Structure, Formation, and Mechanics of Nanofibrillar Spider Silk

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William & Mary, Applied Science Department, 2023
Field: Nanomaterials & Imaging Degree: PhD

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Abstract

Spider silk rivals the best synthetic materials in terms of strength and toughness. It is widely accepted that these properties arise from its internal structure. Despite extensive research, comprehensive experimental evidence of the formation, morphology, mechanics, and protein makeup of its internal structures are still limited, controversially discussed, or not studied at all. First, we report the complete mechanical decomposition of natural silk fibers from the golden silk orb-weaver into ≈10 nm-diameter nanofibrils, the material's apparent fundamental building blocks. Also, we produced nanofibrils of virtually identical morphology by triggering an intrinsic self-assembly mechanism of the silk proteins. By analyzing protein self-assembly, we revealed independent physico-chemical fibrillation triggers which assemble proteins from stored precursors "at-will". We also presented the first evidence-based structural model for spider silk fibers.

According to our experimental work determining the nanofibrillar structure of spider silk, nanofibrils tend to align in parallel to the fiber (axial) direction. The axially oriented nanofibrillar structure of spider silk gives rise to a significant mechanical anisotropy. This mechanical anisotropy is extremely difficult to quantify, especially for microscopically small materials such as spider silk, but has the potential to reveal important knowledge about the material's structure-property relationships. We developed a novel method utilizing atomic force microscope (AFM) nanoindentations and finite element analysis (FEA) to characterize the mechanical anisotropy of such systems. We successfully used this method to measure the mechanics of nonfibrillar silk ribbons of the Chilean recluse spider, revealing the tensile and transverse elastic moduli as 9 GPa and 1 GPa, respectively, and the binding strength between silk nanofibrils as 159 ± 13 MPa. Furthermore, based on this binding strength, we derived the nanofibrils' surface energy, as 37 mJ/m^2, and conclude that van der Waals forces play a decisive role in inter-fibrillar binding. Due to its versatility, this technique has many potential applications including early disease diagnostics, as underlying pathological conditions can alter the local mechanical properties of tissues.

The impressive mechanical properties of spider silk nanofibrils can be further understood by studying their secondary protein structure, especially in the presence of fiber strain. We conducted strain-dependent Raman spectroscopy on nanofibrillar recluse silk and observed strain-dependent red shift in amide III protein band and strain-induced relative peak height changes in amide I/II/II bands. A wealth of knowledge about the behavior of protein secondary structures in the presence of fiber strain can be extracted by decomposing the amide bands into their subpeaks which correspond to each of the secondary protein structures.

This extensive investigation of the structure, formation, and mechanics of nanofibrillar spider silk furthers our understanding of this exceptional material, and ultimately, leads us toward the realization of high-performance silk-based materials.