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論 文 内 容 の 要 旨

Dragline silk, produced by spiders to form the outer rim and spokes of their webs, has long been admired for its remarkable mechanical properties such as high tensile strength and great extensibility. On the contrary, most manmade fibers exhibit either high tensile strength and stiffness or low strength and high extensibility. The mechanical properties of spider silk have been studied for over 40 years. But the characterization of spider silks from a few species has been extensive. The mechanical properties of spider dragline silk fibers vary from species to species and from individual to individual within a species reflecting its use. In addition, under different solvents and environmental conditions, spiders can change the material and mechanical properties of their dragline silk. The mechanisms of these changes in silk properties are not completely known. The aim of this research is to analysis the variation by comparing the mechanical properties of dragline silk by different spiders or in different spinning conditions.

In chapter 1, the background and research purpose are described.

In chapter 2, the relationship between the mechanical properties of *Argiope amoena* spider dragline fiber and reeling speeds were investigated. To obtain the strongest spider silk fiber from *Argiope amoena*, the effects of reeling speed on the mechanical properties and microstructure of the dragline silk fiber were investigated. The dragline silk of A. amoena was obtained at forcible reeling speeds of 2, 7, 11, 20, 60 and 100 mm s-1. It was found that the breaking stress and initial modulus of the spider's dragline silk have maximum values of 1.41 GPa and 7.95 GPa, respectively, when reeled at a speed of 20 mm s-1. The strain at breaking was observed to decrease with an increase in reeling speed. Moreover, the breaking energy dropped significantly at reeling speeds above 20 mm s-1. In addition, the mechanism of tensile properties was investigated by Fourier transform infrared (FT-IR) spectroscopy and X-rag diffraction (XRD) were investigated. The results also indicate that dragline fiber reeled at 20 mm s-1 contains the most β-sheet polypeptides and that the orientation function is enhanced with reeling speed. Our results reveal that the mechanical properties of dragline silk are significantly affected by reeling speed.

In chapter 3, the mechanical properties and microstructures of dragline fibers collected from *Nephia clavata*, *Nephia pilipes*, *Argiope bruennichi* and *Argiope amoena* were investigated. It was found that the mechanical properties of spider dragline fiber were variable. Among the four different species, the larger spiders did not always extrude thicker dragline fibers and produce fibers with the maximum breaking force. The dragline fibers could sustain one to three times the body weight of the spider at a reeling speed of 20 mm s-1. *N. clavata* dragline fiber showed a stronger breaking stress and initial modulus than that of *N. pilipes*, *A. bruennichi* and *A. amoena*. With an increasing reeling speed, the breaking strain decreased; the initial modulus increased in *N. clavata*, *N. pilipes* and *A. bruennichi*, but the breaking stress exhibited a difference tendency. In order to analyze the variation of silk fiber's microstructures, Raman spectra were obtained. The results also revealed that dragline fiber of *N. clavata* contained the most β-sheet polypeptides and an excellent orientation of β-sheet molecular chains.

In chapter 4, Raman spectra of *Nephia clavata* spider dragline silks were obtained by three different spinning methods: crawl spinning, drop spinning and artificial reeling at 20 mm s-1. Based on a rational decomposition of the amide I spectra, the structural conformation of dragline silk proteins and the proportion of those secondary structures were determined. This analysis shows that spider dragline silk contains β-sheet, β-turn, α-helix and unordered structure elements; however, the proportions in which these structures appear changes with the spinning method. The β-sheet content of silk fiber obtained by artificial reeling at 20 mm s-1 is higher than that of spider spun fibers, indicating that some of the α-helix and other structures are transformed into β-sheet during the spider's spinning process.

Finally, the conclusions of main results are remarked in chapter 5.