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Wild silkworm cocoon waste conversion into tough regenerated silk fibers by solution spinning

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1 Introduction

We produced regenerated silk fibers using cocoon waste of wild silkworms, *Antheraea yamamai*, which is a Japanese oak silkmoth of the family Saturniidae (Fig.1). The degumming process for removing sericin layers and calcium oxalate crystals on the surface of cocoons under an alkaline condition decreases the molecular chain length of the silk fibroin due to a hydrolysis reaction, thereby degrading mechanical properties. Therefore, we first pulverized wild silkworm cocoons, and then, the cocoons were washed in boiling water without using an alkaline solution to remove sericin layers and surface minerals. Thus, the molecular length of the wild silkworm silk was maintained after the degumming procedure. As a result, the wild silkworm silk-based regenerated silk fibers exhibited comparable mechanical properties to native silk fibers. This study is not only useful for reusing wild silkworm cocoon waste and old silk products but also expands the use of wild silkworm silk as structural and medical materials.

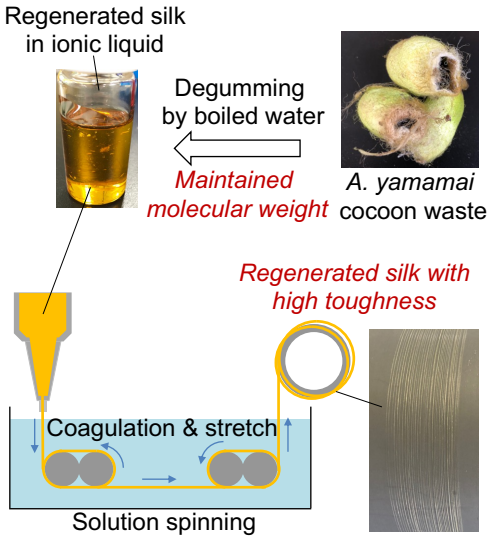

Fig.1. Regenerated silk fiber production using wild silkworm cocoon waste.

2 Experiment

The synchrotron WAXS of the samples was performed at the 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 235 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 background scattering, and crystallinity was calculated from the area of the crystal peaks divided by the total area of the profile by fitting the Gaussian function using Igor Pro 8.03 (WaveMetrics, Inc., Portland, OR). A full width at half maximum (FWHM) value was evaluated from the azimuthal integration profile of the (210) peak according to a previous study.

3 Results and Discussion

The coherent interference of X-ray scattering through crystal regions of protein-based fibers can be detected by WAXS measurements, which enables the investigation of crystal regions consisting mainly of β-sheet structures. The molecular orientation and crystallinity of the regenerated silk fibers were investigated using WAXS data. Two-dimensional WAXS scattering of the regenerated fibers were transformed into one-dimensional data after radial integration. The peaks in the one-dimensional WAXS data originated from crystal regions consisting mainly of polyalanine motifs in the wild silkworm silk. In contrast, the broader peaks are most likely due to amorphous regions. The one-dimensional WAXS profiles were next deconvoluted into amorphous and crystal regions using Gaussian functions. The crystallinity of the native silk was calculated to be 18.4%. Meanwhile, the crystallinity of the regenerated wild silkworm silk fibers after post-drawing at draw–down ratios of 1, 2, 3, and 4 was

calculated to be 20.1, 18.7, 25.7, and 22.9%, respectively. Thus, the β-sheets of the regenerated silk fibers were most likely formed when the silk dope sample was added to the methanol coagulation bath. Methanol facilitates the β-sheet formation of silk fibroin presumably due to the dehydration of silk molecular chains. We found that the (010) peak was not detected in the WAXS profiles of the native silk fiber even though the (010) peak was confirmed in the WAXS profile of the regenerated silk fibers. The disappearance of the (010) peak in the case of the native silk fiber could be explained by the extinction rules for the WAXS measurement of silkworm silks. Conversely, the regenerated silk fibers exhibited the (010) peak, probably due to the less three-dimensionally ordered crystal structure than the native counterparts. The crystallite size of the native and regenerated fibers was estimated using the (210) peak on the basis of the Scherrer equation. The crystallite size of the regenerated silk fiber was 8.6 nm for the as-spun fiber without the stretching process. Then, the crystallite sizes of the regenerated silk fiber were 8.4, 7.4, and 7.3 nm after post-drawing at the draw–down ratios of 2, 3, and 4, respectively. The gradual decrease in the crystallite size could be explained by the break of the crystallite during the post-drawing process.

Next, we evaluated the degree of molecular alignment of the regenerated silk fibers by the azimuthal intensity profile based on the WAXS data. The FWHM of the (210) peak along the equatorial direction was used to evaluate the molecular alignment of the regenerated and native silk fibers. Smaller FWHM values indicate higher molecular alignment along the fiber axis. The FWHM value of the native silk fibers was 49°. On the other hand, the FWHM value of the regenerated silk fiber was lower compared with that of the native silk fiber, indicating that the molecular alignment was improved after dry–wet spinning compared with the native silk fiber. Although the post-drawing process was not applied, the degree of molecular orientation of the as-spun silk fiber was higher compared with that of the native silk fiber. This is probably because the gravitational force was added to the regenerated silk solution at the air-gap region during dry–wet spinning. Accordingly, the regenerated fibers with draw–down ratios of 2, 3, and 4 exhibited the FWHM of 30, 29, and 27°, respectively. Therefore, the molecular alignment was improved by post-drawing during the drawing process.

It should be noted that the WAXS peak of the as-spun fiber without stretching was observed not only in the equatorial direction but also in the meridional direction. The scattering peak along the meridional direction shows that the silk molecular chains were aligned perpendicular to the fiber axis. The scattering intensity along the meridional region gradually decreased with the increased draw–down ratio. Although the post-drawing procedure contributes to an increase in the degree of molecular orientation along the fiber axis of the regenerated silk fiber, some of the molecular chains of the regenerated fiber at a draw–down ratio of 4 were still aligned perpendicular to the fiber axis. Conversely, the scattering peak of the native fiber was observed along the equatorial direction. This suggests that the molecular chains of the native silk were oriented parallel to the fiber axis. In nature, silkworm silk molecules are secreted in a liquid crystalline state and aligned preferentially, along with the lumen of the silk gland. Additionally, the figure-of-eight movement of silkworms can improve the degree of molecular orientation. Thus, the native silk fibers are formed by silk molecular chains oriented parallel to the fiber axis. Once the silk fibers are dissolved into a solution, micro/nanofibrils consisting of silk fibers dissociate randomly, and fibrils do not assemble into the native molecular structure due to polymorphism of polymers. As a result, the molecular assembly of the regenerated silk fiber was different from that of the native silk fiber.

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References

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