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Rheological aspects in fabricating pullulan fibers by electro-wet-spinning

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ABSTRACT

Electro-wet-spinning was used to fabricate continuous nonwoven microscale and nanoscale fibers from pullulan. We investigated the rheological properties of pullulan dispersions using DMSO:water mixtures as solvents with varying compositions. The relationship between electrospinnability and rheological properties were studied. In order to obtain well-formed pullulan fibers, the concentration of pullulan dispersion had to be 1.88–2.25 times the entanglement concentration, depending on DMSO:water ratio in the solvent. Shear viscosity was another important factor. The shear viscosities at 100 s^{-1} of electrospinnable pullulan dispersions fell into a range between 0.06 and 2.2 Pa s, regardless of solvent composition. Yet, there may still be other factors governing the fiber size as DMSO concentration changed. Pullulan fibers in the order of hundreds of nanometers to tens of microns were obtained. Increase in DMSO concentration in the solvent generally increased the fiber size and pore size in the electrospun pullulan fiber mat.

1. Introduction

Electrospinning is a cost-efficient technique to produce continuous nonwoven microscale and nanoscale fibers from a wide variety of materials. Among the materials of interest, polysaccharide biopolymers have been identified as potential substitutes for synthetic polymers (Kong, Ziegler, & Bhosale, 2010). In addition to a sustainable and renewable supply of their constituent biopolymers, biofibers have advantages pertaining to their inherent biodegradability and biocompatibility. Therefore a variety of biopolymers, including polysaccharides, proteins, and DNA, have been successfully spun into fibers, especially by electrospinning (Kong & Ziegler, 2012, 2013; Kong et al., 2010).

Pullulan is a linear polysaccharide produced extracellularly by strains of *Aureobasidium pullulans*. The basic repeating unit of pullulan is α-(1→6) linked maltotriose, where three glucopyranose units are linked by α-(1→4) glycosidic bonds (Fig. 1). Other structures may exist as maltotetraose connected by α-(1→6) linkage. The regular alternation of (1→4) and (1→6) bonds are believed to be responsible for several distinctive properties of pullulan, for instance, structural flexibility, high solubility in water, adhesiveness, oxygen impermeability and excellent fiber/film forming capacities (Leathers, 2003; Singh, Saini, & Kennedy, 2008). Hence pullulan has many potential biomedical, food, paper and electronic applications (Cheng, Demirci, & Catchmark, 2011). Compared with films and gels, fibers possess porous 3-dimensional structure and high surface area that would benefit air permeation, moisture absorption, and action of active agents. Fiber mats made of pullulan are thus potentially useful in certain food applications, e.g. food packaging materials, and biomedical applications, e.g. wound dressing and drug delivery.

Production of pullulan fibers has been disclosed in a number of patents (Domoto & Tsuji, 1978; Fujii, Mori, & Tabuchi, 1991; Nomura, 1976; Ozaki, Nomura, & Miyake, 1996). The utilization of electrospinning for fabricating pullulan fibers appeared only in a few recent reports (Sun, Jia, Kang, Cheng, & Li, 2013). Pullulan/montmorillonite (MMT) blend nanofibers with diameters in the range of 50–500 nm were prepared by electropsinning (Karim et al., 2009). The introduction of MMT improved the tensile strength and thermal stability of the pullulan matrix. Stijnman et al. studied the rheological properties and electrospinnability of a series of polysaccharides including pullulan (Stijnman, Bodnar, & Hans Tromp, 2011). For successful electrospinning, the polysaccharide dispersion had to fall into a narrow range defined by shear viscosity at 1000 s^{-1} and the ratio of concentration to overlap concentration. Nanoscale pullulan fibers were obtained by using aqueous dispersions in these studies, and we have found it difficult to electrospin microscale pullulan fibers from aqueous dispersions. Though nanofibers are of interest because of their high surface area and small pore size, preference can be given to

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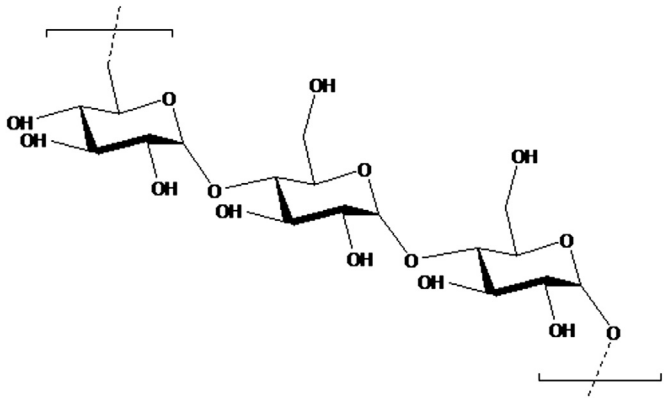

Fig. 1. Repeating unit structure of pullulan.

microscale fibers in some cases, for instance, combined nanoscale and microscale fibers may be the most appropriate architecture for mimicking extracellular matrix in tissue engineering application (Santos et al., 2008; Tuzlakoglu et al., 2005). The productivity of manufacturing nanofibers by electrospinning is usually much lower than that of microscale fibers. In addition, there are some safety concerns with the use of nanostructures in food, medical, and engineering applications (Meng, Xia, George, & Nel, 2009).

Therefore, it was the interest of this study to investigate the effect of electrospinning parameters on fabrication of both microscale and sub-microscale pullulan fibers. First, we investigated the effect of solvent composition and concentration on the electrospinnability of pullulan fibers with an emphasis on the rheological properties of pullulan dispersions (Kong & Ziegler, 2012). Then, we studied the effect of dimethyl sulfoxide (DMSO):water ratio in the solvent on fiber diameters and pore sizes.

2. Materials and methods

2.1. Materials

Pullulan was kindly provided by Hayashibara Biochemical Laboratories Inc. (Okayama, Japan). Dimethyl sulfoxide (DMSO) and ethanol were obtained from VWR International (Radnor, PA). Deionized water was used in the study.

2.2. Electrospinning

The preparation of spinning dope involved dissolving the appropriate amount of pullulan in an aqueous DMSO solution. The pullulan dispersion was heated in a boiling water bath with continuous stirring on a magnetic stirrer hotplate for about two hours. The pullulan dispersion was then allowed to cool to room temperature and deaerated if necessary. 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 high 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. 2). 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. Electrospinning was conducted at room temperature.

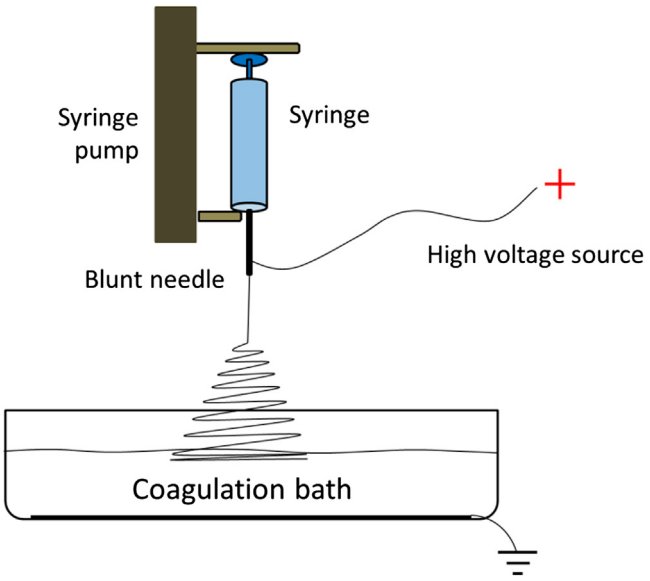

Fig. 2. Schematic drawing of the electrospinning setup.

The electrospinnability was not evaluated under constant process parameters. Instead, the electrospinnability of each pullulan dispersion was evaluated while varying three spinning parameters (feed rate, voltage, and spinning distance) within predetermined ranges: feed rates from 0.01 to 0.4 mL/h, and spinning distances from 5 to 10 cm. At each feed rate and spinning distance combination, the voltage was gradually increased from 0 to 15 kV. The onset and ending voltages of continuous jet formation were recorded. The electrospinnability for pullulan dispersions was determined by visual and microscopic observation of the fibers formed.

2.3. Rheology

Pullulan dispersions in aqueous DMSO solutions (0%, 20%, 40%, 60%, 80%, and 100% v/v) were prepared for rheological characterization. For each DMSO concentration, pullulan concentrations of 0.1–20% (w/v) were prepared. Flow curves, i.e. shear viscosity versus shear rate, were generated using a cone and plate geometry on an ARES strain-controlled rheometer (TA Instrument, New Castle, DE). The cone and plate diameters were 50 mm and the gap was set at 0.043 mm. The cone angle was 0.04 radians. Viscosity data were collect in the shear rate range from 0.1 s^{-1} to 100 s^{-1} at 20 °C.

2.4. Characterization

Fiber morphology was examined using a Phenom G2 Pro SEM (Eindhoven, The Netherlands) at an accelerating voltage of 5 keV. Five random fiber images were analyzed for fiber size and pore size using the Fibermetric application in the Phenom Pro Suite package. 500 different fiber segments were randomly measured by the software to obtain a diameter histogram.

3. Results and discussion

3.1. Rheological properties

Flow curves of pullulan in DMSO dispersions with varying pullulan concentrations are given in Fig. 3. Unreliable data, i.e. out of the detection limit of the rheometer, were not plotted. In all DMSO