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The Influence of Process Parameters on the Properties of Electrospun PLLA Yarns Studied by the Response Surface Methodology

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ABSTRACT: Poly (L-lactide) (PLLA) fibrous yarns were prepared by electrospinning of polymer solutions in 2,2,2-trifluoroethanol. Applying spinning from two oppositely charged needles the spontaneous formed triangle of fibers at a grounded substrate could be assembled into fibrous yarns using a device consisting of a take-up roller and twister. The effect of processing parameters on the morphology, diameter and mechanical properties of PLLA yarns was investigated by the response surface methodology (RSM). This method allowed evaluating a quantitative relationship between polymer concentration, voltage, take-up rate and distance between the needles' center and the take-up unit on the properties of the electrospun fibers and yarns. It was found that at increasing concentrations up to 9 wt % uniform fibers were obtained with increasing mean diameters. Conversely, the fiber diameter decreased slightly when the applied voltage was increased. The take-up rate had a significant influence on the yarn diameter, which increased as the take-up rate decreased. The tensile strength and modulus of the yarns were correlated with these variables and it was found that the polymer concentration had the largest influence on the mechanical properties of the yarns. By applying the RSM, it was possible to obtain a relationship between processing parameters which are important in the fabrication of electrospun yarns. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41388.

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INTRODUCTION

Electrospinning, a technique in which electric forces are subjected to polymer solutions or melts, is an efficient method to produce fibers from both synthetic and natural polymers with submicron diameters.[1–3] Fiber deposition may be either randomly, leading to nanofiber webs, or structures composed of aligned fibers using collection devices or by manipulating the electric field.[2,4] Compared to nanofiber webs, aligned nanofiber bundles hold more lateral interaction and friction between fibers. These interactions can be further increased by twisting the nanofibers on collection providing yarns. As a result of the increased interfiber interaction and cohesion, the mechanical properties of such structures are highly improved. Aligned fiber bundles or yarns are currently studied for their potential applications in, for example, the biomedical field, especially as scaffolds in tissue engineering, microelectronics, as reinforced composites, sensors, and protective clothing textiles.[5]

In recent years, it has been shown that yarns with uniaxially aligned fibers can be produced by a variety of spinning techniques. Recently, Shuakat and Lin[6] and Abbassipour and Khajavi[7] summarized these electrospinning techniques and fiber alignment in a twisted or nontwisted form for the production of nanofiber bundles and yarns. These reviews show that much progress has been made in the assembly process of nanofibers and defined fibrous structures and materials. One of these methods as developed more recently in our laboratories is the use of two oppositely charged needles. In this technique oppositely charged nanofibers create a triangle of fibers in the area between a neutral cylindrical surface and yarn convergence point, where nanofibers will be finally converged and twisted into yarn.[5,6,8–10]

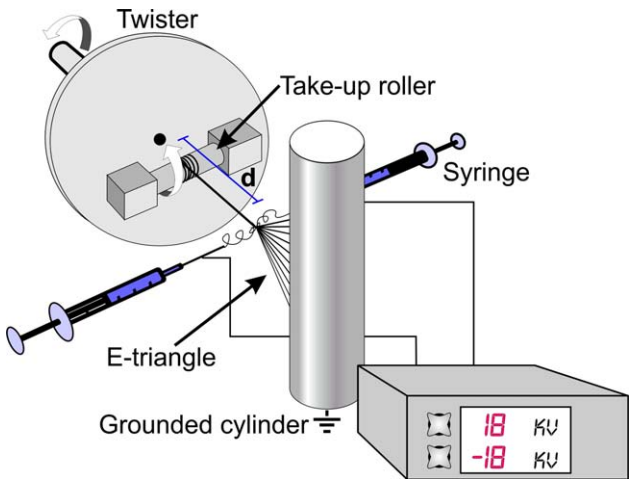

Figure 1. Schematic illustration of the electrospinning setup used in the production of fibrous yarns. The distance between the center of the two needles and the take-up unit (d) is indicated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In the preparation of yarns by electrospinning, variables can be separated in three categories namely polymer solution parameters, processing conditions, and ambient parameters like temperature and humidity.[11–13] These processing conditions directly influence the fiber diameter of the polymeric fibers and likely influences the mechanical properties of fibrous deposits like yarns. Moreover, the morphology of the fibers may influence the surface properties and thereby the hydrophobic nature of materials prepared.[14–17]

In this study, the preparation and properties of twisted yarns from electrospun poly (L-lactide) (PLLA) fibers by a continuous process is presented. PLLA is a thermoplastic polymer made from renewable resources and due to its biocompatibility, biodegradability, and mechanical properties has many applications especially as biocompatible/bioabsorbable medical devices.[8,18] The response surface methodology (RSM) was used to systematically investigate process parameters that influence the fiber and yarn diameter and thereby the mechanical properties of the electrospun yarns. Processing parameters investigated were the solution concentration, applied voltage, take-up rate, and distance of the center between the needles and the take-up unit. RSM has been applied recently to analyze the effect of electrospinning parameters on the final properties of nanofibers.[12,19–22] Using this method, an empirical relationship between independent variables and one or more response variables is obtained. Moreover, the use of this model allows a straightforward and systematic representation of the processing parameters inflencing fiber and yarn formation, and can be used to predict the results of the experiments applying different combinations.[21,23]

EXPERIMENTAL

Preparation of Polymer Solution

PLLA (inherent viscosity 2.51 dL/g) was a gift from Purac Biomaterials, The Netherlands. 2,2,2-Trifluoroethanol (TFE) was obtained from Merck. PLLA/TFE solutions having concentrations varying from 5 to 9 wt % were stirred at 45°C for at least 12 h to obtain homogenous solutions.

Electrospinning Setup

To produce continuous twisted fiber yarns, an electrospinning setup consisting of two oppositely charged nozzles was used (Figure 1). This setup consists of two digitally controlled syringe pumps (TOP-5300, Japan) and flat-tipped needles (22-gauge, ID = 0.4 mm, OD = 0.7 mm) to provide a 0.3 mL/h constant solution feed rate during the electrospinning process. A DC high voltage-power supply was used to charge the needles with the same values of voltage but at different polarization. A grounded aluminum cylinder (6 cm diameter × 30 cm length) was placed vertically at a distance of 2 cm from the center of the two nozzles. The take-up/twister unit consists of a take-up roller and a rotating plate for twisting the yarn. The twister rotation speed can be varied up to 440 rpm. To obtain a constant twist per meter (TPM) yarn over all experiments the twister rotation and take-up rate were adjusted according the relationship; TPM = twister rotation speed (rpm)/take-up rate (m/min). The linear take-up speed is dependent on the solution feed rate and can be controlled using a stepper motor. To produce the yarn, electrospinning was started between two nozzles and the grounded cylinder.

At the convergence point, a triangle of fibers was formed, called the "electrospinning triangle (E-triangle)." The fibers at the convergence point were collected with a piece of yarn, which was then pulled toward the take-up roller. The fibers were twisted by rotating the yarn around its axis and the yarn was taken up by the roller mounted to the twister plate.[5,8] Based on this setup, the yarn production process was continuous. The electrospinning was performed at a temperature of 21 ± 2°C and a humidity of 26 ± 2%. The electrospinning setup parameters such as take-up speed, rotation rate of the twister, distance between the center of the two needles and the take-up unit, solution feed rate, and applied voltage are all important parameters that were considered to produce a continuous fibrous yarn.

Characterization

Morphology. The morphology of the yarns and electrospun fibers in the E-triangle region were examined by scanning electron microscopy (SEM; XL 30, Philips). The samples were sputtered with a thin layer of gold prior to SEM analysis. An accelerating voltage of 20 kV was applied. Based on SEM images, the average diameter of yarns and electrospun fibers were determined by means of Image J 1.44p software. The results are reported as average values of 100 measurements.

Mechanical Properties. The twisted fibrous yarns were cut at random into pieces with an equal length of 100 cm and accurately weighed to obtain the linear mass density (Tex) of the yarns. Mechanical properties of the twisted electrospun PLLA yarns were measured using a tensile tester (Instron Elima EMT-3050). The selected gauge length and crosshead speed were 20 mm and 10 mm/min, respectively. The data obtained in cN per Tex (cN/Tex) were converted into MPa.

Experimental Design

Experiments Based on a Central Composite Design. In this work, a central composite design (CCD) was used to study the

Table I. Experimental Range and Coded Levels of Numerical Independent Process Variables

Variable	Code	Real values of the coded levels		
		−1	0	1
Concentration (wt %)	x_1	5.00	7.00	9.00
Voltage (kV)	x_2	9.00	13.50	18.00
Take-up rate (m/min)	x_3	0.02	0.05	0.08
Needles's center/take-up unit distance (cm)	x_4	22.00	30.00	38.00

effects of electrospinning processing parameters on the diameter and mechanical properties of PLLA fibrous yarns by using the RSM (Design Expert 8.0.7.0, Stat-Ease). In preliminary experiments, we determined the experimental boundaries for fiber formation and yarn production by changing the concentration, voltage, take-up rate and the distance of the needles' center to the take-up unit (d in Figure 1). The experimental range and coded levels of independent variables are presented in Table I. Within the given boundaries in all cases yarns could be produced. From these experiments, 30 further experiments were designed using the CCD methodology. The experimental conditions are shown in Table II. The fiber diameter in the E-triangle zone (Y_1), the yarn diameter (Y_2), yarn strength (Y_3), and yarn modulus (Y_4) were set as the response variables.

Mathematical Modeling. In general, the functional relationship between the experimental variables, x_1, x_2,..., x_k and the observed response Y can be described in a mathematical form[24]:

$$Y = f(x_1, x_2, ..., x_k) + e \quad (1)$$

where f is the response function and e is defined as a statistical error which is assumed to follow a normal distribution. The form of the response function should be approximated. A second-order polynomial model represents the relationship between factors and response:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j + e_i \quad (2)$$

The coefficients b_0, b_1, b_2, ... b_{ij} in the polynomial model will be called parameters of the model. The term b_0 is a constant and estimates the response when all variables are set to zero values. The terms b_i and b_{ii} are the linear and quadratic coefficients respectively. The b_{ij} parameters provide a measure of the interaction between the variables x_i and x_j.[25,26]

Statistical Analysis. The regression correlation coefficient (R^2) is used in the context of statistical models and provides a measure of how well the observed response values fit the model. This coefficient ranges from 0 to 1. When R^2 approaches 1, the actual data fit the polynomial model properly. Low values of R^2 imply that the dependent variables in the applied model do not correlate well.[24]

As more independent variables are added to the regression model, R^2 will generally increase. Thus, a large value of R^2 does not necessarily imply that the regression model is consistent. To take this into account, an adjusted R^2 (R^2_{adj}) is defined by eq. (3), which is generally considered to be a more accurate measure than R^2:[24]

$$R^2_{adj} = 1 - \frac{n-1}{n-p-1}(1-R^2) \quad (3)$$

where n is a number of observations and p is the total number of regression coefficients. The statistical significance of the model is set to 0.05.[27] The probability values (p-value) are utilized to consider the statistical significance of the determined model, with a threshold value of $p < 0.05$.

RESULTS AND DISCUSSION

As shown in previous work, using a setup with two oppositely charged needles close to a grounded cylinder a triangle of

Table II. Experimental Conditions in the Electrospinning of PLLA-TFE Solutions

Run No.	X_1 (wt %)	X_2 (kV)	X_3 (m/min)	X_4 (cm)
1	9.00	18.00	0.02	38.00
2	9.00	9.00	0.08	38.00
3	7.00	9.00	0.05	30.00
4	9.00	18.00	0.08	38.00
5	7.00	13.50	0.05	22.00
6	5.00	18.00	0.08	22.00
7	7.00	13.50	0.05	30.00
8	7.00	13.50	0.05	30.00
9	7.00	13.50	0.05	30.00
10	9.00	18.00	0.02	22.00
11	5.00	13.50	0.05	30.00
12	5.00	9.00	0.08	22.00
13	7.00	13.50	0.05	30.00
14	7.00	13.50	0.05	38.00
15	7.00	18.00	0.05	30.00
16	9.00	13.50	0.05	30.00
17	9.00	18.00	0.08	22.00
18	7.00	13.50	0.08	30.00
19	7.00	13.50	0.05	30.00
20	9.00	9.00	0.02	22.00
21	5.00	18.00	0.08	38.00
22	5.00	18.00	0.02	22.00
23	5.00	18.00	0.02	38.00
24	9.00	9.00	0.08	22.00
25	7.00	13.50	0.05	30.00
26	5.00	9.00	0.02	22.00
27	7.00	13.50	0.02	30.00
28	5.00	9.00	0.02	38.00
29	9.00	9.00	0.02	38.00
30	5.00	9.00	0.08	38.00

X_1: polymer concentration; X_2: voltage; X_3: yarn take up rate; X_4: distance from center of the needles to the take up unit.

Table III. The Analysis of the Variance of the Response Surface 2FI Model for the E-Triangle Fiber Diameter

Source	Sum of squares	df	Mean square	*F* value	*p*-value Prob > *F*	
Model	5.860	10	0.590	44.65	<0.0001	Significant
X_1-concentration (wt %)	5.140	1	5.140	391.60	<0.0001	Significant
X_2-voltage (kV)	0.260	1	0.260	19.95	0.0003	Significant
X_3-take-up rate (m/min)	0.023	1	0.023	1.73	0.2045	
X_4-center between needles/take-up unit distance (cm)	0.050	1	0.050	3.81	0.1660	
X_1 X_2	0.340	1	0.340	25.90	<0.0001	Significant
X_1 X_3	0.011	1	0.011	0.80	0.3814	
X_1 X_4	0.002	1	0.002	0.12	0.7380	
X_2X_3	0.005	1	0.005	0.41	0.5283	
X_2 X_4	0.015	1	0.015	1.15	0.2963	
X_3 X_4	0.013	1	0.013	1.00	0.3310	

electrospun fibers was formed (Figure 1, E-triangle zone). With a piece of yarn, these fibers could be carefully pulled toward a twister plate with a rotating take-up roller. In this way, a continuous yarn composed of electrospun PLLA fibers was obtained.[8] It was also shown that solvents with a low vapor pressure like TFE allowed enough time for the PLLA crystals to grow during fiber formation resulting in a high crystallinity. Moreover, uniform yarns with a diameter of ~150 μm composed of fibers with a diameter of ~2 μm were obtained.[8] To optimize the properties of such yarns that may well be applied in the biomedical field, like in sutures and scaffolds for tissue engineering, the processing conditions were studied. Changing polymer concentration, applied voltage, distance to collector and collector speed would require a very large number of individual experiments. This can be circumvented by performing a set of experiments according the RSM. This method includes the design of experiments and linear regression of the obtained results. This approach enables experimental investigation of the individual variables or parameters and their interactions simultaneously as opposed to determining a single parameter while keeping the other parameters constant. In this way, optimum values for the different parameters can be gained by a generic algorithm.[12,14,20,28]

First, a set of preliminary experiments were performed to determine the boundaries for electrospinning of PLLA/TFE solutions. The poly (lactide) used in this study has an inherent viscosity of 2.51 dL/g and an average molecular weight M_w of 3.10.[5] Within a polymer concentration range between 5 and 9 wt % electrospinning resulted in fiber formation. At concentrations lower than 5 wt % the viscosity of the PLLA solution was not high enough to electrospin fibers and it was observed that the electrospinning jet broke up into small droplets.[29] Moreover, at concentrations higher than 9 wt % the solution became too viscous to pass through the needle at a constant rate. Voltages lower than 9 kV caused droplet formation at the needle tip and a jet was not formed. At voltages higher than 18 kV, fibers could not be properly being focused within an E-triangle near the grounded cylinder and yarn formation was not possible, but at intermediate values fibers could be electrospun and yarns could be produced. The take-up rate of the yarn at the roller was set to values in between 0.02 and 0.08 m/min. This range was effective, since it avoided breakage of the yarn at higher values and yarns with varying diameters at low values. A distance of 22–30 cm between the center of the two needles and take-up unit allowed a continuous process. At distances higher than 30 cm, because of fibers flying, yarn breakage occurred and a nonuniform yarn was obtained. Within the ranges given for concentration, voltage, take-up rate and the distance between needles and take-up roller, a series of 30 experiments were carried out and the results were evaluated by the RSM.

E-Triangle Fiber Diameter (Y_1)

The analysis of variance (ANOVA) results showed that the diameter of fibers in the E-triangle zone was most suitably described with a two-factor interaction (2FI) model (Table III). The 2FI model includes all terms up to the two-factor interactions. This will provide the aliases for the main effects and two-factor interactions.[25] The *p*-value ($p < 0.0001$) was much lower than 0.05 while the values of R^2 ($R^2 = 0.96$) and R^2_{adj} ($R^2_{adj} = 0.94$) approached unity. In addition, for the 2FI model the *p*-value for lack of fit was calculated. The lack of fit test compares the residual error (from the model error) to the pure error (from replicated experiments) and measures how well the model fits the data. Significant lack of fit ($p < 0.05$) is an undesirable property, because it indicates that the model does not fit.[27] A *p*-value of 0.4234 is calculated implying that the lack of fit is not significant. Therefore, it can be concluded that the 2FI model adequately fits the response surface.

The experimental results obtained for the fiber diameter in the E-triangle zone were fitted in terms of processing parameters; concentration, voltage, take-up rate, needles center to take-up unit distance and their interactions, and is represented by eq. (4):

$$Y_1 = 0.92 + 0.53x_1 - 0.12x_2 + 0.035x_3 - 0.053x_4 - 0.15x_1x_2 + 0.026x_1x_3 - 0.0097x_1x_4 - 0.018x_2x_3 + 0.031x_2x_4 - 0.029x_3x_4 \quad (4)$$

Considering the *p*-values, only the concentration (x_1), voltage (x_2), and their interaction (x_1x_2) have significant effects on the

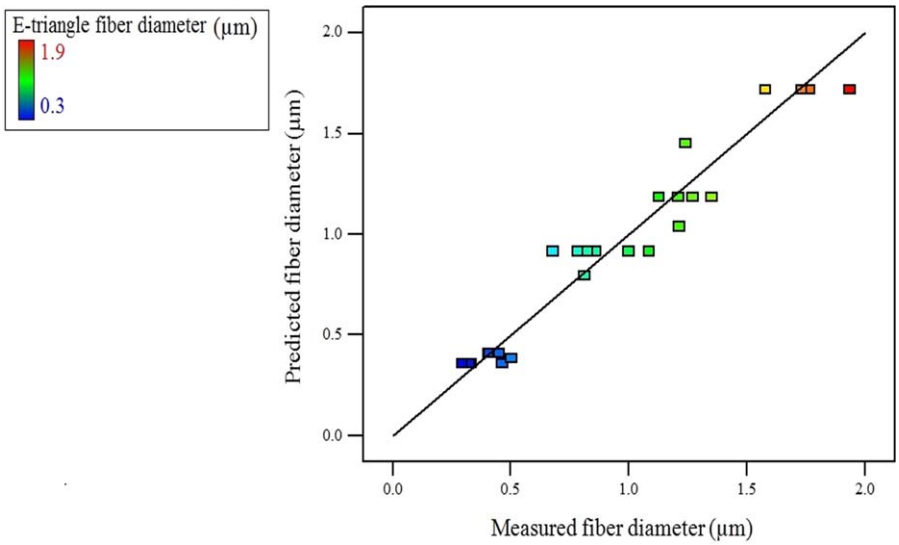

Figure 2. Predicted versus measured values of E-triangle fiber diameter (μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

average fiber diameter in the E-triangle zone (Table III). Removing the insignificant terms eq. (4) can be simplified to eq. (5):

$$Y_1 = 0.92 + 0.53x_1 - 0.12x_2 - 0.15x_1x_2 \quad (5)$$

The average fiber diameters (E-triangle zone) obtained from experiments at different concentrations as shown in Table II and predicted fiber diameters from the model are presented in Figure 2. The values determined were in agreement with the predicted values, which suggest that the model was accurate.

From the results of the experiments at different polymer concentration and applied voltage (as indicated in Table II) a 3D surface plot [Figure 3(a)] was generated from the variables x_1 (concentration) and x_2 (voltage), while the other variables were set to the central coded values as given in Table I. The surface plot gives an overall impression on the dependence of the fiber diameter on these two variables over the entire operating range studied. In Figure 3(b) a contour plot of the mean fiber diameter is presented. These plots indicate that the average fiber diameter is highly dependent on the polymer concentration applied.[14,30,31] Moreover, it is shown that the voltage had little effect on the fiber diameter at solution concentrations of 5 and 7 wt %. At the higher polymer concentration of 9 wt %, the fiber diameter decreased as the voltage increased. Finally, an interaction plot showing the interdependence of concentration and applied voltage on the E-triangle fiber diameter was generated. Only values of the fiber diameters were used from experiments at a take-up rate of 0.05 m/min and center between needles and take-up unit distance of 30 cm. From Figure 3(c), it can be seen that the change in fiber diameter depends on the settings of the two factors. This indicates that the effect of one factor depends on the level of the other one.[24] Although the trend lines cross at a low concentration the slope of the lines revealed a clear dependence of these two variables.

Although the analysis of data concerning the E-traingle fiber diameter suggest that the polymer concentration is the most important factor, the applied voltage may affect factors like volume of solution drawn from the tip of the needle, elongation of the jet by the electrical force, and thereby the resultant fiber morphology. To control the diameter of the fibers and their morphology a balance between applied voltage and polymer concentration is likely to be met.[32,33] An analysis of the morphology by SEM was subsequently performed.

The morphology and diameter distribution of the fibers obtained from 5, 7, and 9 wt % PLLA solutions in TFE are presented in Figure 4. Experiments were performed at a voltage of 13.5 kV and the distance between the center of the needles and take-up unit was 30 cm. At a low PLLA concentration of 5 wt % thin beaded fibers were formed, whereas at higher concentration beadles fibers were obtained. The beaded fiber morphology is generally due to low viscosity polymer solutions.[34,35] As shown by Koski et al.[36] electrospinning nanofibers can take place in a certain concentration range depending on the molecular weight of the polymer. At low concentrations generally beaded fibers are generated, whereas at to high concentrations and high molecular weight flattening of the fibers may occur. Also solvents with a low vapor pressure like TFE influence fiber formation and morphology as was shown in the fiber and yarn formation of PLLA.[8] At a concentration of 9 wt %, the average fiber diameter (1.24 ± 0.15 μm) was the highest. At lower concentrations of 7 wt %, fibers with mean diameters of 0.96 ± 0.25 μm were produced and this value decrease to approximately 0.5 ± 0.1 μm at the lower concentrations limit of 5 wt %. The decreasing fiber diameter at lower concentrations is due to the easier stretching of jets in the applied electrical field at lower viscosities. Moreover, the bending instability by columbic repulsion between charged parts within the jet can result in less uniform fiber diameters.[37]

Yarn Diameter (Y_2)

The results of a statistical analysis of the yarn diameter as a function of concentration, voltage, take-up rate and distance between the center of the needles and take-up unit are

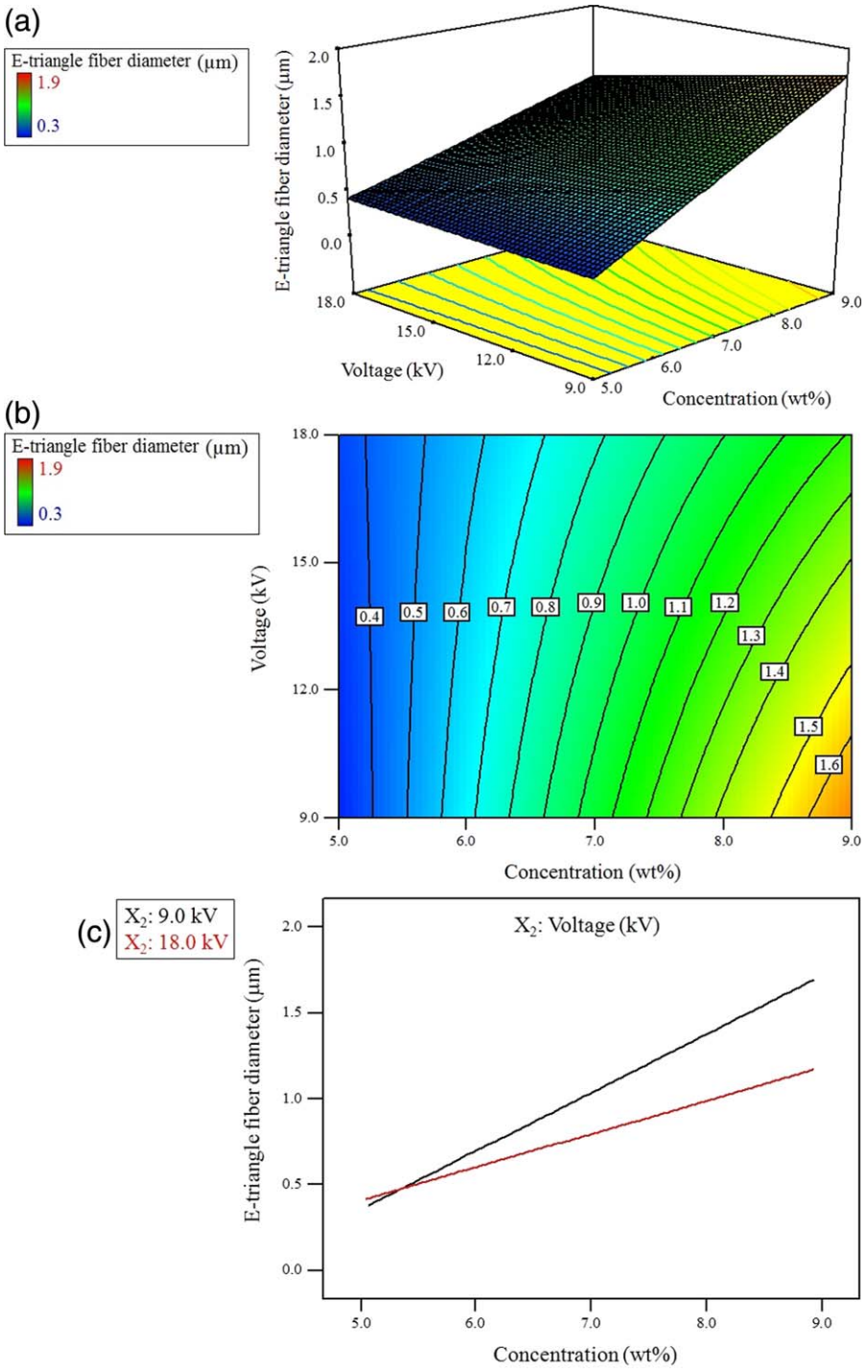

Figure 3. (a) Three-dimensional response surface plot, (b) contour plot, and (c) interaction plot of concentration (wt %), and voltage (kV) for E-triangle fiber diameter (µm) at a take-up rate of 0.05 m/min and center between needles /take-up unit distance of 30 cm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

presented in Table IV. The linear model was statistically reliable ($p = 0.0011$) and had no significant lack of fit ($p = 0.4665$). The relationship between the four factors and the yarn diameter as the response was approximated by the linear eq. (6):

$$Y_2 = 381.96 + 8.24x_1 + 40.99x_2 - 145.78x_3 + 14.29x_4 \quad (6)$$

From the ANOVA results it was shown that the effect of take-up rate on yarn diameter (x_3) is significant and does not vary significantly when the other three factors are changed (Table IV). By removing the insignificant parameters, eq. (6) can be simplified to:

$$Y_2 = 381.96 - 145.78x_3 \quad (7)$$

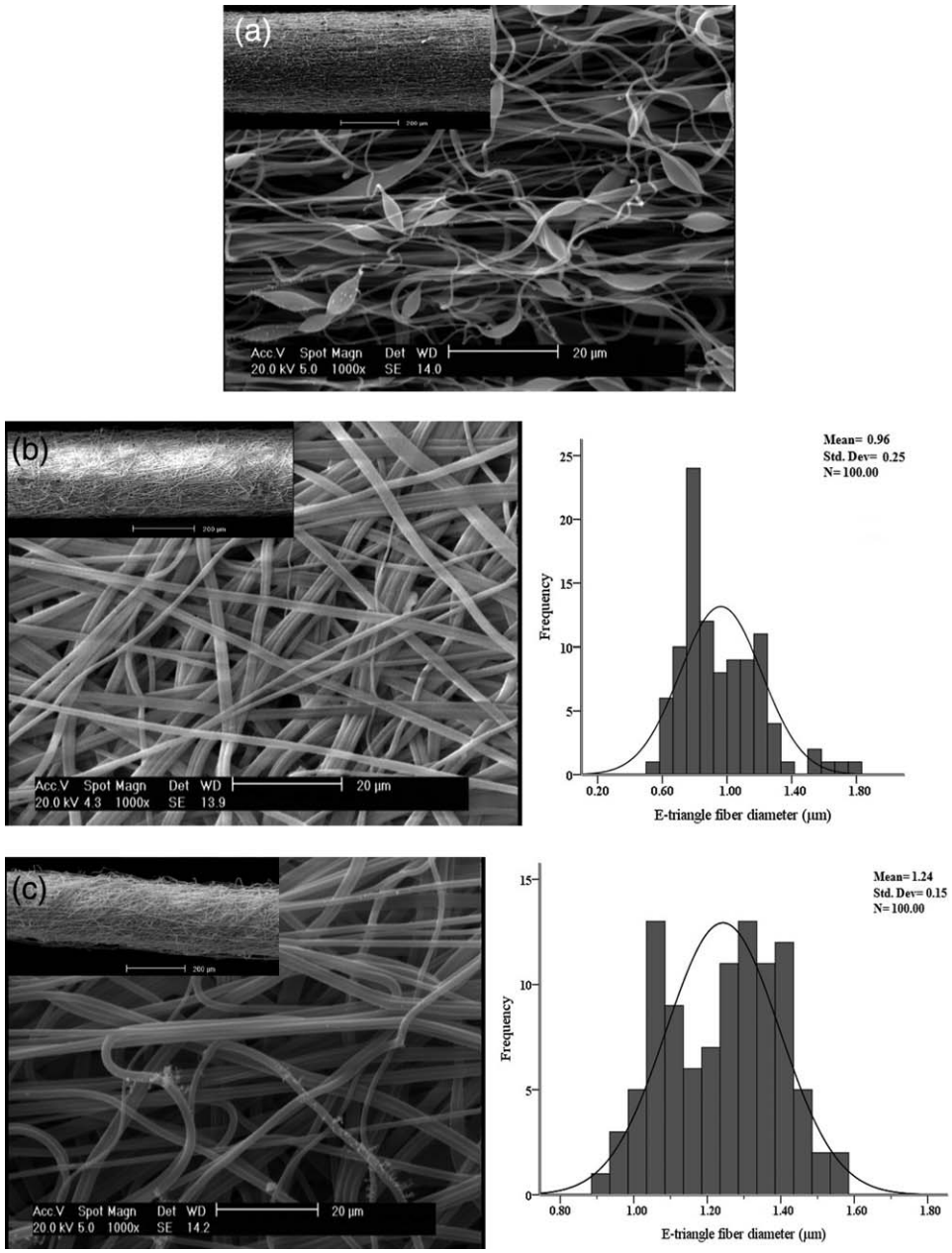

Figure 4. Morphology of nano/microfibers and their diameter distributions at an applied voltage of 13.5 kV, take-up rate of 0.05 m/min, center between needles/take-up unit distance of 30 cm and concentrations of (a) 5 wt %, (b) 7 wt %, and (c) 9 wt %.

SEM images of the electrospun yarns prepared at different take-up rates and corresponding diameter distributions are shown in Figure 5. The images show that the take-up rate caused significant changes in the diameter and size distribution of the yarn. Yarns collected at a take-up rate of 0.08 m/min had a diameter of 350 ± 50 μm. As the take-up rate decreased, the accumulated fibers in the E-triangle increased and as a result, the number of fibers in the yarn body increased. Subsequently, the effect of take-up rate on the linear mass density (Tex) of yarns was evaluated. The statistical results indicated that at constant values of applied voltage, needle's center/take-up unit distance and concentration, the linear mass density of yarns was significantly changed with take-up rate. The linear density of the yarn decreased from 36.6 Tex at a take-up rate of 0.02 m/min to 15.5 Tex at higher take-up rate of 0.08 m/min. At a take-up rate of 0.02 m/min, the yarn diameter showed a slightly wider distribution (440 ± 70 μm).

Mechanical Properties (Y_3 and Y_4)

The designed experiments using CCD were performed and a quadratic model was fitted to the results of strength (Y_3) and modulus (Y_4) as responses. Statistical analysis data are presented in Tables V and VI and illustrate that fitted models are significant for both strength ($p < 0.0001$) and modulus ($p < 0.0001$). Adequate quadratic models for prediction of the response variables are given by the following equations:

Table IV. Analysis of the Variance of the Response Surface Linear Model for the Yarn Diameter

Source	Sum of squares	df	Mean square	*F* value	*p*-value Prob > *F*	
Model	4.18E+005	4	1.04E+005	6.350	0.0011	Significant
X_1-concentration (wt %)	1220.99	1	1220.99	0.074	0.7875	
X_2- voltage (kV)	30241.31	1	30241.31	1.840	0.1873	
X_3-take-up rate (m/min)	3.83E+005	1	3.83E+005	23.250	<0.0001	Significant
X_4-center between needles/take-up unit distance (cm)	3674.66	1	3674.66	0.220	0.6406	

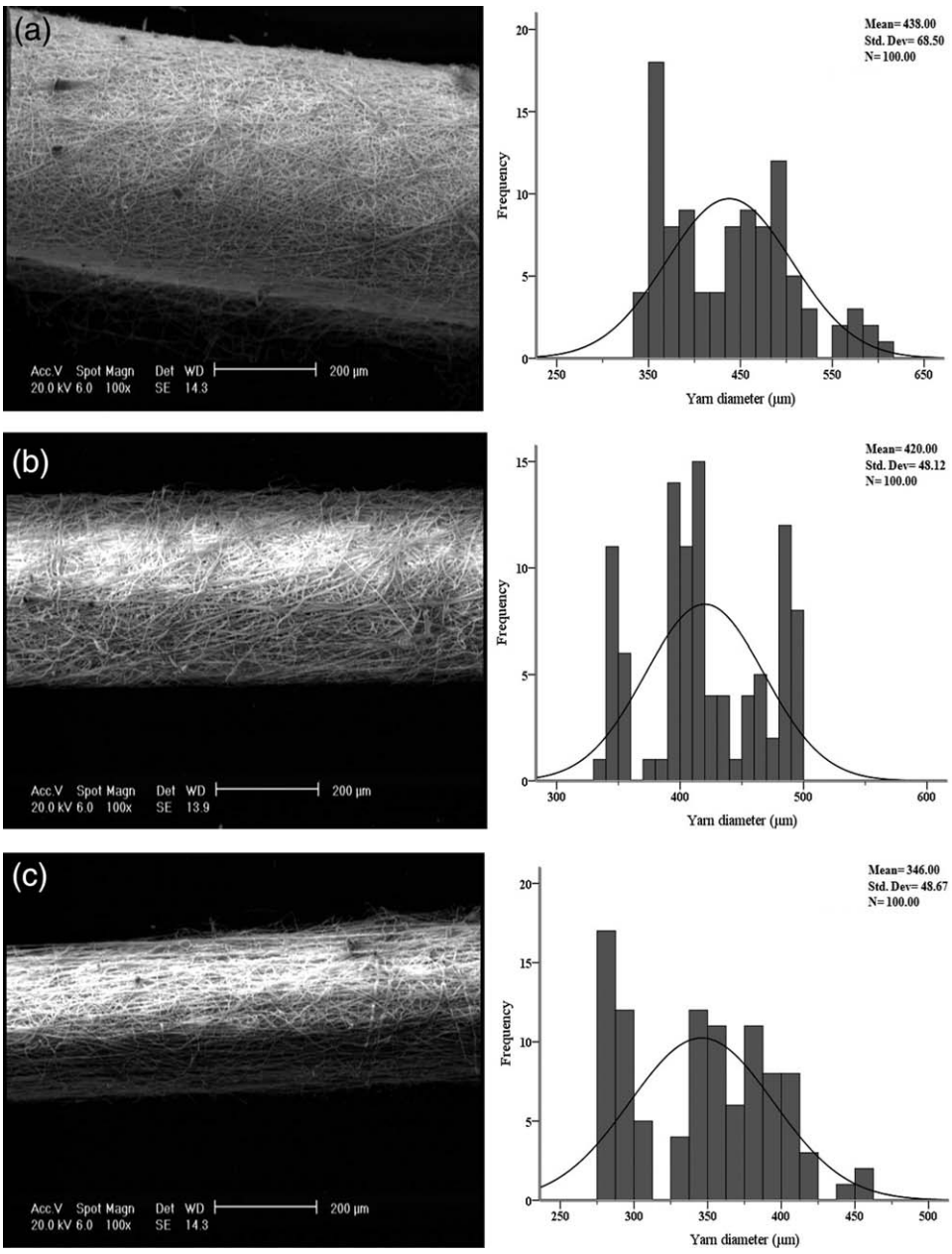

Figure 5. SEM images of continuous electrospun yarns at a voltage of 13.5 kV, 7 wt % polymer concentration, and needles center/take-up unit distance of 30 cm at a take-up rate of (a) 0.02 m/min, (b) 0.05 m/min, and (c) 0.08 m/min.

Table V. The Analysis of the Variance of the Quadratic Model for Strength

Source	Sum of squares	df	Mean square	*F* value	*p*-value Prob > *F*	
Model	3.230	14	0.230	13.37	<0.0001	Significant
X^1-concentration (wt %)	1.800	1	1.800	104.20	<0.0001	Significant
X^2-voltage (kV)	0.099	1	0.099	5.73	0.0301	Significant
X^3-take-up rate (m/min)	0.021	1	0.021	1.22	0.2875	
X^4-center between needles/take-up unit distance (cm)	2.721E-003	1	2.721E-003	0.16	0.6970	
X^1 X^2	0.110	1	0.110	6.53	0.0219	Significant
X^1 X^3	3.333E-003	1	3.333E-003	0.19	0.6667	
X^1 X^4	8.734E-003	1	8.734E-003	0.51	0.4878	
X^2X^3	1.038E-003	1	1.038E-003	0.06	0.8096	
X^2 X^4	0.016	1	0.016	0.91	0.3564	
X^3 X^4	0.011	1	0.011	0.61	0.4472	
X_1^2	0.170	1	0.170	9.75	0.0070	Significant
X_2^2	3.458E-004	1	3.458E-004	0.02	0.8893	
X_3^2	0.021	1	0.021	1.21	0.2883	
X_4^2	0.017	1	0.017	1.01	0.3307	

$$\begin{aligned}\mathrm{Log}_{10}Y_3 = {} & 1.66+0.32x_1+0.074x_2+0.034x_3+0.012x_4-0.084x_1x_2 \\ & -0.014x_1x_3+0.023x_1x_4+0.008x_2x_3+0.031x_2x_4 \\ & -0.026x_3x_4-0.25x_1^2-0.012x_2^2-0.090x_3^2-0.082x_4^2\end{aligned} \quad (8)$$

$$\begin{aligned}\mathrm{Log}_{10}Y_4 = {} & 2.48+0.44x_1+0.059x_2+0.026x_3+0.023x_4-0.093x_1x_2 \\ & -0.005x_1x_3+0.019x_1x_4+0.009x_2x_3-0.009x_2x_4 \\ & +0.008x_3x_4-0.27x_1^2+0.045x_2^2-0.17x_3^2-0.084x_4^2\end{aligned} \quad (9)$$

The ANOVA results show that the *p*-values for x_1, x_2, x_1x_2, and x_1^2 are smaller than 0.05 and thus have a significant effect on the tensile strength and modulus of electrospun yarns. Equations (8) and (9) can thus be simplified to eqs. (10) and (11):

$$\mathrm{Log}_{10}Y_3 = 1.63+0.32x_1+0.074x_2-0.084x_1x_2-0.39x_1^2 \quad (10)$$

$$\mathrm{Log}_{10}Y_4 = 2.44+0.44x_1+0.059x_2-0.093x_1x_2-0.42x_1^2 \quad (11)$$

The values of R^2 ($R^2 = 0.89$), R^2_{adj} ($R^2_{adj} = 0.87$) and lack of fit ($p = 0.9479$) for the yarn strength and R^2 ($R^2 = 0.92$), R^2_{adj} ($R^2_{adj} = 0.90$) and lack of fit ($p = 0.9269$) values for the modulus

Table VI. The Analysis of the Variance of the Quadratic Model for Modulus

Source	Sum of squares	df	Mean square	*F* value	*p*-value Prob > *F*	
Model	5.090	14	0.360	19.010	<0.0001	Significant
X^1-concentration (wt %)	3.430	1	3.430	179.630	<0.0001	Significant
X^2-voltage (KV)	0.062	1	0.062	3.230	0.0424	Significant
X^3-take-up rate (m/min)	0.012	1	0.012	0.640	0.4347	
X^4-needles center/take-up unit distance (cm)	9.291E-003	1	9.291E-003	0.490	0.4962	
X^1 X^2	0.140	1	0.140	7.290	0.0165	Significant
X^1 X^3	3.891E-004	1	3.891E-004	0.020	0.8884	
X^1 X^4	5.821E-003	1	5.821E-003	0.300	0.5891	
X^2X^3	1.225E-003	1	1.225E-003	0.064	0.8036	
X^2 X^4	1.156E-003	1	1.156E-003	0.061	0.8090	
X^3 X^4	9.673E-004	1	9.673E-004	0.051	0.8250	
X_1^2	0.190	1	0.190	10.200	0.0060	Significant
X_2^2	5.209E-003	1	5.209E-003	0.270	0.6092	
X_3^2	0.072	1	0.072	3.770	0.0711	
X_4^2	0.018	1	0.018	0.950	0.3454	

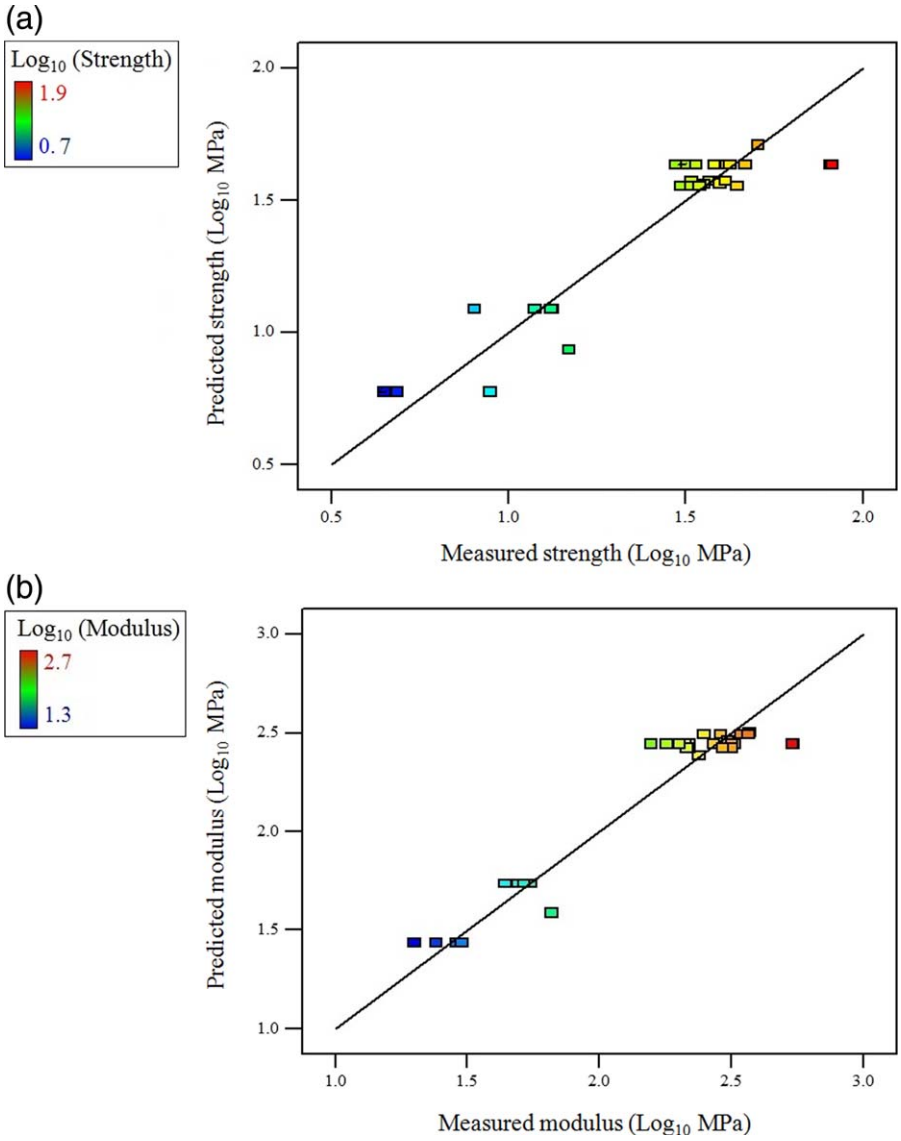

Figure 6. Predicted versus measured values of (a) strength and (b) modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicate that the quadratic model is acceptable for experiments applied. Figure 6(a,b) represent predicted versus actual values for strength and modulus, respectively.

Among all factors, the polymer concentration appeared to have the most significant effect on the mechanical properties of the yarns (Tables V and VI). Surface and contour plots of strength and modulus of electrospun yarns are presented in Figures 7 and 8. These plots show an increase in tensile strength and modulus by increasing the polymer concentration up to around 7.5 wt %. It has to be noted that beaded fibers were obtained at a lower concentration of 5 wt %, which largely influences the mechanical properties of the electrospun fibers and yarns. By increasing the concentration from ~7 wt % up to 9 wt %, the fiber diameter increases but both tensile strength and modulus decreased. It is well known that the tensile strength and modulus increase when the fiber diameter decreases.[38–40] At low polymer concentrations, the orientation of macromolecular chains can be induced due to less polymer entanglement, or less resistance to the stretching force, which results in smaller fiber diameters. The higher strength and modulus are likely a consequence of highly aligned polymer chains along the fiber axis. The tensile strength and modulus of the electrospun yarns also increased by increasing the voltage. Higher voltages cause larger stretching forces and thereby an increased molecular orientation in the electrospun fibers. As a result, fibers showed a higher resistance to tensile forces. This phenomenon might not only result in a decreased fiber diameter. We cannot exclude that also higher shear between fibers in the yarn would occur. In fact, with decreasing fiber diameter, a correspondent increase in number of fibers and available surface could be expected.

As shown in Figures 7(c) and 8(c), the crossing of the lines means that the responses are demonstrating different behavior on the settings of both concentration and applied voltage. The trend lines show that at lower concentrations, the effect of the

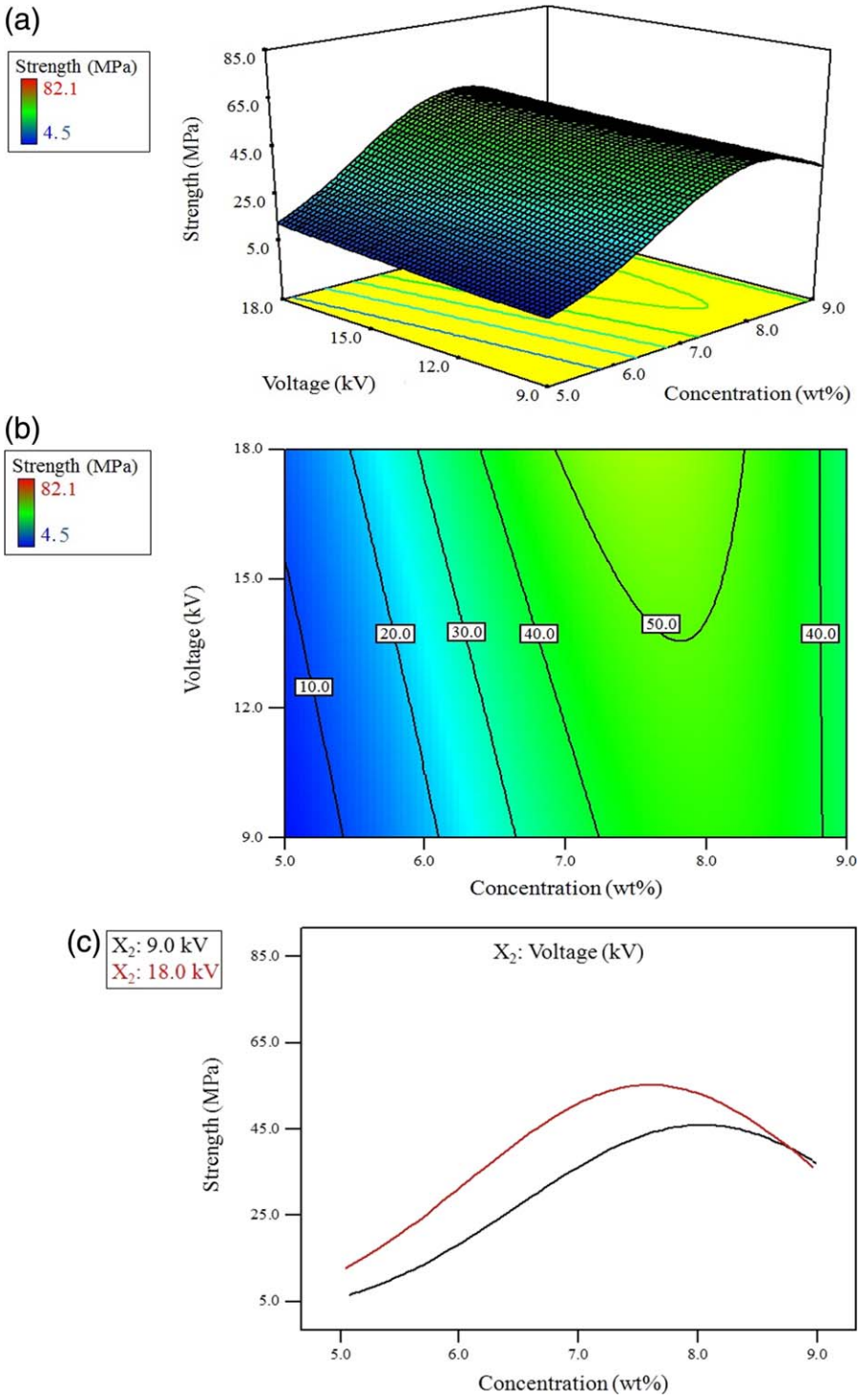

Figure 7. (a) Three-dimensional response surface plot, (b) contour plot, and (c) interaction plot of concentration (wt %) and voltage (kV) for strength of electrospun yarns (MPa) at a take-up rate of 0.05 m/min and center between needles /take-up unit distance of 30 cm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electrical field on the jet was larger than at higher concentrations. This could be likely due to the increased bending instability at lower concentrations, which resulted in a greater stretch of the jet. Moreover, a slower solidification process takes place, which also results in an increased elongation of the jet and increases the molecular orientation in the electrospun nanofibers.

At very low concentrations beaded fibers are generated, which largely influence the mechanical properties of the yarns. At higher polymer concentrations chain entanglements increase and polymer stretching becomes more difficult due to the short relaxation time of the entangled polymer chains. In addition, at high polymer concentration,

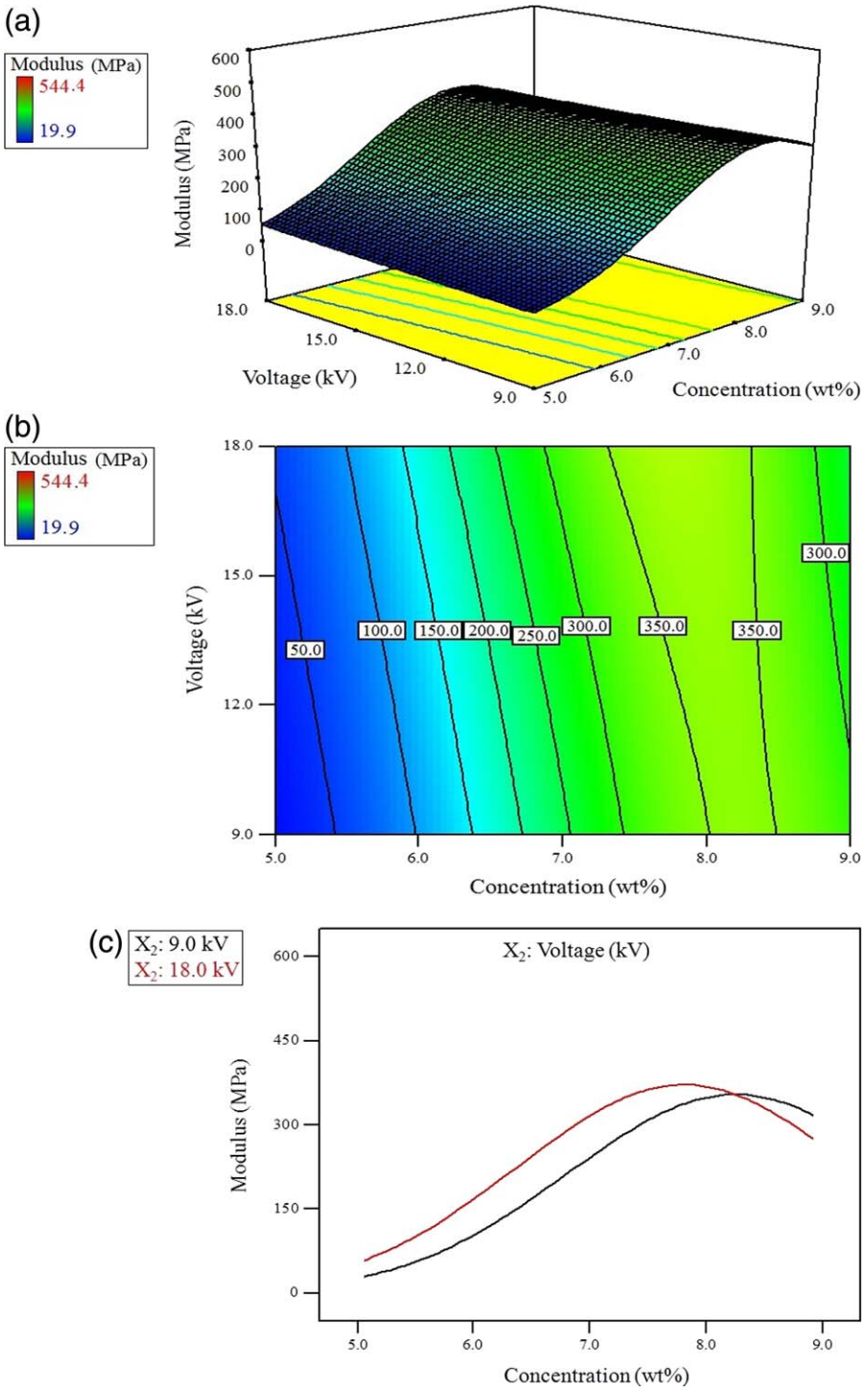

Figure 8. (a) Three-dimensional response surface plot, (b) contour plot, and (c) interaction plot of concentration (wt %) and voltage (kV) for modulus of electrospun yarns (MPa) at a take-up rate of 0.05 m/min and center between needles /take-up unit distance of 30 cm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the rapid evaporation of solvent also leads to less extension of the jet.[18,41–44]

CONCLUSIONS

Electrospinning of PLLA solutions from two oppositely charged needles generates spontaneously a triangle of fibers at a grounded substrate. The fibers could be assembled into fibrous yarns using a device consisting of a take-up roller and twister. In this study, the effect of electrospinning process parameters on the ultimate properties of fibers and yarns, produced by taking up and twisting the fibers, was investigated. The CCD response surface method and subsequent

statistical analysis allowed studying the influence of concentration, voltage, take-up rate, and distance between needles and take-up unit, by a minimal set of experiments on fiber and yarn properties. First, the analysis revealed that the diameter of the fibers was predominantly affected by the concentration and to a lesser extent by the applied voltage. At increasing concentrations the mean diameter increased and slightly decreased at higher applied voltages. The yarn diameter was mainly depending on the take-up rate and increased when the take-up rate was decreased. The experimental data on strength and modulus of the yarns revealed that polymer concentration, voltage, and a combination of these parameters had the most significant effect on the mechanical properties of the yarns.

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