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Higher molecular weight fibroin extracted from silkworm cocoon waste produced regenerated silk fibers with high strength and toughness

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1 Introduction

We produced the regenerated silk fibers consisting predominantly of H chain component using silkworm cocoon wastes (Figure 1). To maintain the molecular weight of silk fibroin, we performed degumming of silk fibroin not by alkaline solution but by boiled hot water. The H chain was extracted as precipitation from silk fibroin by a treatment with formic acid and the subsequent centrifugation. The crystallinity and molecular alignment of the regenerated silk fibers were improved by postdrawing during the reeling process. We obtained the regenerated silk fibers with tensile strength comparable to the native counterpart. This study will be useful to the recycling of silkworm cocoon wastes and used silk clothes. Moreover, the regenerated silk fibers with tensile strength comparable to the native counterpart will contribute to the broader use as a protein-based structural material.

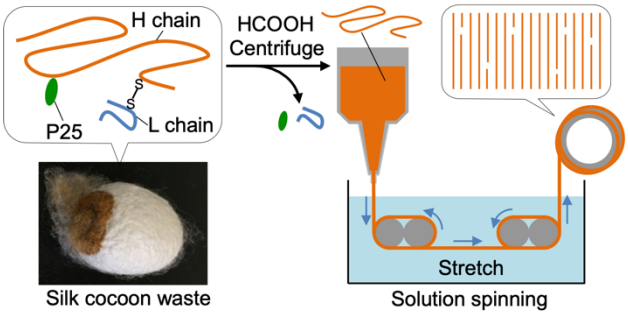

Figure 1. Dry-wet spinning of silk dope solution consisting of higher molecular weight fibroin extracted from silkworm cocoon waste.

2 Experiment

The synchrotron WAXS of the silk samples was performed at BL-10C beamline at Photon Factory, Tsukuba, Japan, using an X-ray energy of 12.4 keV (wavelength: 0.1 nm). The sample-to-detector distance for the WAXS measurement was 238 mm, and the exposure time for each scattering pattern was 15 s. The obtained scattering data were converted into one-dimensional radial integration profiles using the software Fit2D. The data were corrected for the background scattering, and the crystallinity was calculated from the area of the crystal peaks divided by the total area of the crystal peaks and the amorphous halo by fitting the Gaussian function using Igor Pro 8.03 (WaveMetrics, Inc., Portland, OR) [1].

3 Results and Discussion

WAXS measurement can detect the coherent interference of scattered X-rays through crystal region of the material. Accordingly, the structural information such as crystallinity and molecular alignment of the regenerated silk fiber can be evaluated on the basis of WAXS scattering data. Two-dimensional WAXS data of the regenerated silk fibers were converted into one-dimensional data by radial integration. The one-dimensional WAXS plot was deconvoluted into crystal and amorphous fractions using Gaussian function. The crystallinity of the regenerated silk fibers was improved along with the increase in the draw-down ratio. The crystallinity was calculated to be 19.5%, 20.1%, 22.3%, and 23.2% in the case of the draw-down ratio of 1, 2, 3, 4, respectively. Based on the structural data of the native silk fiber, the crystallinity of the regenerated silk fiber was lower than that of the native silk fiber.

On the other hand, we evaluated the molecular alignment of the regenerated silk fiber based on the full width at half maximum (FWHM) value of the azimuthal integration profile of the (210) peak. It is known that the degree of molecular orientation improves as the FWHM value is lower. The degree of orientation of the regenerated fiber was not influenced by postdrawing during the reeling process but improved compared with that of the native silk fiber. Although the as-spun regenerated silk fibers were not applied into postdrawing during the reeling process, air gap between the spinneret and coagulation bath in the dry-wet spinning played a role in enhancing molecular orientation of the silk dope solution by the gravimetric effect. Furthermore, it is noted that the scattering peak of the as-spun fiber was detected not only in the equatorial region but also in the meridional region. The scattering peak at the meridional region indicate that the silk molecular chains are located perpendicular to the fiber axis as illustrated in Figure 2a. The scattering intensity at the meridional region was gradually decreased when the draw-down ratio was increased. The postdrawing process contributes to the increase in the molecular alignment along the fiber axis of the regenerated silk fiber. When the regenerated fibers were postdrawn at the draw-down ratio of 4, some of the silk molecular chains were located perpendicular to the fiber axis (Figure 2b). The silk dope solution was prepared

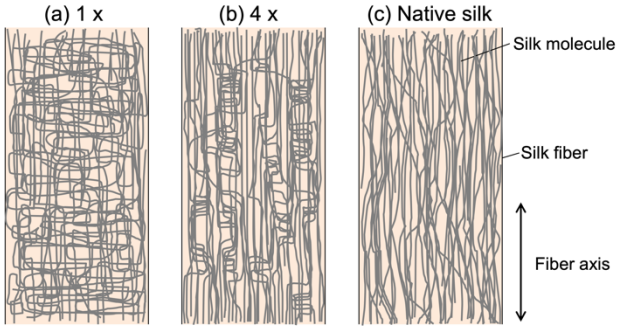

Figure 2. Proposed illustrations of silk molecular chains consisting of silk fibers. The regenerated silk fibers reeled at the draw-down ratio of (a) 1 and (b) 4 are compared with (c) the native silk fiber.

by dissolving the silk fibers, and the silk molecular chains were randomly oriented. In contrast, the scattering peak of the native silk fiber was detected at the equatorial region. This indicates that the native silk molecular chains were aligned parallel to the fiber axis (Figure 2c). The silkworm silk molecules are known to be stored as the liquid crystalline state and ordered preferentially along with the lumen of the silk gland. In addition, figure-of-eight movement of silkworms can enhance the molecular alignment of the silk fibers. Thus, the native silk fibers consist of silk molecular chains aligned parallel to the fiber axis.

Acknowledgement

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References

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