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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.

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, 2012a). We have recently demonstrated a method to produce pure starch fibers by an electrospinning technique (Kong & Ziegler, in preparation).

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, 2012b). 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.

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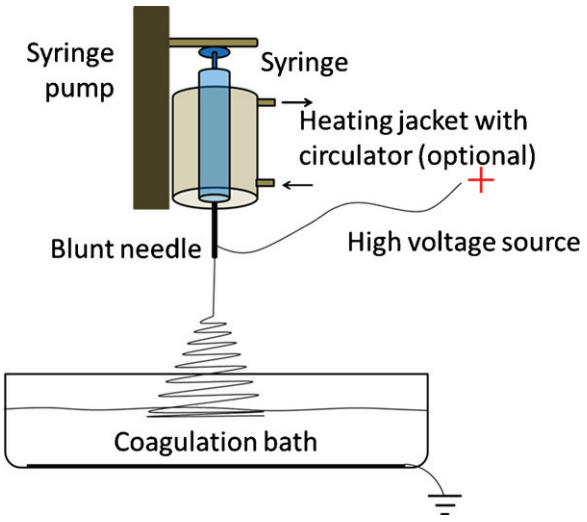

Fig. 1. Schematic drawing of the electrospinning setup.

2. Materials and methods

2.1. Materials

Hylon VII starch was supplied by National Starch and Chemical Company (now Ingredion Incorporated, 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 (10–15%, w/v), voltage (6–10 kV), spinning distance (5–8 cm), and feed rate (2–4 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 three 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. 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 four-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.