

BE.342/442 Tuesday, October 18, 2005
Topic: Silk

Administrative:

Take-home midterm is out! You have almost 1 month to turn it in. On question 10, you are asked to design a creative, novel material. In the past, students have designed ingenious materials. Graduate students are required to write a 5-page experimental design. Drawings are helpful! Undergrads don't have to (but are encouraged to) produce an original design. They may, alternately, write a review paper.

We have covered the material in the textbook. From now on, the course will rely on articles that will be posted on the course website.

Spiders and silkworms can produce long continuous fibers. Silk had enormous impact on civilization. In China, people started spinning silk about 3,000 years ago, which traders distributed via the Silk Road toward Afghanistan, Iran, Turkey and on through Europe to Britain. China still produces enormous quantities of silk, ranging from blankets to works of art.

Silkworm silk and spider silk both contains large amounts of Gly and Ala.

Silkworm silk contains mostly alternating Ala and Gly and forms over 80% beta-sheets. The remaining 20% is mostly loops. One of the fibroins contains 5263 residues (391 kDa) – multiplying by 3.4 angstroms per residue in the beta-sheet structure, we get a length of approximately 15,000 angstroms, or 1.5 microns, per fibroin. These short silk fibroins overlap to form well-ordered silk fibers as long as 2 kilometers: that's 1.3 billion times longer than the individual fibroin! When silk worms mature, the entire body becomes transparent: essentially, it is full of a gel. Once exposed to air, the silk becomes insoluble, and can never be returned to its original state of a gel.

The genetic sequence of silkworm silk is almost entirely composed of alternating codons for Gly and Ala, with occasional substitutions of Tyr or Ser for Ala. Recall that collagen contains the repetition $(\text{Gly X Y})_n$ where X is typically proline, and Y is typically hydroxyproline. Glycine is the most conformationally free amino acid, and people have observed the presence of glycine in intergalactic dust! Glycine is important because it adds flexibility to proteins, allowing, in this case, the silk gel to be squeezed out of a small opening in the animal.

The peptide sequence of silk contains hydrophilic ends and small patches of hydrophilic regions, but is mostly hydrophobic. This causes the fiber to fold onto itself, reducing its length from 1.5 microns to approximately 20 nanometers. Silk proteins can also form a micelle structure, with the hydrophilic ends lining the outside and the inside containing loops of the hydrophilic residues. Experiments of globules of these micelles reveals their individual mechanical properties, and the rheology of the gel that they form.

The globular structure of silk gel can be described as fractal due to its self-similarity on multiple lengthscales, from a few nanometers up to several microns.

Spider silk contains both alpha-helices and beta-sheets, like a block copolymer. Beta-sheets form crystalline packing for strength, and alpha-helices provide flexible extension. Different types of spider silk – dragline, capture, and others – contain different amounts of alpha-helices, 3_{10} -helices, and beta-sheets.

A single strand of silk can bear little force, but combined, bundles of spider's silk is stronger than steel fibers, and incredibly elastic. Have you ever noticed drops of dew stuck to a spider web? Spider's silk is slightly more hydrophilic than silkworm silk.

The oldest spiders found were approximately 470 million years old – way older than dinosaurs – and they will probably outlive humans on Earth! Most spiders have three pairs of spinnerets, each with hundreds of silk-releasing spigots. An individual spider can produce a variety of types of silk. Dragline silk has immense strength, but is less elastic than capture silk. It differs in composition and, of course, in the use the spider makes of it. Capture silk is used to immobilize prey. Sometimes many spiders band together to capture a much larger creature, for which one spider alone could not produce enough silk – like in *Gulliver's Travels*!

Genetic engineering has allowed us to produce spider's silk in the milk of goats. Spider's silk can now be synthesized, but only in small (milligram) quantities. Kevlar, a bullet-proof polymer fabric, was inspired by spider's silk. Another material inspired by spider's silk is PEO, a polymer synthesized from petrochemicals and known for its biocompatibility and resulting utility in medical applications. This polyether has the chemistry $(\text{CH}_2\text{-O-CH}_2)_n$ where n can be as small as 200 or as large as 20,000. Mixed with PEO, silk separates into a separate phase.

Resources about synthetic spider silk materials through bioengineering:

David Kaplan & colleagues at Tuft's University.

BioSteel® Man-made spider dragline silk by startup company Nexia Biotechnologies, Inc., in Quebec, Canada.

NMR and other methods can predict possible structures of spider's silk. Low-resolution NMR allows us to compare silk conformations to Ramachandran plots. Due to the flexibility of the chain produced by the high glycine content of silk, conformations are seen in all regions of the Ramachandran plot, though over more restricted areas than for pure polyglycine. These models propose crystalline beta-sheet blocks rich in Ala, and loops rich in Gly and Pro. The loops form an amorphous matrix in which the crystalline beta-sheets are suspended. Some amyloid diseases cause the human brain to adopt a similar structure.

In "Elasticity and Modular Nature of Spider Silks," Hayashi and Lewis compared the compositions of dragline, capture, and web frame/radii silk. The authors predicted compositions based on the silk behavior, and then measured the corresponding compositions, with comparable

results. Highly oriented alanine methyl residues in dragline silk fibers are associated with a low (37%) alanine content, whereas less oriented residues are associated with high (63%) alanine content. Spider's silk contains many repeats of the patterns Gly-Gly-X and Gly-Pro-Gly-Gly-X. The various motifs contain high percentages of glycine (in the 80's and 90's on percents). Patterns of individual motifs or ensemble repeats make silk a relatively simple, repeating structure. Some structures and associated motifs in spider's silk are:

Structure	Motif
beta-spiral	GPGXX
"linker"	GP(S,Y,G)
crystalline beta-sheet	Ala-rich sequence
3_{10} -helix	GGX
"spacer"	unknown