solvents for both PCL and PLA. Analysis of our findings reveals that PCL nanofibers exhibit an average 72.7% greater thickness compared to PLA nanofibers. This observation can be attributed to variations in the viscosity of the respective solutions.

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References

[1] Frenot, A., Chronakis, I. S. "Polymer nanofibers assembled by electrospinning", Current Opinion in Colloid and Interface science, 8(1), pp. 64–75, 2003. https://doi.org/10.1016/S1359-0294(03)00004-9

[2] Li, D., Xia, W. Y. "Electrospinning of nanofibers: reinventing the wheel?", Advanced Mateirals, 16(14), pp. 1151–1170, 2004. https://www.doi.org/10.1002/adma.200400719

[3] Deitzel, J. M., Kleinmeyer, J., Harris, D., Tan, N. C. B. "The effect of processing variables on the morphology of electrospun nanofibers and textiles", Polymer, 42(1), pp. 261–272, 2001. https://doi.org/10.1016/S0032-3861(00)00250-0

[4] Sivan, M., Madheswaran, D., Hauzerova, S., Novotny, V., Hedvicakova, V., Jencova, V., Kostakova, E. K., Schindler, M., Lukas D., "AC electrospinning: impact of high voltage and solvent on the electrospinnability and productivity of polycaprolactone electrospun nanofibrous scaffolds", Materials Today Chemistry, 26, 101025, 2022. https://doi.org/10.1016/j.mtchem.2022.101025

[5] Sivan, M., Madheswaran, D., Valtera, J., Kostakova, E. K., Lukas, D., "Alternating current electrospinning: The impacts of various high-voltage signal shapes and frequencies on the spinnability and productivity of polycaprolactone nanofibers", Materials and Design, 213, 110308, 2022. https://doi.org/10.1016/j.matdes.2021.110308

[6] Ishii, Y., Sakai, H., Murata, H., "A new electrospinning method to control the number and a diameter of uniaxially aligned polymer fibers", Materials Letters, 62, pp. 3370–3372, 2008. https://doi.org/10.1016/j.matlet.2008.03.038

[7] Petrut, H., Vészi, A., Muntean, N., Cadar, O., Barabás, R. "Mathematical modelling of the electrospinning process for production of polyvinyl alcohol nanofibers", Studia Universitatis Babes Bolyai – Studia Chemia, 3, pp. 117–118, 2022. https://doi.org/10.24193/subbchem.2022.3.09

[8] Li, Z., Wang, C. "Effects of working parameters on electrospinning", In: One-Dimensional nanostructures, Springer Berlin, 2013, pp. 15–28, ISBN: 978-3-642-36427-3 https://doi.org/10.1007/978-3-642-36427-3_2

[9] Thompson, C. J., Chase, G. G., Yarin, A. L., Reneker, D. H. "Effects of parameters on nanofiber diameter determined from electrospinning model", Polymer, 48(23), pp. 6913–6922, 2007. https://doi.org/10.1016/j.polymer.2007.09.017

[10] Meyva-Zeybek, Y., Kaynak, C. "Electrospinning of PLA and PLA/POSS nanofibers: use of Taguchi optimization for process parameters", Journal of Applied Polymer Science, 138(3), 49685, 2020. https://doi.org/10.1002/app.49685

[11] Ramirez, M., Vaught, L., Law, C., Meyer, J. L., Elhajjar, R. "Electrospinning processing techniques for the manufacturing of composite dielectric elastomer fibers", Materials, 14(21), 6288, 2021. https://doi.org/10.3390/ma14216288

[12] Agarwal, S., Wendorff, J. H., Greiner, A. "Use of electrospinning technique for biomedical applications", Polymer, 49(26), pp. 5603–5621, 2008. https://doi.org/10.1016/j.polymer.2008.09.014

[13] Deng, W., Gomez, A. "Full transient response of Taylor cones to a step change in electric field", Microfluid Nanofluid, 12, pp. 383–393, 2012. https://doi.org/10.1007/s10404-011-0882-6

[14] Södergård, A., Stolt, M. "Properties of lactic acid based polymers and their correlation with composition", Progress in Polymer Science, 27(6), pp. 1123–1163, 2002. https://doi.org/10.1016/S0079-6700(02)00012-6

[15] Xu, W. Shen, R., Yan, Y., Gao, J. "Preparation and characterization of electrospun alginate/PLA nanofibers as tissue engineering material by emulsion electrospinning", Journal of the Mechanical Behavior of Biomedical Materials, 65, pp 428–438, 2017. https://doi.org/10.1016/j.jmbbm.2016.09.012

[16] Casasola, R., Thomas, N. L., Trybala, A., Georgiadou, S., "Electrospun poly lactic acid (PLA) fibers: effect of different solvent systems on fibre morphology and diameter", Polymer, 55(18), pp. 4728–4737, 2014. https://doi.org/10.1016/j.polymer.2014.06.032

[17] Mondal, D., Griffith, M., Venkatraman, S. S., "Polycaprolactone-based biomaterials for tissue engineering and drug delivery: current scenario and challenges", International Journal of Polymeric Materials and Polymeric Biomaterials, 65(5), pp. 255–265, 2016. https://doi.org/10.1080/00914037.2015.1103241

[18] Zhang, Y., Venugopal, J. R., El-Turki, A., Ramakrishna, S., Su, B., Lim, T. C., "Electrospun biomimetic nanocomposite nanofibers of hydroxyapatite/chitosan for bone tissue engineering", Biomaterials, 29(32), pp. 4314–4322, 2008. https://doi.org/10.1016/j.biomaterials.2008.07.038

[19] George, E. P., Box, J. S., Hunter, W. G., "Statistics for experimenters: design, innovation, and discovery", Wiley, 2005, ISBN: 10 0-471-71813-0

[20] Badawi, M. A., El-Khordagui, L. K., "A quality by design approach to optimization of emulsions for electrospinning using factorial and D-optimal designs", European Journal of Pharmaceutical Sciences, 58, pp. 44–54, 2014. https://doi.org/10.1016/j.ejps.2014.03.004

[21] Czarnecka, K., Wojasiński, M., Ciach, T., Sajkiewicz, P., "Solution blow spinning of polycaprolactone–rheological determination of spinnability and the effect of processing conditions on fibre diameter and alignment", Materials, 14(6), 1463, 2021. https://doi.org/10.3390/ma14061463

[22] Jahangir, M. A., Rumi, T. M., Wahab, A., Khan, I., Rahman, M. A., Bin Sayed, Z., "Poly Lactic Acid (PLA) fibers: different solvent systems and their effect on fibre morphology and diameter", American Journal of Chemistry, 7(6), pp. 177–186, 2017. https://doi.org/10.5923/j.chemistry.20170706.01