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Effect of degumming ratio on wet spinning and post drawing performance of regenerated silk

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ABSTRACT

Regenerated silk fiber has attracted considerable attention because of its good blood compatibility and cytocompatibility, and the advantages of regenerated fiber, such as control of structure and properties. In this study, wet spun regenerated silk fibers were fabricated by controlling degumming ratio and silk concentration. Rheometry, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were used to examine wet spinning and post drawing performance of silk. Dope solution viscosity was found to be a key factor determining the continuous fiber formation of silk and 0.07 Pa·s was essential for continuous fiber formation. Maximum draw ratio of the as-spun silk fiber was strongly affected by two factors: (1) crystallinity index from FTIR spectroscopy and (2) degumming ratio of silk. XRD of the wet spun silk fibers was not changed by the degumming ratio, silk concentration, and draw ratio. However, the crystallinity indices from FTIR were changed by these factors. Drawing-induced short-range crystallites of the silk were proposed based on FTIR and XRD. These results also show that XRD and FTIR can be used to characterize the micro-structure of silk complementarily because of their different detection characteristics: XRD and FTIR spectroscopy are sensitive to the detection of long- and short-range ordered crystallites of silk, respectively.

1. Introduction

Silk is a naturally occurring material that consists of fibroin and sericin. The material has been used as an excellent textile material for a long time owing to its good luster and touch. Silk has good blood compatibility [1,2], low inflammability [3], good biodegradation [4], and excellent cyto-compatibility [5]. These properties have prompted extensive studies into the biomedical applications of silk, such as a tissue engineering scaffold [6–8], artificial ear drum [9,10] and wound dressing [11].

The morphology, structure and properties of natural silk fiber are fixed when the silk fiber is produced by silkworms. On the other hand, when silk is dissolved in a solvent and is regenerated to the fiber form using a wet spinning technique, the structure and properties of silk can be controlled diversely. For example, the wet spun silk fiber can have circular or dog-bone shape cross-section [12]. In addition, its density and crystallinity can be controlled, resulting in a range of physical properties including biodegradability and mechanical properties. Silk can be mixed with other polymers to fabricate a blended fiber [13,14] and the preparation of other components (e.g. cellulose nano fibril, carbon nano tube, etc.) embedded composite fiber is also possible [15]. A silk biosensor fiber containing an enzyme can also be fabricated.

Studies of the fabrication of regenerated silk filament by solution spinning have been conducted for decades [12–23] owing to the useful properties of silk as a biomedical material and the advantages of regenerated silk fiber, even though the natural silk already has a fiber form.

Recently, Ki et al. reported that residual sericin can increase the crystallinity and tensile strength of wet spun fibers [17]. They also reported that the crystallization of silk is accelerated by the presence of sericin [24]. The residual sericin strongly affected the solution properties and electro-spinnability of the silk formic acid solution [25] and the electro-spinning rate of a silk formic acid solution can be increased approximately 5 fold by controlling the degumming condition (i.e. residual sericin content) [26]. In addition, the presence of sericin in regenerated silk was reported to increase the cholesterol lowering effect [27] and the blood glucose lowering effect [28] in mice.

Sericin was removed in studies of the biomedical applications of silk due to the reported immune reaction to silk sutures containing sericin [29,30]. On the other hand, the positive features regarding biomedical use were recently unveiled. Aramwit et al. [31] reported that sericin-treated wounds exhibited rapid wound healing and a

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Table 1
Degumming conditions, degumming ratio and residual sericin content in silk.

Degumming conditions			Degumming ratio (%)	Residual sericin content (%)
Sodium oleate (%(w/v))	Sodium carbonate (%(w/v))	Degumming time (h)		
0.6	0.4	1	27.7	0
0.1	0.067	1	25.2	1.1
0.024	0.016	1	22.7	4.3

lower level of inflammatory mediators. Nagai et al. [32] reported the enhancing effect of sericin on corneal wound healing.

Considering that silk is an expensive material and pollution occurs during the elimination of sericin from silk (i.e. degumming process), it is quite desirable to utilize sericin in silk rather than remove it totally from silk.

Although Ki et al. examined wet spun silk fiber with different residual sericin contents [17], more detailed features, including the dope solution rheology and post drawing has not been examined. Therefore, this study examined the more detailed features of wet spinning of silk with different sericin contents by rheometry, X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy. First, the rheology of silk solution with different degumming ratios (i.e. residual sericin content) and its effect on fiber formation by wet spinning were examined. In addition, the effects of the degumming ratio and silk concentration on the post drawing of as-spun regenerated silk fiber as well as the effect of the post drawing on the crystallization of regenerated silk fiber were examined by XRD and FTIR.

2. Experimental

2.1. Preparation of regenerated silk

The regenerated silk was prepared using a previously described method [25,26]. Briefly, to prepare silk with different degumming ratios, the *Bombyx mori* cocoons were degummed with a sodium oleate (0.024–0.6% (w/v)) and sodium carbonate (0.016–0.4% (w/v)) aqueous solution at boiling temperature for 1 h. Table 1 lists the degumming conditions, as well as the degumming ratio and sericin content in silk. The liquor ratio was 1:25. After the degumming process, the cocoons were rinsed thoroughly with purified water and dried. The purified water was obtained using a Water Purification System (RO50, Hana Science, South Korea) with a reverse osmosis membrane.

The degummed silk was dissolved in an aqueous 9.4 M LiBr solution at 60 °C for 3 h. The liquor ratio was 1:20. The aqueous silk solutions were obtained by dialyzing the dissolved silk solutions in a cellulose tube (molecular weight (MW) cut-off = 12,000–14,000 Da) against circulating purified water for 5 days at room temperature. The silk solutions were filtered and dried to obtain the regenerated silk powder.

MW distribution of regenerated silk samples was not measured directly in this study. However, in the previous our studies, MW distribution of regenerated silks was measured and reported. Briefly, regenerated silk dissolved in 9.4 M LiBr solution showed a main MW peak at 450 kDa [33]. When the residual sericin existed in silk, a 330 kDa MW peak was additionally presented with the 450 kDa main peak and the intensity of 330 kDa band was increased by increasing sericin content [25].

2.2. Wet spinning of silk

The regenerated silk powder was dissolved in a 98% formic acid solution to prepare the silk formic acid dope solutions with a range of silk concentrations for wet spinning. The dope solutions were filtered twice through nonwoven fabric with a pore size of c.a. 0.1 mm to remove the insoluble particles before wet spinning. The regenerated silk filaments were spun using a syringe and syringe pump by extruding the dope solution through a 22-gauge needle (inner diameter = 0.337 mm) into methanol as the coagulation bath. The flow rate of the fiber extrusion was controlled to 20 ml/h. The as-spun silk filaments were left to stand in the coagulant for 1 h and stored in water to remove the solvent and coagulant prior to post drawing. Post drawing of the as-spun silk filament was performed manually at a drawing speed of approximately 15 cm/s at 25 °C in air to fabricate the wet spun silk filament at different draw ratios.

2.3. Measurement and characterization

The degumming ratios were calculated using the following equation: Degumming ratio (%) = (1 − dry mass of degummed cocoons/dry mass of native cocoons) × 100. The dry masses of the cocoons were measured using a moisture analyzer (XM60, Precisa, Swiss). The residual sericin content was obtained using the following equation: residual sericin content (%) = [1 − {(1–0.26)/(1 − d)}] × 100, where d is the degumming ratio. The sericin content of the silk used in this study, 26%, was determined qualitatively by scanning electron microscopy (SEM) [25,26].

A photograph of the wet spun silk filament in the coagulant was obtained using a digital camera (IXUS 980 IS, Canon Inc., Japan). The rheological properties of the silk solutions were evaluated using a rheometer (MARS III, Thermo Fisher Scientific, Germany) with a 60 mm cone and a plate geometry with a 1° cone angle at 25 °C over a shear rate range of 0.1–100 s^{-1}. The maximum draw ratio was calculated from the ratio of the maximum drawn length of the fiber and the length of the as-spun fiber. The drawing of the as-spun silk filament was performed manually with a ca. 15 cm/s drawing speed at 25 °C in air. The fiber lengths were measured at 20 different parts of the filament, and the maximum draw ratio was determined from the mean. To examine the crystalline structure and crystallinity of the regenerated silk filaments, Small-Angle X-ray Scattering with a General Area Detector Diffraction System (GADDS, Bruker-Axs, Germany) using Cu K_α radiation was applied to X-ray diffraction (XRD) analysis. The irradiation conditions were 45 kV and 40 mA. The XRD patterns were obtained by 2θ scanning for the fiber diagram. The FTIR (Nicolet 380, Thermo Fisher Scientific, USA) spectra were obtained using the attenuated total reflection method. The crystallinity index was calculated as the intensity ratio of 1260 and 1235 cm^{-1} from the FTIR spectrum using the following equation [14,21,26,34]:

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

$A_{1235cm}{}^{-1}$: absorbance at 1235 cm^{-1}.
$A_{1260cm}{}^{-1}$: absorbance at 1260 cm^{-1}.