

# Monday Afternoon, October 31, 2011

## Marine Biofouling Focus Topic

Room: 105 - Session MB+BI+PS-MoA

## Marine Antifouling Coatings

Moderator: A. Rosenhahn, Karlsruhe Institute of Technology, Germany

2:00pm **MB+BI+PS-MoA1 Advances in Sustainable Technologies for the Prevention of Marine Biofouling**, R. Deshmukh, University of Texas at Arlington, P. Sheth, University of North Texas Health Science Center, R.B. Timmons, University of Texas at Arlington, J.A. Schetz, University of North Texas Health Science Center

INVITED

The cost associated with preventing the attachment of marine organisms to underwater surfaces (biofouling) is billions of dollars annually impacting numerous sectors including shipping, aquaculture, offshore drilling, and offshore tidal and wind power. Invariably the most effective biofouling control methods are ones that are biocidal in nature whereby a coating is impregnated with a toxin that leaches out over time. However, persistence and bioaccumulation of heavy metal-based and organic biocides, creates environmental and health problems that have resulted in their regulation. Vigorous hull cleaning, aimed at periodically removing biofouling organisms, disperses fine biocide-impregnated coating particles and this significantly increases biocide persistence in sediments where they are ingested by a variety of marine organisms and bioaccumulate.

Coatings that peel off under conditions of high shear, so called foul-release coatings, are another approach but such coatings are easily damaged, not amenable to grooming and ineffective against microfouling. Further, the most effective foul-release coatings are silicon-based and it is becoming increasingly apparent that leaching of toxic silicon oils from the coating matrix plays a role in their superior antifouling performance. Other approaches have been to develop durable coatings with little antifouling activity but that can withstand repeated intense grooming. One of our long term objectives is to identify coating materials with surface properties discouraging the settlement of biofouling organisms but also durable enough to withstand cleaning.

Here we report on the discovery of a transparent, conformal, pin-hole free, and plasma-polymerizable polymer coating made from an inexpensive monomer material that drastically reduces (>90%) algae (*Ulva*) sporeling settlement and biomass accumulation without any observable toxicity towards *Ulva* or a non-target brine shrimp species (*Artemia*). Further the unpolymerized monomer has no antifouling effect indicating that potential leaching of monomer from coated surfaces does not account for the observed antifouling activity. Rather the antifouling effect is believed to rely on the presence of a specific chemical moiety because chemical modification of that moiety abolishes antifouling activity. Testing of other marine antifouling species such as microfouling bacteria (*Cellulophaga*) and macrofouling mussels (*Ischadium*) suggests that the antifouling properties of the polymer surface are selective for algae. Potential unique applications for this technology include the coating of algae bioreactor walls or light fixtures allowing for maximal illumination and easy cleaning.

3:00pm **MB+BI+PS-MoA4 Development of a Comparative Protocol for Anti-Fouling Surfaces Based on Polymer Brushes**, A. Serrano, S. Zürcher, S. Tosatti, SuSoS AG, Switzerland, N.D. Spencer, ETH Zurich, Switzerland

Marine surfaces are known to accumulate fouling material through the starting point of adhesion and settlement of proteins and cells. This effect can be manipulated through the modification and control of the substrate properties via surface functionalization. This approach has led to successful anti-fouling coatings based on biocidal agents containing copper or zinc compounds<sup>1,2</sup>. The environmental toxicity of these latter materials, however, has increased the demand for less adverse coatings. The use of ultra-thin films consisting of polymer brushes has been considered a promising alternative and many studies have been published in this field<sup>3,4</sup>. None, however, has focused on developing a protocol that allows a reliable comparison between the efficiency of different well-known anti-fouling polymers. This is one of the aims of this work and has been achieved by using a common, azide-terminated monolayer to which different non-fouling polymers, such as PEG, PEOXA, PVP and PVA, have been covalently bound. The different materials were compared by characterizing the structure-property relationship of the formed polymeric brushes. Also investigated was the role of the solvent used in the anti-fouling polymer solution as a key element to better control the surface homogeneity. A thorough analysis of the influence of this parameter on the conformation of the final polymer brush was based on ellipsometry, XPS and imaging ToF-

SIMS. Finally, the anti-fouling surfaces were subjected to a comparative biological study by exposure to complex proteins solution and *Ulva* zoospores, in order to validate the developed protocol.

References:

- [1] Magin, C.M.; Cooper, S.P.; Brennan, A.B., *Materials Today*, **2010**, *13*, 36-44.
- [2] Chambers, L.D.; Stokes, K.R.; Walsh, F.C.; Wood, R.J.K., *Surface & Coatings Technology*, **2006**, *201*, 3642-3652.
- [3] Banerjee, I.; Pangule, R.C.; Kane, R.S., *Advanced Materials*, **2011**, *23*, 690-718.
- [4] Krishnan, S.; Weinman, C.J.; Ober, C.K.; *Journal of Materials Chemistry*, **2008**, *18*, 3405-3413.

3:40pm **MB+BI+PS-MoA6 Surface Modification of Polymers via Self-Stratification: Decoupling of Bulk and Surface Properties**, D.C. Webster, North Dakota State University

INVITED

Since materials interact with their surroundings via their surfaces, controlling the surface properties of a material are of critical importance. For materials to be used to mitigate biofouling, having the correct surface properties means the difference between a useful material and one that is unsuitable for the application. In many cases, the material properties of compositions which yield useful surface properties are not suitable for the bulk properties of the material. Thus, being able to decouple the surface and bulk properties is of interest in many areas.

Combining polydimethylsiloxane (PDMS) with other polymer systems generally results in materials covered with PDMS due to its low surface energy and incompatibility with other polymers. However, if the PDMS is not chemically bound into the system, it can be easily removed from the surface. Thus, forming a copolymer of the PDMS with the other polymer is required for a durable system. Since polyurethanes are known as tough polymers due to extensive internal hydrogen bonding, combining PDMS with a polyurethane could lead to a material which is tough, but has a low surface energy surface provided by the PDMS. Thus, we have found that incorporating a reactive PDMS into a crosslinked polyurethane system can result in a material which has a low surface energy which is stable when immersed in water. High throughput screening has been used to aid in the identification and optimization of PDMS molecular weight, composition of end groups, and the amount of PDMS in the coating. A unique coating was also identified having discrete domains of PDMS on the surface. Coatings having good fouling-release properties have been prepared and tested in ocean immersion testing.

4:20pm **MB+BI+PS-MoA8 Antifouling Behavior on the Surface of Polyelectrolyte Brushes in Water**, M. Kobayashi, M. Terada, Jst, Erato, Japan, A. Takahara, IMCE, Kyushu University, Japan

Nature utilizes super-hydrophilic surfaces under wetted state by water to achieve oleophobicity and self-cleaning behavior. For example, fish can maintain a clean body surface by surrounding a thin layer of mucus containing calcium phosphate and protein, which protects oil attachment, marine fouling, and adhesion of marine organisms. In this study, high-density hydrophilic polymer brushes were prepared on Si-wafer by surface-initiated controlled radical polymerization of methacrylate monomers with ionic functional groups.[1] For example, poly(3-sulfopropyl methacrylate potassium salt) (PSPMK) and poly[2-(methacryloyloxy)ethyl phosphorylcholine] (PMPC) brushes with 50 - 100 nm thickness repelled both of air bubble and hexadecane droplet in water.[2] Even when the silicone oil was spread on the polyelectrolyte brush surfaces in air atmosphere, once the oil-sitting brush substrates were immersed in water, the oil quickly rolled up and detached from the brush surfaces due to the low adhesion force between the brush and oil caused by excellent affinity of polyelectrolyte brushes to water. Similar oil detachment behavior was observed on the hydrophilic poly(sodium methacrylic acid) (PMANa) and poly[3-(dimethyl(2'-methacryloyloxyethyl)ammonio) propanesulfonate (PMAPS) brushes.[3] whereas the oil still remained attached on the hydrophobic poly(2-perfluorooctylethyl acrylate) (PFA-C8) brush even though the PFA-C8 brush shows relatively oleophobic property under air atmosphere. These hydrophilic brush surfaces would contribute to the excellent self-cleaning, antifogging, and antifouling properties without any surfactants

[1] M. Kobayashi, M. Terada, Y. Terayama, M. Kikuchi, A. Takahara, *Macromolecules* 2010, 43 8409.

[2] M. Kobayashi, Y. Terayama, N. Hosaka, M. Kaido, A. Suzuki, N. Yamada, N. Torikai, K. Ishihara, A. Takahara, *Soft Matter* 2007, 3, 740.

[3] Y. Terayama, M. Kikuchi, M. Kobayashi, A. Takahara, *Macromolecules* 2011, 44, 104.

4:40pm **MB+BI+PS-MoA9 Non-fouling Polymer Chemical Gradients for the Investigation of Marine Bioadhesion**, *O. Sterner*, ETH Zurich, Switzerland, *S. Zürcher*, SuSoS AG and ETH Zurich, Switzerland, *S. Tosatti*, SuSoS AG and ETH Zurich, Switzerland, *N.D. Spencer*, ETH Zurich, Switzerland

The accumulation of marine organisms on submerged man-made structures (referred to as marine biofouling) has great economical and environmental impact [1]. Numerous strategies to prevent or lower the extent of marine biofouling have been developed, ranging from biocidal coatings to coatings that either prevent adhesion, lower the strength of adhesion or combinations thereof [2-4]. Surface gradients offer a high-throughput approach to investigate the potency of such coatings, and have the additional advantage of reducing the error in experiments by replacing a set of single samples, including positive and negative controls, with a single substrate [5]. In this project, polymeric ultrathin coatings have been prepared using a versatile surface functionalization system based on a self-assembled monolayer of poly(allyl amine) grafted with photo sensitive perfluorophenyl azide functional groups. Gradients have been prepared using a straightforward approach to control the extent of azide to nitrene conversion over the surface, forming a polymer density gradient. Gradients of poly(ethylene glycol), poly(2-ethoxy-2-oxazoline) and poly(vinyl pyrrolidone) have been prepared and investigated for non-fouling action against zoospores from green macrofouling algae *Ulva* and two strains of marine bacteria. The gradients reveal a drastic reduction in bacterial adhesion at low polymer densities for all polymers investigated. Gradients have been characterised with variable angle spectroscopic ellipsometry (VASE) and the properties of the polymer coatings have been evaluated with time-of-flight secondary ion mass spectroscopy (TOF-SIMS) and XPS.

#### References:

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2. Chambers, L.D., et al., *Surf Coat Tech*, 2006. (6): p. 3642-3652.
3. Grozea, C.M. and G.C. Walker, *Soft Matter*, 2009. (21): p. 4088-4100.
4. Krishnan, S., C.J. Weinman, and C.K. Ober, *J Mater Chem*, 2008. (29): p. 3405-3413.
5. Morgenthaler, S., C. Zink, and N.D. Spencer, *Soft Matter*, 2008. (3): p. 419-434.

5:00pm **MB+BI+PS-MoA10 Development of Poly(silyl urethanes) with Tethered Quaternary Ammonium Biocides as Antifouling Marine Coatings**, *P.N. Coneski*, *N.K. Weise*, *J.H. Wynne*, Naval Research Laboratory

Due to the significant economic burden posed by high operational and maintenance costs of biofouled ships, the design of environmentally benign, antifouling marine coatings has been a significant interest for many researchers since the ban on traditional coatings was enacted. Current approaches for developing new marine coating materials have primarily focused on the preparation of low surface energy materials, such as modified polydimethylsiloxane (PDMS) and fluorinated polymers. These materials have shown great promise for reducing the adhesion strength of various fouling organisms, thus allowing hydrodynamic forces to release the foulants as the ship moves through water. Unfortunately, no existing material has been shown to eliminate adhesion of all of the numerous different fouling organisms, including zoospores, microalgae and diatomaceous species. As such, the development of marine coatings with multiple mechanisms of fouling prevention may be an important avenue of antifouling materials research. Poly(silyl urethanes) coatings have been developed via the reaction of various quaternary ammonium modified orthosilicates with polyisocyanates. Material properties including glass transition temperature, surface energy, and thermal stability have been investigated as a function of orthosilicate and polyisocyanate composition as well the inclusion or omission of low surface energy soft segments. The low surface energy of these materials should provide excellent fouling release properties, as has been seen with other PDMS-like materials, while the inclusion of bound quaternary ammonium biocides should further reduce the adhesion and propagation of fouling organisms at the material interface. Finally, the hydrolysable silyl ether crosslinking may prove to enhance the antifouling capabilities of these materials by allowing any fouled portions of the coating to slough away over time, generating a new active biocidal interface.

5:20pm **MB+BI+PS-MoA11 A Preliminary Study on Porous Pt-TiO<sub>2</sub>/Ti Electrodes with Electrochemically Microbubble-Induced Superhydrophobic Surfaces for Drag Reduction and Antifouling**, *K.R. Wu*, *C.H. Hung*, *C.W. Yeh*, *J.C. Sun*, *J.K. Wu*, National Kaohsiung Marine University, Taiwan, Republic of China

We investigate a novel device that features a reduction in frictional resistance and antifouling hull surface of seagoing ships which are activated electrochemically by a series of porous Pt-TiO<sub>2</sub>/Ti electrodes. This device includes of a series of anodic and cathodic porous Pt-TiO<sub>2</sub>/Ti electrodes insulatedly mounted on the hull surfaces of which are electrically connected to a direct current (DC) power supply. The above-mentioned porous Pt-TiO<sub>2</sub>/Ti electrodes are fabricated by two steps; porous TiO<sub>2</sub>/Ti plates are firstly prepared on pure titanium plates via a micro-arc oxidation technique and Pt nanoparticles are thereafter deposited on the porous TiO<sub>2</sub>/Ti samples using magnetron sputtering. The DC power supply provides an adequate DC bias to the Pt-TiO<sub>2</sub>/Ti electrodes where hydrogen and oxygen microbubbles are electrochemically nucleated and formed herein in seawater. As a result, the microbubble-induced superhydrophobic surfaces are created and the reduction in frictional resistance and antifouling hull surface are obtained. Our preliminary tests reveal that no attachment organisms are found on the Pt-TiO<sub>2</sub>/Ti electrodes after 15 days of field seawater tests at an applied potential of 1.2 V and an energy consumed rate of about 4 W/m<sup>2</sup>. On the other hand, organisms, mainly *Crassostrea gigas* and barnacles, attached and grew on the Pt-TiO<sub>2</sub>/Ti electrode that was not applied a DC potential. That is to say that attachment of organisms can be prevented. Furthermore, the Pt-TiO<sub>2</sub>/Ti electrodes yields a gas production rate of 800 cm<sup>3</sup>/min m<sup>2</sup> by electrolysis of seawater at an energy consumed rate of about 18 W/m<sup>2</sup>. Hence, the microbubble-induced superhydrophobic surfaces can be realized with this gas production rate for drag reduction of the ship hull.

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