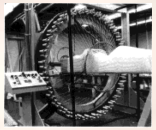
Electrospinning of Spider Silk Carbon Nanotubes Composites

Milind Gandhi[1] and Frank Ko[2]

1-Biomedical Engineering, Sciences and Health System, Drexel University, Philadelphia, PA 19104

2- Fibrous Materials Laboratory, Department of Materials Science and Engineering, Drexel University , Philadelphia, PA 19104



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Background

•Dragline silk from major ampullate glands of spider, *Nephila clavipes* is a fibrous protein with unique characteristics of combined strength and elasticity. It is stronger than steel, as extensible as rubber and has a water uptake comparable to wool.

• The silk fiber has crystalline regions of anti-parallel β-sheet interspersed with elastic amorphous segments similar to liquid crystalline polymers. These two segments are represented by two different proteins, MaSp1 (Major Ampullate Spidroin 1) and MaSp2 (Major Ampullate Spidroin 2) coded by different genes.

•Nexia Biotechnologies Inc., in 1999 introduced an innovative technology of using transgenic approach to produce recombinant spider silk. They produced recombinant spider silk, Biosteel[R] in BELE[R] (Breed Early Lactate Early) goat system. The milk produced by Nexia's transgenic goats contains spider silk proteins which can be isolated and purified to homogeneity. They have successfully isolated MaSp1 as well as MaSp2.

•While the biotechnology pathway to large scale manufacturing of spider silk is promising, the strength of the recombinant silk is far from satisfactory in spite of its high level of elongation at break.

Objective

•Taking advantage of the super strength of a carbon nanotube (CNT), we hypothesize that the composite consisting of recombinant spider silk and CNT will have the mechanical properties comparable or superior to those of natural spider silk.

•We plan to test this hypothesis by fabricating a novel composite material in a process of co-spinning of spider silk and CNT in electrostatic field.

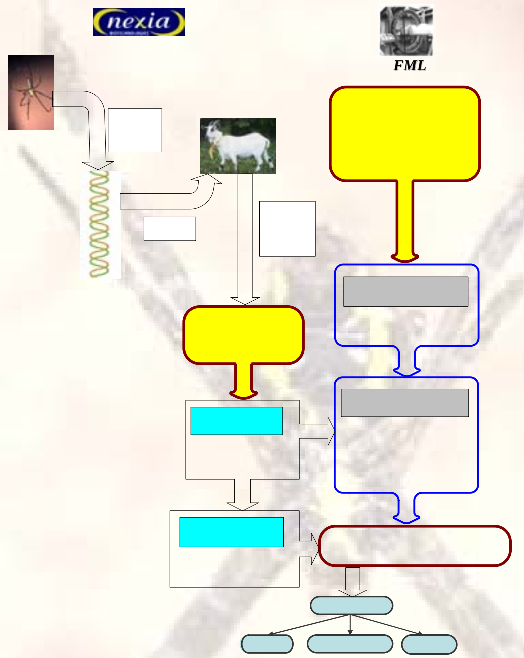
On the basis of elongation balance we concluded that the spider silk (20-30% elongation at break) and CNT (6-30% elongation at break) are compatible material systems

•We intend to combine these tailorable superior mechanical properties with the biocompatible nature of spider silk at a nanoscale level and explore the feasibility of the "super silk' as tissue engineering scaffolds.

Hypothesis

- Mixing MaSp1 and MaSp2 in different ratios to prepare the spinning dope might produce silk nanofibers with unique and tailor made properties. For silk-CNT composite preparation, CNTs must be dispersed in the silk solution so that individual tubes are well separated from each other, approaching the level of mono-dispersion.
- The electrostatic charge during electrospinning along with the polymer flow will help in aligning the CNT in the spider silk polymer matrix therefore resulting in strong and tough fibrils unmatched by any known synthetic materials.
- Nanofibrous structures fabricated by the electrospinning process are characterized by ultrahigh surface area to volume ratio with morphology similar to natural extracellular matrices, a wide range of pore size distribution, and a high porosity. Cells seeded on the biocompatible silk nanofibrous structure might proliferate and migrate under the guidance of fiber orientation.

Materials and Methods

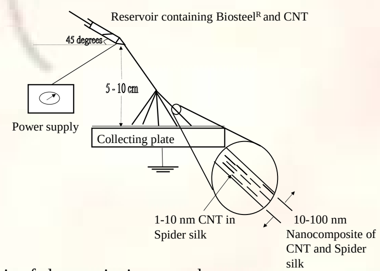


Results

•MaSp1 was successfully electrospun at 12 % wt in formic acid at spinning distance of 10 cm and voltage of 3 kV/cm. 1% CNT was added to MaSp1 and was spinnable at 10 % at similar distance and electric field. Both aligned as well as random fibers were formed. The aligned fibers with and without CNT were tested by Kawabata microtensile tester .

•MaSp2 was spinnable at 12% but with beads at similar spinning conditions.

•Ratios of MaSp1 to MaSp2 - 3:1 was spinnable at 12 % but for 1:1 and 1:3, viscosity was too high and had to reduce it to 10% and 6% respectively.

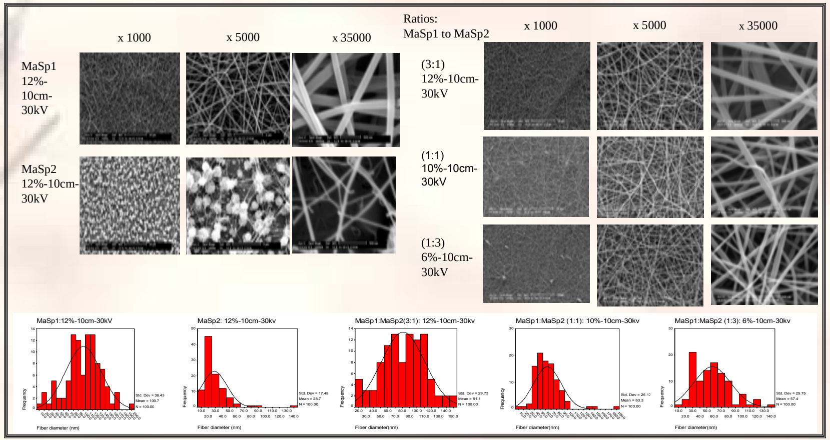


Schematic of electrospinning procedure

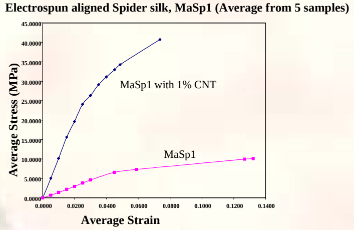
Spinning parameters used in the experiments…

•Concentration of spider silk (%wt): 6 - 12
•Solvent: Formic acid
•Electric field (kV/cm): 1-6
•Diameter of spinneret: 18-G needle
•Angle of spinneret: 45°
•Spinning distance (cm): 5 - 10

Fiber Morphology and Diameter

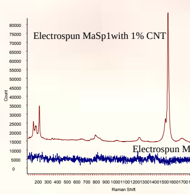


Tensile Properties

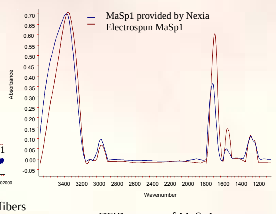


	Modulus (MPa)	Maximum Stress (MPa)	Elongation at break (%)
MaSp1	123.2982 ± 29.2264	9.5948 ± 3.7077	14.33 ± 3.98
MaSp1 + 1% CNT	1004.3658 ± 546.76	40.7422 ± 18.0545	7.3973 ± 2.6103

Chemical Composition



Raman spectra of electrospun MaSp1 fibers with and without CNT



FTIR spectra of MaSp1 powder and electrospun fibers

Conclusion

•Individual components of spider silk (Biosteel[R]) in different ratios produced by transgenic technology were successfully electrospun to obtain nano scale diameter aligned as well as random fibers.

•Incorporation of carbon nanotubes (CNT) in spider silk improved the mechanical properties of fibers.

•Preliminary analysis with FTIR proved electrospinning does not change the chemical composition of spider silk.

•Raman spectroscopy results proved that CNT are in the fibers.

Future direction

Further optimization of electrospinning parameters to produce continuous uniform fibers.

Incorporation of CNT having higher concentrations.

Chemical and thermal annealing to improve the mechanical properties.

In vivo cell culture study to investigate biocompatibility of spider silk scaffolds for tissue engineering applications.

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