BE.342/442 Thursday, October 27, 2005
Topic: Bioadhesives

How does the body glue things together? You couldn't build a building without cement. Even in ancient times, people used dirt to glue together structures. In biology, adhesives are very different from adhesives on the macroscale.

Mussels

Reading:

Read about the common mussel or blue mussel at
http://weichtiere.at/Mollusks/Muscheln/miesmuschel.html

Check out Prof. Herbert Waite's work at UC Santa Barbara
http://www.lifesci.ucsb.edu/mcdb/faculty/waite/index.html

Papov, et al. "Hydroxyarginine-containing Polyphenolic Proteins in Adhesive Plaques of the Marine Mussel *Mytilus edulis*." *J. Biol. Chem.* **270** (34) 25 August 1995, 20183-20192.

The common mussel *Mytilus edulis* glues itself to surfaces using *byssal threads*. A stem attached to the animal's retractor muscles attaches the animal to the thread. The thread has two subunits:

Closer to the animal, the *proximal thread* has an untimate tensile stress on 30 MN/m^2, an ultimate strain of 2, and a modulus (stiffness) of 20 MN/m^2.

Between the proximal thread and the attachment plaque, the *distal thread* has an untimate tensile stress on 85 MN/m^2, an ultimate strain of 0.6, and a modulus (stiffness) of 150 MN/m^2.

Finally, an attachment plaque connects the byssal thread to the surface.

The distal thread is much stronger, stiffer, and less extensible. It is proposed that the protein content ranged from a D-rich distal end to a P-rich proximal end. The thread is composed of a biological block copolymer containing alanine-rich flanking blocks at either end, and histidine-rich ends, which, along with cysteine, is one of the amino acids that is key for metal coordination. This may explain why this His group is useful for binding to rocks. For example, a "histidine tag" of two to six His residues can surround a metal ion, such as nickel or zinc, to coordinate around it. This chemistry was observed in animals and is now being used in protein purification!

Recall the collagen motif (GXY)n: this motif is found in the byssal thread collagen structure as well! In the protein se quence of the distal block PreCol-D collagen precursor, we observe:

A terminal histidine block for metal coupling
A stiff silk-fibroin-like region
A collagen region witht eh $(GXY)_n$ motif, but with more X, Y diversity than in human collagen
An acidic region

A stiff silk-fibroin-like region
A terminal histidine block for metal coupling

By comparison, the PreCol-P block contains:
A terminal histidine block for metal coupling
An elastic glysine-rich region
A collagen region witht eh $(GXY)_n$ motif, but with more X, Y diversity than in human collagen
An acidic region
An elastic glysine-rich region
A terminal histidine block for metal coupling

The overall structure is rich in Gly, Dopa (Tyr*), Asp/Aln, and Arg-OH. His can conjugate directly to a metal ion such as zinc to form His-Zn^{2+} coordination. Alternately, the DOPA can cross-link with His (Type A) and mediate conjugation around an ion, such as DOPA-Fe^{3+}. Arg-OH can also form a hydrogen bond to and adjacent O-DOPA residue, increasing the strength of the structure.

Summary of glysine-rich structural proteins

Collagens
Silkworm silk
Spider silk
Byssal threads

Barnacles

Check out Kei Kaminos' work at the Marine Biotechnology Institue, Japan. He is one of few professors in the world who dedicates his work to bioadhesives. The slides from this lecture come from his lecture, "Barnacle underwater adhesive: Significance to supramolecular chemistry and peptide-based material design."

Marine sessile invertebrates are specialists in underwater attachments.

Consider how the following organisms achieve bioadhesion:
Ascidians
Barnacles
Mussels
Sponges
Polychaetes
Algae

In the early 1970's, scientists performed histological studies of barnacle cement glands. Later in the 1970's, they analyzed the chemical composition of the cement, and discovered it to be proteinaceous. The challenge of the 1980's was to discover what can render the cement soluble, in order to purify the proteins to analyze their sequences. Today’s challenge is to identify the sub-function of each cement protein.

Two types of cement have been identified: primary cement, and secondary cement. Multi-protein complexes were discovered, including:

cp-100k: *hydrophobic* major cement protein
cp-25k: *hydrophobic* major cement protein with content to cp-100k, and primary structure composed to repeating sequences of cp-68k
cp-68k: S, T, G, A –rich protein
cp-20k: rich in charged amino acids and Cys
cp-16k: lysozyme analogue
cp-160k: unknown

By purifying certain proteins, NMR and crystallography have been used to determine the structure of cp-20k.

It is believed that barnacles achieve adhesion by a carefully timed mixing of multiple proteins with several sub-functions. The specific tactics employed by bivalves, mussels, crustaceans, and barnacles are quite distinct.

Other forms of adhesion include:
Capillary adhesion: Frog. tubercles provide suction forces at a walking gate.
Suction: Salamander. Slow locomotion by suction cups, one foot at a time, on smooth surfaces only.
“Sticky leaves:” Geckos. fibers arranged into lamellar stacks in a fractal pattern. Fibers branch like trees into setae and spatulae for enhancement of van der Waals interactions. Type in “gecko’s toe” into Google Image Search to learn more!