Biomaterial Interfaces Division
Room 318 - Session BI+AS+PS-MoM

Biomolecular Interfaces and Underwater Adhesion
Moderator: Morgan Alexander, University of Nottingham, UK

8:20am **BI+AS+PS-MoM-1 Supported Lipid Bilayers as Model Systems to Understand Molecular Interactions at Complex Solid/Liquid Interfaces***, **Pierluigi Bilotto**,* Centre for Electrochemistry and Surface Technology, Austria*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria

Generating a detailed molecular understanding of complex, simultaneous inter actions at reactive and/or dynamic solid|fluid interfaces is a challenge across disciplines, and has intrigued researchers for decades.[1, 2] Whether it is, for example, in medical adhesives, friction of articular cartilage,[3] or the adhesion of organisms in seawater,[2] complex macroscopic properties at crowded biologic solid|liquid interfaces are mediated by large numbers of individual nanoscale interactions.[4] Exactly this complex competition and molecular structuring at interfaces are central to a multitude of interfacial phenomena, such as membrane transport,[5] membrane conductance, [6,7] cellular adhesion [8] and adhesion regulation in the marine environment. [9]

In our previous works, we characterised a lipid-based model system (LMS) in terms of its stability and bending properties by employing atomic force microscopy and surface forces apparatus. [10] Then, we further modified its outer face with amine-terminating polymers to investigate the specific electrostatic interaction between the amine and a negatively charged mica surface. Then, we examined how interaction forces are affected by the electrolyte concentration, funding a direct exponential like decay between adhesion and electrolyte concentration. Specifically, we found a decrement of 90% in adhesion in a 1M sodium chloride environment. These fundings suggested the presence of a competing mechanism which was confirmed by a kinetic model at the interface involving two competing Langmuir isotherms. Finally, we could estimate ion/surface interaction energies from the experimentally recorded interaction force measurements.[11]

In the talk we will discuss these works and present the new research opportunities coming out from these results.

(1) Israelachvili, J.; Wennerstr̈om, H. Nature 1996, 379, 219–225

(2) Stock, P. *et al,* ACS Nano 2017, 11, 2586–2597

(3) Shoaib, T. *et al,* Biomater. Sci. 2020, 8, 3944–3955

(4) Cai, L. *et al,* ACS Nano 2017, 11, PMID: 28383885, 3727–3732

(5) Gage, P. W.; Quastel, D. M. J. The Journal of Physiology 1966, 185, 95–123

(6) Stieve, H.; Bruns *et al* Zeitschrift f̈ur Naturforschung C 1978, 33, 574–579

(7) Stieve, H.; Pflaum *et al,* Zeitschrift f̈ur Naturforschung C 1985, 40, 278–291

(8) Ohgaki, M. *et al,* Journal of Biomedical Materials Research 2001, 57, 366–373

(9) He, X.; *et al,*Colloids and Surfaces B: Biointerfaces 2016, 146, 289–295

(10) Bilotto, P.; Lengauer, M.; *et al* Langmuir 2019, 35, 15552–15563

(11) Bilotto, P *et al* ACS Physical Chemistry Au 2021, 1, 45-53

8:40am **BI+AS+PS-MoM-2 Recombinant Lubricin Improves Anti-Adhesive, Wear Protection and Lubrication of Collagen II Surface***, H. Yuan,* Tianjin University, China*; **Laura Mears**,* Vienna University of Technology, Austria*; R. Su,* Tianjin University, China*; M. Valtiner,* Vienna University of Technology, Austria

Lubrication in articular joints is regulated by a number of biomolecules including the collagen of the cartilage, lubricin and lipids in the synovial fluid. Camptodactyly-arthropathy-coxa vara-pericarditis syndrome (CACP) is a joint disease, which causes a lack of lubricin, leading to failed lubrication as well as abnormal deposition at cartilage surfaces. Injection of recombinant lubricin (R-LUB) is a promising way to treat the disease. Here, the protein adsorption and lubrication behavior of type II collagen (COL II), mimicking the cartilage surface, upon R-LUB injection were followed by a surface plasmon resonance spectroscopy and surface forces apparatus. The results indicated R-LUB can bind well on COL II surface and the layer of COL II/R-LUB complex exhibited a much lower nonspecific adsorption of BSA (3.25 ng/cm^2) and LYS (0.26 ng/cm^2) compared to those of the COL II layer (32.7 ng/cm^2, 7.26 ng/cm^2), respectively. Normal force measurement demonstrated there were repulsive forces between the COL II/R-LUB complex and different surfaces with -COO^-, -NH_3^+ and -CH_3 groups. Likewise, COL II had a high coefficient of friction ($\mu\sim0.48$) with surface damage at 2 μm/s and wear pressure of 1.56 MPa. In contrast, the coefficient of friction of COL II/R-LUB complex was dramatically decreased to ∼0.014-0.13 with surface damage at 13 μm/s, the complex even shows an ultralow coefficient of friction of 0.008 at the lowest loading <3 mN. Furthermore, R-LUB modification boosts the strength of the surface against abrasive wear (damage) of 11.96 MPa, which was 7.7 times higher than that of COL II alone. Hence, R-LUB may act as an anti-adhesive and lubrication layer adsorbed on COL II surfaces to develop strong steric-repulsive interactions and lubrication to prevent direct surface contact. Our results provide fundamental insights into the adsorption and lubrication behavior for understanding biological lubrication, especially using R-LUB for CACP disease treatment.

9:40am **BI+AS+PS-MoM-5 Hyaluronic Acid-Dopamine Conjugate for Facile Deposition onto Collagen I with Enhancing Anti-Adhesion and Lubrication***, H. Yuan,* Tianjin University, China*; L. Mears, M. Valtiner,* Vienna University of Technology, Austria*; **Rongxin Su**,* Tianjin University, China

Collagen I matrix (COL I) has been applied clinically for repairing damaged cartilage, but it has poor protein resistance and insufficient lubrication performance, which seriously affects the repairing performance for cartilage. Hyaluronic acid (HA) has good anti-adhesive and lubrication properties, and seems to be a potential candidate to improve treatment with COL I, but it cannot be immobilized onto the collagen surface. Inspired by mussels, dopamine (DA) was chemically grafted to HA to form the HADA conjugate, which could firmly adhere to the surface of COL I by dopamine oxidation and reacted with amine from COL I. The protein resistance and lubrication properties of COL I and HADA-modified COL I (COL I/HADA) surfaces were followed by quartz crystal microbalance with dissipation and surface force apparatus techniques. The optimal modified time of HADA on COL I surface was 8 h. The nonspecific adsorption of bovine serum albumin (BSA) and lysozyme on COL I/HADA were reduced to 1/25 and 1/42 of that on COL I. COL/HADA also displayed very good resistant to high concentrations of BSA. Upon HADA modification, the interaction force between COL I and the surfaces with positive and negative charges sharply decreased from 2-6 mN/m to 0, demonstrating that the COL I/HADA surface had a strong anti-adhesion property. The coefficient of friction of COL I (∼0.65) was quite high displaying poor lubricating ability, while that of COL I/HADA reduced to ∼0.16. Upon HADA modification, the wear occurred at a shear rate of 14 μm/s, and the surface resistance to abrasive wear (damage) was greatly improved to 9.7 MPa, about 12 times higher than the COL I surface. These results indicated that HADA-modified COL I is a promising anti-adhesive and lubricating joint repair material, especially in the field of osteoarthritis treatment.

10:00am **BI+AS+PS-MoM-6 Anti-Fouling Properties of Amphiphilic Zwitterionic Hydrogels***, **Lisa Schardt**,* Ruhr University Bochum, Germany*; A. Martínez Guajardo,* University of Potsdam, Germany*; J. Koc,* Ruhr University Bochum, Germany*; J. Clarke, J. Finlay, A. Clare,* Newcastle University, UK*; H. Gardner, G. Swain, K. Hunsucker,* Florida Institute of Technology*; A. Laschewsky,* University of Potsdam, Germany*; A. Rosenhahn,* Ruhr University Bochum, Germany

Hydrogels exhibit excellent biocompatibility and resistance against nonspecific attachment of organisms most likely due to their stable hydration shell.[1] Zwitterionic polymers like the sulfobetaine N-(2-methacryloxy)-ethyl-N,N-dimethylammoniopropansulfonate (SPE) are promising candidates foranti-fouling coatings. However, due to low mechanical strength, their performance in the field is limited.[2] N-butyl methacrylate (BMA) was added in amounts between 0 and 50% to copolymers containing SPE and the photocrosslinker 2-(4-benzoylphenoxy)ethyl methacrylate (BPEMA) to tune the hydrophilicity of the resulting hydrogel properties. The rearrangement of the polymer upon immersion in seawater was characterized by under-water contact angle goniometry. The swelling and resistance against mineral particles were measured with surface plasmon resonance (SPR) and sediment immersion tests. Biological anti-fouling experiments were performed using *Ulva linza* and field tests. Upon immersion in saltwater, the polymer chains rearranged to form hydrophilic surfaces and the degree of swelling depended on the salt concentration. The incorporation of BMA successfully altered the mechanical properties of the coatings resulting in a lower silt uptake. At the same time, the amphiphilicity did not hamper the anti-fouling performance in laboratory assays and a decrease of the settlement was observed in field tests.[3]

[1] A. Laschewsky, *Polymers*, **2014**, 6, 1544-1601.

[2] J. Koc, *Biofouling*, **2019**, 4, 454-462.

[3] L. Schardt, *Macromolecular Rapid Communications*, **2021**, 2100589.

10:40am **BI+AS+PS-MoM-8 Mussel Adhesion: A Fundamental Perspective on Factors Governing Strong Underwater Adhesion***, L. Mears, J. Appenroth, A. Celebi, A. Imre, H. Yuan,* TU Wien, Austria*; P. Bilotto,* CEST Centre for Electrochemistry and Surface Technology, Austria*; R. Su,* Tianjin University, China*; **Markus Valtiner**,* TU Wien, Austria

Tuning interfacial electrochemistry is central to the principle of the strong underwater adhesive of mussels. Here we critically discuss recent progress in the field, and we discuss how interfacial electrochemistry can vary interfacial forces by a concerted tuning of surface charging, hydration forces and tuning of the interfacial ion concentration. Mussel foot proteins contain a number of different functional groups, with much focus directed towards the catechol moiety. Therefore, we discuss some of our recent results in the area of adhesion of different functional groups in a saline environment. We also present new data from electrochemical surface force apparatus experiments that explore the difference in adhesion for oxidized and reduced forms of the catechol functional group against a mineral, mica, in different environments. These results raise interesting questions about the role of the catechol group. We propose new paths into understanding and utilizing redox-proteins and derived polymers for enhancing underwater adhesion in a complex salt environment.

11:00am **BI+AS+PS-MoM-9 Bioinspired Underwater Adhesives Using Amyloids from Commonplace Proteins***, M. Wilson,* NRC Post-doctoral Fellow sited at the Naval Research Laboratory, Chemistry Division*; M. Beasley,* NRC post-doc sited at the Naval Research Laboratory, Chemistry division*; K. Fears,* Naval research laboratory, Chemistry Division*; E. Yates,* US Naval Academy, Chemistry Department*; **Christopher So***[1], Naval Research Laboratory, Chemistry Division

Barnacles adhere permanently underwater using proteins that are delivered as a liquid, triggered to assemble, and cure as a bulk amyloid material in extreme seawater environments. More cosmopolitan than most other fouling organisms, barnacles rely on these materials to remain stuck at frigid ocean depths, as well as on hot intertidal coasts. We have previously been successful in designing sequences that can mimic the natural glue chemistry and structure, however bridging the gap between natural sequences and materials of practical use remains a challenge. Here, we mimic protein aggregation from the barnacle with unmodified food proteins as model systems and fabricate adhesives by curing them at the adhesive joint. We use temperature and time to control protein assembly and define the relationship between biophysical state and adhesive strength. Using thermal processing, we fabricate adhesives that approach the underwater lap shear strength of commercial marine and contemporary bioinspired chemistries. Though we observe differences in adhesive behavior between the examined proteins and their aggregation state, the presence of amyloids improves underwater performance across all proteins studied. We show that commonplace proteins can be delivered as a liquid, triggered to cure with chemistry or heat, and form strong underwater adhesives at the contact. The aggregation of commonplace proteins is therefore a viable pathway in creating strong underwater adhesives which, like the organisms that use them, can operate in extreme underwater conditions.

11:20am **BI+AS+PS-MoM-10 Incorporation of Antimicrobial Cyclic Peptides in Polymeric Materials***, D. Regan, Q. Lu, D. Barlow, **Kenan Fears**,* US Naval Research Laboratory

Polymeric coatings are used universally to protect structural materials and extend their operational lifetime. Microbial growth on these coatings, if unmitigated, present health risks and can diminish the protective performance of the coatings. For example, fungi have been linked to the degradation of aircraft surface coatings which can lead to corrosion of the underlying metals. After bans on heavy metal mixtures within surface treatments, a commercial void remains for a solution to prevent biodegradation of material surfaces. Building on the advancements within cyclic peptide synthesis, we test the antimicrobial activity of alpha and beta conformations of cyclic peptides against microorganisms of medical and industrial interest. Minimum inhibitory concentration (MIC) and microbial growth assays showed that cyclic peptides exhibited broad spectrum activity against gram-positive and gram-negative bacteria, yeasts, and algae. Furthermore, the cyclic peptides were mixed into a commercial polyester polyurethane coating, Irogran, and exposed to cultured isolates of biodegrading yeasts. For both cyclic peptide-Irogran blends, zero colony forming units were detected after a one-week exposure. These findings demonstrate how synthesized cyclic peptides retain their antimicrobial activity after incorporation into polymeric surface coatings to prevent the growth of problematic microorganisms.

11:40am **BI+AS+PS-MoM-11 Tuning Amphiphilicity of Alginic Acid-Based Polyelectrolyte Multilayers to Enhance Marine Fouling Resistance***, **Jana Karthäuser**, T. Gnanasampanthan, S. Spöllmann, R. Wanka, H. Becker, A. Rosenhahn,* Ruhr University Bochum, Germany

Polysaccharides are among other naturally occurring polymers commonly used in fouling-resistant coatings for both marine and medical applications. The anionic polysaccharide alginic acid (AA) is a non-toxic, eco-friendly, and readily accessible biopolymer that is widely used for biomedical purposes because of its high water-binding capacity. Thus, alginic acid is an interesting and promising building block to produce marine antifouling coatings. Unfortunately, in seawater, the biopolymer loses its antifouling efficacy due to the complexation of bivalent ions. An approach to overcome the susceptibility of charged polysaccharides, such as AA, is the blocking of the carboxylate groups by hydrophobic functional groups. The incorporation of amphiphilic moieties additionally changes the physicochemical properties of the coating and enables the tuning of fouling-resistant properties.[1]Layer-by-layer assembly of polyelectrolytes is a versatile and common technique to produce highly defined and reproducible coatings. The use of different or differently modified polyelectrolytes with opposite charges enables the charge-driven assembly.[2] To introduce amphiphilicity, different degrees of carboxyl groups of alginic acid were modified with pentafluoropropylamine. The influence of the amphiphilicity on the physicochemical characteristics of the modified alginic acid itself as well as of the coatings, when used alternately deposited with polyethyleneimine in multilayers, were investigated. Subsequently, the different degrees of modification of the AA-containing coatings with respect to the non-specific attachment of proteins by surface plasmon resonance spectroscopy and marine fouling organisms by attachment assays were examined in more detail and revealed an improved fouling resistance with increasing amphiphilicity.

1. Bauer, S. *et al.* Resistance of Amphiphilic Polysaccharides against Marine Fouling Organisms. *Biomacromolecules***17**, 897–904 (2016).

Gnanasampanthan, T. *et al.* Effect of Multilayer Termination on Nonspecific Protein Adsorption and Antifouling Activity of Alginate-Based Layer-by-Layer Coatings. *Langmuir***37**, 5950–5963 (2021).

Gnanasampanthan, T. *et al.* Amphiphilic Alginate-Based Layer-by-Layer Coatings Exhibiting Resistance against Nonspecific Protein Adsorption and Marine Biofouling. *ACS Appl. Mater. Interfaces***14**, 16062–16073 (2022)

[1] **BID Early Career Researchers Award**

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