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Effects of electric field on the maximum electro-spinning rate of silk fibroin solutions

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ABSTRACT

Owing to the excellent cyto-compatibility of silk fibroin (SF) and the simple fabrication of nano-fibrous webs, electro-spun SF webs have attracted much research attention in numerous biomedical fields. Because the production rate of electro-spun webs is strongly dependent on the electro-spinning rate used, the electro-spinning rate becomes more important. In the present study, to improve the electro-spinning rate of SF solutions, various electric fields were applied during electro-spinning of SF, and its effects on the maximum electro-spinning rate of SF solution as well as diameters and molecular conformations of the electro-spun SF fibers were examined. As the electric field was increased, the maximum electro-spinning rate of the SF solution also increased. The maximum electro-spinning rate of a 13% SF solution could be increased 12 × by increasing the electric field from 0.5 kV/cm (0.25 mL/h) to 2.5 kV/cm (3.0 mL/h). The dependence of the fiber diameter on the present electric field was not significant when using less-concentrated SF solutions (7–9% SF). On the other hand, at higher SF concentrations the electric field had a greater effect on the resulting fiber diameter. The electric field had a minimal effect of the molecular conformation and crystallinity index of the electro-spun SF webs.

1. Introduction

Silk has long been used as a textile material because of its good luster, desirable texture and good mechanical properties. Recently, reports regarding the good cyto-compatibility [1,2] and biodegradability of regenerated silk fibroin (SF) [3,4] have fostered additional research into SF for its biomedical applications, including as membranes for guided bone regeneration [5], bone substitutes [6], tissue engineering scaffolds [7,8], and nerve guidance conduits [9].

Electro-spinning is a simple method used to produce nanoscale fibrous webs. The electro-spinning of SF has attracted research attention ever since electro-spun SF webs were first shown to be effective tissue engineering scaffolds [8,10–12]. However, the low production rate of electro-spun SF webs is an obstacle in its industrialization and mass production [17].

A number of different electro-spinning conditions can be controlled to alter the electro-spinning performance of SF solutions. These include SF concentration [13–15], SF molecular weight (MW) [4], residual sericin content of silk [16,17], degumming method [18], silkworm variety [19], solvent [20], and applied electric field [21–23]. However, most studies have only focused on electro-spinnability (i.e. stable fiber formation) and fiber diameter of electro-spun webs; fewer have been conducted to understand and improve the electro-spinning rate.

Yoon et al. recently used control of the residual sericin contents to increase the maximum electro-spinning rate of SF solutions, finding that this control over the sericin content and viscosity can significantly increase the electro-spinning rate [17]. Kim and Um also reconfirmed that the maximum electro-spinning rate of SF solution is increased by increasing the solution viscosity (i.e., MW of SF) [18]. In this process, an electric field is used to power the electro-spinning of the polymer and overcome the inherent viscosity and surface tension of the dope solution. Although the effect of electric field on the electro-spinning of SF has been considered in previous studies [21–23], further details regarding the electro-spinning rate and the structure and properties of the resulting webs has not been conducted from the perspective of the electric field. Therefore, the present study examines the electro-spinning of SF solutions under different electric fields, and the effect that electric field has on the electro-spinning rate of SF solution and the fiber morphology and molecular conformation of resulting SF webs.

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2. Experimental

2.1. Preparation of regenerated SF powder

Regenerated SF was prepared using previously published methods [4,19,24]. In brief, *Bombyx mori* cocoons were degummed with a solution containing sodium oleate (0.3% [w/v]) and sodium carbonate (0.2% [w/v]) at 100 °C for 1 h (1:25 liquor ratio). The cocoons were rinsed thoroughly with purified water and dried after the degumming process.

A ternary solvent containing $CaCl_2/H_2O/EtOH$ (1:8:2 molar ratio) was then used for dissolving the degummed silk, performed at 85 °C for 30 min (1:20 liquor ratio). After dissolution, the SF solution was dialyzed with a cellulose tube (molecular weight cut off [MWCO]) = 12,000–14,000) against purified water for 4 days at room temperature. The purified water was produced using a Water Purification System (RO50, Hana Science, South Korea) with a reverse osmosis membrane. Regenerated SF powder was then obtained by drying the regenerated SF solution.

2.2. Electro-spinning of regenerated SF solution

The electro-spinning method used has been introduced previously [19]. Regenerated silk powders were dissolved in formic acid (98%) and filtered using a non-woven mat to prepare 7–13% regenerated SF dope solutions. A solution was loaded into a plastic syringe with a 21-gauge stainless steel needle (inner diameter = 0.495 mm) at the tip, and electro-spinning was carried out at voltages of 5–25 kV. The tip-to-collector distance was fixed at 10 cm.

2.3. Measurement and characterization

Various regenerated SF dope solutions (7–13% (w/w)) were used to measure the rheological properties. The shear viscosity was obtained by a rheometer (MARS III, Hakke, Germany) using a cone and plate geometry, at a 60 mm cone radius and 1° cone angle. Measurements were performed at a shear rate of 0.1–100 s^{-1} at 25 °C.

The maximum electro-spinning rate of the dope solution was measured under a fixed voltage and tip-to-collector distance [17,19]. The feed rate of the dope solution was controlled using a syringe pump (KDS100, KDScientific, USA) until the electrified jet was stable (e.g. continuous spinning without dripping and Taylor cone stability). To observe the electro-spun fibers at the maximum electro-spinning rate, field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan) was used after Pt-Pd coating of the fibers. Mean fiber diameters were determined by counting 60 fibers in the SEM data.

Fourier transform infrared (FTIR, Nicolet 380, Thermo Fisher Scientific, USA) spectroscopy in an attenuated total reflection (ATR) mode was used to examine the molecular conformation and the crystallinity index of the electro-spun silk webs [19]. The crystallinity index was calculated from FTIR data using the intensity ratio of the 1260 cm^{-1} and 1235 cm^{-1} bands using the following equation

$$\text{Crystallinity index}\,(\%) = \frac{A_{1260\text{cm}^{-1}}}{A_{1235\text{cm}^{-1}}} \times 100,$$

where $A_{1235\,\text{cm}^{-1}}$: Absorbance at 1235 cm^{-1}.
$A_{1260\,\text{cm}^{-1}}$: Absorbance at 1260 cm^{-1}.

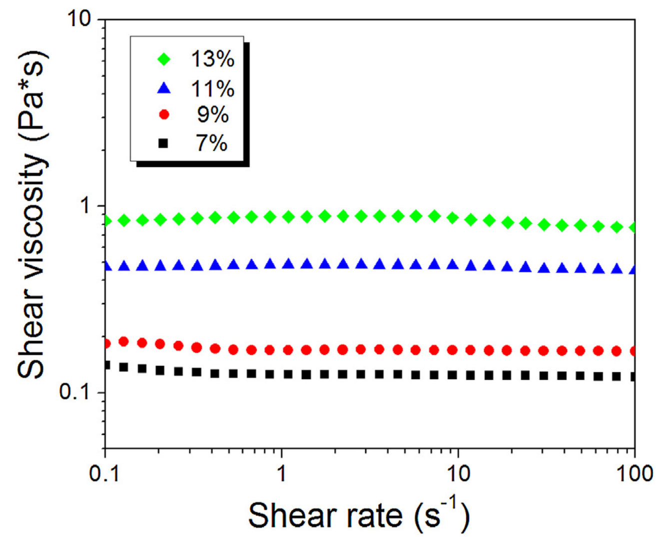

Fig. 1. Steady state flow of regenerated SF dope solutions with different SF concentrations.

3. Results and discussion

3.1. Rheological properties of regenerated SF dope solutions

The electro-spinning performance of a SF solution is strongly affected by its rheological properties [17,18,27]. Therefore, a steady state flow test was performed on the regenerated SF solutions with different concentrations (Fig. 1). All SF formic acid solutions showed nearly Newtonian fluid behavior, consistent with results in previous studies [19,24,26]. As the SF concentration increases from 7% to 13%, the solution viscosity increases from 0.1 to 0.9 Pa s.

3.2. Effect of electric field on the electro-spinning performance of SF

The electro-spinning rate is very important to the future industrialization and mass production of electro-spun fibers. However, the electro-spinning rate of SF solution is normally relatively low (0.2–0.3 mL/h) [4,28]. As mentioned in Introduction, Yoon et al. increased the electro-spinning rate of SF solution to 1.4 mL/h by controlling sericin contents and silk concentration [17], while Kim and Um increased it to 1.3 mL/h through control over the degumming method and silk concentration [18]. Although these studies report significantly improved electro-spinning rates, further improvements in the electro-spinning rate are necessary to promote mass production of nanoscale silk webs. This study further examines the effects of electric field on the maximum electro-spinning rate of SF solutions.

As shown in Fig. 2, the maximum electro-spinning rate of SF solution was increased by increasing the electric field and SF concentration. In the range from 7% to 11% SF concentration, the maximum electro-spinning rate increased linearly with a linear increase in the electric field. In this SF concentration range, the maximum electro-spinning rate of SF was slightly increased as well by increasing the SF concentration. However at 13% SF, the maximum electro-spinning rate increased remarkably with this same increase in the electric field, compared to other SF concentrations (7–11%). In addition, the maximum electro-spinning rate increased abruptly above 1.0 kV/cm when increasing the electric field. Finally, a maximum electro-spinning rate of 3.0 mL/h was obtained at 2.5 kV/cm and 13% SF. Considering the electro-spinning rate of SF solutions in most studies is 0.2–0.3 mL/h and previously published improve-