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Fabrication of silk sericin nanofibers from a silk sericin-hope cocoon with electrospinning method

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ABSTRACT

In this study, silk sericin nanofibers from sericin hope-silkworm, whose cocoons consist almost exclusively of sericin were successfully prepared by electrospinning method. Scanning electron microscopy (SEM) was used to observe the morphology of the fibers. The effect of spinning conditions, including the concentration of sericin cocoon solution, acceleration voltage, spinning distance and flow rate on the fiber morphologies and the size distribution of sericin nanofibers were examined. The structure and physical properties were also observed by Fourier transform infrared (FT-IR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The optimum conditions for producing finely thinner fibrous sericin nanofibers without beads were the concentration of sericin solution above 6–8 wt%, acceleration voltage ranging from 25 to 32 kV, spinning distance above 9 cm, and flow rate above 0.06 cm min^{-1}. The mean diameter of as spun sericin fibers varied from 114 to 430 nm at the different spinning conditions. In the as-spun fibers, silk sericin was present in a random coil conformation, while after methanol treatment, the molecular structure of silk sericin was transformed into a β-sheet containing structure. Sericin hope nanofiber demonstrated thermal degradation at lower temperature than the sericin hope cocoon, which probably due to the randomly coiled rich structure of the sericin hope nanofiber.

1. Introduction

Electrospinning is a spinning technique to generate fibers with diameter ranged from 2 nm to several micrometers, yielding a three-dimensional porous network (a random mat) of nanofibers with high aspect ratio and a large specific surface area by stretching and splitting polymer solution under high-voltage electric field [1].

The sizes of nanofibers with nano scale order primarily depend on the major factors of specifications of solvents, such as viscosity, conductivity and surface tension as well as the electrospinning conditions, including applied voltage, spinning flow rate and working distance [2]. Among them, viscosity and molecular weight of the sample are the most important factors to decide the fibrous nanofiber size. Very smooth, thinner nanofibers without beads can be produced with using sample solvents with low viscosity [3]. Surface tension favors the formation of beads and bead fibers. As for electric field strength, it is illuminated that the jet diameter firstly decreased with the electric field strength increasing, and then increased when the electric field strength increased further. Very low and high flow rate are not preferable to produce very thin nanofibers. Too high flow rates did not produced fibers because the polymer solution was pushed out of the syringe so fast that it did not have time to evaporation. Since the time needed to eject the solution, very low flow rate was also not chosen [4]. The working distance between the needle and collector varies the path length and solvent evaporation, so it greatly influences the mean diameter and uniformity of the fibers [5].

The micro/nanometer scale bears helpful specialties, high aspect ratio, high-specific surface area and high porosity with very small pore size. Therefore, the micro/nanofibers can simulate the extracellular matrix (ECM) and enhance the cell migration and proliferation and be applied in biomedical domain, involving drug delivery, wound dressing, tissue engineering scaffolds, and others [6,7].

Silk fiber derived from silkworm *Bombyx mori* (*B. mori*) is a natural biopolymer that is mainly composed of two different macromolecular proteins, i.e., fibroin (the inner brins) and sericin (outer coating). Silk sericin (SS) is a family of adhesive silk proteins synthesized exclusively in the middle silk glands of silkworms, which envelops the fibroin fiber with successive sticky layers that help in the formation of a cocoon [8]. SS constitutes 25–30% of

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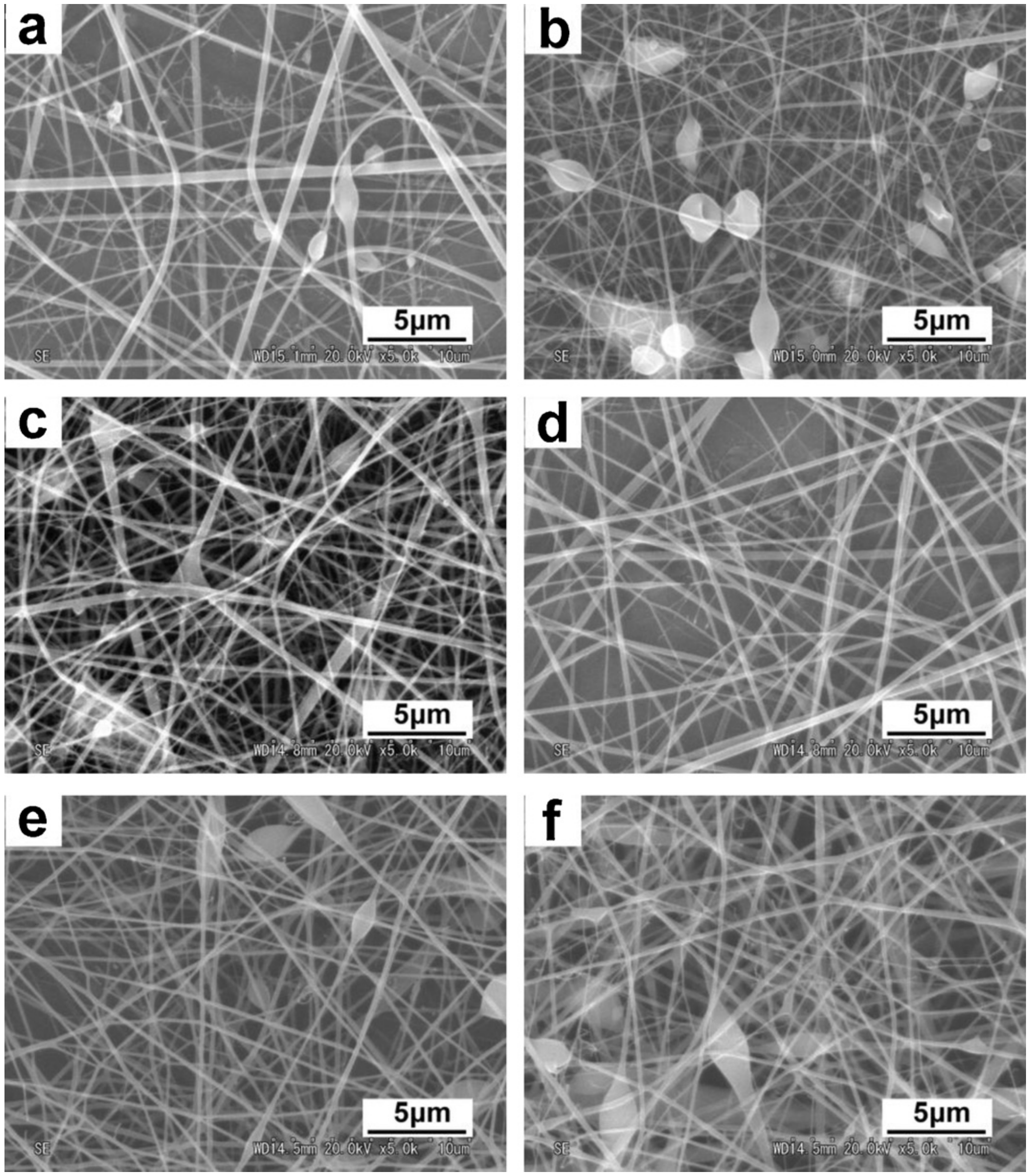

Fig. 1. The surface morphology of electrospun silk sericin fibers spun at the voltage of 25 kV with a constant spinning distance of 15 cm at the concentration of solution: (a) 2%; (b) 4%; (c) 6%; (d) 8%; (e) 10% and (f) 12%.

silk protein and ensures the cohesion of the cocoon by gluing silk threads together. SS consists of 18 kinds of amino acids most of which have strong polar side groups such as hydroxyl, carboxyl, and amino groups, and are characterized by a high serine content, about one third of the total amino acids [9,10], which lends it high hydrophilicity. Abundant hydroxyl groups in sericin are hoped to play a significant role in structural formation.

Recently it has been shown that SS resists oxidation, and is anti-bacterial, biocompatible, UV resistant, absorbs and releases moisture easily, can be cross-linked, copolymerized, and blended with other macromolecular materials [11–13]. Moreover, it exhibits a lot of biological activities, such as, tyrosinase activity inhibition [14], pharmacological functions such as anticoagulation [15], anti-cancer activities [16], promote digestion [17], and nitrogen source for culture medium [18]. Mandal et al. [19] prepared and characterized novel silk sericin/gelatin 3-D scaffolds and 2-D films for potential tissue engineering applications. They showed that blended sericin/gelatin 3-D scaffolds were highly porous with an optimum pore size of $170 \pm 20\,\mu$m. The scaffolds were robust with enhanced mechanical strength and showed high compressibility. Hence it is anticipated that SS is a promising natural resource for developing novel protein based materials. One important materials option for biomaterials such as, SS is the formation of nanofibers. The nanofibers from SS would be the most attractive materials in view of medical and industrial applications. The silk protein nanofibers with very thin and smooth surface, with smaller diameter and its narrow standard deviation, and with thick bead free nanofibers are important morphological feature for using in industrial fields.

Silk textile materials are composed mainly of silk fibroin and not of sericin, which can be almost removed by the elevated alkali and enzymatic solution. Thus sericin is the by-product proteins which are produced in the course of reeling process of raw silk fibers. The molecular weight of SS significantly decreased in the degumming process by the action of alkali solution. Actually it is impossible to get native SS without decreasing of molecular weight by collecting the SS from the sericin solution which obtained by the conventional technique.

Many gene scientists have been paid a great attention to produce novel SS cocoon by genetically modification and diversification