Biofouling and Anti-Biofouling Interface

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Outline
- Biofouling/Protein adsorption
- Procedure of biofouling
- Surface energy, adhesion
- Strategy of anti-biofouling
Biofouling

- Biofouling is non-desirable accumulation and growth of living matter (micro-organisms) on material surface;
- World wide problem with
  - Pulp and paper manufacturing
  - Food industry
  - Cooling tower
  - Ship hulls, fishing farms
  - Heat exchangers
  - Water desalination systems
Marine organisms and bacteria

Marine biofouling systems Algae, barnacle, mussel,

Bacteria, proteins, etc.
Procedure of Biofouling

Extracellular Polymeric Substrances (EPS)

Steps in biofilm formation

a) Formation of conditioning film
b) Primary adhesion, reversible and irreversible
c) Formation of microcolonies, surrounded by EPS
d) Development of a continuous biofilm
e) Sloughing off of biofilm parts
f) Transport of biofilm particles (flocs) throughout the system, initiation of further biofilm formation
Strategy for anti-biofouling

- Mechanical detachment of biofoulers if possible;
- Killing biofoulers using antibiotics, biocides, cleaning chemicals, etc.;
  - TBT-Silver Bullet: get rid of biofouling once and forever!
  - Toxic, banned by the year 2008

tributyltin
Strategy for anti-biofouling

- Surface engineering:
  - Low energy
  - Low adhesive
  - Non-sticking

S. Krishnan et al. J. Mater. Chem. 2008, 18, 3405
Surface Energy, the Work of Adhesion

- Work can be expressed in terms of surface energies and interfacial energies

\[ W_{AB} = \gamma_A + \gamma_B - \gamma_{AB} \]

- Contact angle \( \theta \)

\[ \gamma_{sa} = \gamma_{ls} + \gamma_{la} \cos \theta \]

- Young-Dupre equation

\[ W_{sl} = \gamma_l (1 + \cos \theta) \]
Surface Energy, the Work of Adhesion

- For an organism (O) in aqueous medium (w) in the presence of a surface (S)

- $W_{sow} = -\gamma_{so} + \gamma_{sw} + \gamma_{ow}$

- For dispersion forces $W_{AB} = \sqrt{W_{AA}W_{BB}}$

- The work of adhesion can be expressed using contact angle as

- $W_{sow} = 1/2\gamma_{w}(1-\cos\theta_o)(1-\cos\theta_s)$
Strategy I: low Energy hydrophilic surface

- \[ W_{sow} = \frac{1}{2} \gamma_w (1-\cos\theta_o)(1-\cos \theta_s) \]
- According to the equation, as \( \theta_s \) approaches zero (hydrophilic surface) the work of adhesion does too;
Strategy I: low Energy hydrophilic surface

- Interfacial energy (work of adhesion) – Strong hydrophilic interface
  - Poly(ethlyene glycol) (PEG) self-assembled monolayer (SAM)
  - OEG SAM
  - Very low surface energy about 5 mJ/m²

OEG and PEG SAM: Preparation of SAM

- Immersion
  ~ 200-500 μM Thiol solution in Ethanol

Au on Si wafer or SiO2 block for NR

12-24h
adsorption & organisation
Cell Adhesion

Steric Repulsion of Poly-EG

competing interactions:

- **attractive:**
  - van der Waals:
    \[
    \frac{\Delta F_s}{kT} = -\frac{A}{6kT} \left( \frac{R_d}{d} + \frac{R}{d + 2R} + \ln \frac{d}{d + 2R} \right)
    \]
    - hydrophobic attraction
    - entropic (excluded volume)

- **repulsive (steric, entropic):**
  \[
  \frac{\Delta F_s}{kT} = \frac{k_1}{a^2} \left( \frac{7k_2}{5k_1} \right)^{5/12} N \sigma^{11/6} \left[ \left( \frac{L_0}{L} \right)^{5/4} - 1 \right] + \frac{5}{7} \left( \frac{L_0}{L} \right)^{7/4} - 1 \]
  - osmotic & elastic
  - de/compression of PEG chains
  - solvation energy
  - long chains, high density

PEG

Long chains

Hydration

Conformational changes

Additional ‘steric’ repulsion

e.g. HS-(CH$_2$)$_{11}$-(EG)$_3$

Short chains

Pure low interfacial energy
Strategy II: low Modulus $\times$ Energy

- Only consider the interfacial energy, we have:
  
  $$W_{\text{so}} = \frac{1}{2} \gamma_{\text{w}} (1 - \cos \theta_{\text{o}})(1 - \cos \theta_{\text{s}})$$

- An organism cannot distinguish a hydrophilic surface from a watery environment and attaches preferentially to a hydrophobic surface.

- Now we consider also the mechanical property of the coating materials:
Strategy II: low Modulus x Energy

Siloxane elastomer coating
hydrophobic
Surface energy ~50 mJ/m²

- $W_{sow} = \frac{1}{2} \gamma_w (1-\cos \theta_0)(1-\cos \theta_s)$
- Peeling force: $P \sim (E\gamma)^{1/2}$
- Detaching by the weight of fouling materials
- Detaching by shearing/weight
- PDMS (polydimethylsiloxane)
Strategy III: Non-sticking structured interface
surface roughness, 3D patterning, energy and modulus

- Surface roughness leads to superhydrophobic
- Low hysterisis of contact angle
- Low friction, reduction of drag in fluid flow
  - Lotus leaf
  - Shark skin

Dermal denticles ribbed with longitudinal grooves.
Reduce vortices formation,
Water flow more efficiently
Protection from marine fouling:
against adhesion and growth of organisms
Strategy III: Non-sticking structured interface
surface roughness, 3D patterning, energy and modulus
Summary

- Biofouling is a complex procedure involving chemical, physical and biological processes.
- Current strategy focus on surface engineering:
  - Low interfacial energy: strong hydrophilic (water like)
  - Low modulus and energy (elastomers): weak peeling force
  - 3D structure: disturbing the settlement of marine organisms