Marine Biofouling Topical Conference

Room: 609 - Session MB+BI-MoA

Control of Marine Bioadhesion

Moderator: G.P. Lopez, University of New Mexico

2:00pm **MB+BI-MoA1 Engineered Polymer Coatings for Foul-Release Applications**, ***J. Genzer***, *A.E. Özçam*, *K. Efimenko*, North Carolina State University **INVITED**

Marine biofouling is a serious and complex problem resulting in losses of operating efficiency of ships. Current coating technologies derived from copper- and tin-based compounds are being banned because of detrimental effects on marine environment. Hence there is need for developing efficient marine coatings that would possess no ecological concern. In addition to various chemical approaches, surface topography has also been shown to be important for mechanical defense against biofouling. For instance, Hoipkemeirer-Wilson and coworkers reported that topographically corrugated surfaces are capable of reducing biofouling. The degree to which fouling was reduced was found to depend on the dimensions of the geometrical protrusions as well as the chemistry of the surfaces. Because biofouling includes a very diverse range of various species, whose sizes span several orders of magnitude, one single topographical pattern will not likely perform as an effective antifouling surface. Rather, surface corrugations having multiple length scales acting in parallel should be used in designing effective antifouling surfaces. We have developed a method leading to substrate comprising hierarchically wrinkled (H-wrinkled) topographies. These specimens were prepared by first uniaxially stretching poly(dimethylsiloxane) films, exposing them to ultraviolet/ozone (UVO) radiation for extended periods of time (30-60 minutes), and releasing the strain. After the strain was removed from the specimens the surface skin buckled perpendicularly to the direction of the strain. A detailed analysis of the buckled surface uncovered the presence of hierarchical buckling patterns; buckles with smaller wavelengths (and amplitude) rested parallel to and within larger buckles, forming a nested structure. At least 5 distinct buckle generations (G) were detected with their wavelengths ranging from tens of nanometers to a fraction of a millimeter. The method for producing coatings with H-wrinkled topographies may represent a convenient platform for designing foul-release surfaces. Our recent sea water immersion experiments involving testing over an extended time period indicated that these coating are far superior to flat coatings. We will discuss how the H-wrinkle topographies can be applied to make coatings from just about any type of material and offer methodologies for preparing amphiphilic foul-release coatings from commercially available materials. While more work still needs to be done, the initial observations suggest that the H-wrinkled coatings may represent a new and promising platform for fabricating efficient foul-release marine coatings.

2:40pm **MB+BI-MoA3 Nanoscopically-resolved Amphiphilic Surface Features as Non-toxic, Treacherous Terrain to Inhibit Marine Biofouling**, ***K.L. Wooley***, Washington University in Saint Louis **INVITED**

This presentation will detail amphiphilic nanostructured material systems, constructed from a general methodology that involves the kinetic, in situ crosslinking of thermodynamically-driven phase segregated states of polymer assemblies. Macroscopic crosslinked networks composed of amphiphilic nanodomains presented on the surface and dispersed throughout the material are obtained by crosslinking of the assemblies in bulk samples. Of particular interest for these materials are the complex surface topographies and morphologies that allow for the materials to exhibit antifouling characteristics. The crosslinked macroscopic networks have been focused upon compositions that include hyperbranched fluoropolymers and linear poly(ethylene glycol)s, although the compositional profiles are being expanded. The domains or channels that are present throughout the samples offer interesting opportunities for the packaging and release of guest molecules. The nanoscale dimensions and large interfacial surface areas provide for high loading capacities within uniform host environments, but then also promote the release of these guests at significantly reduced temperatures. The uptake and release of guests from hydrophobic vs. hydrophilic, of varying compositions, structures, and sizes, will be discussed. Most recently, unique mechanical properties have also been observed, and these data will also be presented.

3:40pm **MB+BI-MoA6 Basic Surface Properties and Their Influence on the Adhesion of Marine Organisms**, ***A. Rosenhahn***, University of Heidelberg, Germany **INVITED**

The prevention of biofouling is a major challenge for all man made objects which are in long term contact with seawater. In order to systematically develop non toxic coatings, a fundamental understanding of basic surface properties that inhibit or encourage settlement of marine inhabitants is required. Together with biological partner groups within the EU IP AMBIO[1] we investigate the influence of surface properties such as wetting, charge or morphology on the adhesion and on the removal properties for different marine organisms. To tune wetting and chemical surface properties, self assembly is used as highly versatile technique. For preparation of well defined micro- and nanomorphologies, different lithography and multilayer approaches are used. The interaction of different marine inhabitants with these surfaces will be discussed and compared to general protein resistive properties. Although one main focus of this work is inhibition of settlement, also release properties are tested as important measure of adhesion strength. Apart from established ways of evaluating anti fouling properties, we use digital in-line holography as new tool to study and compare the exploration of different surfaces by swimming marine organisms.[2] Following the original idea of D. Gabor,[3] coherent scattering of radiation can be used to record scattering patterns which contain three dimensional information about investigated objects due to the presence of a reference wave. Holography therefore allows the investigation of three dimensional processes e.g. by tracking particles in real time with sub¬micrometer resolution.[4] We use this novel technique to visualize and analyze the motion and exploration behavior of swimming marine organisms towards surfaces with systematically changing properties. The goal of these three dimensional tracking experiments is to gain a more detailed understanding about surface sensing and the early attachment stages of marine organisms.

[1] Ambio : Advanced Nanostructured Surfaces for the control of biofouling, FP6 EU integrated project, http://www.AMBIO.bham.ac.uk/

[2] M. Heydt, A. Rosenhahn, M. Grunze, M. Pettit, M.E. Callow, J.A. Callow, The Jornal of Adhesion, in press

[3] D. Gabor, Nature 1948, 161, 777

[4] W.Xu, M.H. Jericho, H.J. Kreuzer, Opt. Lett. 2003, 28(3), 164

4:20pm **MB+BI-MoA8 Bioresponse to Engineered Topographies**, ***A.B. Brennan***, University of Florida **INVITED**

This study examines hierarchical combinations in polymers that have been used to produce engineered surfaces, which elicit micro-topographical and chemical cues in biological systems. Nature provides complex chemical forms of polymers that are manipulated through both conformational and configurational forms to yield specific functions. Our recent studies have been focused on the design of polymeric surfaces that can be used as models in the study of biological adhesion mechanisms. The recent expansion of bioengineering has increased our need for better models of cellular adhesion and chemical manipulation of surfaces. A process commonly referred to as contact guidance has been shown to modulate cell shape and function in a variety of cell types. Control of endothelial cell (EC) shape using micropatterned chemical substrates is shown in numerous studies by influencing cell adhesion to proteins, which selectively adsorb to the chemical micropatterns. This presentation will focus on the polymer structures that we have been developing for a topographically modified surface with a range of surface energies and bulk modulus values developed through nanostructural modifications on larger microstructures. In this model, we have been able to study the interactions of the biological-induced factors with the polymer chemistry.

5:00pm **MB+BI-MoA10 Development of Environmentally Benign and Durable Nonfouling Marine Coatings**, ***S. Jiang***, University of Washington

Biofouling on ship hulls and other marine surfaces has become a global environmental and economic issue. Traditionally, the best antifouling coating is TBT (tributyltin)-based paint. Due to increased environmental concern, TBT antifouling coatings have been restricted. Non-toxic, fouling-release coatings based on silicone or fluorinated compounds are under development. These coatings are only effective on vessels moving at high speeds. Currently, we are developing environmentally benign, durable, and cost-effective nonfouling coatings, to which marine microorganisms can not attach, as the next-generation marine coatings. In this work, zwitterionic-based materials will be shown to be effective against various marine microorganisms in laboratory and field tests. We have demonstrated for the first time that poly(sulfobetaine methacrylate) [p(SBMA)] and poly(carboxybetaine methacrylate) [p(CBMA)] based materials and coatings are superlow biofouling. In addition, we have explored various approaches to apply p(SBMA) or p(CBMA) materials onto surfaces and developed several noncoatings for marine applications. Laboratory tests confirmed the excellent performance of sulfobetaine (SB)-based coatings against marine microorganisms (Ulva spores and barnacle cypris larvae). Recently, we developed SB-based paints and spray-coated them onto surfaces covered with an epoxy primer. Initial field tests of these panels clearly demonstrated that our coatings effectively deferred the settlement of hard foulants. Because of their excellent stability and high effectiveness at preventing microorganisms from adhering to surfaces, SB and carboxybetaine-based materials are excellent candidates for marine coatings. The objective of our work is to create products that will effectively defer biofouling under static conditions over a long period of time.

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