Surface Elastic Modulus of Barnacle Adhesive and Release Characteristics from Silicone Surfaces

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Barnacle Adhesion leads to Fuel Inefficiency of Ships (can be 20% loss)

- Ship hull surface becomes covered with barnacles.
- Commonly used Cu poisons the environment.
- How to design a non-toxic non-stick hull coating? Low surface energy coating like PDMS? Need to understand barnacle release mechanics.
Baseplates grown on hard surface look uniform, but baseplates on PDMS are abnormal

- *Balanus eburneus* on glass - adhesive is transparent and consistent
- *Balanus eburneus* removed from a 2000 um silicone coating
  - Adhesive is variable - ranging from soft and amorphous to hard and transparent
  - Values represent detachment stress (MPa)

See also Berglin

Experiment:

Detachment stresses and baseplates of different barnacles
Predicted Coating Thickness vs Release Stress

Thickness dependence in Kendall limits

\[ \sigma_I = \sqrt{\frac{2EG_c}{\pi a(1-\nu^2)}} \]

\[ \sigma_I = \sqrt{\frac{2KG_c}{h}} \]

Stud diameter: 7.2 mm

Singer, NRL
Research Design: AFM test of 48 barnacles on different PDMS coatings:

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thickness</th>
<th>Addition</th>
<th># barnacles</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC 3140</td>
<td>600 (microns)</td>
<td>none</td>
<td>3</td>
</tr>
<tr>
<td>DC 3140</td>
<td>200</td>
<td>&quot;oil&quot;</td>
<td>8</td>
</tr>
<tr>
<td>DC 3140</td>
<td>50</td>
<td>&quot;oil&quot;</td>
<td>10</td>
</tr>
<tr>
<td>DC 3140</td>
<td>600</td>
<td>none</td>
<td>3</td>
</tr>
<tr>
<td>DC 3140</td>
<td>50</td>
<td>none</td>
<td>12</td>
</tr>
<tr>
<td>T2 Silastic</td>
<td>50</td>
<td>none</td>
<td>12</td>
</tr>
</tbody>
</table>

Barnacles were selected to represent three groups from panels:
Max, Mean, and Min adhesion values (measured at FIT)

Targeted Surface Properties (measured at Pitt):
- AFM-based modulus
- % soft area (hand inspection)
- Max center depth ($\alpha$ 1/curvature of baseplate)
- Contact angle
AFM Height and Phase Images: Sometimes glue looks fibrillar

All images are 20 x 20 microns

Barnacle glue contains 3 primary proteins, with disulfide cross-linking with curing
Some globular components

Some smaller fibrillar components
Some mineral-like substrate

Probably CaCO$_3$, whose modulus is $\sim 35000$ MPa.
Using AFM tip indentation to study the surface modulus of barnacle base plates.

- Silicon nitride AFM tip radius ~ 40nm.
- Experiments in artificial sea water, mostly on live barnacles.
- A maximum indentation force (about 30 nN) for all barnacles and all locations on each barnacle
- ~ 30 measurements per barnacle, in groups of 3 per location
- All force plots were converted into indentation vs. force plots. The Hertz model, where $F \propto \text{indentation}^2$, was used to fit the data. Parabolic tip assumed.
Simple force plots can be fit directly with one modulus

E = 1.85 MPa
R² = 0.999
Some force plots show multiple modulus components

\[ E = 0.60 \text{ MPa} \]
\[ R^2 = 0.933 \]
\[ E_1 = 0.41 \text{ MPa} \]
\[ E_2 = 2.50 \text{ MPa} \]
Modulus Profile

- There are different component moduli of barnacle base plates. Most of them fall into 0.01 MPa – 500 MPa, some of them are over 1000 MPa, and a few showed extreme hardness, presumably CaCO₃.
Summary over first batch of barnacles: 48 organisms

mean surface modulus of baseplate vs adhesion strength

Barnacles selected to represent low, medium, and high shear adhesion strength
Baseplate modulus predicts adhesion strength for all 3140, T2 and 3140+oil coatings, independent of coating thickness

- The dependent variable Adh(MPa) can be predicted from a linear combination of the independent variables (alpha=0.01):
  - \( P \) 0.028
  - Coating Type 0.028
  - coat thickness 0.631
  - % soft area 0.411
  - Max center depth 0.073
  - Mean Baseplate Modulus (MPa) 0.004

Unexpected Result: Modulus of outer 100nm of barnacle base-plate correlates with barnacle release stress.
AFM measured modulus of freshly released barnacles

There are several major peaks: around 1, ~5 and 20 MPa. They probably correspond to the moduli of different adhesive layers of baseplate multilayer structure.
For small shear adhesion, moduli are narrowly distributed. For large shear adhesion, moduli are widely distributed.

\[ y = 128.84x + 2.86 \]
\[ R^2 = 0.34 \]
\[ p=0.01 \]

• Abnormal large E values (>200 MPa) were excluded.

**Question:** Does large shear adhesion correspond to a mixture of failure modes, while small shear adhesion corresponds to a simpler failure mode?
Staining PDMS for detached barnacle protein

FL03V4-01
Be

FL03R1-02
Bv

Stained surface on left barnacle on right
Summary

• For ALL DATA and the 3 x 50um COATINGS (3140, T2, 3140+oil)
• Mean or Median Barnacle Modulus of outer 100nm predicts Barnacle Adhesion Strength.
• Mostly adhesive failure, but some cohesive failure.