Biomaterial Interfaces Division
Room 101B - Session BI-ThA

Biolubrication and Wear / Women in Bio-surface Science

Moderators: Anna Belu, Medtronic, Inc., Sally McArthur, Swinburne University of Technology, Australia

2:20pm **BI-ThA-1 Super Lubrication and Extremewear Protection using Bioinspired Polymers**, ***Xavier Banquy***, *J Faivre,* Universite de Montreal, Canada*; G Xie, M Olszewski,* Carnegie Mellon University*; L David, T Delair, G Sudre, A Montembault,* Univ. Claude Bernard Lyon I*; K Matyjaszewski,* Carnegie Mellon University*; B Shrestha,* Universite de Montreal, Canada **INVITED**

The coming end of earth's fossil energy is pressing humanity to develop more efficient and environmentally friendly technologies. Control of wear and fatigue of machine parts has become one of the most important field of research to meet the outstanding energy crisis the world is currently facing. The design of lubricating fluids able to protect surfaces against wear and high friction has been one the several tools used by engineers to improve machines' life time and decrease energy consumption. Inspired by many different biological systems that can resist fatigue wear for decades such as our synovial joints, different coating/lubricating technologies involving polymer brushes either in their molecular form or grafted on the surface have emerged. All these strategies require the lubricating or wear protecting molecules to be strongly anchored to the surfaces in order to avoid close contact between the surfaces. Strong anchoring of molecules on surfaces requires a good knowledge of the chemistry and the structure of the surface which complicates dramatically the translation of these technologies towards industrial settings.

We will describe our efforts in the design of lubricating and wear protecting fluids based on synergistic mixtures of bottle brushes (BB) and linear polymer solutions that mimic human synovial fluid. Individually, these two polymers exhibit poor wear protecting capabilities compared to saline solutions. Mixture of the two polymers in pure water or in saline allows to drastically increase wear protection of surfaces under a wide range of shearing conditions. We demonstrate that this synergy between the BB and linear polymer emerges from a strong, yet transient, cohesion between the two components forming the boundary film due to entanglements between both polymers. We show that this concept can be applied to other types of linear polymers and surfaces and is independent of the chemical and mechanical properties of the surfaces. We further extended this approach by engineering different types of molecular interactions between the BB polymer and the linear partner and showed that wear protection can be finely tuned independently of the lubricating properties of the mixture. Different applications of these materials will be described in the biomedical field.

3:00pm **BI-ThA-3 A Billion Force Runs: The AFM/Single-molecule Version of the Pitch Drop Experiment**, ***Laila Moreno Ostertag***, Vienna University of Technology, Austria*; T Utzig,* Max Planck Institute for Iron Research, Germany*; C Klinger,* TU Bergakademie Freiberg, Germany*; M Valtiner,* Vienna University of Technology, Austria

The "fly-fishing" and breaking of single molecular bonds to study their properties has been extensively studied via Atomic Force Microscopy (AFM) and optical tweezers. A good example for this are various ligand-receptor bonds or surface to molecule bonds such as the gold-amine bond, for which a free energy of ~ 37 k_BT has been determined. The experimental setup and design has evolved over the years, and so have the technology and analysis strategies involved. In the last 15 years, using Jarzynski's equality emerged as a powerful theoretical tool for estimating interaction free energies via the analysis of non-equilibrium work distributions from single-molecule pulling experiments with optical tweezers and AFM. [1] However, some of the questions remain the same and others appear as the field becomes broader. For example, what happens when the chemical model used to connect the probe with the interacting surface and head groups is varied? We recently tested the variation of linker lengths and changing pulling speeds [2] and found strong correlations that confirm the predictions of bias in such experiments by Gore *et al*. [3] in 2003. In particular, the longer the length of the polymeric chain, the more work dissipates during the retraction of the tip, and so does in turn the estimated ΔG_0, which leads to an increasing bias between the average values and those calculated using Jarzynski's equality. This is also reflected in the broadening of work distributions when using the same sample size. Longer polymeric chains show no convergence, unless millions or even billions of events were used. With this order of magnitude in mind, we started our very own "pitch drop experiment": an ambitious project which aims to collect an ever-increasing number of single-molecular force runs for a single system, which will allow us to directly and step-by-step further evaluate equations, work-distributions, convergence behavior, and expected biases in single-molecule experiments. This work will continue along the PhD times of many students - first non-converged results will be discussed in detail and compared to systems that are well converged. Part of this mammoth task is the development of an automated single-molecule recognition algorithm that is capable of distinguishing with high reliability very low work single-molecule events from thermal noise. Some of our advances in this direction will be discussed in detail as well.

References:

[1] Jarzynski, C., *JSMTE* **2004,** *2004* (09), P09005.

[2] Moreno Ostertag, L.; Utzig, T.; Klinger, C.; Valtiner, M., *Langmuir* **2018,** *34* (3), 766-772.

[3] Gore, J.; Ritort, F.; Bustamante, C., *PNAS* **2003,** *100* (22), 12564-12569.

3:20pm **BI-ThA-4 Ionic Liquid Behaviour in Biologic Environments: Structuring and Lubrication at Aqueous Solid/liquid Interfaces**, *H Cheng,* TU Wien, Germany*; H Weiss, M Mezger,* Max Planck Institute for Polymer Research, Germany*;* ***Markus Valtiner***, Vienna University of Technology, Austria

Bio and aqueous applications of ionic liquids (IL) such as catalysis in micelles formed in aqueous IL solutions, lubrication or extraction of chemicals from biologic materials rely on surface-active and self-assembly properties of ILs. Here, we discuss qualitative relations of the interfacial and bulk structuring of water-soluble and highly surface-active ILs on chemically controlled surfaces over a wide range of water concentrations using both force probe and X-ray scattering experiments. Our data indicate that IL structuring evolves from surfactant-like surface adsorption at low IL concentrations, to micellar bulk structure adsorption above the critical micelle concentration, to planar bilayer formation in ILs with <1 wt % of water and at high charging of the surface. Interfacial structuring is controlled by mesoscopic bulk structuring at high water concentrations. Surface chemistry and surface charges decisively steer interfacial ordering of ions if the water concentration is low and/or the surface charge is high. We also demonstrate that controlling the interfacial forces by using self-assembled monolayer chemistry allows tuning of interfacial structures. Both the ratio of the head group size to the hydrophobic tail volume as well as the surface charging trigger the bulk structure and offer a tool for predicting interfacial structures. Based on the applied techniques and analyses, a qualitative prediction of molecular layering of ILs in aqueous systems is possible. Potential applications in biomedical applications will be discussed.

4:00pm **BI-ThA-6 Synergistic Mechanisms of Selenium and Tellurium based Nano-Alloys Towards Biofilm Inhibition**, ***Kelly Nash***, *S Tek, B Vincent, C Smith, R Robledo,* University of Texas at San Antonio **INVITED**

Selenium (Se) and Tellurium (Te) are two elements under-utilized in medicinal treatments that naturally occur in the human body. Selenium is a bioessential element that exists as a micronutrient throughout most biological systems. In mammalian species, selenium is found in the form of selenocycteine, an amino acid found in selenoproteins. Selenoproteins play an important role in cell metabolism and is an active participant in anti-oxidant glutathione peroxidase mechanism which aids in DNA synthesis. Given selenium's crucial role within biological functions, recent efforts have investigated the antimicrobial properties of selenium as a means to reverse, suppress or prevent the development biofilms. Tellurium, belonging to the same family as oxygen, sulphur and selenium, has been far less studied for its bioactivity. In part, this is due to its classification of being a non-essential biological element. However, recent evidence points to the possible existence and role in biological activity, abet to a lesser extent than selenium. Given that Selenium (Se), a bioessential element, and tellurium (Te), its related analog, are under-utilized elements in the medicinal libraries of antimicrobial treatments, recent research on these elements reveals that they may have numerous therapeutic applications beyond antimicrobial effects including for anti-inflammatory, anti-fouling and anti-cancer treatments. The focus of the work has been to develop novel nano-alloys composed of Se and Te by bio-friendly and chemical free synthesis methods and to evaluate their antimicrobial effects in conjunction with complementary studies on their toxicity against normal cells. Using nano-alloy formulations of these elements will form the basis of a new type of nature-inspired microbial prevention. We demonstrate that

the Seand Te nano-alloys provide a reduced toxicity to normal cells while providing enhanced therapeutic efficiency of these compounds towards biofilm inhibition including on surfaces. The short-term impact of this work will provide novel approaches to inhibiting biofilm formation. The long-term impact of this work will provide the basis for treatment of some difficult to treat nosocomial infections caused by *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *E. coli* and *Candida albicans*.

4:40pm **BI-ThA-8 From Bedside Back to Bench: Combining Human Centered Design with Biointerfacial Research**, *P Nguyen, T Martin, D Cuylear, L Mckenney, B Matheson, A Yingling, L Ista,* ***Heather Canavan***, University of New Mexico

In 1978, the Worth Health Organization's Alma Ata Declaration asserted individuals' "right and duty to participate individually and collectively in the planning and implementation of their health care". The expansion of these policies began in the 1980s and by the 1990s, social movements across the world demanded greater public accountability and the inclusion of regular citizens in the decision-making process. Today, patient-centered healthcare has continued to progress, and in 2009 a new definition was made by the president of the Institute for Healthcare Improvement Donald Berwick "The experience (to the extent the informed, individual patient desires it) of transparency, individualization, recognition, respect, dignity, and choice in all matters, without exception, related to one's person, circumstances, and relationships in health care". These ideas have transformed over time to become “patient-centered design.” In patient-centered design, the focus is to redefine how people experience healthcare by focusing on their needs. The focus of the design is on the wants, needs, and skills of the products’ end-users, including patients, doctors, nurses, caretakers, and others.

In our laboratory, we apply our expertise in bioactive and stimulus-responsive polymers, cell/surface interactions, and cytotoxicity to create therapies that improve patient outcomes by improving the patient’s experience. For example, we have developed a pH-responsive hydrogel to control the release of the medications used to prepare patients for colonoscopy screening. Using standard surface science techniques such as NMR, FTIR, and XPS, the chemical identity, robustness of the hydrogels in varying environments, and uniformity of size of the hydrogels have been assessed. Using standard cytotoxicity assays such as Live/Dead, XTT, and MTS, the biocompatibility of the hydrogels have been established at increasing concentrations from 1-25% out to four days in vitro with appropriate mammalian cell lines. Our model also shows promise in targeted delivery of biotherapeutics and encapsulated bacterial strains within the GI tract of immunocompromised individuals.

5:00pm **BI-ThA-9 Liquid-Infused Surfaces Coated on Paper Improve Bacteria Handling Efficiency and Detection**, *D Regan, C Lilly, A Weigang, H Patanwala,* ***Caitlin Howell***, University of Maine

Issues such as the rise of antibiotic resistance highlight the need for constant innovation in the field of point of care (POC) microbial diagnostics. Current approaches that do not require the use of energy for storage or detection are hindered by low sample concentration and adhesion challenges which arise when handling these often “sticky” organisms. To overcome these limitations, we combine two approaches in complex analyte handling: infused polymers, which provide a universal anti-adhesion surface against microorganisms, and paper-based microfluidics, which present a lightweight, rugged, and low-cost platform for POC diagnostics, to create paper-supported liquid-infused polymer surfaces. The results showed that the liquid-infused system could be created on multiple different types of paper, including commercially-available silicone release paper which is already manufactured at an industrial scale. Folding the paper liquid-infused surfaces produced chambers which could be used to concentrate the organisms into single point via evaporation with >60% efficiency, compared to <20% efficiency for controls without an infused polymer layer. Sample containing bacteria could be moved from point to point without the loss of cells due to surface adhesion. Finally, integrated proof-of-principle tests showed that the use of liquid-infused surfaces to handle bacteria in this way resulted in positive colorimetric indication of *Staphylococcus aureus* significantly faster than control surfaces. These results demonstrate the use of paper-supported liquid-infused surfaces for improved microorganism handling in POC diagnostics.

5:20pm **BI-ThA-10 Tailoring Interactions at the Nanoparticle-nucleic Acid Interface using Molecular Modelling**, *M Manning, J Nash,* ***Yaroslava Yingling***, North Carolina State University

The design of nanoparticles (NPs) that can induce specific structural transitions in nucleic acids (NA) is important for nanotechnology applications including gene delivery and nanoelectronics. NP biocompatibility and efficacy is determined by geometry, charge, and surface chemistry. Advancing NPs to the clinic requires optimization, which is prohibitively expensive, and a mechanistic understanding of NP-NA interactions, which remains unknown. This project will advance tailored NP gene delivery by a multiscale optimization employing all-atom molecular dynamics (MD) simulations and leveraging machine learning algorithms. It is known that in biological systems, the binding of cationic proteins induces structural changes in DNA or RNA, which can affect gene expression or cause the compaction of DNA into chromatin. The anionic backbone of the nucleic acids DNA and RNA allow for non-specific electrostatic interactions with cationic proteins, nanoparticles, or dendrimers. The interaction of nucleic acids and nanoparticles may be tuned through changes in nanoparticle size, charge, polarity, or shape. However, the factors that affect structural transitions are not fully understood. We performed atomistic molecular dynamics simulations of the binding of nucleic acids to monolayer-protected gold nanoparticles to elucidate structural changes that take place for nanoparticles and DNA upon binding. Results from these simulations were analyzed to determine modes of DNA and RNA bending with nanoparticles. Our simulations show that highly charged nanoparticles cause DNA to bend with little damage to the helix structure, similar to DNA in the nucleosome. Nanoparticle shape as well as charge is shown to affect the wrapping of nucleic acids with the nanoparticle. Low salt concentrations and high nanoparticle charge cause greater disruptions to DNA structure. We find that the roll parameter is the most important base-pair parameter for DNA bending. Requirements for bending differed significantly between DNA and dsRNA. The degree of DNA bending is controlled by the charge of the NPs, but ligand flexibility played a more significant role in dsRNA bending. These results allowed us to determine the training data for machine learning algorithms and design a novel ligands capable of controlled wrapping of NA around NP. We have shown that the designer gold NPs are capable of wrapping NAs with fine control of binding strength through NP charge and ligand stiffness. These findings are useful for designing gene delivery systems with enhanced biocompatibility and selectivity.

5:40pm **BI-ThA-11 Biomolecule Interaction with Polymer Thin Films Based on Zwitterions and Polymer Nanoparticles**, ***Eva Bittrich***, *C Naas,* Leibniz-Institut für Polymerforschung Dresden e.V., Germany*; F Mele,* Leibniz-Institut für Polymerforschung Dresden e.V. and Polytechnic University of Turin, Italy*; A Münch,* Leibniz-Institut für Polymerforschung Dresden e.V., Germany*; P Uhlmann,* Leibniz-Institut für Polymerforschung Dresden e.V.,Germany, Germany*; D Appelhans, K Eichhorn, B Voit,* Leibniz-Institut für Polymerforschung Dresden e.V., Germany

Controlling and understanding the interaction behavior of biomolecules with polymer surfaces is one key aspect for the design of new biomaterials. Thin hydrogel coatings offer a huge variety of possibilities to tune physical and chemical surface properties and to create functional biocompatible interfaces supported on a substrate material. Among polymer architectures studied for biocompatible systems are dendritically structured polycations decorated with oligosaccharide shell [1, 2], and zwitterionic copolymers based on phosphorylcholine groups [3]. We prepared two types of thin hydrogel films: 1) based on dendritic polymer core-shell nanoparticles of hyperbranched poly (ethylene imine) (PEI) with maltose shell and 2) based on the statistical copolymer poly[(2-methacryloyloxyethyl phosphorylcholine)-co-(glycidyl methacrylate)] (MPC-*co*-GMA). For both surface types swelling and the interaction with selected biomolecules from small drug molecules to proteins and phospholipids was analyzed quantitatively by in-situ spectroscopic ellipsometry and quartz crystal microbalance with dissipation monitoring. The adsorbed amount of biomolecules was correlated to changes in hydration, thickness and viscoelastic properties of the films to obtain new insights into the specific interaction processes.

References

[1] M. Warenda, K.-J. Eichhorn, B. Voit, D. Appelhans et Al., Macromol. Rapid Commun. 33 (2012) 1466.

[2] D. Wrobel, D. Appelhans, B. Voit et Al., Colloid. Surf. B: Biointerfaces 152 (2017) 18.

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