Adhesives at the Beach

Jon Wilker
Purdue University



- Reduce turbulence
- Deter predators
- Reproductive efficiency


• sea stars

• cucumbers

• soft coral

• giant clams

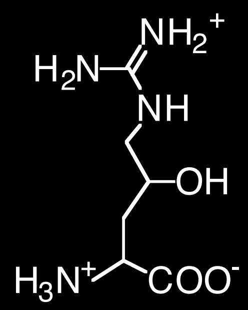
• sea squirts

• kelp

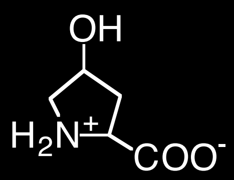
How Do They Stick?

Mussel Adhesive Proteins

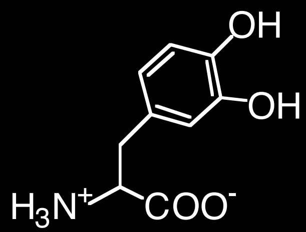
Mefp-1	(Ala-Lys-Pro-Ser-Tyr-Hyp-Hyp-Thr-DOPA-Lys)$_{75}$
Mefp-2	(Cys-Val-Gly-Gly-DOPA-Ser-Gly-Pro-Thr-Cys-Gln-Glu-Asn-Ala-Cys-Lys-Pro-Asn-Pro-Cys)$_{11}$
Mefp-3	Rich in Arg, Asn, DOPA, Gly, Hyr, Trp
Mefp-4	Rich in Arg, DOPA, Gly, His
Mefp-5	Rich in Gly, DOPA, Lys, Ser
Mefp-6	Rich in Asx, Cys, DOPA, Gly, Lys, Tyr



Hyr: 4-Hydroxyarginine



Hyp: Hydroxyproline



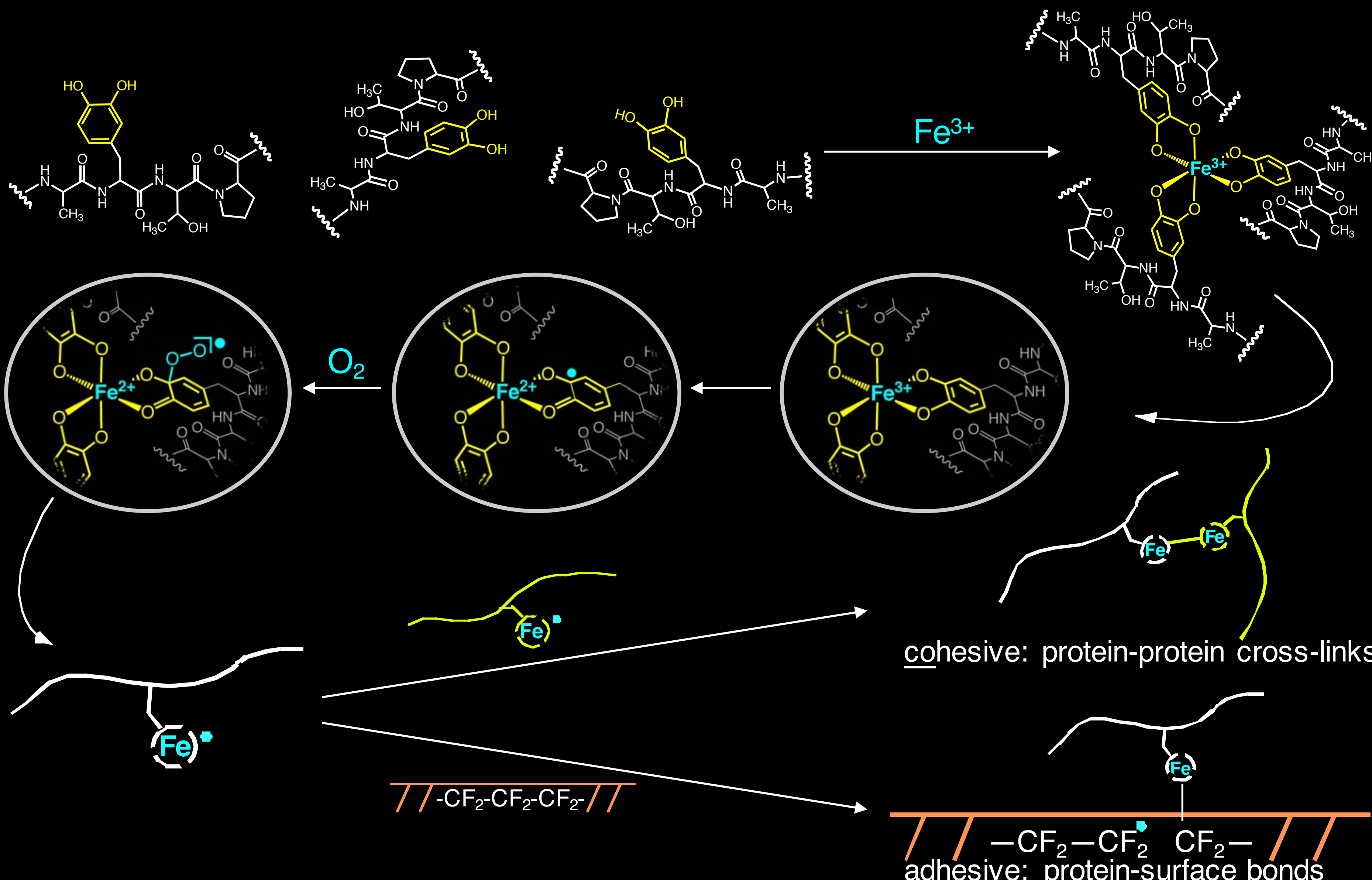
DOPA

Barnacles: No DOPA, but Cys thiols (0.6 - 7.8%)

-Work of Herb Waite, also David Kaplan, Dan Rittschof, Kei Kamino

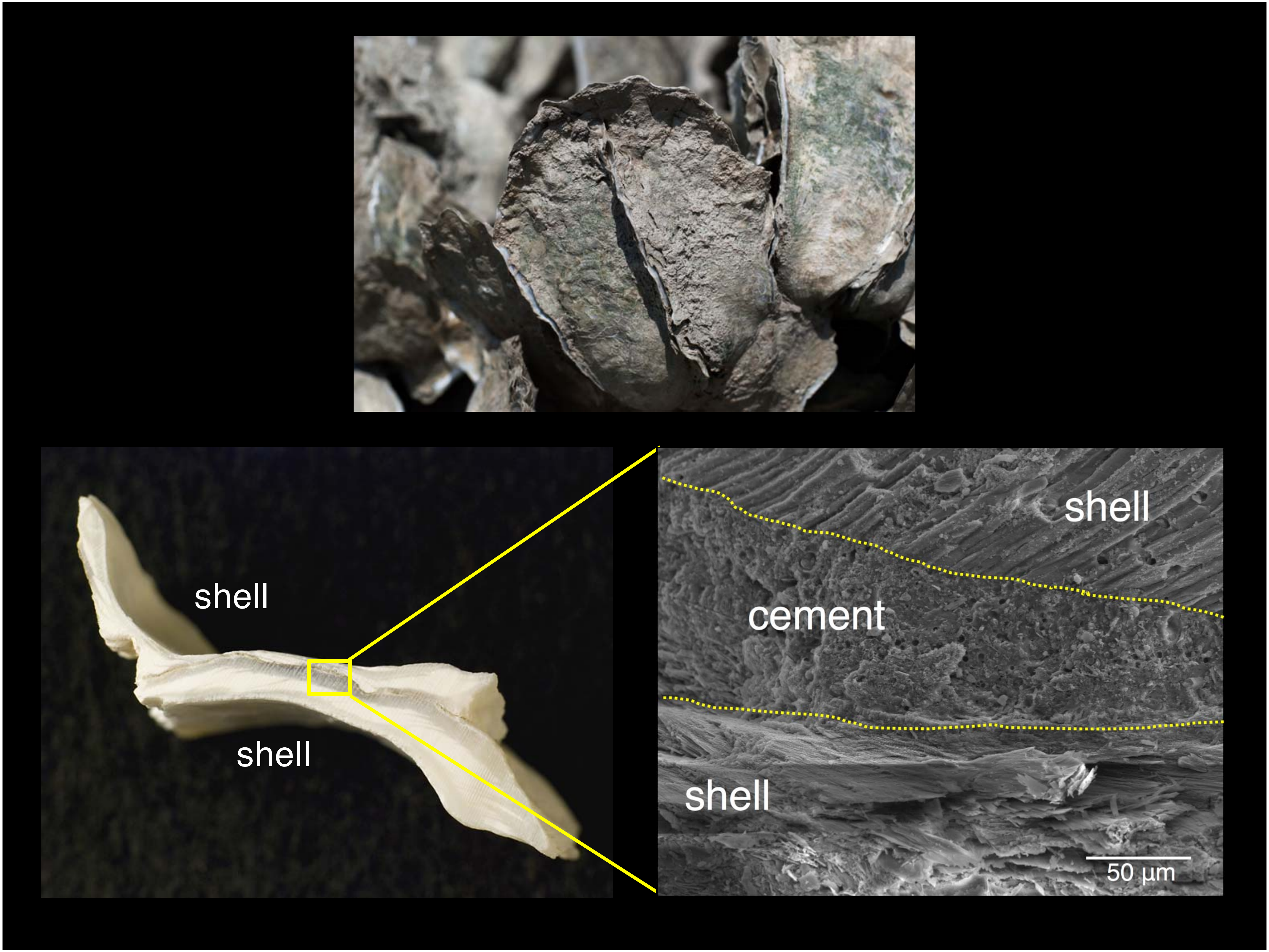
Proposed Mechanism of Mussel Adhesion

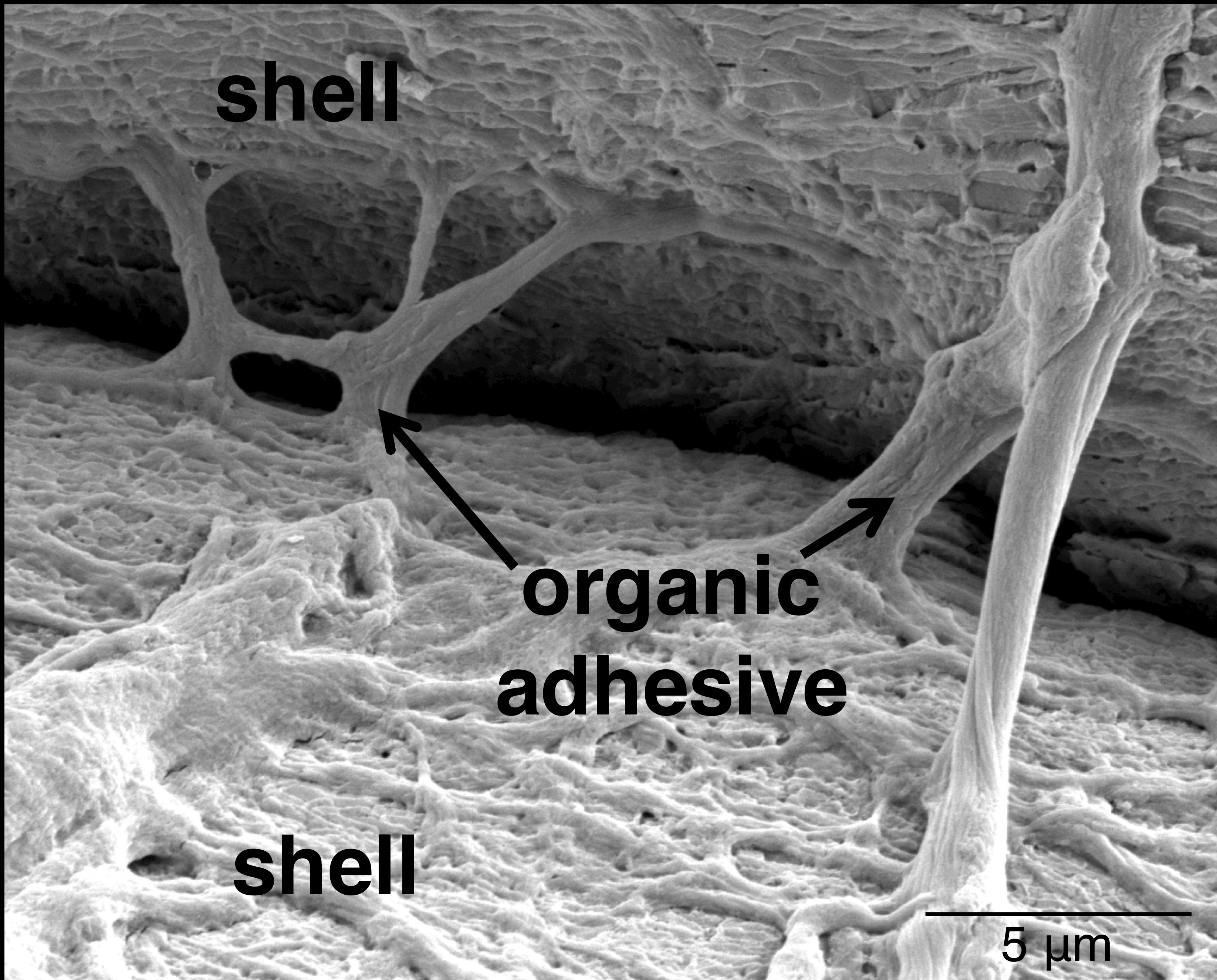
- Data from animal, protein, peptide, surface chemistry studies



Oyster Reefs and Adhesion

- Oyster reefs provide a major influence on coastal ecosystems
- Reefs filter water, prevent erosion, protect from storms, give habitat
- 98% of US reefs are gone
- What is the nature of oyster cement?

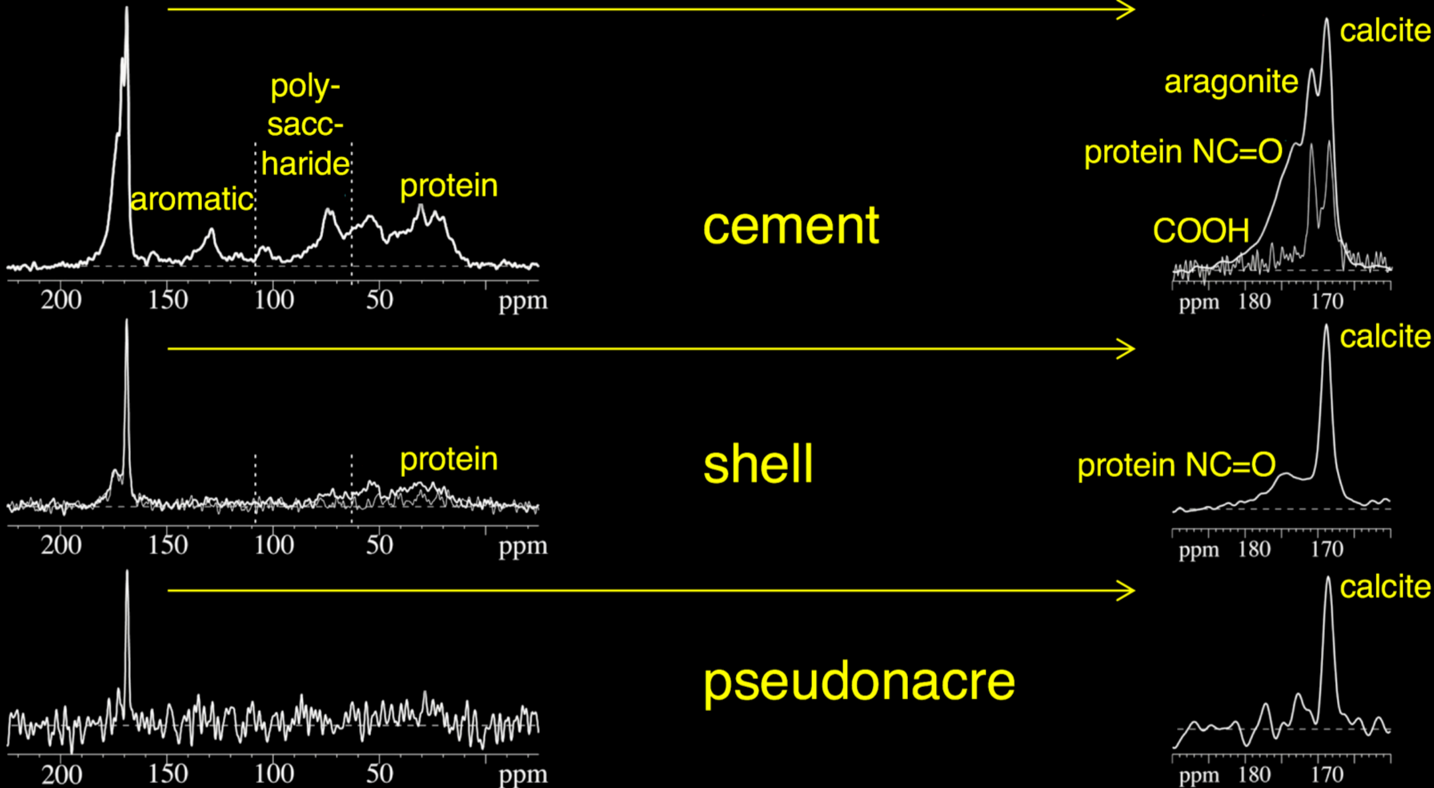

shell
shell
shell
cement
shell
50 µm


shell
organic
adhesive
shell
5 µm

Adult Cement: ^{13}C Solid State NMR Spectrometry

• With Keith Fritzching and Klaus Schmidt-Rohr at Brandeis U.

• several samples:
  - isolated cement powder
  - shell powder
  - acid etched cement film
• several NMR techniques



• Can observe proteins in cement.

Cement Protein Insights from SS NMR

	oyster cement	spider silk
alanine	33 ± 10%	3-43%
glycine	12 ± 3%	3-39%
serine	13 ± 4%	4-36%
phenylalanine/ tyrosine	12 ± 4%	1-7%

- Cement proteins have unusual amino acid composition.
- Looks somewhat similar to spider silk, but not the same.
- Have seen fibers in larval adhesive.
- Silk-like proteins seen in barnacle cement.[1]

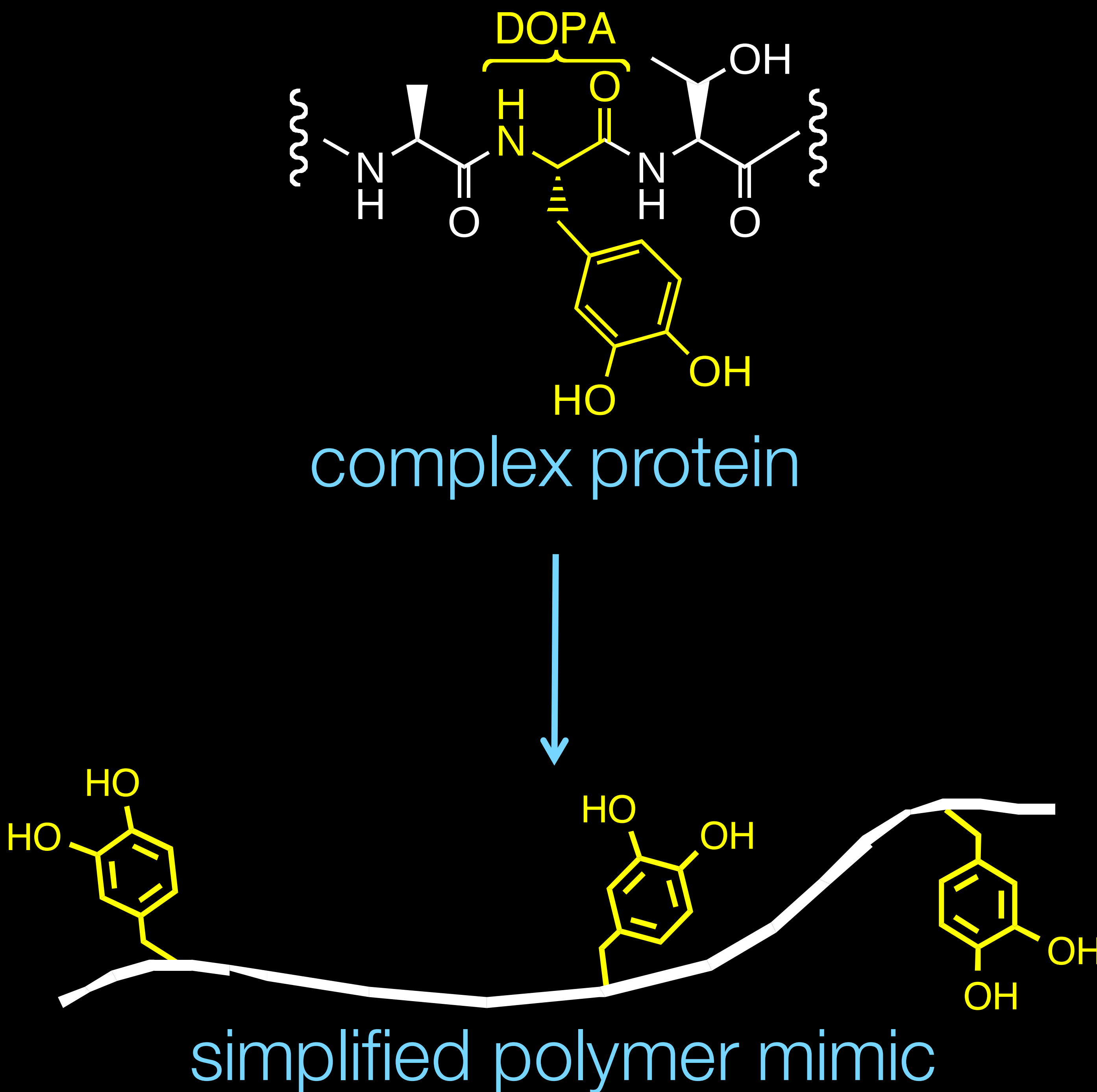
- With Keith Fritzching and Klaus Schmidt-Rohr at Brandeis U.

[1] So, Fears, Leary, Scancella, Wang, Liu, Orihuela, Rittschof, Spillman, Wahl, *Sci. Reports*, 2016, 6, 35219

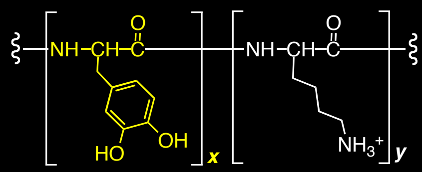
Why Do We Care About This Technology?

Why Do We Care About This Technology?

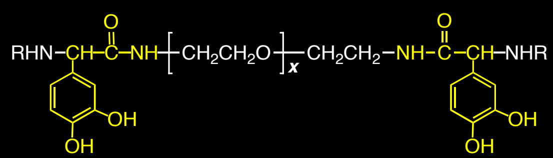
Why Do We Care About This Technology?


DOPA
H
N
O
N
H
O
N
H
O
OH
HO
OH
complex protein
HO
HO
HO
OH
OH
OH
simplified polymer mimic

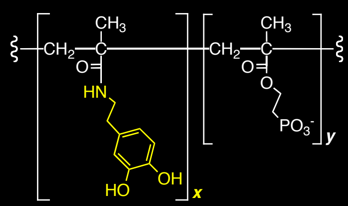
Polymer Mimics of Mussel Adhesive Proteins



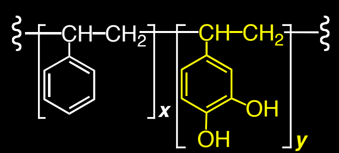
- Deming Lab
- *Macromol.*, 1998, *31*, p. 4739



- Messersmith Lab
- *Biomacromol.*, 2002, *3*, p. 397



- Stewart Lab
- *ACS Appl. Mat. & Interfaces* 2011, *3*, p. 941



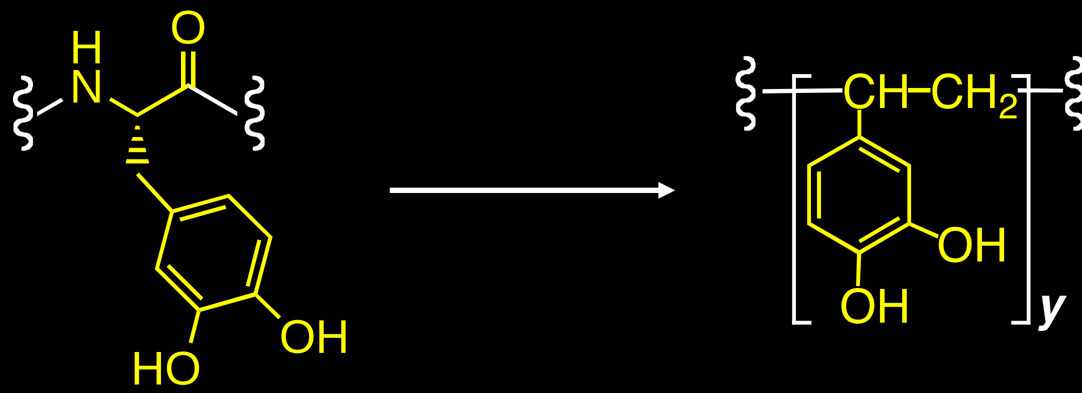
- Our Lab
- *Macromol.*, 2007, *40*, p. 3960

Jiang- Polyacrylates
Lee- Polycaprolactones
H. Lee- Polydopamine
Zurcher- Polypeptides
Patton- Thiol-enes
Washburn- Polyacrylates
Sedo- Polydopamine
Liu- Polypeptides
Dhinojwala/Joy- Sebacic acid
Kamperman- Polyacrylates
Kuroda- Polyacrylates
Chung- Polyacrylates
B. Lee- PEG
X. Wan- Polyvinylacetates

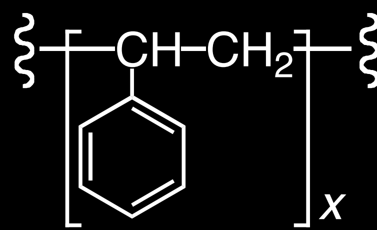
- Coatings
- Adhesives
- Hydrogels
- Surface couplings
- Drug delivery
- Nanoparticle coatings
- Tissue engineering
- Sensors
- Biosynthesis (e.g., melanin)
- Non-fouling surfaces
- Membranes
- Surface catalysis

Polystyrenes

DOPA simplified:

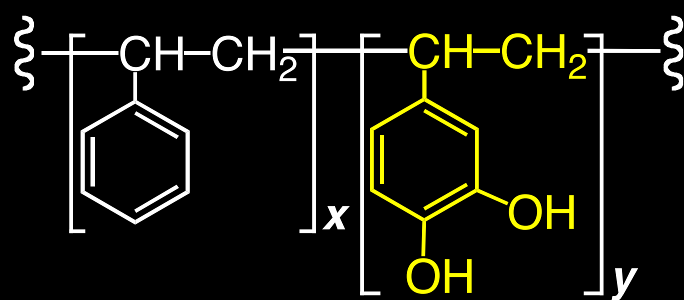


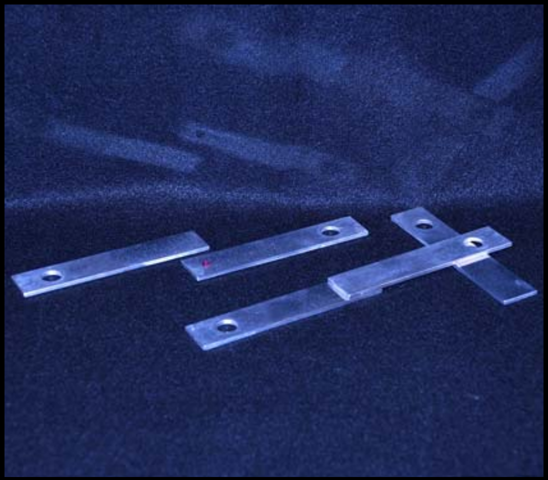
polystyrene:

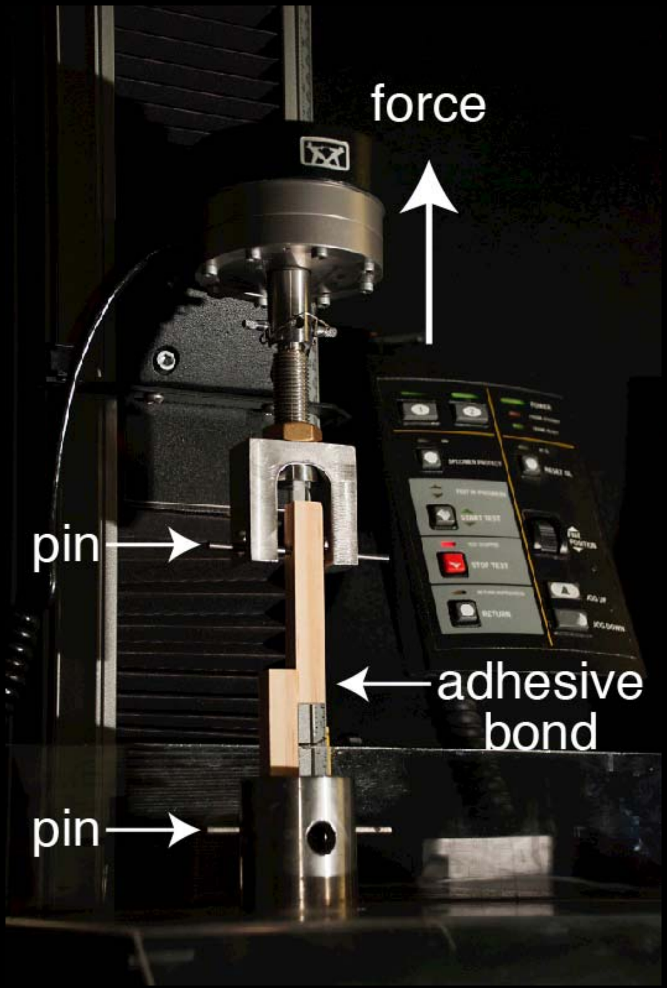


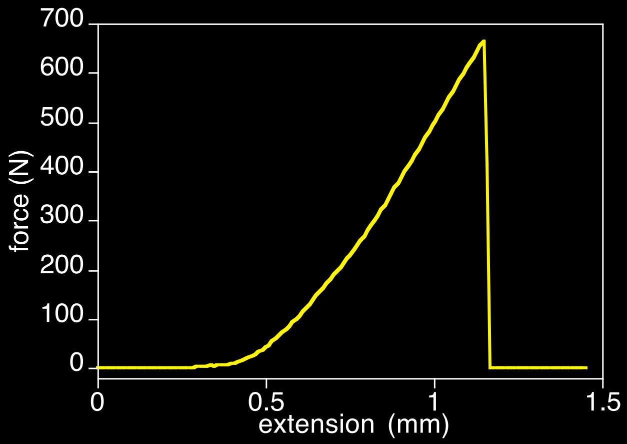
-similar structure
-easy synthesis
-no adhesion

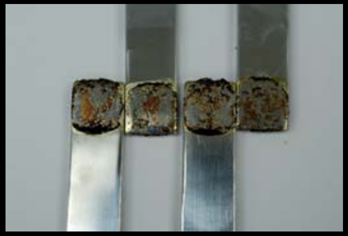
target random copolymers:

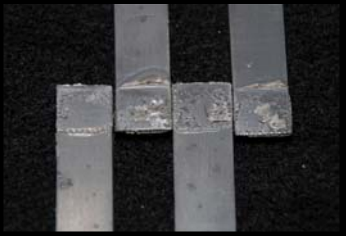


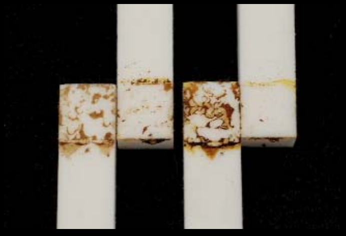






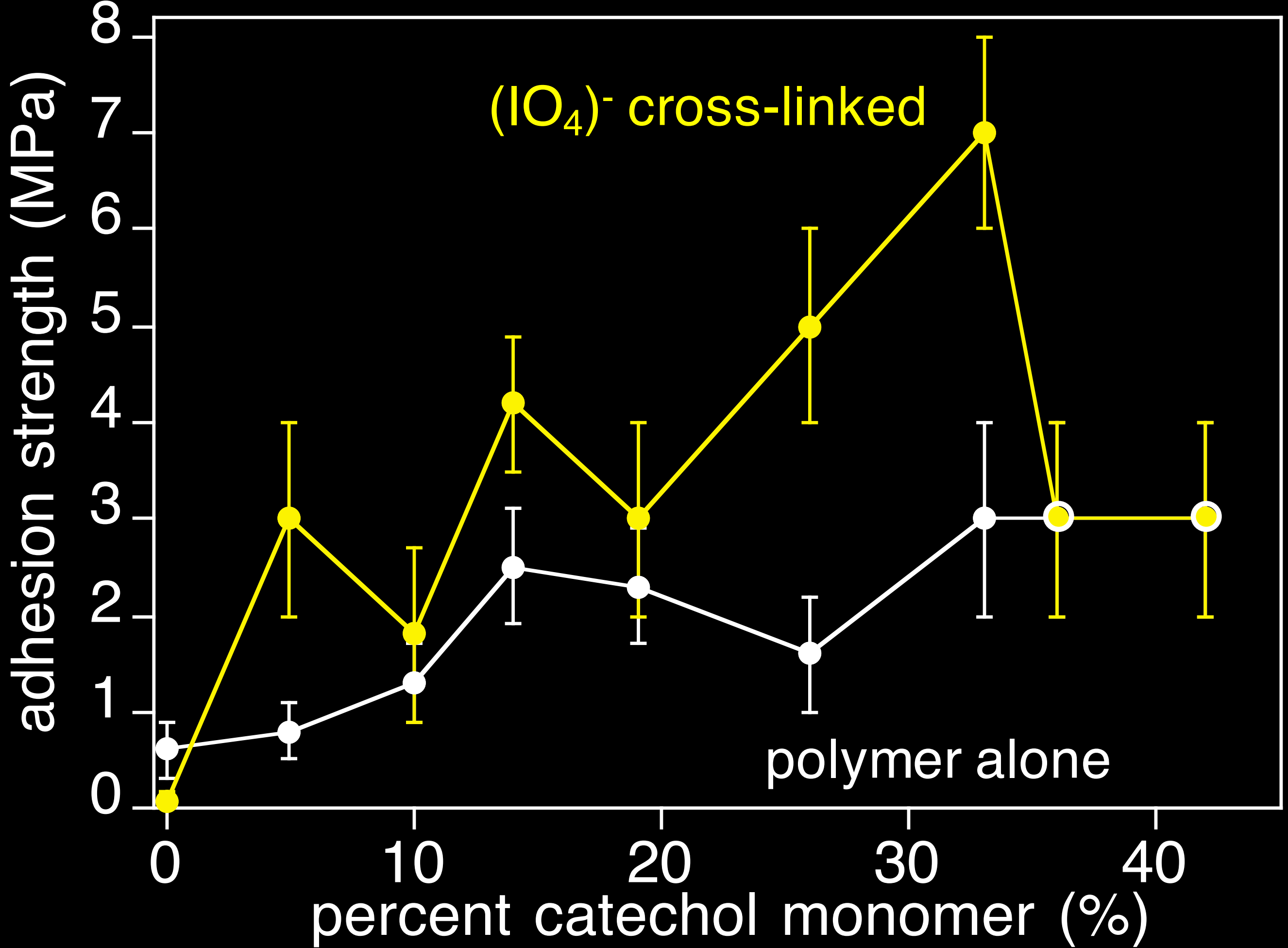


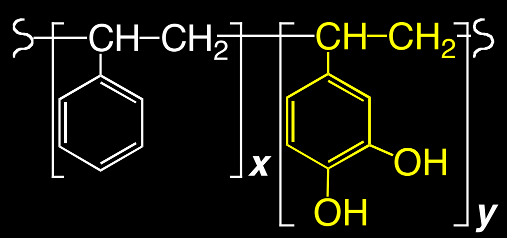




• Metals, plastics, and woods

Polymer Composition and Adhesion



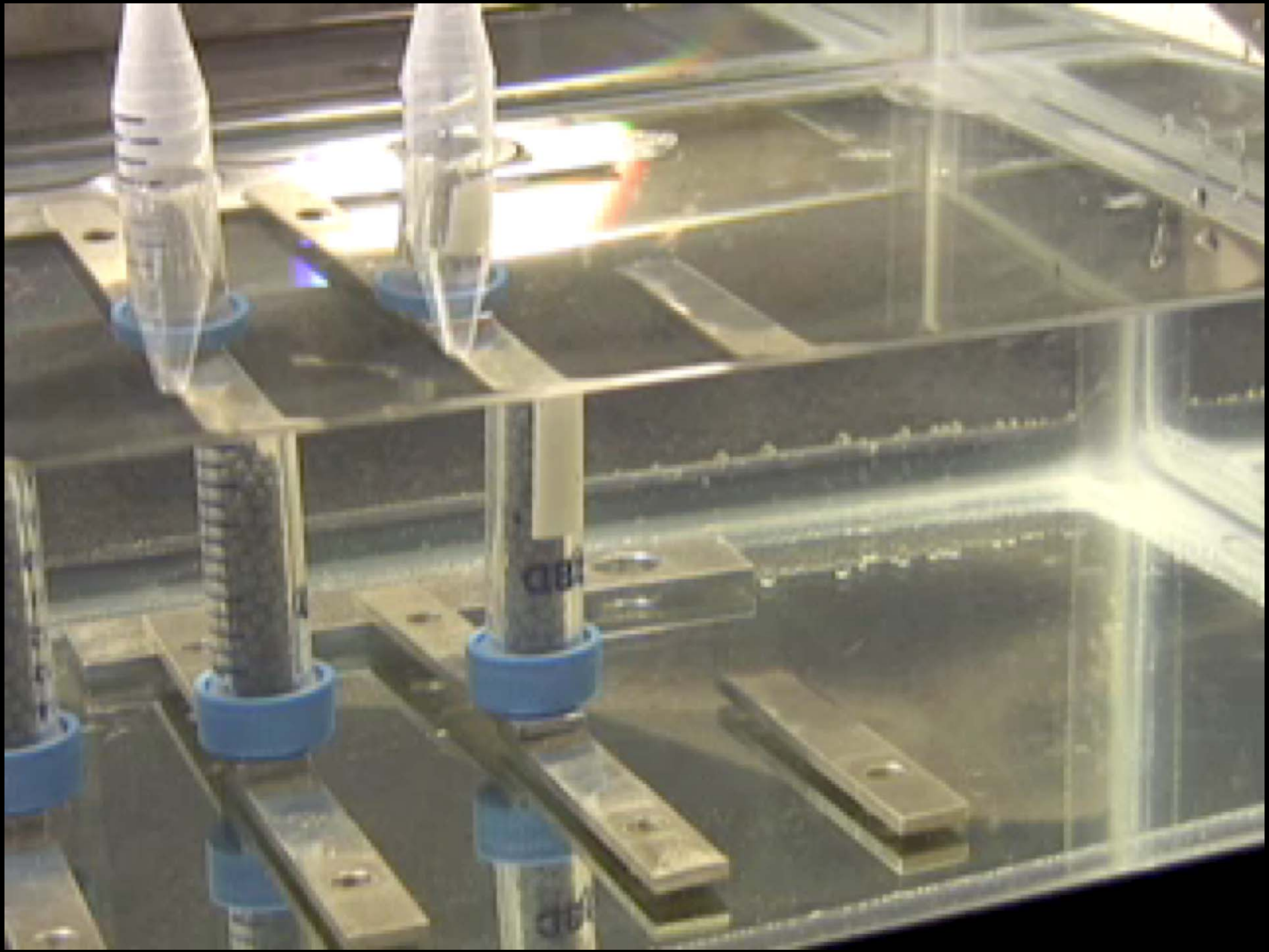


$M_n \approx$ 32,000 - 57,000
$M_w \approx$ 38,000 - 84,000

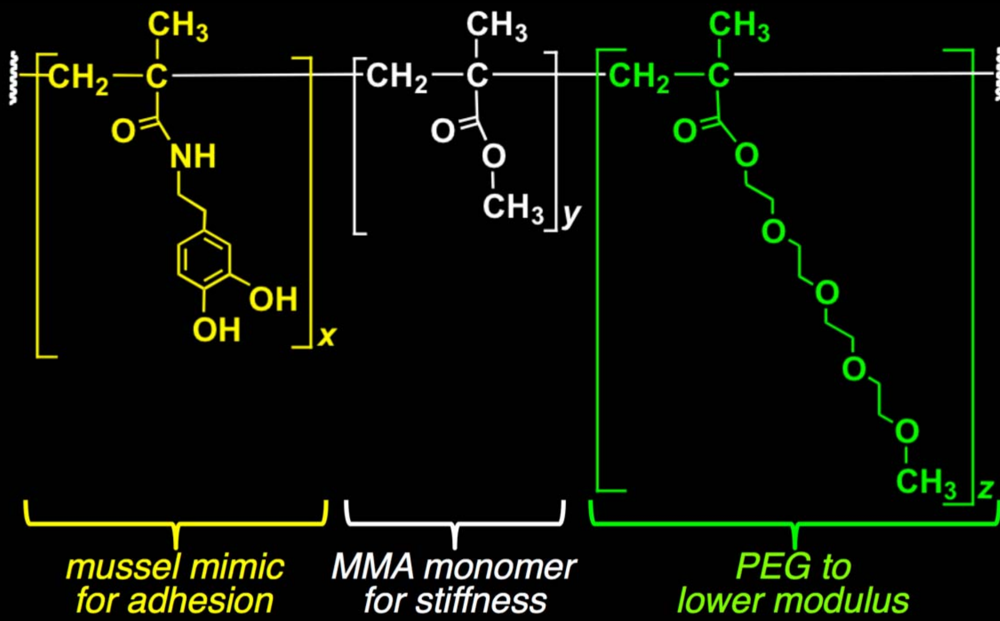
Adhesive Strengths on Etched Aluminum

Gorilla Glue, urethane	3.3 (±0.8) MPa
Elmer's white PVA glue:	3.8 (± 0.6) MPa
Super Glue, cyanoacrylate	5.0 (± 0.7) MPa
Epoxy glue, Loctite Quick Set	18 (± 2) MPa
Our biomimetic copolymers:	11.0 (± 0.5) MPa

Underwater Adhesion Testing



Flexibility of Adhesive Polymers

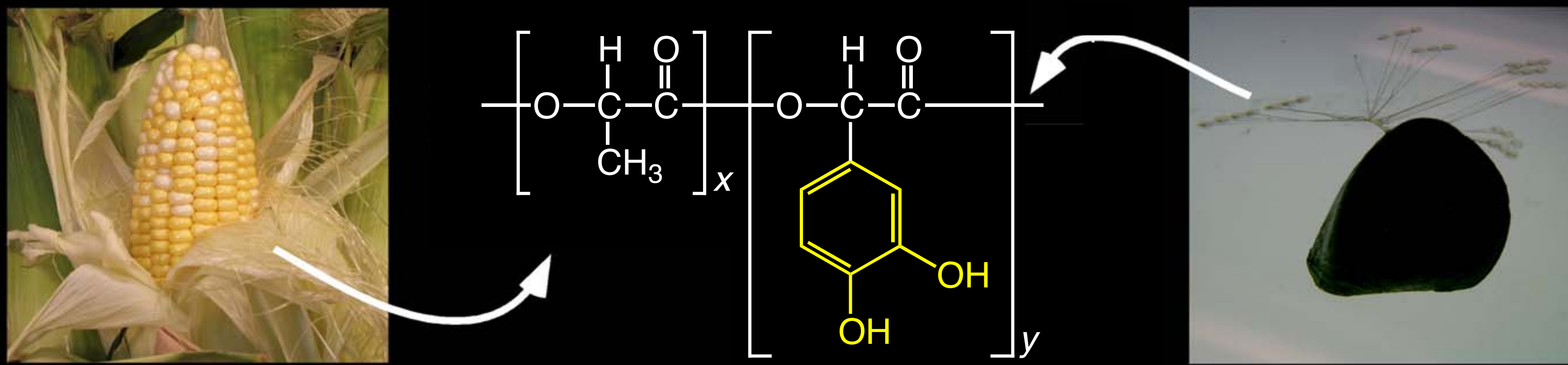


0% PEG

72% PEG

- PEG reduces polymer modulus
- Implications for bonding soft versus hard tissues

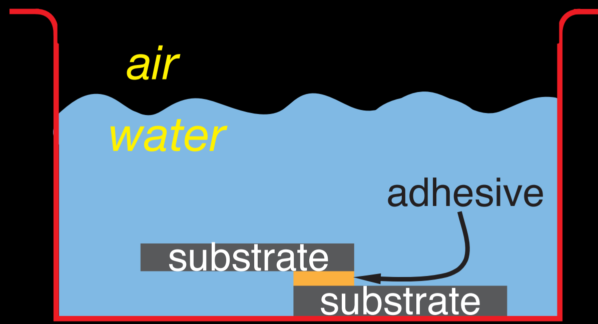
Adhesives from Renewable Resources

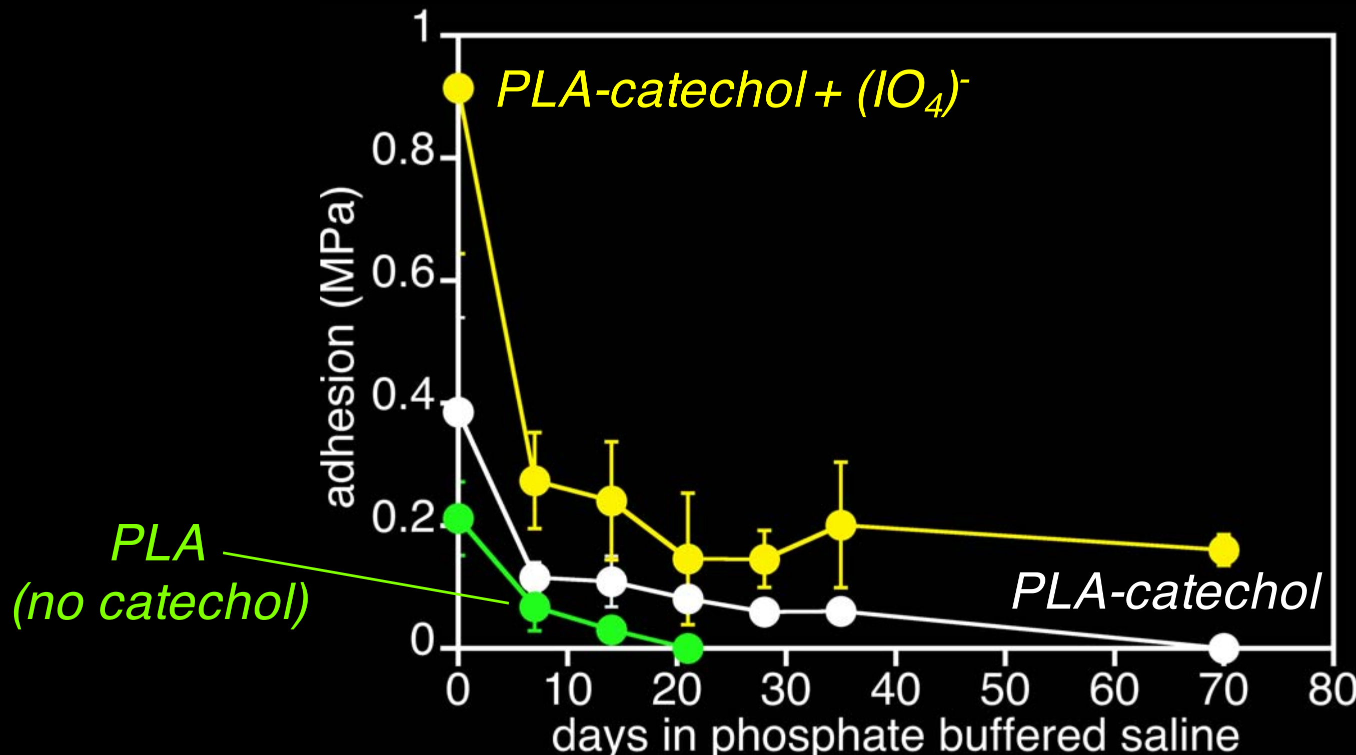


- Current high strength adhesives are all made from petroleum
- Toxic formaldehyde is in 4 of 9 billion kg of glues/year (e.g., wood)
- Permanent nature of glues prevents recycling of cars, furniture, electronics
- Combine polylactic acid and mussel adhesion
- The resulting materials may be sustainable, degradable, and biocompatible
- Entry into removable adhesives

Debonding

- Polyesters can hydrolyze
- Bond dry
- Submerge under water
- Monitor adhesion kinetics





- Adhesives can be debonded
- Debonding times can be <10 days or >3 months

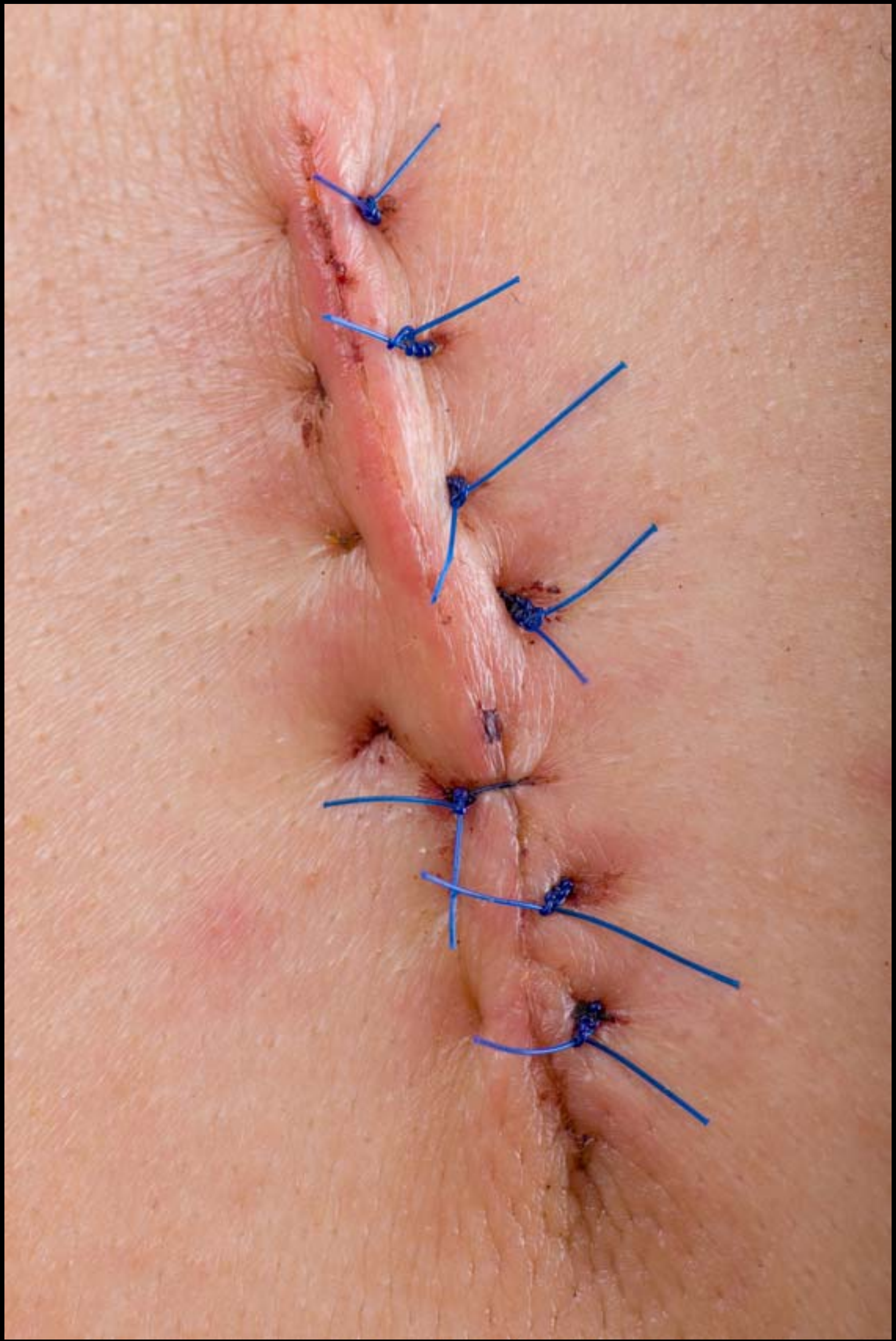


Photo: uwimages/Fotolia


Photo: Whyona/Fotolia

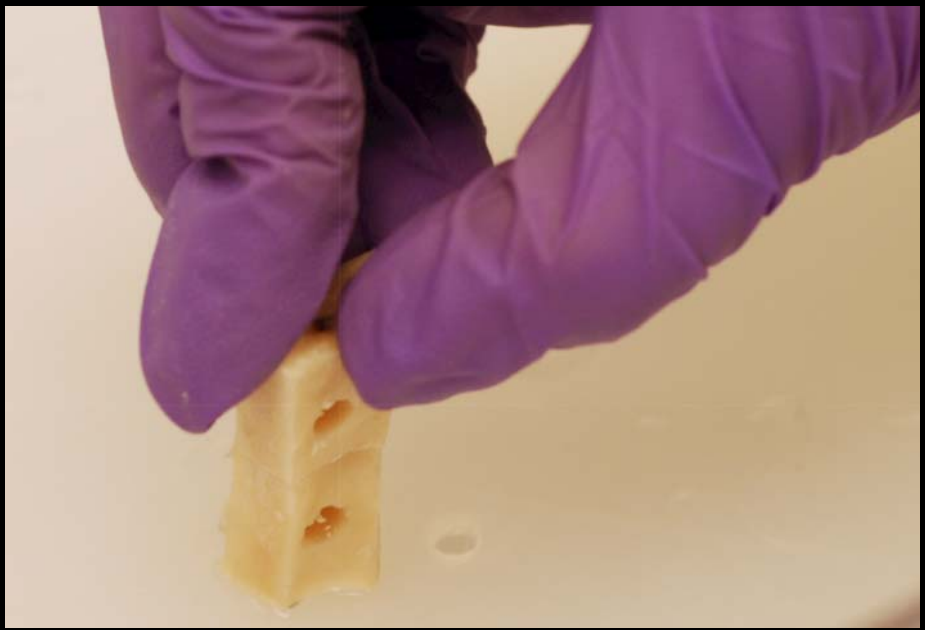
Biomedical adhesive needs:

- Sets wet
- Strong bonding
- Non-toxic





JUSTRITE



SPECIMEN PROTECT
RESET GL
START TEST
STOP TEST
RETURN
JOG UP
JOG DOWN

Conclusions

- Mussels: Iron → protein radicals → cross-linking and adhesion
- Oyster cement has a unique composition and structure
- Oyster cement is a cross-linked organic + $CaCO_3$ hybrid material
- Organics make interfacial contacts
- Similarities to spider silk proteins
- Developing new biomimetic, cross-linking polymers
- Strong adhesion achieved, comparable to "super glues"
- High strength underwater adhesion found
- Making adhesives from renewable resources and degradable
- Future: Biomedical materials

Acknowledgments

Uma Haryal & Victoria Hedrick, Purdue
Janie Bryan & Julie Liu, Purdue
Tara Essock-Burns & Dan Rittschof, Duke
Keith Fritzching & Klaus Schmidt-Rohr, Brandeis
Christa Crain & Robyn McCain, Purdue
Neeraj Gohad & Andy Mount, Clemson
Eric Holm, NSWC Carderock
Chia Ping Huang, Chris Gilpin & Debby Sherman, Purdue
Paul Kenny, Baruch Marine Lab, S. Carolina

Office of Naval Research

Defense Advanced Research Projects Agency

Gert Breur & Craig Georgen, Purdue
Chuan Leng, Yuwei Liu & Zhan Chen, U of Michigan
Emily Ralston & Geoff Swain, FIT
Rebecca Rist & Rebecca Metzler, Colgate U
Axel Rosenhahn, Bochum U, Germany
Gudrun Schmidt, Purdue
Karen Sider, VIMS
Erik Soderblum & Arthur Moseley, Duke
John Supan, LSU