

# Spider Silk Proteins as Carbon Fiber Precursors

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**PI: Felix Paulauskas**

(Oak Ridge National Laboratory)

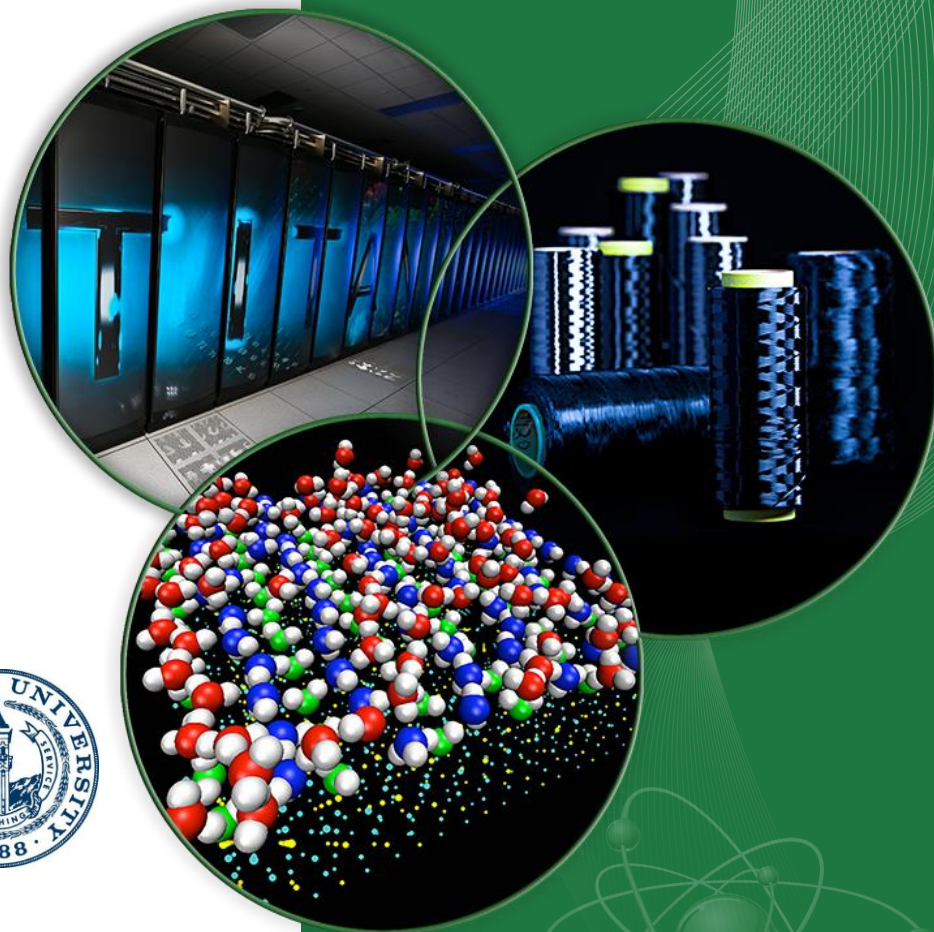
**Presenter: Pol Grappe**

(4X Technologies, LLC.)

**Partners:**

Utah State University (USU)

4X Technologies, LLC.



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# Overview

## Timeline

- Project Start: 1/1/18
- Project End: 12/31/19
- Progress: ca. 50%

## Budget

Total project funding:

- FY18: \$420k (phase II)
  - DoE share: 100%
  - Contractor share: 0%

## Barriers

- Barriers addressed
  - Sourcing: increase the variety of feedstock material suitable for carbon fiber (CF) production.
  - Low-cost high-volume manufacturing of carbon fiber  
(2017 U.S. drive MTT Roadmap report, Section 4)

## Partners

- Project lead: ORNL
- Partners:
  - USU
  - 4X Technologies  
(formerly RMX Technologies)

# Relevance

- Match with DoE goals by:
  - DoE goals for carbon fiber
  - Enable lightweight materials used for vehicles
  - Reduce high cost carbon fiber
- Project Goals
  - Protein production via *E. coli*:
    - Maximization: (volume of the production)
    - Optimization: (maintaining or increasing full-length proteins)
    - Diversification: Generate transgenic silkworms
  - Fiber spinning process: enhance the scale of production
  - Mechanical properties: improved compare to previous batches
  - Stabilization and conversion: determine optimal process
  - Techno-economic analyses

# FY18 Milestones

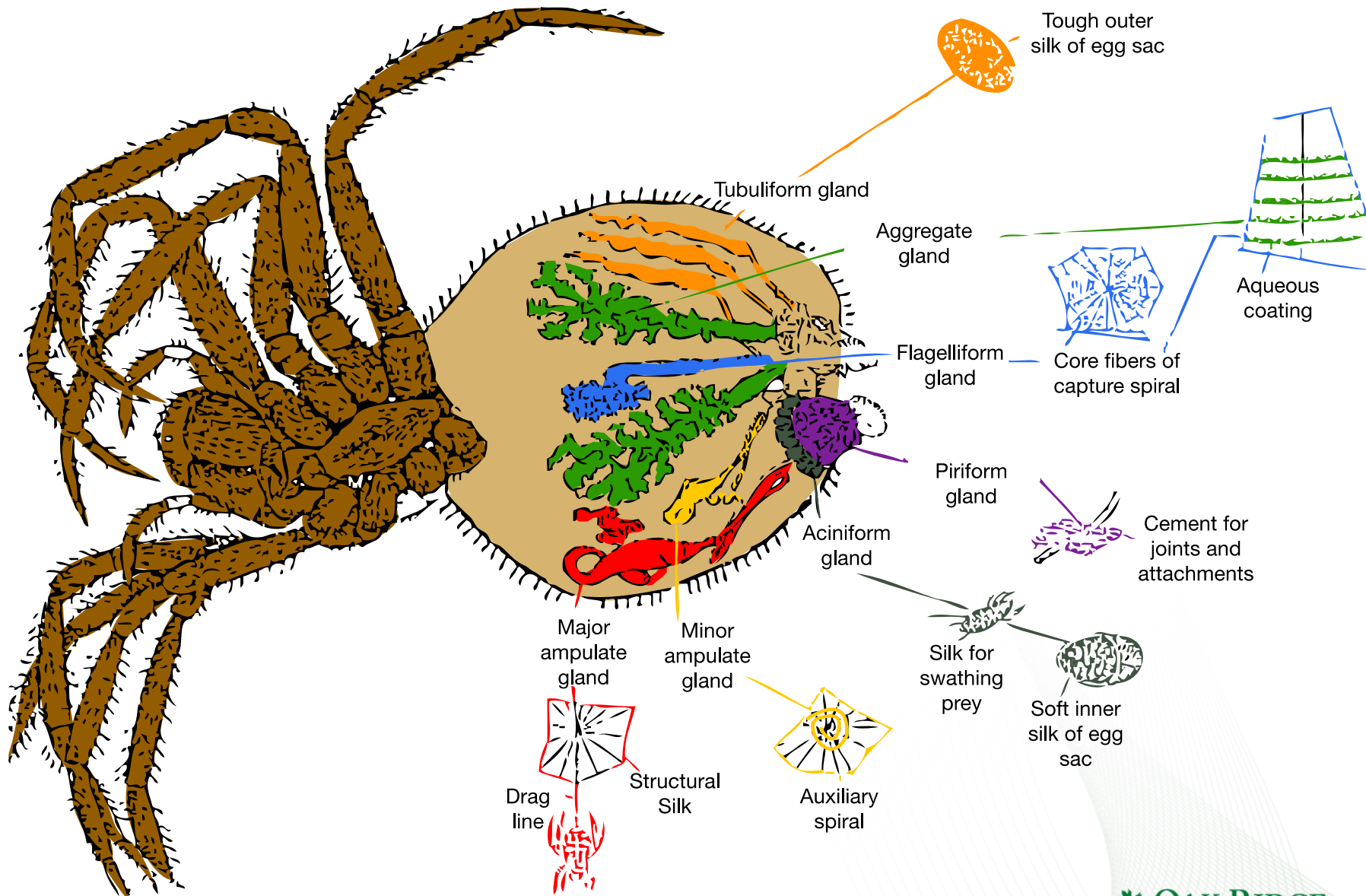
Date	Milestone	Status
March 29, 2018	<b>M1:</b> Production of 25ft of 24 filaments from two spider silk proteins.	<b>Completed</b> <b>March 29, 2018</b>
June 28, 2018	<b>M2:</b> Produce five samples of 1000ft of 24 filaments from the best two proteins in M1.	<b>Completed</b> <b>June 15, 2018</b>
September 30, 2018	<b>M3:</b> Increase production by 2-fold from 1g/l to 2g/l.	<b>Completed</b> <b>Aug, 2018</b>
December 31, 2018	<b>M4:</b> Develop conversion parameters and exceed best results of prior work (100ksi)	<b>Not achieved</b>

# Historical Development

- Origins of the project (2013-2014)
  - Hand collection of spider silk filament → impossible
  - Use of synthetic material Partnership with Pr. Lewis at USU
- Phase 1 (2015): silkworm silk (SWS) and spider silk (SS) synthetic materials
  - Modification of the production and spinning
  - Conversion possible – Results ~100ksi
- Phase 2 (2018): Scale up of the material production
  - Improvement of the process of material production:
    - Increase the production capability (one of the major impediments)
    - Diversify the variety of proteins
  - Figure out and optimize a process of conversion



# Approach Background



Proteins of main interest: from **Major** and **Minor Ampullate**

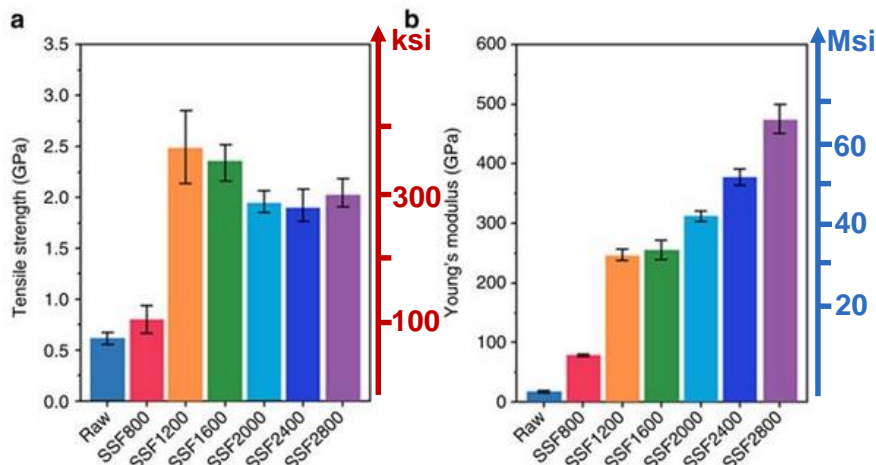
# Approach

- Feasibility already demonstrated by prior works:
  - using natural silks (Korea)



Pictures: 1) B. Mori flying, 2) B. Mori worm on a leaf, 3 and 4) silk cocoon extraction at “Suzhou no1 silk mill”.

Experimental work of conversion conducted by Cho and al. gave interesting persuasive results:



## Source (pictures):

- 1) <http://fyeahcutemoths.tumblr.com/post/21370639716/moth-of-the-week-the-silkworm-moth-bombyx-mori>
- 2) [http://www.wormspit.com/bombyxsilkworms\\_files/silkwormdimesm.jpg](http://www.wormspit.com/bombyxsilkworms_files/silkwormdimesm.jpg)
- 3) <http://Tripadvisor.com>
- 4) <http://antematters.com/wp-content/uploads/2013/03/Silk-Extraction-Vietnam.jpg>

# Approach (continued)

- using synthetic silks (USU/ORNL in 2016)

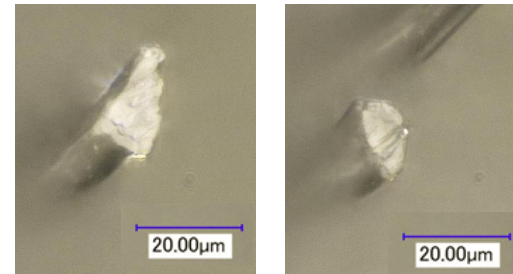
Sample ID	Max. temp. of treatment [°C]	Equivalent diameter [μm]	peak stress [ksi]	Modulus [Msi]	Strain at break [%]
Bundles type 1	1300	29.37 (1.58)	99.7 (41.0)	7.5 (0.9)	1.28 (0.42)
Bundles type 2	1300	29.34 (1.51)	77.3 (41.1)	7.3 (1.1)	1.06 (0.67)
Bundles type 3	1500	28.52 (1.35)	69.2 (43.6)	8.9 (1.4)	0.78 (0.50)
Bundles type 4	1700	26.08 (3.11)	101.9 (61.9)	7.4 (2.0)	1.32 (0.67)

- Experimental work conducted by Pr. R.Lewis and Dr.-Eng. F.Paulauskas
  - Precursor production, composition, and morphology not optimized:
    - Protein selection (choice between several proteins).
    - Spinning process parameters (temperature, speed, stretch ratio, etc.).
    - Fused filaments.
    - Reduced amount of material available (small tow, short lengths, few grams at a time).
  - Optimization of the process of conversion insufficient.



# Technical accomplishments (precursor)

- Production capacity of precursor improved:
  - New 24 filament spinning head.
  - New fermentation method at lower temperature (pCold).
    - Double the production of protein.
    - Yield of full length protein increased from ~45% to ~80%.
- Precursor characteristics still not ideal:
  - Fused filaments.
  - Random cross section.



Cross section of MaSp1 non degummed (precursor)

- Mechanical properties of 3 precursors:

Samples name	Diameter (μm)	Diameter SD (μm)	Tensile strength (ksi)	Tensile strength SD (ksi)	Modulus (Msi)	Modulus SD (Msi)	Strain at break (%)	Strain at break SD (%)
MaSp1 degummed (single filament)	10.0	1.1	62.2	7.8	1.8	1.1	18.8	5.0
MaSp1 degummed (single filament)	9.5	N/A	68.7	N/A	2.0	N/A	21.9	N/A
MIsp degummed (single filament)	9.8	1.0	71.7	10.6	1.9	0.2	17.0	4.2
MIsp stabilized (BUNDLE)	53.5	5.9	12.7	5.8	1.8	0.4	0.6	0.2

# Technical accomplishments (conversion)

- Carbonization possible with one precursor only (MaSp1 non-degummed).
- Overall morphology of the filaments preserved:



- Mechanical properties (bundles) did not meet expectation:

Samples name	Diameter (μm)	Diameter SD (μm)	Tensile strength (ksi)	Tensile strength SD (ksi)	Modulus (Msi)	Modulus SD (Msi)	Strain at break (%)	Strain at break SD (%)
MaSp1_ND_B1	43.4	3.9	2.2	1.3	N/A	N/A	N/A	N/A
MaSp1_ND_B2	53.5	5.8	8.8	3.3	2.5	N/A	0.4	0.1
MaSp1_ND_B3	56.6	N/A	2.4	N/A	N/A	N/A	0.3	N/A
MaSp1_ND_B4	53.5	5.9	12.7	5.8	1.8	0.4	0.6	0.2
MaSp1_ND_B5	59.67	N/A	8.6	N/A	0.1	N/A	0.93	N/A
MaSp1_ND_B6	49.01	4.82	6.1	1.9	1.2	0.5	0.56	0.33
MaSp1_ND_B7	57.13	8.89	9.2	2.6	2.4	0.1	0.41	0.007

# Response to Previous Year Reviewer's Comments

- This project did not participate to the previous annual merit review.
- Following answers will be provided to the comments the reviewers formulated the year before (AMR 2017).
- Question 1:

*Approach to performing the work—the degree to which technical barriers are addressed, the project is well-designed, and well planned.*

– Summary of the comments:

- “interesting subject, good approach to develop a fundamental understanding”.
- “Heating duration and material loss are similar to that in conventional CF: these barriers still need to be overcome.”
- “Overall approach was good, but missing the establishment of a Go/No-Go target for suitable replacement for CF ”.
- “developed properties are still far lower than the performance of commercial CF”.

Answer:

- With the new work, the time to stabilize the biopolymer remains greater than the time for conventional CF, while the char yield remains lower (between 20% to 40% compare to ~50% for PAN). This is expected due to the nature of the material. Compared to other type of precursors, its carbon content is on the low side.
- Techno-economic estimates need to be reevaluated once the mechanical performance reaches acceptable level.
- Other work on the conversion of natural material showed that silk has a real potential.

# Response to Previous Year Reviewer's Comments

- Question 2:

*Technical Accomplishments and Progress toward overall project goals—the degree to which progress has been made and plan is on schedule.*

- Summary of the comments:

- “The project met the milestones in timely manner”.
- “ The project demonstrated the feasibility of using E. coli-derived spider silk proteins as precursors for CF, but underlined that meeting the cost targets is still uncertain”
- “The technical accomplishment seems satisfactory, but the explanation of the cost impact could have been further improved with examples”
- “The commercial application is not there”.

Answer:

- Feasibility for the conversion of the spider silk and similar materials into CF was demonstrated.
- Cost impacts are too premature for a firm estimate.

# Response to Previous Year Reviewer's Comments

- Question 3:

*Collaboration and Coordination Across Project Team.*

- “The existing collaboration appeared to be good, but it would have been more appropriate to have other industry partners involve in addressing the overall feasibility”.

Answer:

- *This work was mostly oriented to demonstrate the feasibility. At the time this project was designed, no similar work had yet been performed. At that low technology readiness level (TRL), industry partners are usually hard to convince or achieve a partnership with.*



# Response to Previous Year Reviewer's Comments

- Question 4:

*Proposed Future Research—the degree to which the project has effectively planned its future work in a logical manner by incorporating appropriate decision points, considering barriers to the realization of the proposed technology and, when sensible, mitigating risk by providing alternate development pathways.*

- “The project is complete”.
- “The project has ended”.

Answer:

- *From a scientific point of view, there is a significant amount of research that needs to be accomplished on this topic in order to achieve a better understanding of the morphological transformation of the biopolymer into CF structure. This would help to make the proper selection of protein, or even redirect the research into other type of biopolymers.*

# Response to Previous Year Reviewer's Comments

- Question 5:

*Relevance—Does this project support the overall DOE objectives?*

- “The low-cost CF is a potential means of light weighting transport vehicles”.
- “It would be useful for the project to identify whether any of the raw materials are derivate from petroleum”.
- “A large amount of energy is required at high temperature. What type of furnaces are used”.
- “Whereas it does not fully support the relevance of meeting DoE objectives, the project will need additional research funding”.

Answer:

- The biopolymer of interest is free of petroleum based substances.
- Whatever the precursor is, the production of CF will require processing above 1000°C. The type of furnaces that are used is electrical radiant, similar to those currently in use in this industry.
- The need of future funds for this research can be justified due to:
  - Early research status.
  - Potential to reduce dependency on petroleum-based material.
  - Potential performance and applications.

# Collaboration and coordination

ORNL performed this project in collaboration with:



Utah State University (USU) — Production of the proteins and extrusion of the filaments



4X Technologies — support to ORNL in the conversion and the characterization of the material

# Remaining Challenges and Barriers

- Production of circular and non-fused filaments.
- Build a database for conversion prediction in function of the protein selection.
- Figure out appropriate formulation for the precursor.
- Improve the process of conversion.
- Achieve acceptable mechanical properties (e.g. strength of 250ksi, and modulus of 25Msi).

# Proposed Future Research

- Comparative studies of the evolutionary morphology during the thermal conversion between natural precursor (silkworm) and synthetic materials.
- More fundamental research and characterization is needed to establish correlation between the selection of the protein and the structure of the material during the process of conversion.
- Further increase the capability of precursor/material production.

Any proposed future work is subject to change based on funding level.



# Summary

- The production of protein has significantly increased (~x4).
- Several combination of proteins were produced and spun without process optimization.
- The generation of the filaments remained not ideal (fused filaments with random cross-sections).
- The conversion was challenging and provided material with poor mechanical properties (~10 ksi).

# Thanks for your attention



With authorization from Prof. R. Lewis

## Questions ?

# Backup

# Technical back-up

Reference mechanical values of different PAN precursors  
(as delivered by manufacturers).

Type	Size	Diameter, um	Tensile Strength, ksi	Modulus, Msi	Strain, %
VHMW 168	.5k	4.84	101.9	1.7	8.0
VHMW 169	.5k	5.38	124.7	1.9	8.7
BlueStar	24k	13.5	63.8	1.4	15.5
Textile <sup>[1]</sup>	26k	11.7	66.7	1.3	14.5
Commodity <sup>[2]</sup>	50k	11.7	73.5	1.5	11.2
Aerospace	3k	12.9	76.6	1.7	10.5

Carbon content for different CF precursors.

Precursor material	Carbon contain (%)
Pitch	~ 85
PAN	68
Cellulosic	~ 44
Synthetic silk	40-44