A Flexible Platform for Adhesion Measurements at Polymer and Biomaterial Interfaces

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Contributors/Acknowledgements

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- Matt Becker

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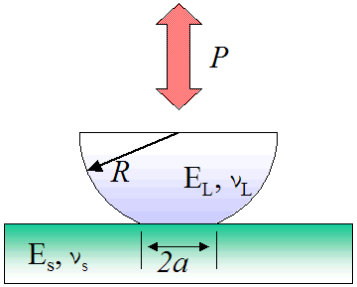
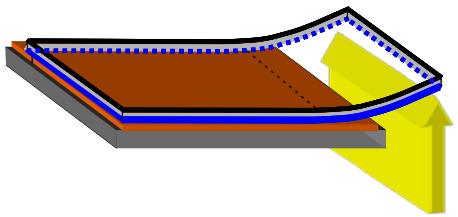
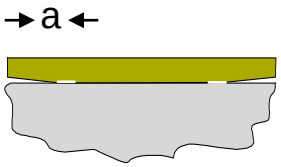
Measuring Adhesion at Complex Interfaces

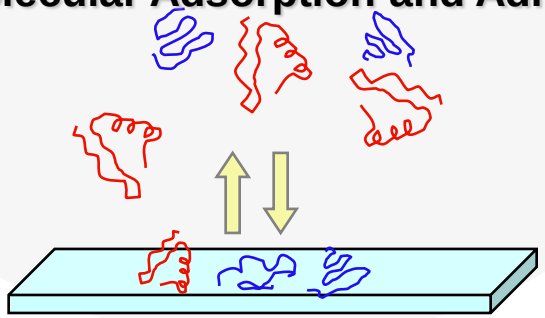






Biomolecular Adhesion

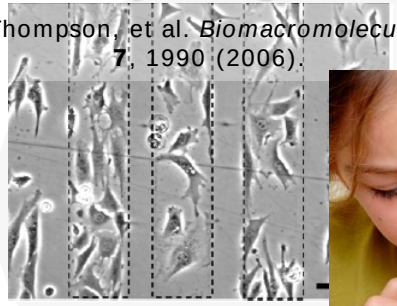
Biomolecular Adsorption and Adhesion

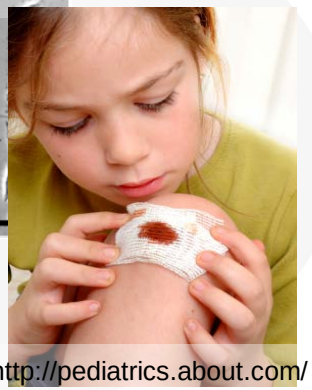


Taylor, et al. *Macromol. Rapid Comm.* (2008)

Physiological Response

Thompson, et al. *Biomacromolecules* **7**, 1990 (2006).





http://pediatrics.about.com/

- Macromolecular adsorption and adhesion governs many important biological processes
  - Wound healing/tissue regeneration
  - Cell signaling
  - Device biocompatibility
- A straightforward measurement method to determine adhesion biointerface adhesion strength can:
  - Advance our understanding of the relationship between surface properties and physiological effects in biomaterials
  - Lead to the development of rapid screening methods for assessing biocompatibility

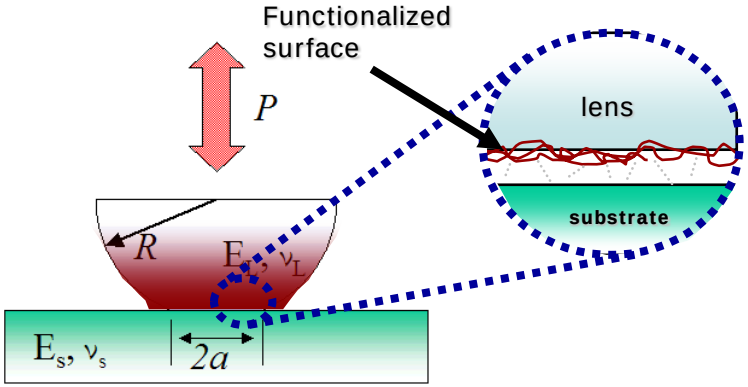
Biomedical Devices

http://www.davidclulow.com

http://www.biomet.com

http://www.endovasc.com

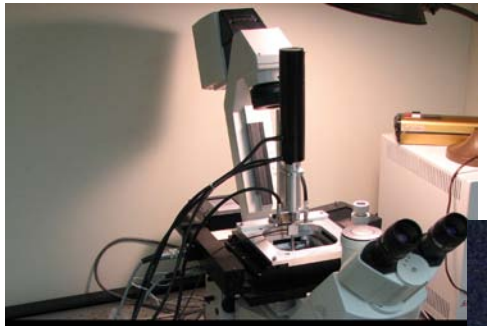
Johnson, Kendall, and Roberts Mechanics (JKR)

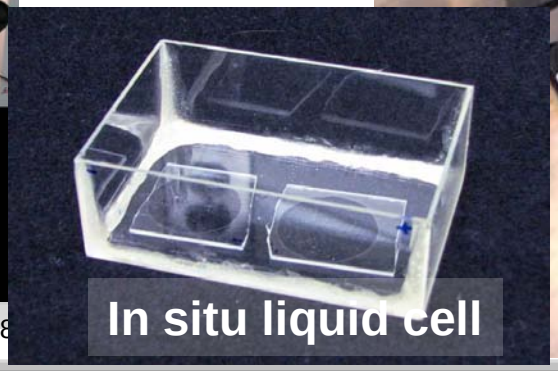


K.L. Johnson, et al. *Proc. Royal Soc. Lon. A.* **324**, 301 (1971).

- **JKR theory**
  - Describes deviations from Hertzian contact mechanics due to surface energetics

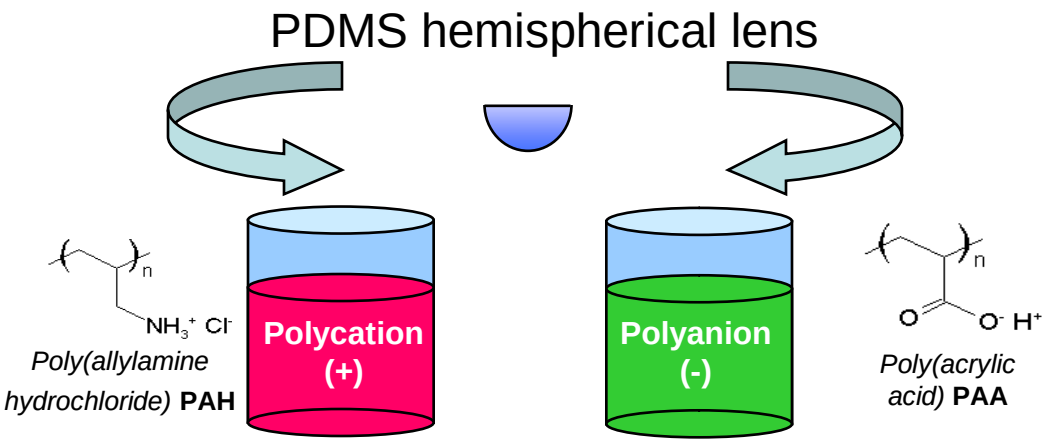
Hertzian Force	JKR Force
$P' = \frac{4E^* a^3}{3R}$	$P = P' - \sqrt{8\pi E^* \mathcal{G} a^3}$



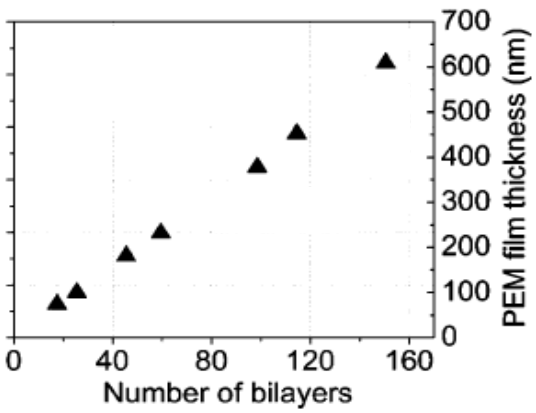


A.M. Forster, et al. *Meas. Sci. & Tech.* **16**, 8

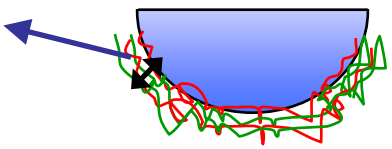
LbL Assembly for Lens Functionalization



- LbL is a flexible technique, allowing incorporation of various water-soluble polymers, polyelectrolytes, and biomacromolecules
- LbL is conformal, and affords precise control of the film thickness
- Young's modulus well-characterized for some systems

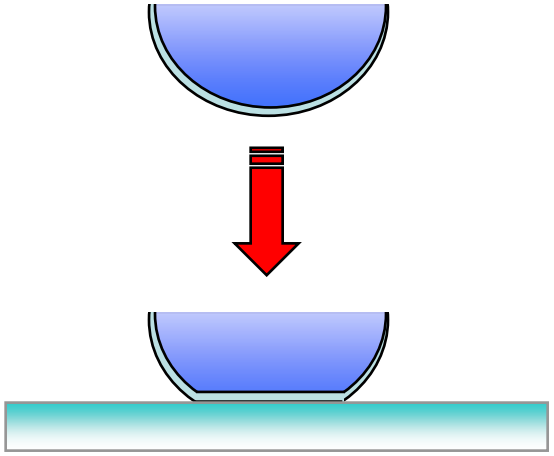


Film thickness increases linearly with number of deposition cycles (bilayers)

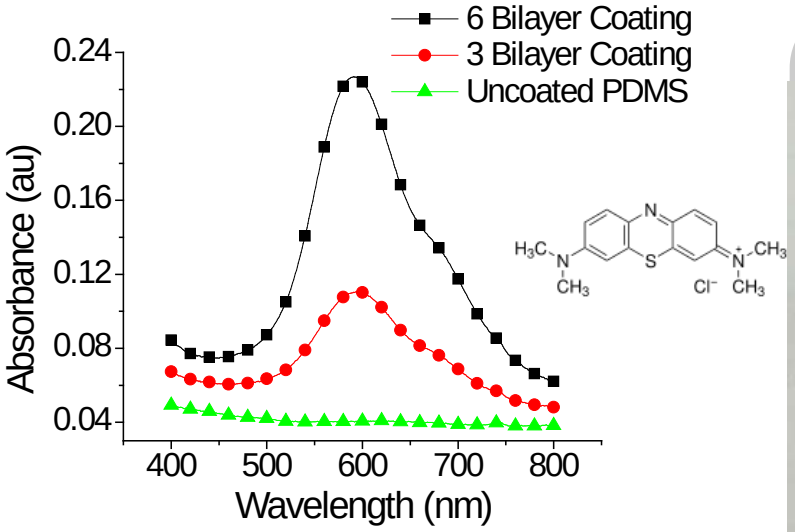


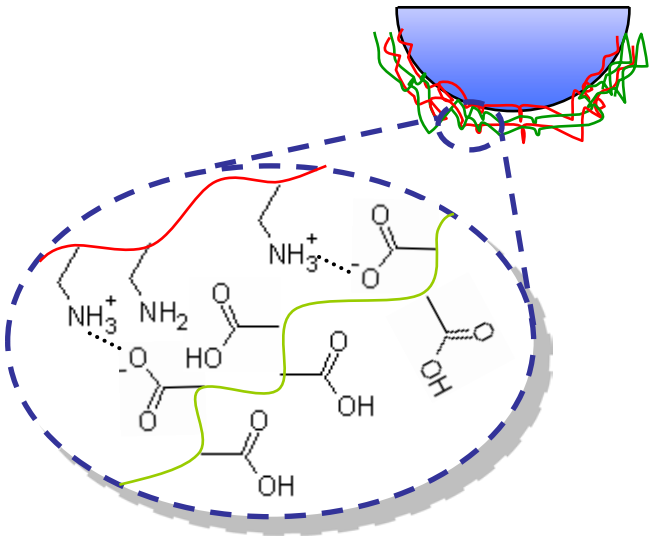
A.J. Nolte, et. al., *Macromol.*, **39** 4841 (2006)

Do thin films change the mechanics?
What types of factors must we consider?

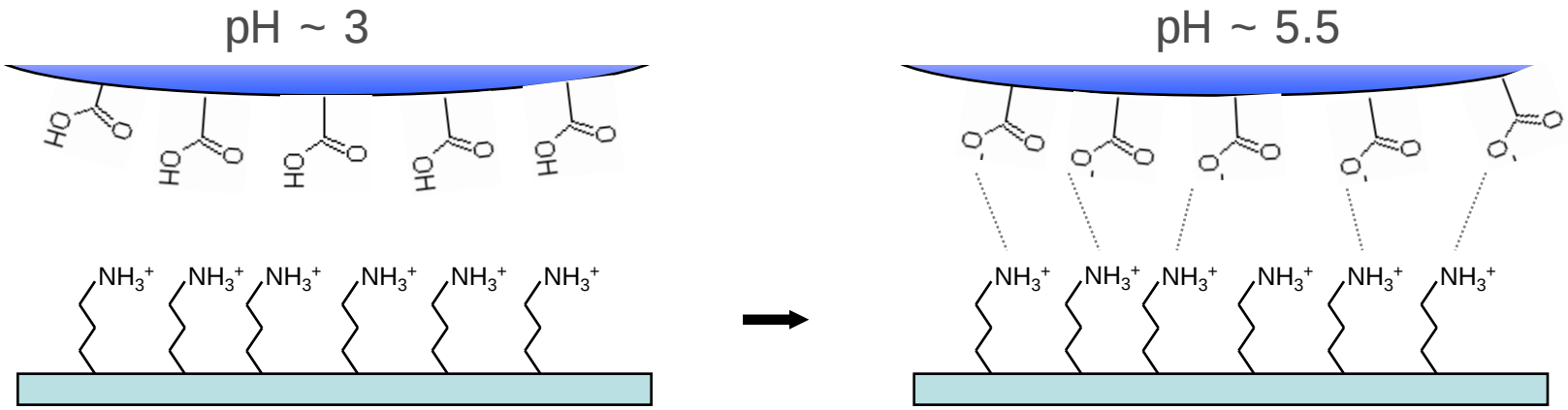


COOH-rich LbL Coatings for Acid-base Adhesion

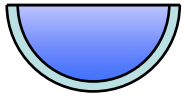


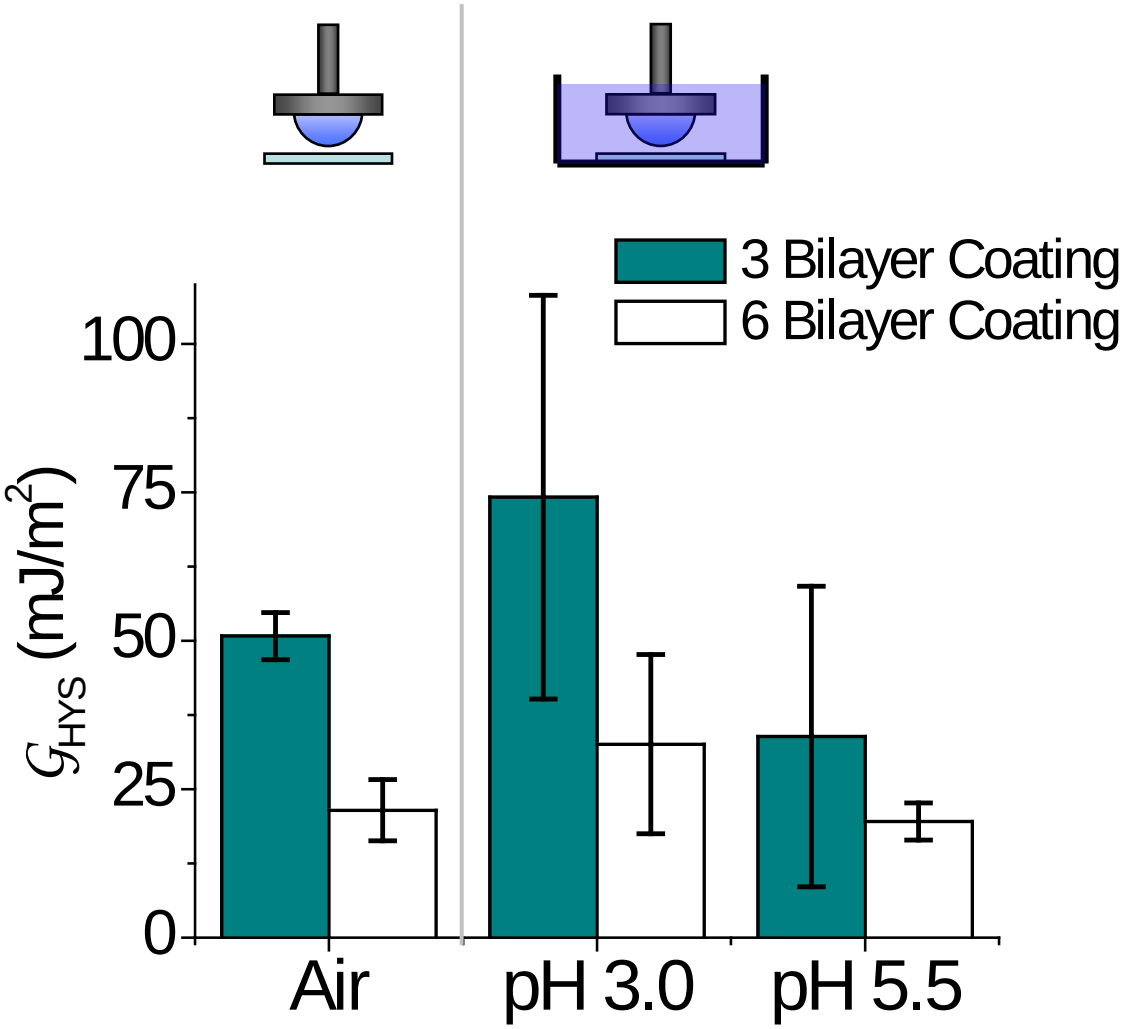


pH-tunable acid-base interactions with 3-aminopropylsilane (APTES)



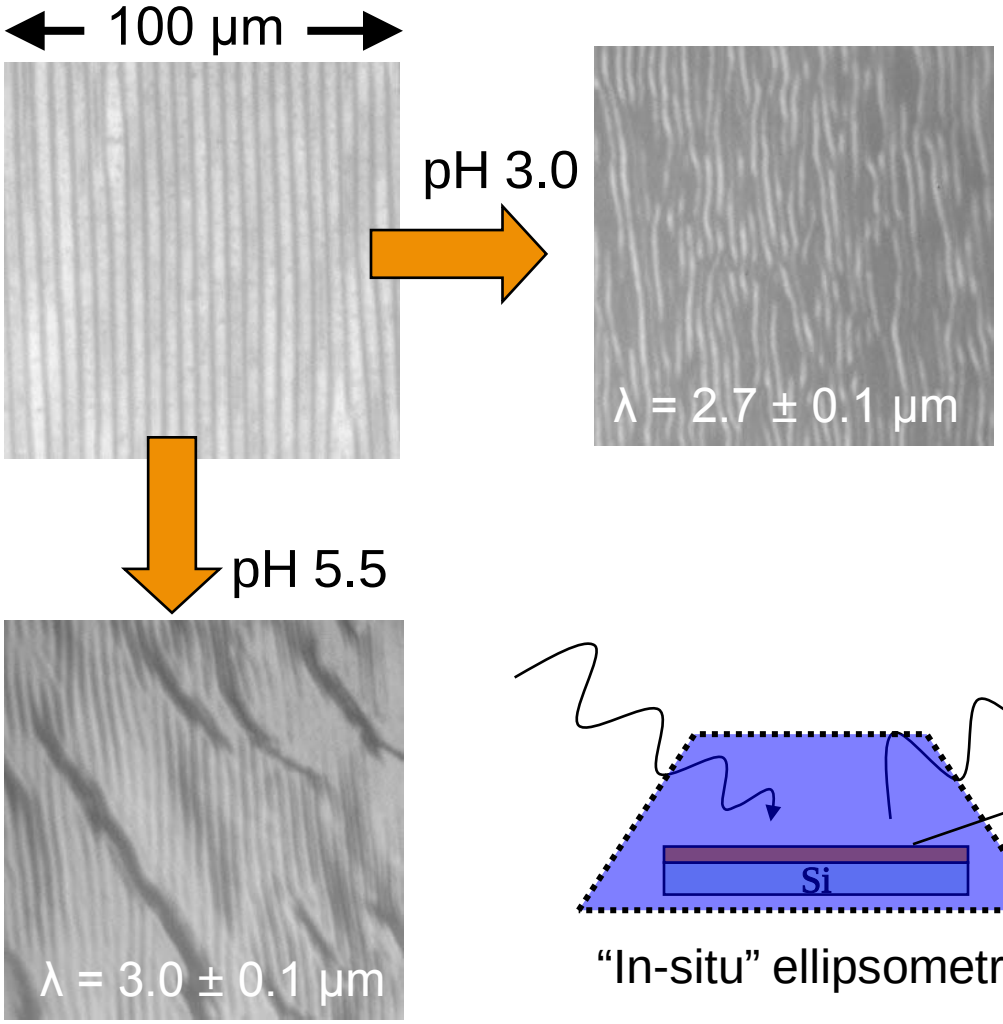
Adhesion Tests: LbL Coatings





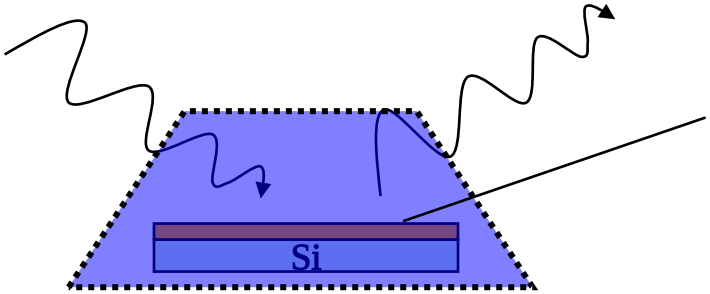
- Specific acid-base interactions suggested by little to no loss of adhesion in moving to aqueous environment
- 3 Bilayer (~ 15 nm) coating shows greater adhesion under all conditions
- pH trend is *opposite* of expected… coatings should be more ionized near neutral pH

Wrinkling Analysis



$$\overline{E}_{coating} \propto \left(\frac{\lambda}{d}\right)^3$$

Ambient	$\overline{E}_{coating}$ (GPa)
Air	5.0 ± 2.0
pH 3.0	0.7 ± 0.2
pH 5.5	1.8 ± 0.8

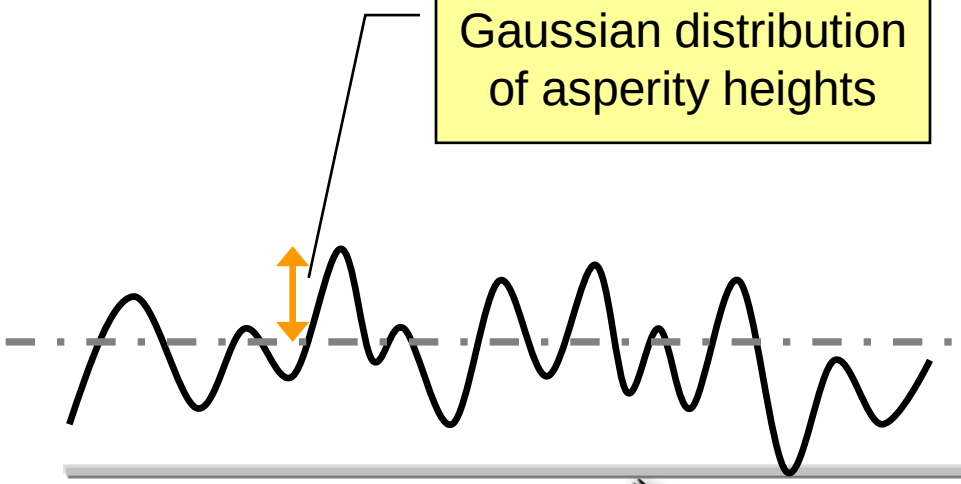


"In-situ" ellipsometry

Change in coating thickness (d), ~ 16% at both pH

Roughness Effects

- JKR theory assumes flat surfaces, perfect contact
  - In the ideal case, coating modulus should not affect adhesion
- Rough surfaces with non-deformable asperities can *decrease* the actual contact area
- Fuller and Tabor introduced an adhesion parameter, θ
  - $\uparrow \theta = \downarrow$ *adhesion*



Adhesion Parameter

$$\theta = \frac{E \cdot R_a^{3/2}}{\beta^{1/2} \cdot \Delta\gamma}$$

Young's modulus

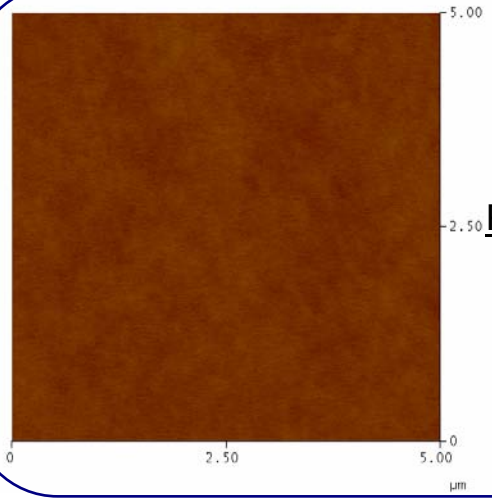
Surface roughness

Asperity radius

Adhesion energy

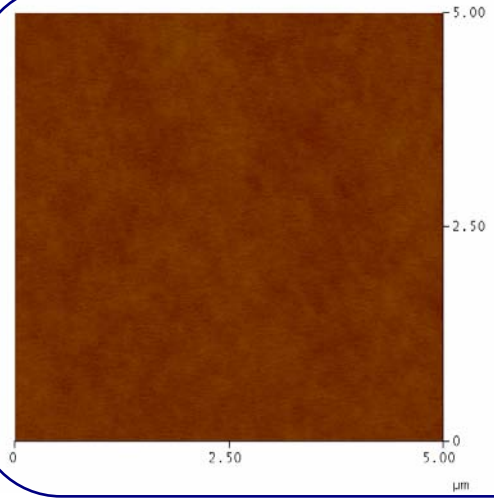
Fuller and Tabor, *Proc R. Soc. Lond.* (1975)

Surface Roughness



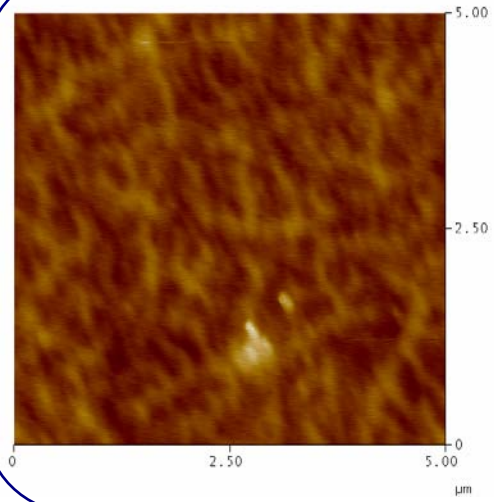
PDMS

Roughness (R_a)
0.5 nm



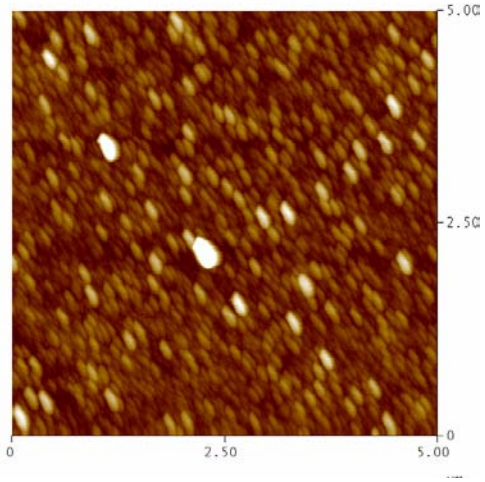
APTES

Roughness
0.7 ± 0.4 nm



3 Bilayers

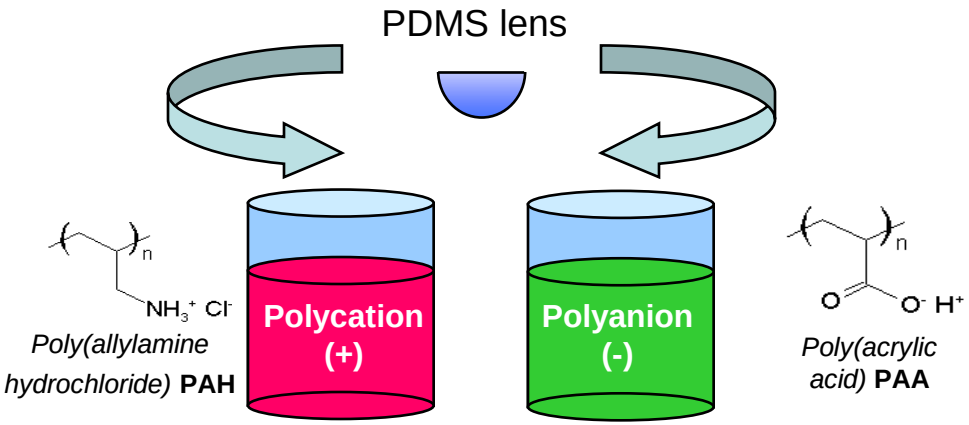
Roughness
2.6 ± 0.7 nm

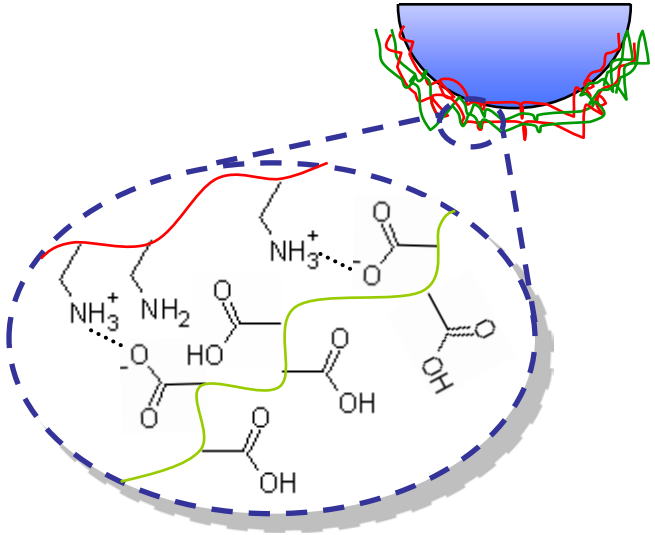


6 Bilayers

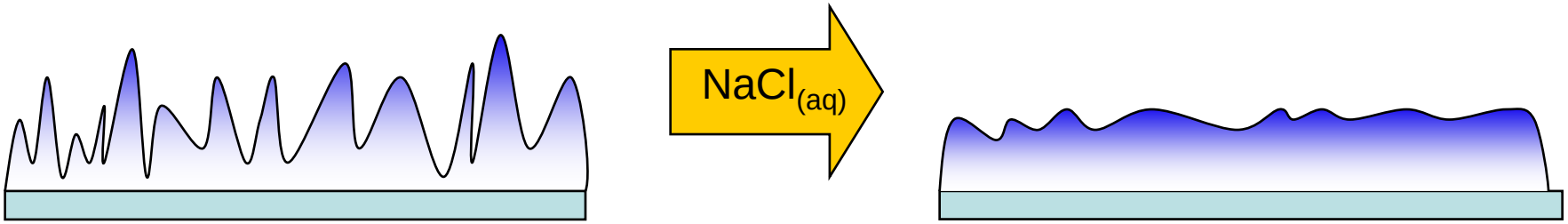
Roughness
10.4 ± 1.3 nm

Smoothing the Roughness: Salt Annealing





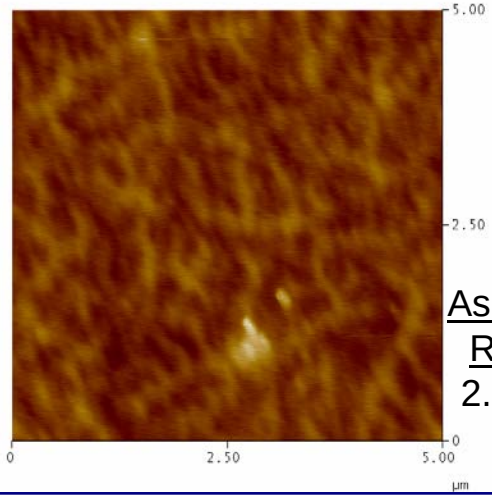
"Salt Annealing"



Dubas and Schlenoff, *Langmuir* (2001)

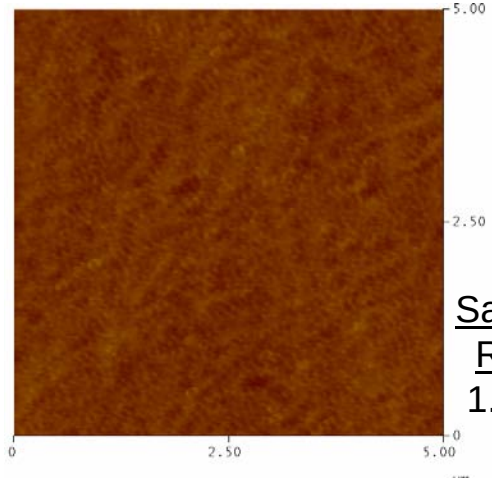
Effect of Salt Annealing (5 µm scans, 40 nm scale)

3 Bilayers



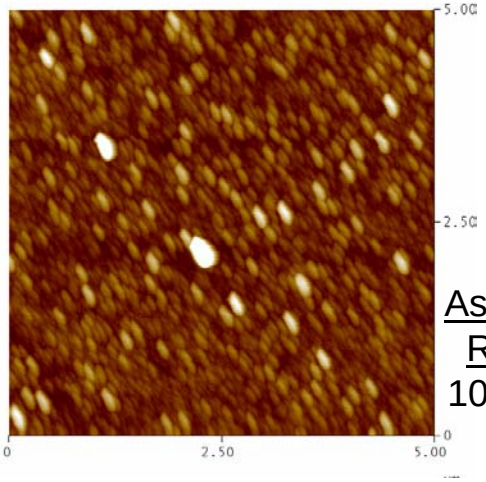
As assembled
Roughness
2.6 ± 0.7 nm

0.1 M NaCl



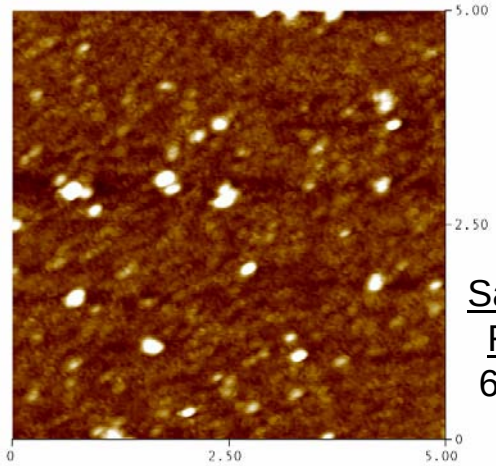
Salt-annealed
Roughness
1.4 ± 0.5 nm

6 Bilayers



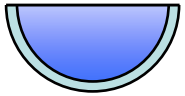
As assembled
Roughness
10.4 ± 1.3 nm

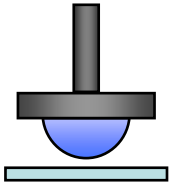
0.1 M NaCl

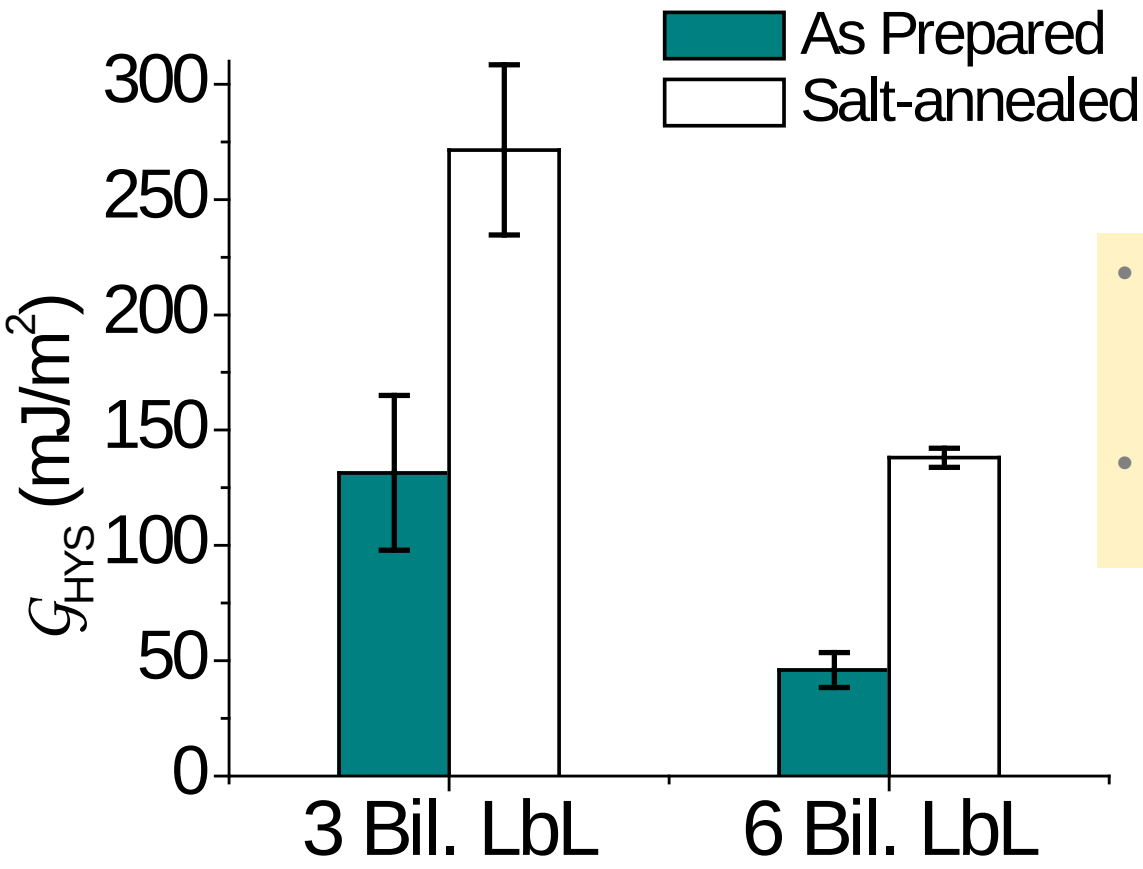


Salt-annealed
Roughness
6.2 ± 3.5 nm

Adhesion Tests of Annealed Coatings



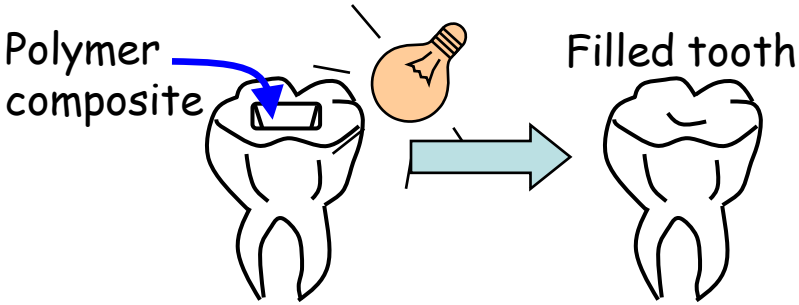


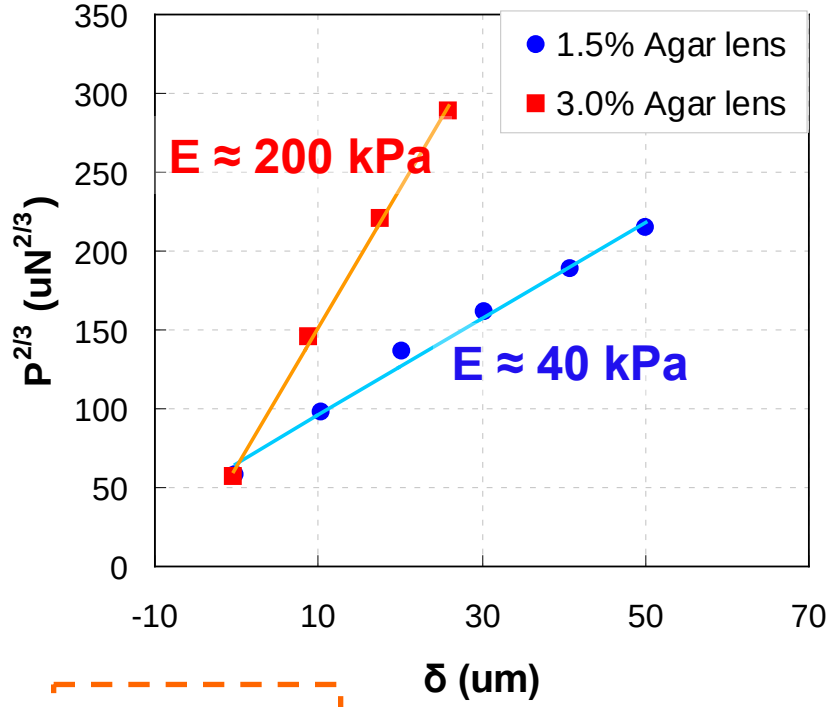


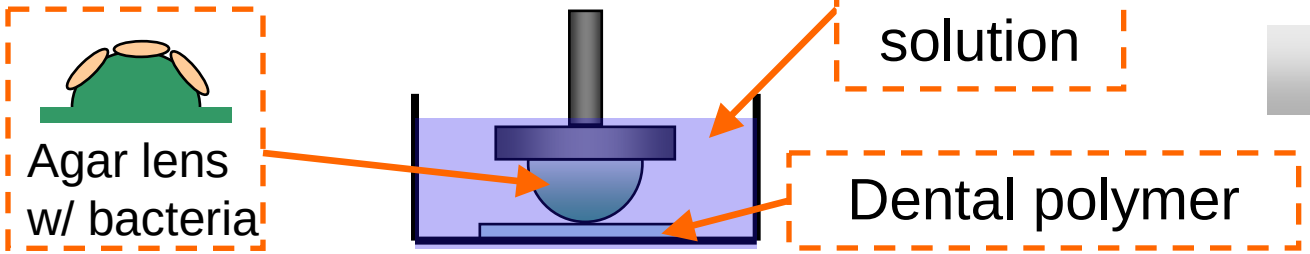
- Significant increase in adhesion for annealed coatings
- Adhesion hysteresis for 3 bilayer coatings > PDMS

Future Work: Bacterial Adhesion to Dental Polymers

- **Bacterial adhesion to dental polymers**
  - Motivation: Develop new methods to measure bacteria affinity dental polymers and composites
  - Bacterial adhesion test in "sandwich geometry" between an agar lens and a dental polymer surface
  - Key result: JKR capable of operating with and measuring the modulus of low-compliance agar lenses
  - Future work: JKR test with bacteria-cultured lenses



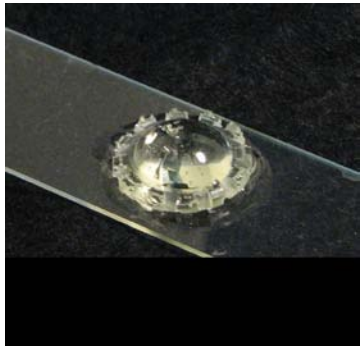




w/ Nancy Lin

Future Work: Measuring Contact Lens Bioadhesion and Young's Modulus

- **JKR indentation of contact lenses**
  - Performed on lenses in their native geometry
  - JKR mechanics used to find Young's modulus
  - Key result: Successful measurement of Young's modulus for different crosslinking densities
  - Future Direction: Protein-functionalized lens for *simultaneous* measurements of modulus and adhesion



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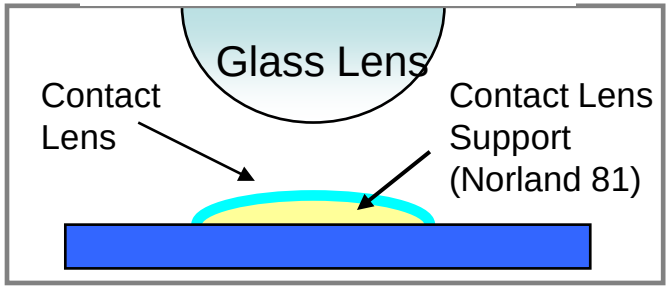
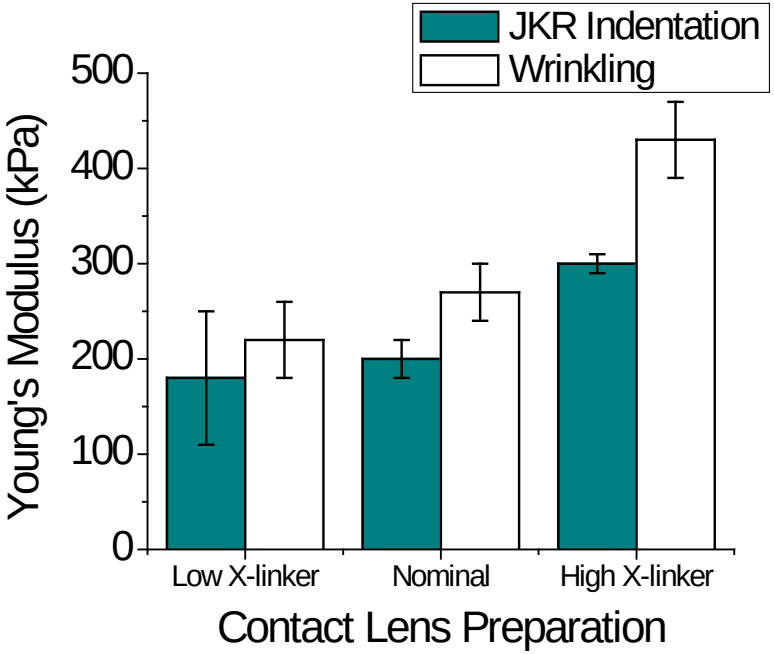
Experiment Geometry





Summary

- The JKR apparatus is an effective measurement tool for characterizing in-situ adhesion between functionalized surfaces
  - The chemistry, roughness, and modulus of the surface all play an important role in determining adhesion
- The basic instrument platform is flexible, and can be used to conduct adhesion measurements on samples in alternative geometries and ambient conditions
- The ability to simultaneously measure both the Young's modulus and the biological adhesive properties of hydrogels make the JKR instrument particularly attractive for biomaterial research and development