Impact of Processing Methods on Synthetic Spider Silk

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Background

Dragline spider silk is among the strongest known biomaterials. It is the silk used for the framework of the web and it is used to catch the spider if it falls. As such, it is stronger and much more flexible than KEVLAR©. Studies show that dragline silk is made of two proteins, Major Ampullate Spider Proteins 1 and 2 (MaSp1 and MaSp2). MaSp1 contains a 3_{10} helix (GGX repeated) , a rod-like structure, and a beta sheet secondary structure motif (poly-A) (Fig. 1A). MaSp2 contains a secondary structure motif known as a Beta spiral (GPGXX-repeated) (Fig. 1B) along with a poly-A beta sheet region.

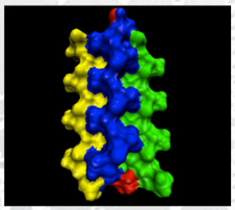


Fig. 1 - A) Beta Sheet Motif

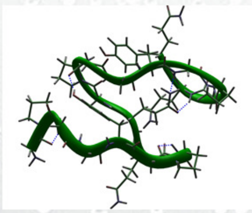


Fig. 1 - B) Beta Spiral Motif

Due to its incredible mechanical properties, spider silk is being considered for use as a new biomaterial for drug delivery and tendon and ligament replacement/repair, as well as athletic gear, military applications, airbags, and tire cords. However, spiders can't be farmed because they are territorial and cannibalistic. Therefore, methods of mass-producing synthetic spider silk have been developed. Transgenic goats were engineered to produce either MaSp1 or MaSp2 in their milk. The spider silk protein is extracted from the milk (Fig 2). It is then dissolved into a viscous solution, called a spin dope. The spin dope is loaded on the DACA unit (Fig 3), which applies pressure, extruding the dope through small diameter PEEK tubing into a coagulation bath of isopropanol. This process converts the spin dope into a solid silk fiber.

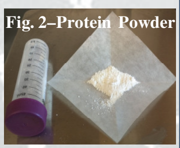


Fig. 2–Protein Powder

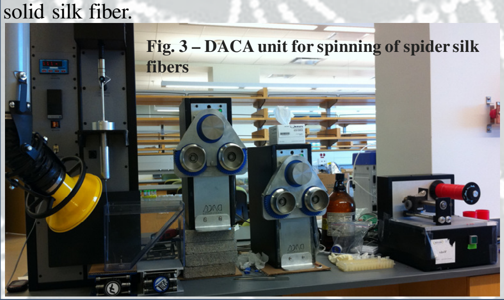


Fig. 3 – DACA unit for spinning of spider silk fibers

Changing Mechanical Properties through Processing

Draw Ratio

Unfortunately, spider silk fibers that are simply spun into a coagulation bath are weak and brittle. However, previous research has shown that by stretching the fibers after they are formed dramatically increases the strength and elasticity of fibers. Up until now this stretching was done by hand after the fiber making process was done. Stretching by hand is impractical as it cannot be scaled up and resulted in inconsistent fibers. Our research has shown by changing the speeds of the two spinning godets on the DACA SpinLine we can stretch the fiber in a liquid and achieve the better, more consistent results. Different draw ratios were tested. The results show that with higher stretch more stress is achieved, but some extension is lost.

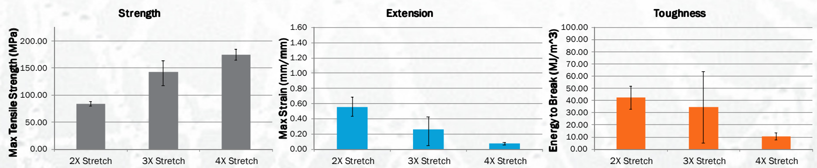


Fig. 4 – Bar charts showing the max stress, max strain and toughness of fibers that were stretched at different ratios. As the max stress increases the max strain decreases.

Stretch Bath Composition

The silk fibers needed to be in a liquid in order for the post-spin draw to be effective. Different bath compositions were tested. Results showed that altering the composition radically changes the mechanical properties of the fibers. A stretch in 50:50 IPA:H_2O resulted in an increased extension but a lower stress. A stretch in either 80:20 IPA:H_2O or 2M ammonium sulfate had a much higher max stress but not as much extension.

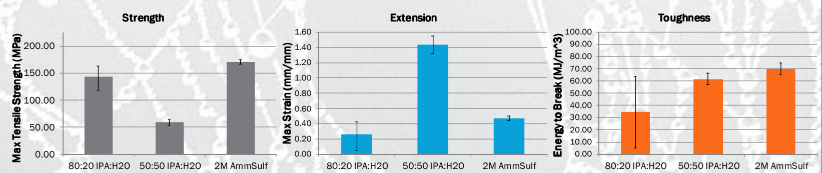


Fig. 5 – Bar charts showing the effect of different stretch bath compositions on the max stress, max strain and toughness of synthetic spider silk fibers.

Effects of Water Treatments After Post-Spin Draw

Recent publications from our lab have shown that water can have a large effect on the mechanical properties of synthetic spider silk fibers. After the 80:20 IPA:H_2O fibers were stretched to three times their original length in a variety of different water treatments. The first was a simple dip in water and the next was a 1.5x stretch in water. The results showed that a dip or a stretch improved all the mechanical properties of the fibers.

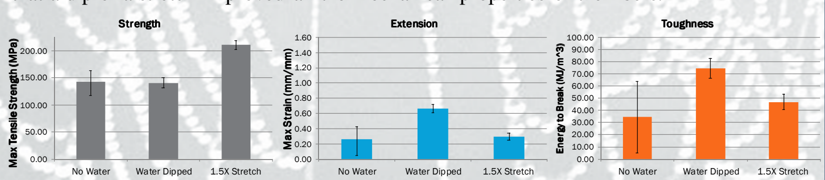


Fig. 6 – Bar charts showing the different water treatments used and their effect on the max stress, max strain and toughness of the fibers.

Conclusions and Future Work

Based on previous results we decided to build a third set of godets. This was done so that the fiber could run through both baths and be stretched in an automated fashion. Early results indicate that a second stretch in 100% water further improves the fibers. The highest values for energy-to-break and max stress have been achieved with this process. Further work is in progress to improve upon this design.

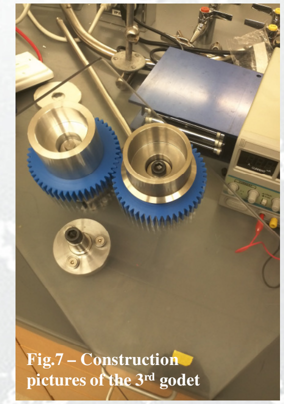
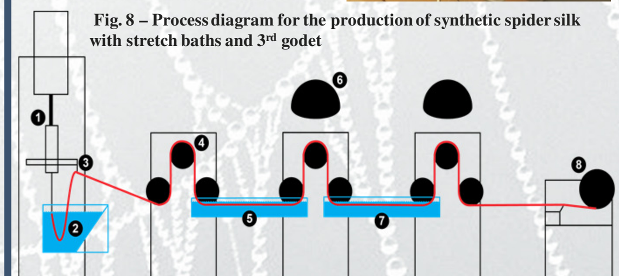


Fig.7 – Construction pictures of the 3rd godet

Fig. 8 – Process diagram for the production of synthetic spider silk with stretch baths and 3rd godet



1) Piston/Extruder - Constant pressure is applied to the spin dope.
2) Coagulation Bath - Generally isopropanol is used to help with fiber formation and extract solvents used in dope
3) Teflon Guide
4) Godets - Wheels that spin in sync along which the fiber runs. Sets of godets can be programmed to different speeds independently. This allows the stretch to be applied.
5) Stretch Bath - As the fiber is stretched by a difference in speed between godet set one and two, the fiber runs through a stretch bath to aid in protein motif formation and alignment.
6) Drying Unit - With either heat or a slight air current, the solvents used in the stretch bath are driven off prior to entering the water bath or before going to the winder.
7) Water Bath - The fiber runs through water or a water/alcohol or water/salt mix to further strengthen and align the fibers. A stretch can also be applied here, between the second and third godet sets.
8) Winder - The fiber is guided to a winder for collection.

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