ELECTROSPINNING SETUP IN THE MORPHOLOGY OF POLY (LACTIC ACID) NANOFIBERS

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ABSTRACT – The diameter of the electrospun fibers is a key parameter for most applications. This study evaluated the influence of the feed rate (0.6 – 1.6 mL.h⁻¹), voltage (10.6 – 17.4 kV) and spinning distance (13.6 – 20.4 cm) on the diameter and continuous and reproducibility morphology of electrospun poly(lactic acid) (PLA) fibers using a rotatable central composite design (RCCD) response surface optimization methodology. The polymeric fiber-forming solutions was prepared by dissolving PLA in 4:1.25:1 (w/v/v) chloroform:methanol:dimethylformamide blend solvent. The fibers morphology and the average diameter were evaluated by the Sauter equation. At a given fixed feed rate, an optimum distance of 15.5 cm and voltage of 13 kV provided consistent fiber morphology with diameter of less than 300 nm.

KEYWORDS: electrospun, RCCD, voltage, distance.

1. INTRODUCTION

Electrospinning is a fiber-forming technology for manufacturing polymer fibers with a diameter ranging from few nanometer to several micrometers. This process uses electrostatic force continuously applied to the polymeric solution, forming a jet that travels from a capillary spinneret to an electrically grounded collector surface. With increasing voltage, the electrostatic force induces the formation of a deformed pendant droplet know as the Taylor cone. The polymer jet erupted from the tip of the Taylor cone develops whipping instability as it travels towards the collector, while the solvent is evaporated from the jet. The dried continuous fibers landed on the collector entangle to form a nonwoven membrane (Fernandez et al., 2009; Li et al., 2009; Mihindukulasuriya & Lim, 2013; Shen et al., 2011).

The main advantages of electrospun membrane, as compared with other products such as films and foams, is the former as relatively high surface area/volume ratio and high porosity, in addition to being used as a matrix for carrying bioactive compounds. This loading ability has drawn attention to various applications, such as for the development of food packaging, especially active and intelligent packaging (Figueira et al., 2016; Lu & Ding, 2008; Morais et al., 2010; Mihindukulasuriya & Lim, 2013; Xu et al., 2009).
Many different materials can be converted into fibers via electrospinning technology, including polymers, metals, ceramics and oxides (Reddy et al., 2010). Among these, poly(lactic acid) (PLA), which is a biodegradable polymer, has been widely studied, mainly due to its mechanical properties, clarity, and UV stability. PLA is produced from lactic acid monomer produced by fermentation of agricultural products (e.g., corn, potato, sugar cane and rice) (Frone et al., 2013).

The objective of this study was to evaluate effect the feed rate, voltage and distance of electrospinning fiber-forming in order to optimize a procedure that allows obtain continuous and uniformly PLA fibers aiming subsequent application in intelligent packaging for food.

2. MATERIAL AND METHODS

2.1 Material

PLA resin (grade 6201D) was donated by NatureWorks LLC (Minnetonka, MN, USA). Chloroform, ethanol and dimethylformamide (DMF) used were supplied by Ggotuzzo (Synth).

2.2 Preparation of the polymeric solution and electrospinning parameters

The 8% PLA solution was prepared by dissolving the polymer in chloroform, methanol and DMF in a ratio of 4:1.25:1, respectively, under magnetic stirring for 2 h. The PLA solution was then placed in a 1 mL syringe equipped with a 0.45 mm diameter blunt end stainless steel needle that acted as a spinneret. The syringe was loaded onto an infusion pump (KD100 KD Scientific Inc., New Hope, PA) to control the flow rate of the polymer solution. The polymer solution was electrospun by applying positive charge to the needle, while the collector was attached to the negative electrode of the power supply. From preliminary testing, a rotatable central composite design (RCCD) (Roberts & Lemma, 2009) was used to optimize the condition for preparation of PLA nanofibers by changing the feed rate, voltage applied (positive electrode), and distance variables (Table 1). A factorial design was used 2³ including 6 axial points and three central points, totaling 17 treatments.

<table>
<thead>
<tr>
<th>Parameters -1.68</th>
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<th>1</th>
<th>1.68</th>
</tr>
</thead>
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<tr>
<td>Feed rate (mL.h⁻¹)</td>
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<td>0.8</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Voltage (kV)</td>
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<td>+12</td>
<td>+14</td>
<td>+16</td>
</tr>
<tr>
<td>Distance (cm)</td>
<td>13.6</td>
<td>15</td>
<td>17</td>
<td>19</td>
</tr>
</tbody>
</table>

2.3 Morphology and diameter of the nanofiber

The morphology of the nanofibers was analyzed by scanning electron microscopy (SEM) (JEOL JSM-6610LV, USA). The fibers were placed on stubs with the aid of a double-sided carbon tape and sputter-coated with Au (Sputtering, Deston Vacuum Deskv, USA). The images were examined under accelerating voltage of 10 kV. The fibers diameter was obtained from the images (35 to 50 measurements) using computer software ImageJ and the average diameter was estimated by the Sauter equation (Foust et al., 1980).

\[ D_{Sauter} = \frac{1}{\sum \frac{f_i \times D_i}{D_{mi}}} \]  
Eq. (1)
Where \( D \) is the Sauter mean diameter; \( x_i \) is the relative frequency between the class adopted diameters (%) and \( D_{mi} \) represents the arithmetic mean diameter between the diameters class adopted in the frequency distribution.

### 3. RESULTS AND DISCUSSION

The SEM micrographs of the fiber, taken based on the RCCD experimental design, are presented in Figure 1 (1-15).

Figure 1 - PLA fibers with different conditions of feed rate, voltage and distance.

As shown, the central points showed slight variation between the average diameters, with a coefficient of variation of 3.9%, indicating good repeatability of the process, accordingly, one only representative micrograph were presented the central point (Figure 1 - 15). Moreover, continuous fibers without beads were observed under all conditions tested, although variations in fiber diameter were detected. Kong and Ziegler (2013) reported an empirical modeling using a fractional factorial experimental design for electrospun starch fiber. They reported that high polymer concentration (15% w/v) and high voltage/distance (10 kV/ 8 cm) ratios resulted in poor fibers.

Figure 2 shows the changes in diameter of the electrospun fibers as affected by the process parameters.
Figure 2 - Diameter distribution of the PLA fibers for each treatment by RCCD.

1 - 0.8 mL.h⁻¹; 12 kV; 15 cm

2 - 1.4 mL.h⁻¹; 12 kV; 15 cm

3 - 0.8 mL.h⁻¹; 16 kV; 15 cm

4 - 1.4 mL.h⁻¹; 16 kV; 15 cm

5 - 0.8 mL.h⁻¹; 12 kV; 19 cm

6 - 1.4 mL.h⁻¹; 12 kV; 19 cm

7 - 0.8 mL.h⁻¹; 16 kV; 19 cm

8 - 1.4 mL.h⁻¹; 16 kV; 19 cm

9 - 0.6 mL.h⁻¹; 14 kV; 17 cm

10 - 1.6 mL.h⁻¹; 14 kV; 17 cm

11 - 1.10 mL.h⁻¹; 10,6 kV; 17 cm

12 - 1.10 mL.h⁻¹; 17,4 kV; 17 cm

13 - 1.1 mL.h⁻¹; 14 kV; 13.6 cm

14 - 1.1 mL.h⁻¹; 14 kV; 20.4 cm

15 - 1.1 mL.h⁻¹; 14 kV; 17 cm

As shown, the diameter of the fibers ranged from 100 to 1500 nm with variable frequency distribution (%). From feed rate and distance interaction was significant, while the effect of quadratic
feed rate and the interaction between the voltage and distance variable were not significant (p<0.05). Therefore, these variables were removed from the model. The Sauter mean diameter for PLA fibers predicted by the model as a function of the coded variables is presented in Equation 1:

$$D_{\text{Sauter}} = 456.02 + 24.46F + 22.00V + 24.41V^2 + 29.27D + 19.98D^2 - 19.88FV - 41.38FD$$  \hspace{1cm} (1)

where $D_{\text{Sauter}}$ represents the average diameter (nm); $F$ is the feed rate (mL.h$^{-1}$); $V$ is the voltage (kV); and $D$ is the distance of the collector (cm).

From ANOVA analysis, the $F_{\text{calculated}}$ value was higher than the $F_{\text{tabulated}}$ ($F_{\text{calculated}}/F_{\text{tabulated}} = 5.5$). Moreover, the variance explained 94.04% of fiber diameter. Therefore, the model is capable of predicting the behavior of the diameter of PLA fibers under the feed rate, voltage and distance conditions used in electrospinning experiments.

The contour plots are shown in Figure 3. The fibers diameter was affected by all three electrospinning process variables. From Figure 3a, it is clear that increasing both distance of the target and voltage had resulted in decreases in fibers diameter, with approximately 16 cm and 13 kV provided the smallest fiber diameter. In all treatments, increasing feed rate caused an increase in fiber diameter. In Figure 3b, the lowest feed rate associated with the lowest voltage resulted in lowest fiber diameters. Therefore, within the ranges of the parameters studied, condition that provided the smallest fiber diameter (300 nm) was 0.8 mL.h$^{-1}$, 12 kV and 15 cm.

Figure 3 - Contour curves for the diameter of fibers (nm) of PLA. Distance x voltage (a) voltage x feed rate (b) distance x feed rate (c).

4. CONCLUSIONS

Feed rate, voltage and distance equal to 0.8 mL.h$^{-1}$, 12 kV and 15 cm, respectively, it is recommended for production of nanofibers with diameters less 300 nm.

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6. REFERENCES


