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Quantitative relationship between electrospinning parameters and starch fiber diameter

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Abstract

The diameter of the starch fibers produced by electrospinning is a key parameter for most potential applications. In this study, a quantitative relationship between fiber diameter and certain electrospinning parameters, i.e. starch concentration, applied voltage, spinning distance and feed rate, was established by empirical modeling using a fractional factorial experimental design in a constrained region. Response surface methodology was employed to analyze the interactions of the electrospinning parameters and predict the direction to minimize and maximize the fiber diameters.

KEYWORDS: starch, fiber, diameter, electrospinning, empirical modeling, response surface methodology

1. Introduction

Polysaccharide based biopolymers are of great interest to researchers in academia and industry as a potential substitute for synthetic polymers because of their sustainable supply, biodegradability and biocompatibility. Fibers spun from polysaccharides are promising materials for a wide variety of applications, e.g. filtration, biomedical, and textiles to name but a few. A number of polysaccharides have been artificially spun into fibers, including cellulose, chitosan, alginate, hyaluronic acid, pullulan, and dextran (Kong, Ziegler, & Bhosale, 2010). Among polysaccharides, probably the most abundant and inexpensive is starch. Therefore, starch spinning has attracted much interest (Kong & Ziegler, 2012b). We have recently demonstrated a method to produce pure starch fibers by an electrospinning technique (Kong & Ziegler, 2012a).

The diameter is a key parameter for fibers envisioned for specific applications. Electrospinning is a simple and efficient technique capable of producing micro- or nano-scale fibers. Compared with normal textile fibers, which are in the order of hundreds of microns, nano-scale fibers have much higher surface-area-to-volume ratio, higher porosity, and smaller pore sizes. The diameter of the starch fibers obtained in our original work was in the order of microns. It's important to systematically investigate the effect of the electrospinnig parameters on starch fiber diameter, and the smallest fiber diameter obtainable without sacrificing fiber qualities, e.g. continuous morphology and reproducibility.

Empirical modeling by response surface methodology has been used successfully for fiber spinning processes in a number of studies including dry-jet-wet spinning of polyurethane elastomer fibers (Reddy, Deopura, & Joshi, 2010), and electrospinning of silk fibers (Sukigara, Gandhi, Ayutsede, Micklus, & Ko, 2004), polylactide fibers (Gu & Ren, 2005), and polyacrylonitrile fibers (Gu, Ren, & Vancso, 2005; Yördem, Papila, & Menceloglu, 2008). In our previous report, we have observed the interaction of some electrospinning parameters (Kong & Ziegler, 2012c). For instance, dispersions with low starch concentration required a high feed rate, high voltage and short spinning distance to be spun; the requirement was reversed for high starch concentrations. Spinning was unsuccessful at certain combinations of spinning parameters. Therefore, it was not possible to employ a full-factorial design to investigate the effects of spinning parameters on fiber diameter. Instead a fractional factorial design in a constrained region (Wheeler, Betsch, & Donnelly, 1993) was used to generate the response surface contours for the influence of starch concentration, voltage, distance and feed rate on fiber diameter without drawing.

2. Materials and Methods

2.1. Materials

Hylon VII starch was supplied by National Starch and Chemical Company (now Corn Products International, Bridgewater, NJ) and used as received. Hylon VII is a corn starch with amylose content of about 70%. Dimethyl sulfoxide (DMSO) was obtained from VWR International (Radnor, PA). Ethanol (200 proof) was obtained from the Penn State Chemistry Stockroom.

2.2. Electrospinning

The preparation of spinning dope involved dissolving the appropriate amount of starch in 95% (v/v) aqueous DMSO solution. The starch dispersion was heated in a boiling water bath with continuous stirring on a magnetic stirrer hotplate for about one hour. The starch dispersion was then allowed to cool to room temperature and deaerated. A 10 mL syringe (Becton, Dickinson and Company, Franklin Lakes, NJ) with a 20 gauge blunt needle was used as the spinneret.

The electrospinning setup comprised a higher voltage generator (ES40P, Gamma High Voltage Research, Inc., Ormond Beach, FL), a syringe pump (81620, Hamilton Company, Reno, NV), and a grounded metal mesh immersed in pure ethanol (Fig. 1). This electrospinning configuration can also be referred to as "electro-wet-spinning". The fibrous mat deposited in the ethanol coagulation bath was then washed using pure ethanol and dried in a desiccator containing Drierite under vacuum.

2.3. Design of experiments

In order to establish a quantitative relationship between fiber diameter and spinning parameters, a fractional experimental design for a constrained region using a quadratic model was created by ECHIP (ECHIP, Inc., Hockessin, DE) (Wheeler, et al., 1993). Four variables were included in the model: starch concentration (10 to 15 %, w/v), voltage (6 to 10 kV), spinning distance (5 to 8 cm), and feed rate (2 to 4 ml/h). The constraints were specified by a "point-percentage" method provided by ECHIP. Within the experiment range, two extreme combinations were identified as non-operational conditions according to previous experiments, i.e. starch concentration at 10% (w/v), voltage at 6 kV, spinning distance at 8 cm and feed rate at 2 ml/h; and starch concentration at 15, voltage at 10, spinning distance at 5 and feed rate at 4. Two pieces of experimental region were cut off by two imaginary planes perpendicular to the vector from the center of the experimental region to the non-operational points and located at 10% of the distance from the center.

The design contained 28 experiments, 25 unique combinations, and 3 replications (Table 1). Five unique checkpoints (runs from 26 to 30) were then used to validate the initial model and added to create a new model.

2.4. Fiber morphology

Observation of fibers was performed using a FEI Quanta 200 environmental scanning electron microscope (ESEM~~ (~~, FEI, Hillsboro, OR) in low vacuum mode at an accelerating voltage of 20 KeV. The fiber samples for ESEM were not coated with metal. Fiber diameter was measured from the ESEM images. Five images were used for each fiber sample and at least 100 different segments were randomly measured to obtain an average diameter.

3. Results and Discussion

3.1. Fiber morphology

Fiber samples from each experimental run were observed using electron microscopy (Fig. 2), and evaluated according to their spinning behavior and fiber morphology (Table 1). The pairs of 3 replicates produced fibers of same appearance. Therefore only one picture was shown representing the replicate runs. 18 out of 30 experimental conditions produced good fibers, i.e. those that are continuous and have few droplets, though the fiber diameter spanned from 3.35 μm (run 26) to 12.16 μm (run 11). Of 30 fiber samples 5 were evaluated as fair. These fibers are largely continuous but may have some droplets (i.e. runs 4, 5, and 14) or thick fibers (i.e. 15 and 19). The final 7 runs produced poor fibers. Some of these runs, i.e. 1, 13, 17, and 23, resulted in thick fibers. These runs resulting in poor fibers used the highest starch concentrations and relatively high voltage/distance ratios. At these electrospinning conditions, the jet did not develop whipping instability and the process appeared like simple wet-spinning. The other two runs, i.e. ~~11~~ 7 and 22, produced too many droplets by electrospraying, instead of electrospinning. These two runs used the lowest starch concentration and the greatest spinning distance. A similar material concentration effect was reported in other studies (Gu, et al., 2005). The fiber morphology can probably be influenced by both surface tension and viscosity. The surface tension tends to reduce surface area per unit mass and thus favors the formation of droplets or particles, while viscoelastic forces promote the formation of fibers. At low material concentrations, surface tension may have a dominating impact over viscoelastic force. However, at high concentrations, high viscosity brings difficulty in the extension of the jet and thus results in thick fibers. With only two constraints for a 4-dimensional experimental design, these combinations were included in the constrained region, because a balance between well-defined operational range and enough space to have distant points has to be considered for the prediction power of the model.

When all of the experimental runs were used to construct a model for the effect of spinning parameters on fiber diameter, starch concentration was the only significant parameter (r^2=0.88, *p*-value = 0.0007). However, when all of the poor fiber data were eliminated, a model with 12 significant terms (r^2 = 0.94, *p*-value = 0.0143) was obtained. The poor fibers were obtained by mechanisms other than true electrospinning and, thus, should not be included in the model construction and refinement for electrospinning.

3.2. Model construction

Fiber diameter data of the good and fair fibers were used for regression analysis. Five additional unique runs were used as checkpoints for model validation. The root mean square of the residuals between checkpoints and predictions was calculated to be 2.08, smaller than the residual standard deviation for non-checkpoints, i.e. 2.09. Therefore, the model can be considered a good one and the predictions reliable (Wheeler, et al., 1993). Insignificant terms were then removed to refine the model. Table 2 provides the coefficients of the final statistical model and the significance of each term. All the terms involving feed rate were insignificant in determining the fiber diameter and thus not included in the final model.

As shown in the footnote, the model used centering values by subtracting the average of the high and low limits of the variables. With centering removed, the fitted second-order equation for average fiber diameter is given by:

$$\begin{aligned} Diameter = {} & 165.924 - 2.465 \times Distance - 6.475 \times Voltage \\ & - 24.825 \times StarchConc - 1.13 \times Distance \times Voltage \\ & - 2.25 \times Distance \times StarchConc + 1.22 \times Voltage \times StarchConc \\ & + 2.38 \times Distance^{2} + 1.32 \times StarchConc^{2} \end{aligned}$$

According to the model, the smallest mean fiber diameter obtainable, without an added process like mechanical drawing, is 3.98 μm at a starch concentration of 10% (w/v), feed rate of 2.8 ml/h, voltage of 10 kV, and distance of 6.8 cm, which is identical the conditions of run 16. The largest mean fiber diameter is outside the experimental design region.

3.3. Electrospinning parameters and their interactions

For starch concentration from 10 to 15 % (w/v), contour plots of the predicted mean fiber diameter were illustrated in Fig. 3. Each contour visualizes the effects of voltage and spinning distance at the corresponding starch concentration. The effect of starch concentration can also be seen by comparing the six contour plots. Increasing starch concentration increases the lower limit of the fiber diameter.

For all starch concentrations, the fiber diameter seems more responsive to spinning distance than to voltage. The interaction of voltage and spinning distance can also be observed according to the nonlinear contour lines. The interaction effect follows a similar trend regardless of starch concentration. The condition for smallest fiber diameter shifted from the high voltage, intermediate distance region to the low voltage, long distance region as starch concentration increased. It is expected from previous rheological studies that low starch concentration requires higher shear rate brought about by higher voltage to distance ratio for aligning the starch molecules in the jet, whereas highly concentrated starch dispersion does not need such high shear rate (Kong & Ziegler, 2012c). Both increasing and decreasing the ratio of voltage to distance from this condition tended to increase the fiber diameter. The ratio of voltage to distance can also be defined as electric field strength (Sukigara, et al., 2004). Lowering the electric field strength will decrease the electric stress on the starch dispersion and the efficiency in drawing the fiber. However, increasing the electric field strength from the center region accelerates the jet so quickly that whipping instability cannot be well developed. This will shorten the spiral loop path of the jet, where the jet is extensively elongated. Further increase of the electric field strength will result in a process like simple wet-spinning, as described for runs 1, 13, 17, and 23.

The contour plots in Fig. 4 and 5 indicate that the fiber diameter is very responsive to starch concentration. The strong dependence of fiber diameter on material concentration has been reported by a number of studies for other materials (Kattamuri & Sung, 2004; Ryu, Kim, Lee, Park, & Lee, 2003; Sukigara, et al., 2004; Yördem, et al., 2008). At short spinning distances (5 and 6.5 cm), the effect of voltage is largely negligible, as can be seen from the slope of the curves. At long spinning distance, the effect of voltage is also not apparent for intermediate starch concentrations. But voltage has more effect on fiber diameter at low and high starch concentrations. It should also be noted that the electrospinnability outside the experimental region cannot be guaranteed. The reason is related to the rheological properties of the starch-DMSO-water dispersions, which has previously been discussed (Kong & Ziegler, 2012c).

The contour plots at constant voltages show that at higher starch concentrations greater spinning distances were needed in order to produce fibers with equivalent diameters. On the one hand, it is reasonable to suggest longer travelling distance enables the development of sufficient whipping of the fibers, where viscous starch dispersion is elongated. One the other hand, long spinning distance should be avoided at low voltage in order to produce small fibers, since low electric stress would be insufficient to align the molecules in the fibers. The predicted condition for the smallest fiber diameter is located near spinning distance of about 6.5 to 7 cm, which can be easily visualized in the contour plot at a voltage of 6 kV (Fig. 5A).

4. Conclusions

Fractional factorial design for a constrained region and quadratic empirical modeling were applied to establish a quantitative relationship between several electrospinning parameters and fiber diameter. Checkpoints were used to validate the model and added for regression analysis. A quadratic empirical model was finalized involving three electrospinning parameters, i.e. starch concentration, voltage, and distance. According to the model, the smallest fiber diameter (3.98 μm) can be obtained within the experiment range. Response surface analysis was employed to create contour plots where the main effects and interactions of individual parameters can be visualized. Fiber diameter was found to be more responsive to starch concentration than to voltage and distance in the experiment range. The ratio of voltage to distance and the ratio of starch concentration to distance were found to be important in predicting the trend of fiber diameter.

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Figure Captions

Fig. 1. Schematic drawing of the electrospinning setup.

Fig. 2. Electron micrographs of fiber samples from experimental runs from 1 to 30. Scale bar represents 500 µm in all figures. Fibers were evaluated and classified into good fibers (++), fair fibers (+), and poor fibers (-).

Fig. 3. Contour plots of fiber diameter as a function of voltage and spinning distance at a constant feed rate of 3 ml/h and different starch concentrations: A, 10%; B, 11%; C, 12%; D, 13%; E, 14%; and F, 15% (w/v). Contour lines with numbers are significantly different ($P < 0.05$). The red lines denote the design boundary; i.e. experimental conditions outside or below the red lines were not included in the design.

Fig. 4. Contour plots of fiber diameter as a function of starch concentration and voltage at a constant feed rate of 3 ml/h and different spinning distance: A, 5; B, 6.5; and C, 8 cm. Contour lines with numbers are significantly different ($P < 0.05$). The red lines denote the design boundary; i.e. experimental conditions outside of the red lines were not included in the design.

Fig. 5. Contour plots of fiber diameter as a function of starch concentration and spinning distance at a constant feed rate of 3 ml/h and different voltage: A, 6; B, 8; and C, 10 kV. Contour lines with numbers are significantly different ($P < 0.05$). The red lines denote the design boundary; i.e. experimental conditions outside of the red lines were not included in the design.