Nanofibrils as the Basic Building Blocks of Spider Silk

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College of William & Mary, Department of Applied Science, 2019
Field: Materials Science & Engineering Degree: Ph.D.

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Abstract

Spider silk is a natural high-performance biopolymer with superior mechanical properties, resulting from its hierarchical structure. With protein nanofibrils observed in various spider and silkworm silks, the critical role of nanofibrils in achieving the silk's mechanical behavior has been widely suggested by both experimental observations and numerical simulations. However, a close review of available evidence of silk nanofibrils reveals many crucial aspects are still largely ambiguous or unknown. This further hinders the development of advanced silk-based materials.

The simple structure of the ribbon-like recluse (*Loxosceles*) silk provides an ideal opportunity to investigate silk nanofibrils. By studying the surface and internal structure of this silk, we showed that it is entirely composed of nanofibrils. Since the recluse ribbons exhibit the outstanding mechanical properties typical of a good spider silk, we can conclude that the properties of recluse ribbons are already implemented at the level of an individual nanofibril. Furthermore, we took advantage of this system to study the protein makeup of pristine silk nanofibrils. Using both polarized FTIR and Raman spectroscopy, we presented the first-ever vibrational spectra of silk nanofibrils. We were able to identify the presence of different secondary structures, as well as their volumetric percentages and orientations. A detailed structure model of recluse silk was proposed based on our results.

To relate the presence of nanofibrils to the natural silk spinning process, we investigated the self-assembly behavior of the native spider spidroin. Both individual and networks of long, thin silk nanofibrils were observed in the presence of shear force and a proper ion concentration. This unprecedented observation suggests the intrinsic tendency of native silk spidroin to form nanofibrils.

In summary, through an extensive investigation of the organization, protein makeup, and formation of silk nanofibrils in various natural and *in-vitro* systems, we revealed the fundamental role of nanofibrils as the basic building blocks of natural spider silk. This will have wide-ranging implications on the understanding of the structure-property relations of spider silk and the development of silk-inspired high-performance materials.