Ocean Pollution Prevention Using Non-leaching, Nontoxic Polymers as Anti-Biofouling Surface Coatings

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Marine Biofouling

Algal slime

Macrofouling: barnacles

Fouled turbidity meter

Membrane filter blocked by microbial biofilm

Images courtesy Dr. James Callow: http://www.ambio.bham.ac.uk
Marine biofouling: Increases fuel consumption up to 40% 
After 287 days in Severn River (Annapolis, MD)

Drag coefficient, $C_D = \frac{\tau_w}{\frac{1}{2} \rho V^2}$

Schultz MP, *J. Fluids Eng.* 2004, 126, 1039-1047
Economics of Biofouling

• Fuel consumption by commercial shipping fleets: 300M tons / year
• Without antifouling coatings: 420M tons / year
• A cost of $30B world-wide cost (estimate by International Paint Ltd.)
• Costs US Navy $2B per year
• Emission of green house gases
  – Fossil fuel consumption will increase by 70.6 million tons per annum = 210M tons of CO₂ and 5.6M tons of SO₂
• Global market for antifouling coatings: $700M per year
Fouling in Desalination Plants

- Fouling of heat exchanges in power plants and desalination plants: $15B per year
- Thermal desalination plants use Cu-Ni alloys as heat exchanger materials
- Brine discharge from 21 desalination plants in Red Sea were studied (Hoepner and Lattemann, 2002)
  - Combined capacity exceeds 1.5 million m$^3$/d
  - 36 kg copper (13.1 tons/year) and 9,478 kg of anti-scalants (polyacrylic acid, polymaleic acid) discharged per day into marine environment.
  - Copper concentration in discharge (15 ppb) was higher than the 3.1 ppb level recommended by US EPA.
‘Self-polishing’ Tributyltin Coatings

- Highly toxic to marine organisms
- Complete ban enforced by International Maritime Organization on January 1, 2008
Copper Biocidal Coatings

• Present day antifouling paints use Cu as biocide.
  – Major source of copper loading into the marine environment.

• Annual copper input into the 64-km stretch of Indian River Lagoon, Florida, is 3.9 tons/year (Srinivasan and Swain, 2007)

• Local copper levels exceed water quality criteria.

• Copper-based AF paints are expected to face environmental regulations similar to those faced by TBT.
Outline

• ‘Green’ approaches to tackle marine biofouling and prevent ocean pollution

1. Foul-release coatings
   – adhered organisms come off easily by flow of water past the surface

2. Antifouling coatings
   – surface is ‘invisible’ to marine organisms
   – surfaces with dynamic surface wettability
   – nanopatterned surfaces

3. Biofouling control using coatings with low elastic modulus
   – Sacrificial skin concept
Settlement and Attachment of Spores of Marine Algae *Ulva*

- **Flagellum**
- **Chloroplast**
- **Nucleus**
- **Adhesive vesicle**
- **Free swimming zoospore**
- **Adhesive pad**
- **New cell wall**

**Callow ME; Callow JA *Biologist* 2002, 49, 1**

- Location of surface; rotation on apical dome: ~1 min
- Discharge of adhesive: ~2–3 min
- Permanent adhesion; retraction of flagella; production of cell wall: ~20 min
Low Surface Energy Hydrophobic Coatings

- Adhesion strength = area of contact $\times$ work of adhesion

$$W_{SL} = \gamma_S + \gamma_L' - 2\sqrt{\gamma_S\gamma_L'}$$

=minimize this $\gamma_S$, cannot change $\gamma_L'$
Differential Scanning Calorimetry

Smectic transition temperatures of 98 °C and 113 °C

Liquid crystallinity prevents underwater surface reconstruction


Liquid Crystalline Fluorinated Block Copolymers

R1 = H (or CH₃), R2 = CH₃ (or H)

Lamellar morphology

Cylindrical morphology

Percentage removal of green algal slime

Green algae adhere poorly to fluoropolymer coatings

Percentage removal of diatoms

Diatoms adhere strongly to fluoropolymer coatings
Polymer Surfaces with Switchable Wettability

Block Copolymer Synthesis by Polymer Analogous Reactions

\[ F(\text{CF}_2\text{CF}_2)_y(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{CH}_2\text{OH} \]

\( x \sim 6, y \sim 3 \) (NMR)

DCC, DMAP

THF/pyridine mixture

RT, 64 h

\( \bar{p} = 3.5, \quad \bar{q} = 3 \)
### Underwater Surface Reconstruction

<table>
<thead>
<tr>
<th>Dynamic water contact angle</th>
<th>Advancing</th>
<th>Receding</th>
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<tbody>
<tr>
<td></td>
<td>94°</td>
<td>34°</td>
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<tr>
<th>Underwater equilibrium contact angle</th>
<th>Air</th>
<th>Octane</th>
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<tr>
<td></td>
<td>31°</td>
<td>55°</td>
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- Polymer-water interfacial energy = 4.4 mJ/m²
- cf. PDMS-water interfacial energy = 52 mJ/m²
High release of both green alga and diatoms from amphiphilic surfaces
Micropatterned Surfaces

Hypotheses

- Chemically heterogeneous surfaces ‘confuse’ algal spores and prevent spore settlement
- Chemically heterogeneous surfaces are unfavorable for protein adsorption
Semifluorinated Alkyl and PEG Groups

Semifluorinated Alkane: Hydrophobic

\( \gamma_s \approx 8 \text{ mJ/m}^2 \)

PEG: Hydrophilic

\( \gamma_d = 30.9 \text{ mJ/m}^2 \)

\( \gamma_p = 12.0 \text{ mJ/m}^2 \)
Pattern Formation by UV Lithography

1. Fluorinated SAM on silicon wafer

2. Coat with positive tone photoresist and expose to 405 nm UV

3. Develop

4. Oxygen plasma etch to remove FOTS

5. Patterned hydrophobic and hydrophilic stripes

6. Backfill with PEG
PEG BG

FOTS

325 μm

PEG

500

500, PEG stripe

FOTS

500, FOTS stripe

200

PEG
Cell Settlement on Chemically Patterned Surfaces

- Significantly lower settlement on PEGylated regions
- Greatly reduced settlement on 2 and 5 µm wide stripes
Nanostructured anti-biofouling coatings

GISAXS map of amphiphilic block copolymer thin film (left) and tapping mode AFM phase image (right). Cylindrical PS domains are oriented parallel to the substrate.

No Settlement of Barnacle Larvae on Amphiphilic Surfaces
- Force plot for determination of adhesion force of bovine serum albumin with amphiphilic copolymer surface. Negligible force of interaction between BSA and nano-structured amphiphilic surface.
Biofouling Control Using ‘Soft’ Coatings

Effects of Surface Modulus, $E$, and Work of Adhesion, $W$, on Adhesion Strength: Theory


\[
F = \pi a^2 \sqrt{\frac{2WE}{3(1-2\nu)h}} \quad \text{when } a >> h, \quad \text{and} \quad F = \sqrt{\frac{8\pi a^3 WE}{(1-\nu^2)}} \quad \text{when } a < h
\]
Experimental Approach

- Bilayer coatings
- Top layer = antifouling polymer
- Bottom layer = inexpensive, thermoplastic elastomer (also used in shoe soles)
- Use the same antifouling polymer
- But two different TPEs, with different moduli
R₁, R₂ = H or R, where R = -CH₂CH₂(OCH₂CH₂)ₓ(CF₂CF₂)ᵧ F
TPE Base Layers

A
Kraton G1652

High-modulus

Nominal Stress (MPa)

E = 18 MPa

\[ \frac{\Delta I}{I_0} \]

B
Kraton MD6945

Low-modulus

Nominal Stress (MPa)

E = 1.2 MPa

\[ \frac{\Delta I}{I_0} \]

\[ \theta_{a,w} = 107^\circ \]

\[ \theta_{r,w} = 26^\circ \]
Removal of *Ulva* Sporelings

% removal vs. Surface pressure (psi)

- **PDMS**
- **High modulus**
- **Low modulus**
Future Work

• Low modulus is desirable for fouling release.
• Mechanical stability and durability of the coating are, however, adversely affected.
• In the sacrificial skin approach, salinity responsive polymers will be used to mimic mucous layer on skins of shark, which is very effective against barnacle adhesion.
• Antifouling polymers that gel in the presence of high ionic strength seawater will be investigated.
  – Low modulus coatings that are self-healing
Acknowledgements

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F(CF₂CF₂)ₓ(CH₂CH₂O)ₓCH₂CH₂OH  \xrightarrow{CBr₄, PPh₃}  \text{(1)}  F(CF₂CF₂)ᵧ(CH₂CH₂O)ₓCH₂CH₂Br

x \sim 6, y \sim 4

\begin{align*}
m &= 135, n &= 75 \\
m &= 595, n &= 630
\end{align*}

Water Contact Angles

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<th>θₐ</th>
<th>θᵣ</th>
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<tbody>
<tr>
<td>PS₁₄k P₄VP₈k-PEG/FA</td>
<td>105°</td>
<td>21°</td>
</tr>
<tr>
<td>PS₆₂₉ P₄VP₆₆k-PEG/FA</td>
<td>112°</td>
<td>15°</td>
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Removal of Ulva sporelings from Quats

Graph showing the percentage removal of Ulva sporelings as a function of surface pressure for different materials:
- Glass
- PDMS
- SEBS
- L
- H

The y-axis represents the percentage removal, and the x-axis represents the surface pressure (kPa).