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

Conference Item

How to cite:


Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online’s data policy on reuse of materials please consult the policies page.
Life in the slip lane: The effect of molecular level friction on algal adhesion

M. E. Pettitt, J. Bowen, M. E. Callow, J. A. Callow, J. A. Preece, G. J. Leggett

School of Biosciences & School of Chemistry, University of Birmingham, UK; University of Sheffield, UK

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 study demonstrates the influence of surface friction on the adhesion strength between two species of fouling algae, Ulva linza and Navicula perminuta.

This Study: As the attributes of self-assembled monolayers (SAMs) can be controlled to provide useful models to investigate the influence of various surface properties on adhesion processes. In this study the adhesion of Ulva species and Navicula cells to methyl-terminated alkanethiol SAMs of varying chain length and known frictional properties, was investigated. Varying the chain length of the alkane from octyl (C₈) to octadecyl (C₁₈) results in a three-fold change in the frictional properties of the surface, whilst minimising the change in surface energy.

Ulva is a major fouling macro-alga that colonises new surfaces through motile 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).

Methods
Methyl-terminated alkanethiol self-assembled monolayers (SAMs) of carbon chain length C₈-C₁₈ were formed on the relevant alkanethiol solutions in CH₃OH. SAMs were attached to 8 × 100mm thick Au film over a Ca 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 were harvested and sprayed onto substrates
- Cells settle and are allowed to adhere by gravity
- Cells are allowed to settle for 15 min
- The settled cells are removed by rinsing with fresh microalgae culture medium

Ulva
- Ulva lineae spores are collected from Ulva lineae culture and rinsed with fresh Ulva culture medium
- Cells are allowed to settle on the substrate
- The settled cells are removed by rinsing with fresh microalgae culture medium

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

Table 1: Characteristics of a methyl-terminated alkanethiol series. - Thickness determined using an atomic force microscope. - Frictional coefficient determined using water contact angle. - Values noted were determined by friction force microscopy. - All the data have been normalised to the alkanethiol of chain length C₁₈. - The alkanethiol of chain length C₈ has been calculated using the von Arx equation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Thickness (nm)</th>
<th>θa (°)</th>
<th>Friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₈</td>
<td>0.53 ± 0.06</td>
<td>111 ± 2</td>
<td>0.51 ± 0.03</td>
</tr>
<tr>
<td>C₁₀</td>
<td>0.70 ± 0.04</td>
<td>112 ± 2</td>
<td>0.35 ± 0.04</td>
</tr>
<tr>
<td>C₁₂</td>
<td>1.45 ± 0.06</td>
<td>113 ± 2</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>C₁₄</td>
<td>1.54 ± 0.08</td>
<td>115 ± 1</td>
<td>0.29 ± 0.05</td>
</tr>
<tr>
<td>C₁₆</td>
<td>2.14 ± 0.08</td>
<td>115 ± 1</td>
<td>0.18 ± 0.05</td>
</tr>
</tbody>
</table>

Progressive extension of the alkanethiol chain 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 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 alkanethiol increases from C₈ to C₁₈, the friction coefficient of the surface drops.

This is a consequence of the intermolecular organisation of the monolayer. Short chain length thiols are disordered structures. The reduced number of methylene groups in the chain limits the potential for intermolecular interactions, primarily van der Waals forces and hydrogen bonding. This has 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 packing occurs at thiol lengths of C₁₂-C₁₄. This coincides with the onset of increasing surface roughness.

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 thiols may simply provide a greater available surface area for the wetting and interaction of the adherents.

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.

Acknowledgments
The authors acknowledge support from the AMBER project (NER/CT/2005-1181629) funded by the European Commission’s 6th Framework Programme. View expressed in this publication reflect only the authors’ views and the Commission is not liable for any use that may be made of information contained therein.

The University of Birmingham and AOPA (a Collaboration on Research into Nanoparticles) are acknowledged for financial support. The authors are grateful to Professor Mark Kendall, Professor Stephen Davies, Dr. Mark Crozier and Dr. Shaping Sun.

References