



Making Electrospun Spider Silk Fibers Stronger

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Results



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Introduction

Spider silk is one of the most robust and versatile fibers making it a topic of interest in the scientific community. Possessing strength and elasticity many have sought to create fibers comparable to natural spider silk. Up until recently many scientists have fallen short of creating said fibers. With the use of a technique called electrospinning, comparable spider silk fibers have been created. Electrospinning is the process of creating fibers from a polymer solution using an electrical field. This method leads to the formation of nanofibers. These Fibers can then be further modified by crosslinking, a technique traditionally used to analyze protein-protein interactions.



Methods

- Silk dope is loaded in syringe with positive electrode attached
- The target (rotating spindle) has the negative electrode attached
- 28 kV field is applied forcing polymer ejection
- Ejected polymer forms nanofibers collected as a mat
- Mat is rotated into a yarn
- Yarn is then irradiated with the CLIP to initiate cross-linking











MTS/Mechanical Testing:

within nylon 6, 6

MaSp1 and nylon

sheets

 Nylon+MaSp1 (up to 5% wt) has increased elastic modulus and ultimate tensile strength compared to nylon

MaSp1 contributed to crystallization

formations; indicates H-bonds between

Increases in intensity of α -helices and β -

Increases in amide I, II, and III

 Cross-linked Nylon+MaSp1 samples have increased stress with decreased strain demonstrating further modification

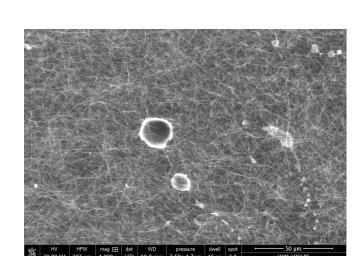
Cross-Link Comparison Strain (mm/mm) Cross-Link Comparison Control XL

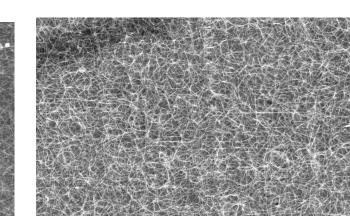
-- Nylon 66 + 10 wt.% MaSp

SEM:

FTIR:

- Cross-linked fibers show better orientation when compared to control
- Diameter of fibers demonstrates nanofiber formation (100-200 nm)





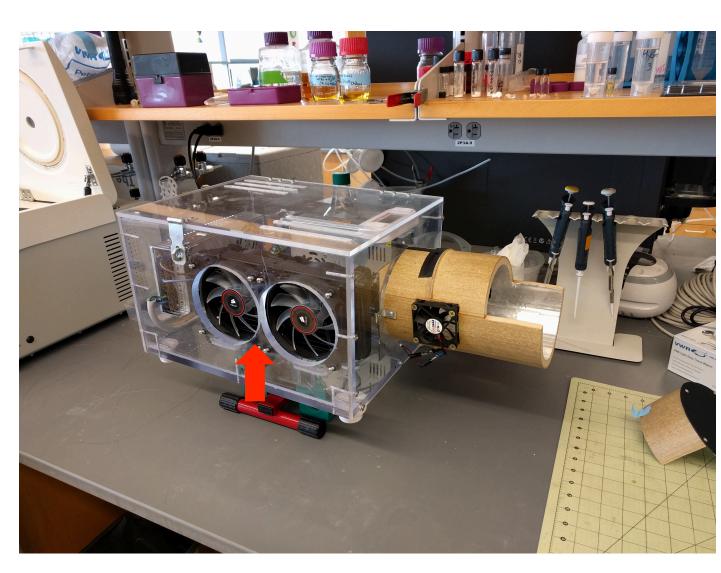
Cross-Linked

Control

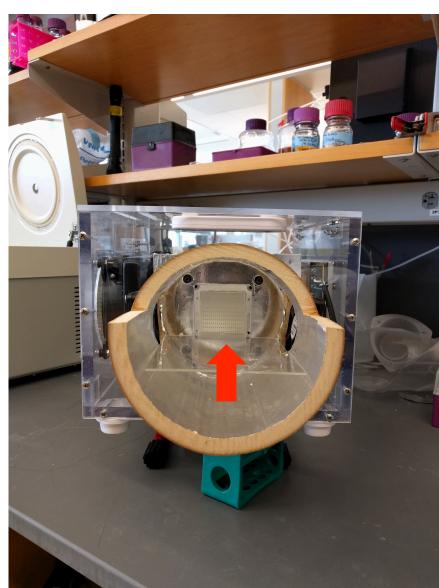
Cross-Linking Modifications

Cross-linking:

- Technique traditionally used to analyze protein-to-protein (protein a + protein b) interactions known as Photo-induced cross-linking of unmodified proteins (PICUP)
- PICUP is being used to further modify proteins through internal reinforcement by creating a direct covalent bond within the spider silk proteins
- Initially a high powered flashlight was used to initiate PICUP to test whether or not cross-linking was possible
- The Cross-Link Initiating Photodiode or CLIP was created for maximum cross-linking of spider-silk proteins.
- The CLIP initially contained a broad spectrum LED, with further testing a specific wavelength (450nm) LED was used to further increase the efficiency of cross-linking
- The 450nm LED was selected because the main cross-linking agent (Ruthenium) is activated at this wavelength which causes a dityrosine crosslink to form between the spider silk proteins in the fiber
- The CLIP can be used with any biomaterial containing spider silk proteins to modify their mechanical properties (lyogels, sponges, fibers, films, etc.)
- Preliminary experiments show 5-10 fold increase in mechanical strength (control: 2N; cross-linked: 20N)



CLIP: The design of the CLIP allows for continuous irradiation without excessive build up of heat promoting longevity of the LED. The red arrow points to the cooling system.



The red arrow indicated the 450nm LED, specific for cross-linking.

Conclusion

- Electrospun spider silk and composite fibers exhibit superb mechanical properties
- Electrospinning allows for production of mats constructed of multiple nanofibers resulting in resilient fibers/yarns
- Combining spider silk proteins with other polymers (nylon, cellulose, etc.) appears to increase mechanical properties of the polymers
- Using the CLIP, electrospun fibers can be further modified
- Cross-linking initiated by the CLIP can be applied to not only electrospun fibers but any biomaterials containing spider silk proteins