

# Can Nature Help Solve This Problem?

## Biomimetic Adhesives for Infrastructure Repair



sandiego.gov

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# The Heroes of Our Story



• mussels



• barnacles



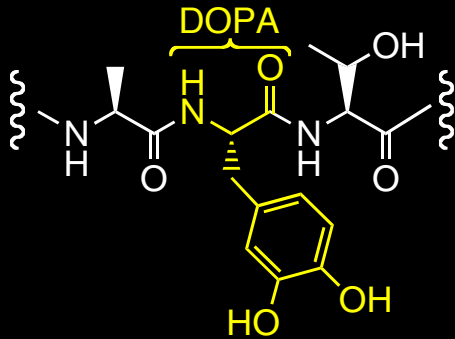
• oysters



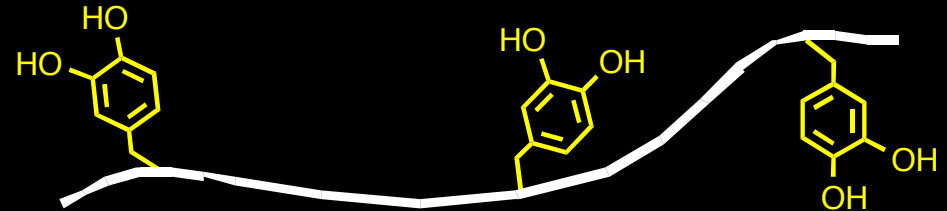
- Reduce turbulence
- Deter predators
- Reproductive efficiency



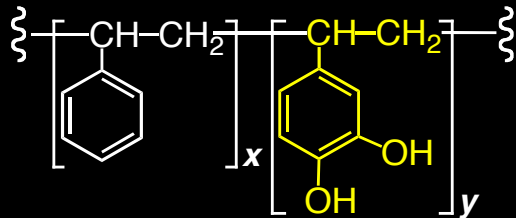
# Reductionist Approach to New Materials



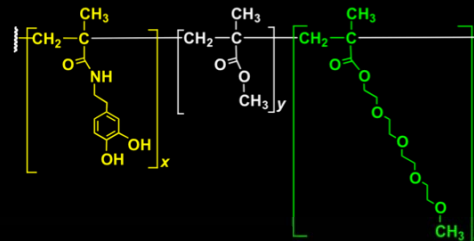
- Complex protein
- DOPA cross-linkable sidechains



- Simple polymer backbone
- Catechol groups



- poly(catechol-styrene)
- highest strength, dry & wet

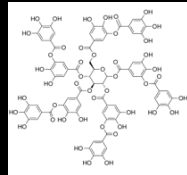


- poly(catechol-MMA-OEG)
- tunable flexibility, modulus

zein protein  
(corn)

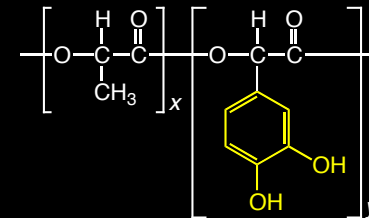


+



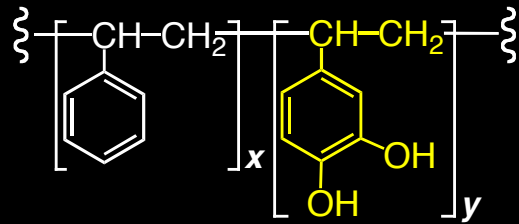
tannic acid  
(trees, coffee)

- zein-tannic acid
- bio-based, cheap



- poly(catechol-lactic acid)
- tunable degradation

# Dry Adhesive Strengths on Etched Aluminum



- poly(catechol-styrene)
- optimized  $M_w$ , catechol %, formulation
- polymer + solvent + filler



Gorilla Glue, urethane 3.3 ( $\pm 0.8$ ) MPa

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Elmer's white PVA glue: 3.8 ( $\pm 0.6$ ) MPa

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Super Glue, cyanoacrylate 5.0 ( $\pm 0.7$ ) MPa

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Epoxy glue, Loctite Quick Set 18 ( $\pm 2$ ) MPa

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Our biomimetic copolymers: 11.0 ( $\pm 0.5$ ) MPa

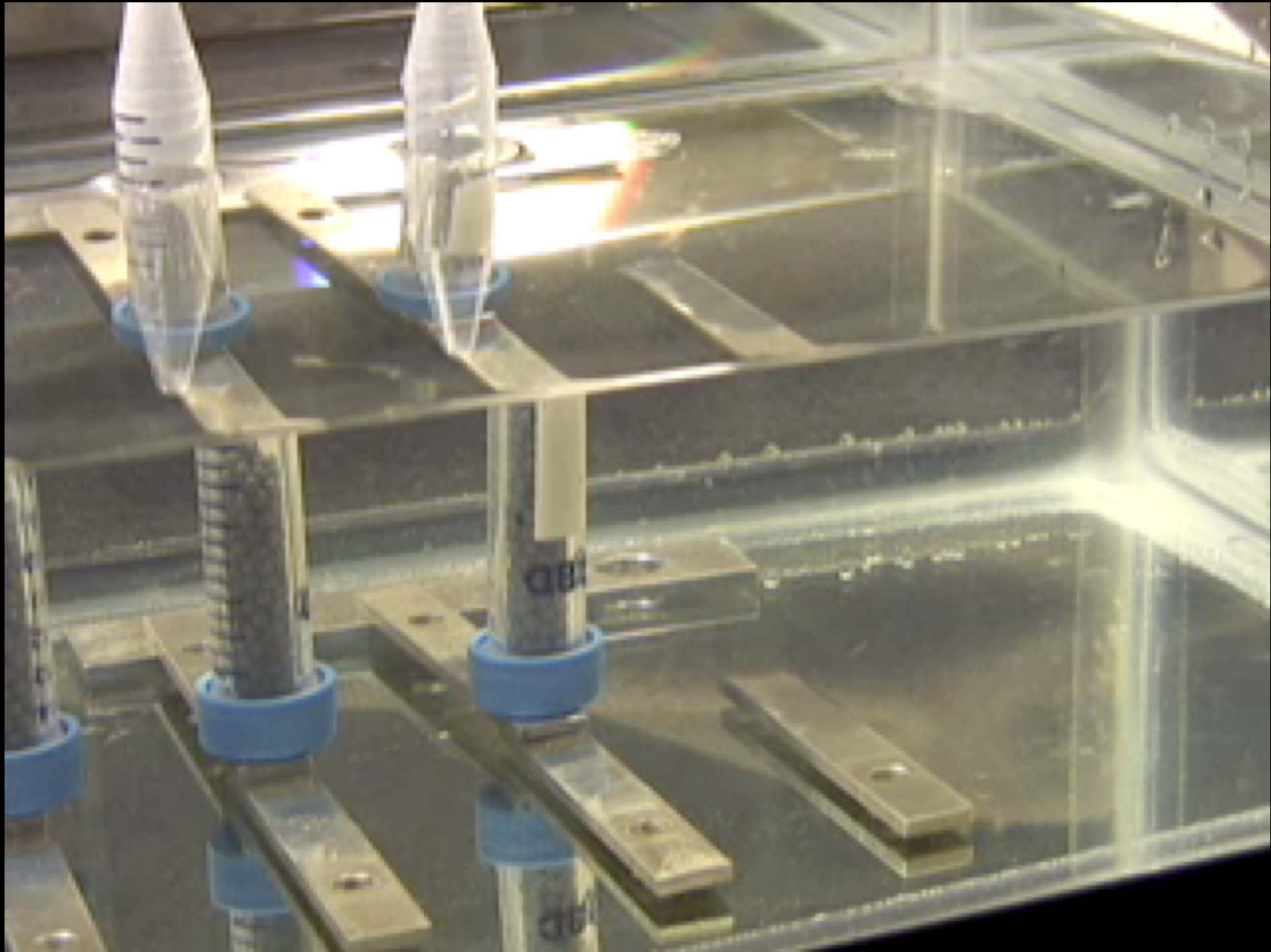
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# Dry Adhesion







	etched aluminum	sanded steel	red oak	Teflon
Elmer's Glue (polyvinyl acetate)	$3.8 \pm 0.6$	$7 \pm 1$	$11 \pm 2$	$0.48 \pm 0.07$
Loctite Super Glue (cyanoacrylate)	$5.0 \pm 0.7$	$7 \pm 1$	$9 \pm 2$	$0.7 \pm 0.2$
Loctite Quick Set (epoxy)	$18 \pm 2$	$18 \pm 2$	$15 \pm 2$	$1.0 \pm 0.1$
biomimetic polymer	$11.0 \pm 0.5$	$10 \pm 1$	$6.0 \pm 0.5$	$0.23 \pm 0.08$

- High performance versus commercial products

# Underwater Adhesion Testing



# Underwater Performance Versus Commercials

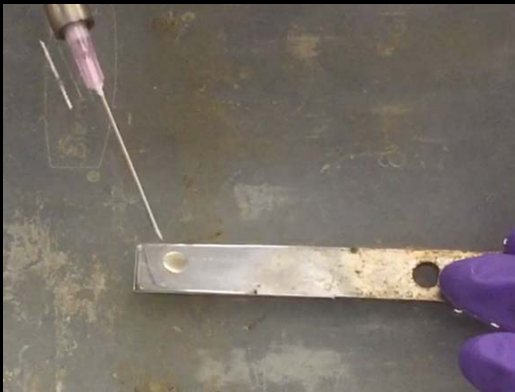
	polished aluminum	etched aluminum	sanded steel	red oak	PVC	Teflon
Gorilla Glue (urethane)	 $0.7 \pm 0.1$	 $0.4 \pm 0.2$	 $0.5 \pm 0.1$	 0	 $3.0 \pm 0.6$	 0
Mr. Sticky's (epoxy)	$1.0 \pm 0.3$	$0.2 \pm 0.1$	$0.4 \pm 0.1$	0	$3.0 \pm 0.6$	$0.10 \pm 0.08$
North Sea Resin (acrylic)	$0.3 \pm 0.1$	0	$0.2 \pm 0.1$	0	0	0
Marine Loctite (epoxy)	$0.6 \pm 0.3$	0	$0.2 \pm 0.1$	0	$2.0 \pm 0.5$	0
3M Marine (urethane)	$0.2 \pm 0.1$	$0.4 \pm 0.2$	$0.5 \pm 0.1$	0	$3.0 \pm 0.6$	0
biomimetic polymer	$3.0 \pm 0.4$ <i>stronger</i>	$0.2 \pm 0.1$ <i>same</i>	$0.10 \pm 0.02$ <i>weaker</i>	$0.2 \pm 0.1$ <i>stronger</i>	$0.4 \pm 0.1$ <i>weaker</i>	$0.3 \pm 0.1$ <i>stronger</i>

- High performance versus commercial products

# Formulation for Practical Use

## Underwater lap shear on polished aluminum

chloroform  
(beads up, rolls away)



$1.3 \pm 0.5$  MPa

dichloroethane/dimethylformamide  
(wets well, persists on slanted substrates)



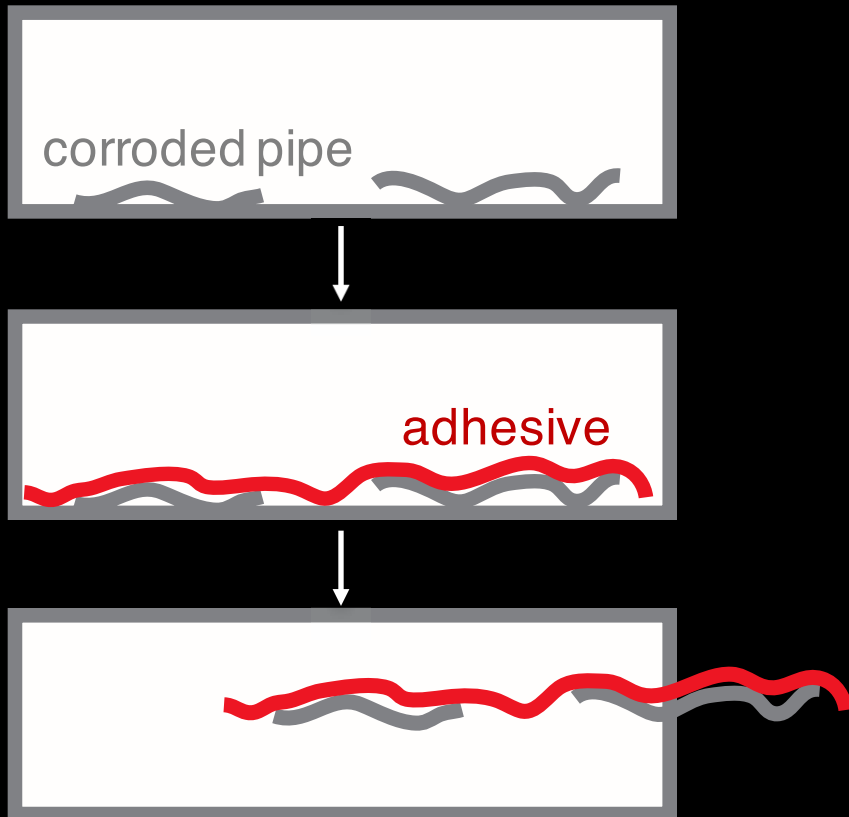
$0.29 \pm 0.05$  MPa

- DCE/DMF has lower adhesion than  $\text{CHCl}_3$ , but is easier to work with
- This lower adhesion is still higher than most commercial glues
- Formulation work is straightforward, but needs to be done.



# Bonding Without Surface Cleaning?

- Bonding to degrading surfaces may lose the adhesive
- Perhaps we can reach the underlying surface



## Potential alternative:



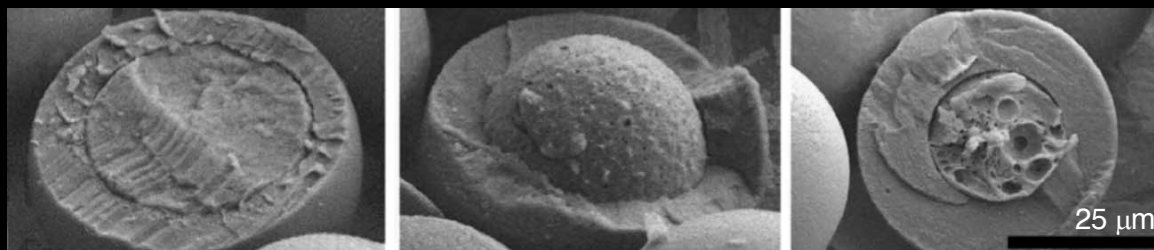
- Current epoxies may be too viscous
- Tailor properties as needed

- We have flexibility in formulation
- Can tune viscosity, etc. as needed
- Change polymer concentration, add fillers, etc.

## Cross-Linking, Encapsulation, Formulation

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- Two part adhesive system can make a gel, rapid curing
- Oxidants can cross-link polymer and cure the adhesive
- $(\text{Bu}_4\text{N})(\text{IO}_4)$ , periodate, is a good example,  $\text{Fe}^{3+}$  salts, too



Park and Yeo, *Encycl. Pharm. Tech.*, 2007, p. 2315

- Encapsulate oxidant in particle, break open to cure
- Not tried yet, but could work
- How to break open? How to fill? How to formulate?

# Conclusions and Future Outlook

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- Biomimetics yields high performance adhesives
- Hydrophobicity and wet bonding may help with pipelines
- Many variables available to change formulations
  
- Define ideal adhesive properties for pipeline repair
- Develop new formulations accordingly
- Test and reformulate



# Acknowledgments



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