Marine Biofouling Topical Conference
Room: Navajo - Session MB+BI+AS-MoA

Preventing & Characterizing Marine Biofouling
Moderator: G.P. Lopez, Duke University

2:00pm **MB+BI+AS-MoA1 Zwitterionic Polymers for Non-Fouling Coatings**, ***G. Tew***, University of Massachusetts Amherst **INVITED**

Biofouling remains a challenging problem for various fields ranging from biomedical applications and marine coatings technology, to water purification, transport, and storage systems. To date, the most widely employed protein repellent materials are poly(ethylene glycol) (PEG) or oligo(ethylene glycol) (OEG) based. Even though PEG shows excellent nonfouling character, it has low stability in the presence of oxygen and transition metal ions found in most biochemical solutions, which pushed the field to search for more robust non-fouling materials. Having hygroscopic nature similar to PEG as well as a biomimetic character, arising from their structural similarity to the head groups of lipids comprising cell membranes, zwitterions such as 2-methacryloyloxyethyl phosphorylcholine (MPC) and more recently carboxy/sulfobetaines have also been investigated as protein resistant materials. These materials concentrate only on hydrophilic modification of the substrates. However, the real biological environment is populated by different species, which have different attachment mechanisms; some prefer to adhere more on hydrophilic surfaces whereas others prefer more hydrophobic substrates. The solution to this problem has been investigated by engineering surfaces that reconstruct depending on the environment they are being exposed to, which has been found to be relatively easy to obtain with amphiphilic materials. However, these approaches are either still not sufficient to inhibit bioadhesion by themselves or they suffer from complex or labor intensive coatings preparation conditions. In this work, we are introducing a new polymeric system which carries dual functionality at the repeat unit level, a zwitterionic functionality coupled with an alkyl moiety that can be varied to adjust the amphiphilicity of the overall system. The alkyl group is varied to include PEG based, hydrocarbon, and fluorinated chains. Using these ring-opening metathesis polymerization (ROMP) based zwitterionic polymers as the foundation for non-fouling coatings, we are trying to understand what role the overall hydrophilicity/amphiphilicity of the materials play in fouling prevention.

2:40pm **MB+BI+AS-MoA3 Resistance of Saccharide-Terminated Alkylthiol Self-Assembled Monolayers to Protein Adsorption and Marine Biofouling**, ***T. Ederth***, *T. Fyrner, T. Ekblad, M. Hederos, H.-H. Lee, A. Mangone, P. Konradsson, C.-X. Du*, Linköping University, Sweden, *M.E. Pettitt, M.E. Callow, J.A. Callow*, University of Birmingham, UK, *S.L. Conlan, A.S. Clare*, University of Newcastle, UK, *F. D'Souza, G.T. Donnelly, A. Bruin, P.R. Willemsen*, TNO Science and Industry, The Netherlands, *B.G. Liedberg*, Linköping University, Sweden

The protein resistance of galactoside-terminated alkanethiol self-assembled monolayers (SAMs) can be tuned by partial methylation of the terminating saccharides, and has a non-trivial dependence on the degree of methylation [1], and for other mono- and oligosaccharide-terminated SAMs, protein resistance may vary considerably with small changes in sugar structure. We have used such mono- and oligosaccharide-terminated SAMs in a series of assays using marine fouling organisms as biological model systems, representing common micro- and macrofoulers. We investigate to what extent protein resistance properties are related to effective prevention of fouling by the marine model organisms, and discuss the results in terms of physicochemical properties of the SAMs.

[1] Hederos, M.; Konradsson, P.; Liedberg, B., *Langmuir* **2005,** 21(7), 2971-2980. DOI: 10.1021/la047203b

3:00pm **MB+BI+AS-MoA4 Influence of the Characteristics of a Mineral Coating on its Ability to Resist to the Biofouling**, ***T.H. Tran***, Ecole Nationale Supérieure des Mines de Saint Etienne, France

Mortars are building material with a high primary bioreceptivity and thus, they are easily colonized by different microorganisms... But green algae and cyanobacteria are the main which affect the aesthetics of the facade. Besides the aesthetical problem, an economical problem exists because of the expensive restoration of facade.

This work aimed to study the influence of the intrinsic parameters of a Portland cementitious mortar (roughness, porosity and surface alkalinity) on the algae development in laboratory and also in situ experiments. The degree of fouling was evaluated by means of colorimetric measurements and image analysis.

The roughness played an important role in algae establishment: the higher the roughness, the easier the algae adhesion. The carbonation, reducing surface alkalinity, shortened remarkably the latency time of the fouling onset.

From experimental results, a model was built to predict the fouling of mortar. This model was based on processes such as "germination" - growth. Each rate law was determined separately by image analysis.

3:40pm **MB+BI+AS-MoA6 Influence of Physicochemical Surface Properties on the Settlement of Biofouling Microorganisms**, ***A. Rosenhahn***, Karlsruhe Institute of Technology, Germany **INVITED**

When manmade surfaces are immersed into the ocean, biofouling rapidly occurs. To support the outphase of toxic coating formulations from the market we derive design rules for environmental benign alternatives. Therefore we study the interaction of biofouling organisms such as zoospores of the green seaweed Ulva linza with well defined surfaces and disentangle the influence of wetting, hydration, morphology, and charge. The obtained results are discussed in the context of time depending formation of conditioning layers. Especially because of its motility, the settlement step of Ulva is highly selective and crucial in their life cycle. A detailed investigation of the relevant phases of approach, exploration and eventually settlement is desired but challenging due to the quick, three dimensional swimming motions of spores. Digital in-line holography is suited for this application as time lapse holograms recorded with a single detector provide the 3D position of microorganisms with high accuracy and at a high frame rate. From such 4D tracking data, the sensitive response of spores and their interaction with surfaces has been studied. Statistical analysis of the motion pattern occurrence, velocity distributions and turning motions on surfaces with different chemical termination can be correlated with the accumulated biomass. By this we obtain quantitative access to the interaction between single spores and surfaces.

4:20pm **MB+BI+AS-MoA8 Interfacial Spectroscopy: *In situ* Approaches to Understand Sticky Contacts**, ***K.J. Wahl***, *D.E. Barlow, R.K. Everett, C.M. Spillmann*, Naval Research Laboratory, *G.H. Dickinson, B. Orihuela, D. Rittschof*, Duke University Marine Laboratory **INVITED**

Proteinaceous secretions are widely recognized to be significant contributors to marine biofouling. The resulting interfacial films can be physisorbed or chemisorbed, and have varying degrees of permanency – they may be highly polymerized and cross-linked, or simply sticky enough to allow surface exploration. Conventional approaches to examining interfacial films derived from bioadhesive junctions is forensic in nature – foulant removal (separating the surfaces) followed by *ex situ* examination of the adhesive composition and surface morphology. While "what" the adhesive is may be gleaned from *ex situ* approaches, "how" the adhesive is applied and cures cannot. These time dependent changes can't be examined "after the fact" and instead require real-time measures of interfacial interactions.

At NRL, we have made significant progress in developing *in situ* methods to demonstrate the chemical, mechanical and rheological processes in interfaces. We are now applying and extending these approaches to examine underwater adhesion in marine organisms, specifically the little striped barnacle, *Balanus amphitrite*. We are developing *in situ* and *in vivo* spectroscopic approaches to determine how protein structure and chemistry influence marine foulant adhesion. We are particularly interested in determining the structure and chemistry of the cement, the biochemical processes influencing polymerization, cross-linking, and water displacement, as well as the physiochemical nature of the adhesion. Our *in situ* approaches include performing temporally- and spatially-resolved microscopy and spectroscopy through adhesive interfaces transparent at UV, visible, IR, and x-ray wavelengths. I will describe how we have used these tools to develop new understanding of the properties and development of the adhesive interface of barnacles.

5:00pm **MB+BI+AS-MoA10 Solid State Circular Dichroism of Insoluble Bioadhesive Films: Determining Protein Secondary Structure by Concentration Independent Analysis**, ***D.E. Barlow***, *J.L. Kulp, K.J. Wahl*, U.S. Naval Research Laboratory

Far-UV circular dichroism (CD) is a valuable method for estimating protein structure components. Analysis of protein CD spectra typically requires

deconvolution to resolve overlapping bands and standard methods require that the concentration and pathlength of the sample are accurately known. While this is usually not an issue for the solution state, it is sometimes desirable or a necessity to analyze samples as solid films, complicating deconvolution. Barnacle cement is one example of a proteinaceous bioadhesive that is insoluble by standard biochemical methods and of inconsistent thickness in the native state. To analyze such samples by CD, we have applied g-factor analysis,[1] where the CD spectra are normalized by absorption spectra. This has been demonstrated as a valid, concentration independent deconvolution method, but so far has not been widely used. We will present protein secondary structure estimation results of barnacle cement films as determined by g-factor analysis and show how these results compare with those obtained by infrared spectroscopy. Potential issues and further applicability of solid state CD for bioadhesion studies will be discussed.

[1] McPhie, P. *Anal. Biochem.* **2001**, *293*, 109.

5:20pm **MB+BI+AS-MoA11 Dissipative Microbalance (QCM-D) Studies of Interfacial Processes at the Nanoscale**, ***M.A. Poggi***, Biolin Scientific

Currently there are many technologies that can study the bulk properties of nanoparticles in solution (such as light scattering) as well as experimental methods that allow one to visualize particles (microscopy or fluorescence). However, there are few technologies that can provide real-time in-situ information regarding how nanoparticles interact with other molecules or materials. Recently we have been using the quartz crystal microbalance with dissipation monitoring technology (QCM-D) to quantify the interaction of particles with surfaces and other materials (biological and organic). We will first present recently published results that address the effect of stagnant and dynamic motion of chemically modified nanoparticles on their adsorption onto silica surfaces. We were able to follow the real-time assembly (in liquid) of these chemically-modified particles. By simultaneously quantifying the changes in surface mass and viscoelasticity during the adsorption process, we were subsequently able to model the adsorption characteristics of these nanoparticles. We will also discuss recent advances that have been made in regards to using QCM-D to follow the assembly of biological nanoparticles (such as cells, viruses and lipids) and polyelectrolytes and touch upon recent electrochemical work that we have been using to study electroactive processes at interfaces.

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