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Life in the slip lane: The effect of molecular level friction on algal adhesion

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Background
The physical properties of a surface have a profound effect on the settlement and adhesion of fouling organisms. Concepts of fracture mechanics have been employed to describe and model release of hard foulers, e.g. barnacles, from fouling-release coatings. The adhesion strength of such organisms has been shown to be influenced by a range of physical factors including:
- Coating modulus
- Coating thickness
- Critical surface tension / surface energy
- Friction and slippage

For soft-foulers, e.g. algae, foul-release mechanics are less well defined, as the organisms often violate the conditions required by models of virtue of their small size and low modulus. This poster demonstrates the influence of surface friction on the adhesion strength of two species of fouling algae, Ulva litoralis and Navicula perminuta.

Ulva is a major fouling macro-alga that colonises new surfaces through multiple spores. Spores adhere to newly colonised surfaces by the secretion of a preformed, fast curing, glycoprotein-rich adhesive that surrounds the spore and anchors it by wetting the surface (Figure 1).

Navicula perminuta (Figure 2) is a diatom (Bacillariophyceae), a member of a family of siliceous microalgae that are a major component of fouling microbial slimes. Diatoms colonise new surfaces by gravitational settlement and adhere through production of a, mainly, polysaccharide extracellular polymeric substance (EPS).

Methods
Methyl-terminated alkanethiol self-assembled monolayers (SAMs) of carbon chain length C₃₋C₉ were formed from the relevant alkanethiol solutions in CH₃OH. SAMs were attached to 3-100nm thick Au film over a Cr adhesion promoter on a glass substrate. (Figure 3). SAMs were prepared shortly before the biological assays and were stored under N₂ until required.

Biological assays. Biological assays were conducted according to the protocols detailed in references 1 and 4. Briefly:

Navicula
- Navicula cells settle on the substrate
- Navicula cells adhere by gravity and adhesion to the substrate

Ulva
- Ulva cells settle on the substrate
- Ulva cells adhere by gravity and adhesion to the substrate

Results
Characteristics of the alkanethiol SAM series are shown in Table 1.

Table 1: Characteristics of a methyl-terminated alkanethiol series. Thickness determined using a multi-spectral ellipsometer. Wettability determined as advancing water contact angle.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Thickness (nm)</th>
<th>0° Contact Angle (°)</th>
<th>Friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃</td>
<td>0.53 ± 0.04</td>
<td>111 ± 2</td>
<td>0.51 ± 0.03</td>
</tr>
<tr>
<td>C₅</td>
<td>0.79 ± 0.04</td>
<td>112 ± 2</td>
<td>0.35 ± 0.04</td>
</tr>
<tr>
<td>C₇</td>
<td>1.45 ± 0.04</td>
<td>113 ± 2</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>C₉</td>
<td>1.54 ± 0.04</td>
<td>115 ± 1</td>
<td>0.29 ± 0.02</td>
</tr>
<tr>
<td>C₁₁</td>
<td>1.73 ± 0.04</td>
<td>116 ± 2</td>
<td>0.23 ± 0.02</td>
</tr>
<tr>
<td>C₁₃</td>
<td>2.14 ± 0.04</td>
<td>115 ± 1</td>
<td>0.18 ± 0.05</td>
</tr>
</tbody>
</table>

Progressive extension of the thiol chain length is verified by the increasing thickness of the coating in the nanometre range. Wettability of the series varied by only 5° but the friction coefficients decreased with increasing length of the thiol chain, this is a consequence of changes in the molecular organisation of the SAM (see Discussion).

Discussion
Table 1 shows that as the length of the thiol chain increases from C₃ to C₁₃, the friction coefficient of the surface drops. This is a consequence of the intermolecular organisation of the monolayer. Short chain length thios are disordered structures. The reduced number of methylene groups in the chain limits the potential for intermolecular interactions, primarily van der Waals, and leads to a 'fluid-like' amorphous nature, which is readily deformable and therefore experiences high levels of surface friction. As chain length increases the SAM becomes more ordered as interactions between the thiol chains increase. This gives the monolayer a more rigid crystalline structure, which is less deformable and consequently has lower friction.

The change from fluid-like to crystalline pack occurs at thiol lengths of C₇-C₁₃. This coincides with the onset of increasing area / cell removal.

The mechanism that accounts for this change in adhesive strength is not yet certain. As Figure 4 shows however, the removal of Ulva and Navicula has the same dynamic. This suggests that the underlying mechanism is independent of the specific composition of the adhesive employed.

Two hypotheses are currently being considered:

1) The amorphous nature of the short chain length thios may simply provide a greater available surface area for the wetting and interaction of the adheres.

2) The short chain length SAMs have a lower elastic modulus (i.e. are more deformable) than the longer chain length, crystalline, SAMs. This may confer the potential for increased energy dissipation through molecular motion. As shear stress (energy) is applied to the adhered spores / cells, an amorphous SAM has the ability to 'absorb' more of the energy.

These results indicate that the frictional properties of a surface affect the dynamics of adhesive release in a consistent manner for these two algal species. 'Newby and Chaudhury' described the importance of friction, lubricity and slippage in the foul-release properties of PDMS (siloxanes). Although the mechanisms they invoked to explain high removal from thick cross-linked polymers cannot be directly applied to release from a monolayer, these results suggest that frictional characteristics are of fundamental importance to the foul-release nature of a surface.

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References

Figure 1: Ulva litoralis spores

Figure 2: Navicula perminuta

Figure 3: Methyl-terminated alkanethiol self-assembled monolayer structures. (a) 1.5nm thick Au film coated with a Cu adhesion promoter. (b) SAMs. (c) SAMs attached to the substrate. (d) SAMs attached through the substrate.

Figure 4: The removal of Ulva spores and Navicula cells from the alkanethiol SAM series is shown in Table 1. Ulva removal from the thiolised SAMs is insensitive to changes in friction coefficient, removal remaining around 25% for Ulva and around 40% for Navicula. C₉ SAMs of thiol length C₉ show both removal of both species scales linearly; as friction coefficient decreases (chain length increases) removal of both species increases.