

Fundamental Aspects of Material Degradation Focus Topic Room A212 - Session DM1+BI+SS-ThA

Low Fouling Interfaces and Environmental Degradation

Moderator: Axel Rosenhahn, Ruhr-University Bochum

2:20pm DM1+BI+SS-ThA-1 Utilizing Experimental and MD Simulation Approaches in the Understanding and Design of Low Fouling Interfaces, *Paul Molino*, University of Wollongong, Australia

INVITED

Biofouling is a ubiquitous problem for a diverse suite of industries, impacting the functionality of materials and devices. Diverse approaches taken in the design of materials and interfaces to prevent microbial fouling often rely on atomic and molecular scale processes, however the fundamental mechanism/s underlying these processes, and their mode of action, in many cases continue to elude researchers. Highly hydrophilic chemistries such as polyethylene glycol and zwitterion-based chemistries, have long been used to generate interfaces that prevent biological interactions at surfaces. Such surface chemistries have been proposed to function through a combination of molecular water organisation and steric repulsion at the interface. Experimental approaches have confirmed the presence of hydration layers associated with hydrophilic polymer-based surfaces, yet the fundamental mechanisms underlying their capacity to inhibit surface fouling, and how such hydration layers differ from equally hydrophilic interfaces that do not prevent surface fouling is still unclear. Molecular dynamic (MD) simulations have gone some way to provide critical insights into their respective mechanism/s of action, however experimental approaches capable of adequately resolving features at a suitable spatial resolution to corroborate and build on these models have been lacking. Herein I will present a highly biofouling resistant coating composed of silica nanoparticles functionalised with a short chain hydrophilic silane. To understand the interfacial environment at the hydrated nanoparticle surface, frequency modulation – atomic force microscopy was used to provide sub-atomic resolution of the water structuring about the nanoparticle interface, which we validate using all-atom molecular dynamic simulations that strikingly predict similar structures of water layers on the original and ultralow fouling surfaces. The convergence of experimental and modelling data reveals that suitably spaced, flexible chains with hydrophilic groups interact with water molecules to produce a connective, *quasi-stable* layer, consisting of dynamic interfacial water, that provides a basis for antifouling performance of ultrathin, hydrophilic surface chemistries. This approach provides a road map for the future development and optimisation of interfacial chemistries and materials designed to combat biofouling and biodegradation.

3:00pm DM1+BI+SS-ThA-3 Study of Environmental Exposure Effects on Pristine and DC Magnetron Sputtering Metallic Coated 3D Printed Polymers, *D Mihut, Arash Afshar, P Chen*, Mercer University

Three dimensional printing is a promising technique for producing complex geometries and high precision structures from different types of materials. The technique is particularly attractive for polymeric materials due to the cost effectiveness; however when compared to other manufacturing techniques the resulting structures have low mechanical properties and low performance as exposed to harsh environmental conditions. ABS (acrylonitrile butadiene styrene) and PLA (polylactic acid) are common thermoplastic polymers used for many applications (e.g. electrical and electronic assemblies, medical devices, implants, toys). For this research, the ABS and PLA specimens for tensile and flexural testing were 3D manufactured according to standards and their mechanical properties were tested using hardness tester, and Mark-10 tensile testing equipment. In order to simulate outdoor environmental conditions while avoiding the uncertainties associated with it, specimens were exposed to controlled environmental chamber. Accelerated exposure was performed using a UV radiation/condensation (Q-Lab QUV/basic) accelerated weathering tester. ABS and PLA samples were exposed to UV radiation, high temperature and moisture cycles for different time intervals. Some ABS samples were coated with optically thick metallic materials (silver and copper) using high vacuum DC magnetron sputtering deposition system and were later exposed to UV radiation, high temperature and moisture cycles using same conditions as for un-coated samples. The surface and cross section morphology of samples and the adhesion of metallic layers to the polymer substrates were examined using scanning electron microscopy and laser scanning microscopy. The crystalline structure of the metallic coatings was analyzed using X-ray Diffraction technique. The mechanical properties were characterized using flexural and hardness tests over the exposure time. The

metallic thin films improved the surface resistance of the substrate materials and enhanced the mechanical behavior of samples exposed to harsh environmental conditions.

3:20pm DM1+BI+SS-ThA-4 Reaction Mechanism of Chloride-induced Depassivation of Oxide Films: a Density Functional Theory Study, *Q Pang, H DorMohammadi, K Oware Sarfo, P Murkute, Y Zhang, O Isgor, J Tucker, LÍney Árnadóttir*, Oregon State University

A protective iron oxide film (passive film) forms on the surface of iron in alkaline environment, such as in reinforced concrete. Chloride and other aggressive ions can cause the breakdown of the passive film (depassivation) in the same environment, leading to active corrosion. The mechanism of the Cl-induced depassivation is studied on flat and stepped $\alpha\text{-Fe}_2\text{O}_3$ (0001) surfaces because $\alpha\text{-Fe}_2\text{O}_3$ has been suggested to be one of the dominant oxides in the outer layer of the passive film.

The oxidation state of the surface metal atoms plays an important role in Cl-surface interactions and depassivation. Cl binds more strongly to metal atoms at lower oxidation state and these adsorption sites can facilitate higher local coverage. Defect sites, such as on a step edge or next to a O vacancy have lower oxidation states, suggesting an important role of defects in the depassivation process. Two main mechanisms of depassivation have been proposed in the literature, the point defect model that proposes a depassivation through Cl enhanced Fe vacancy formation on the surface and void formation at the metal oxide/metal interface, and the ion exchange model, which proposes a depassivation mechanism through subsurface Cl. Our studies of the thermodynamics of Cl ingress into the passive film, Fe vacancy formation, and bulk vacancy stability all support the point defect model for iron oxide. The initial stages of Cl-induced depassivation are proposed through a combination of reactive force field molecular dynamics simulations and DFT calculations.

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