Man-Made Spider Silk Alternatives

A Literature Review

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Introduction

Spider silks are one of the strongest and most elastic fibers that exist in nature. Its high tensile strength, elasticity, and biocompatibility make it a viable candidate for several industrial and biomedical applications. It is also a preferred fiber for wound repairs and closures. Silk proteins can be paired with various substances to confer additional properties such as immunological binding sites and affinity properties. For all these applications, a lot of scientists are trying to produce artificial spider silk fibers that possess mechanical properties comparable to natural spider silk, and also that can be manipulated for using the material for specific purposes.

This literature review provides an analysis of three different studies where artificial spider silk fibers have been produced using different methods and their mechanical properties have been characterized.

"Native-sized recombinant spider silk protein produced in metabolically engineered Escherichia coli results in a strong fiber" – Xia *et al*, 2010

A lot of scientists are trying to recreate the spider dragline silk, as it has very strong mechanical properties making it useful for applications such as parachute cords, composite materials, biomedical implant coatings, and drug carriers. In 2010, Xia *et al* expressed the dragline silk protein of *Nephila clavipes* in *Escherichia coli*, extracted the protein and spun it into fibers, and analyzed its mechanical properties. The glycine-rich 284.9 kDa (4.63 N) major ampullate spidroin 1 (MaSp1) protein was expressed in different sizes using different sized constructs in *E. coli*. The silk proteins of various sizes were purified by fractional ammonium sulfate precipitation followed by further rounds of purifications. These proteins were dissolved in a spinning solvent and spun at a protein concentration of 20%. As mechanical properties are best analyzed on stretched fibers, the spun proteins were stretched by hand to about five times its original size.

In order to assess the mechanical properties of the spun silk fibers, stress-strain curves were drawn for all of them and the tenacity, breaking strain, and Young's modulus was calculated for each curve. It was observed that these values improved with the increase in size of the silk proteins. The largest protein which comprised of 96 amino acids showed mechanical properties comparable to that of native dragline silk fibers. A scanning electron microscopy analysis of the 96-mer showed a uniform fibrillar structure, similar to that of the native protein. In comparison with a recently produced protein from *Araneus diadematus*, the tenacity of this protein is much higher possibly due to its larger size. The protein's similarity in mechanical properties to the native protein opens up the possibility of several applications in the industrial and biomedical fields. It may also be used for the production of biomaterials such as elastin, collagen, and resilin.

"Bioinspired supramolecular fibers drawn from a multiphase self-assembled hydrogel" – Wu *et al*, 2017

In 2017, Wu *et al* derived inspiration from spider silk fibers and produced supramolecular fibers from colloidal hydrogel, a supramolecular polymer. As shown in Figure 1 below, this was fabricated by mixing a hydroxyethyl cellulose derivative and silica nanoparticles in a 1:1 ratio. The silica nanoparticles had previously been complexed with cucurbit[8]uril, which helps in the formation of polymer cross-links. The hydroxyethyl cellulose derivative was prepared by producing a composite of naphthalene isocyanate and hydroxyethylcellulose. The end product of this production process showed elasticity, rigidity, and a persistent shape.

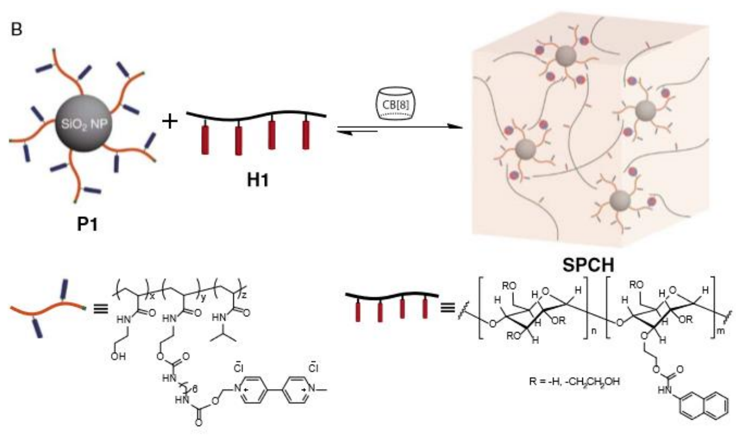

Fig 1: Production process of the colloidal hydrogel. P1 refers to silica nanoparticles, H1 refers to hydroxyethyl cellulose derivative, CB[8] refers to cucurbit[8]uril, and SPCH refers to supramolecular polymer-colloidal hydrogel (*Wu et al*, 2017).

The mechanical properties of this polymer were tested using rheological techniques. Strain-dependent oscillatory rheology measurements and step-strain measurements revealed the highly ductile nature of the fibers and the hydrogel fibers could be cast into a filament of size greater than 250 mm (0.25 m). The filament was found to be smoothly cylindrical having a consistent diameter. Stress-strain measurements of the supramolecular fibers showed that it was elastic and had reasonably high tensile properties, which was higher than textile fibers, cellulose-based viscose, and artificially prepared silks. The toughness of the fibers was found to be higher than that of flax and jute. The elastoviscosity and damping performance of these supramolecular fibers was found to be comparative to that of natural spider silks. The softness of the supramolecular fibers makes them favorable for use in cell culture and tissue engineering.

"Ultrastrong and bioactive nanostructured bio-based composites" – Mittal *et al*, 2017

Another study that was conducted in 2017 by Mittal *et al* described a biological procedure to produce large amounts of recombinant spider silk proteins. They used cellulose nanofibrils present naturally in trees as a reinforcing element with spider silk proteins to generate artificial spider silk fibers. The silk proteins and cellulose nanofibrils were mixed to form a hydrocolloidal dispersion, and following evaporation of water, a planar fibril network was obtained. The simplicity of this technique allowed the formation of stable fibrillar networks over a large area. Microscopic analysis using scanning electron microscopy and atomic force microscopy revealed a uniform network of cellulose fibrils involved in fibril-fibril interactions and small clusters of silk proteins distributed uniformly throughout the network.

An analysis of the mechanical properties of the fibers revealed a high modulus, elevated strength at break, and a high strain-to-failure value. This is the highest measured for fibers made using cellulose as the backbone, and it is evident that these mechanical properties are imparted by the silk proteins. The interactions between the silk proteins and cellulose nanofibrils were responsible for the increased strain of the composite. This study also demonstrated how the silk protein-cellulose complex could be used for immunological and cell culture studies. Hence, the stability conferred by cellulose and strength conferred by silk proteins have widespread applications in the biomedical field for the purpose of cell culture, tissue engineering, and immunological studies.

Conclusion

This literature review describes three different studies where attempts have been made to generate artificial silk spider proteins and their resulting fibers or networks. These composite structures can find suitable applications in several industrial and biomedical processes. Both biological and chemical processes have been used to generate these fibers and their mechanical properties have been characterized using microscopic and stress-strain relationship analyses. The procedure outlined by Mittal *et al* generates a cellulose-silk network which has quite specific applications in the medical field. On the contrary, Wu *et al* uses a supramolecular pathway to produce artificial silk supramolecular polymer which stands out due to its softness and damping capacity. Xia *et al* uses a biological method to produce spider silk proteins using a microbial host. All these three procedures show the promise of strength, scalability, and applicability in the current industrial and biomedical context.

References

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