Biomaterial Interfaces
Room 117 - Session BI2-MoM

Functional Materials

Moderators: Kenan Fears, U.S. Naval Research Laboratory, **Rong Yang**, Cornell University

10:30am **BI2-MoM-10 Customizing Naturally-Derived Polymers Using Plasma-Enhanced Chemical Vapor Deposition***, **Morgan Hawker**,* California State University, Fresno

Naturally-derived polymers are the fastest-growing biomaterials because they are non-immunogenic and are able to recapitulate a range of biological tissues through bulk mechanical property tuning. This remarkable materials class includes silk, collagen and cellulose, all of which have high potential for use as tissue engineering implants, biosensors, and drug delivery devices. One drawback is that naturally-derived polymers are bioinert, exhibiting non-specific interactions with proteins, cells, bacteria, enzymes, and other biological species. Another possible drawback in some applications includes fixed degradation kinetics which may not match the rate required for a given application. Plasma-enhanced chemical vapor deposition (PECVD) is a useful strategy to address both drawbacks, providing a chemically customizable coating that can control interfacial interactions while also modulating degradation.

This talk will highlight our recent work on plasma-enhanced chemical vapor deposition approaches to modify different naturally-derived polymers. First, an acrylic acid and pentane plasma copolymerization strategy has been developed to control silk film wettability. We demonstrate that silk film wettability decreases with increasing pentane in the feedgas, with impressive static water contact angle tunability between 50° and 100°. High-resolution XPS findings provided additional insight into changes in surface chemical composition for coatings deposited with varying proportions of monomers in the feedgas. Second, PECVD coatings were deposited on commercially-available cellulosic wound dressings using a 1,8-cineole precursor. Pulsed and continuous power conditions were utilized with the goal of preserving the 1,8-cineole monomer structure because of the molecule's well-documented antibacterial properties. Although surface analysis revealed minimal difference between films deposited under different powers, films unexpectedly exhibited differing performance when interfaced with *Streptococcus pneumoniae*. Last, novel PECVD systems currently under development in our lab will be presented. One goal of employing new precursors is to develop additional antibacterial coating systems that are stable in aqueous environments. Each of these systems is poised to enhance naturally-derived polymer utility in biomedical contexts through controlling interfacial interactions.

10:45am **BI2-MoM-11 Vascularized Polymers: Optimizing Support Systems for Biotic/Abiotic Living Materials***, E. Leonard, S. Zier, **Caitlin Howell**,* University of Maine

Large-scale detection of and active response to changing conditions at interfaces is a promising pathway to facilitating the long-term growth and stability of the biotic component of biotic/abiotic living materials. In Nature, one method of both detecting and actively responding to environmental changes is by using vascular networks as intermediaries that transport signals and materials from one location to another. In this work, we explore various methods of embedding vascular networks into abiotic polymeric matrices that use widely available fused filament deposition model (FDM) 3D printing. We test each method for the efficacy of diffusion to and from the interface, as well as how well it can be used in both hydrophobic and hydrophilic abiotic polymers. Our goal is to create detection-and/or-response systems to support the growth of biotic systems located at abiotic polymer interfaces in a low-cost, easily scalable manner, paving the way for the creation of durable and adaptable biotic/abiotic living materials.

11:00am **BI2-MoM-12 Preserving the Hydrophilicity of Biodegradable Films Post-Plasma Treatment: Impact of Aging Environment on Hydrophobic Recovery***, **Mina Abdelmessih**, M. Hawker,* California State University, Fresno

Polylactic acid (PLA) and chitosan (CS) are biopolymers with vast potential in the biomedical field. Their biodegradability and non-toxicity *in vivo* makes them useful as tissue engineering scaffolds. The slower degradability of PLA is suitable for slower-healing bone tissues, while the faster degradability of CS is suitable for faster-healing soft tissues. Nevertheless, both polymers are inherently hydrophobic, which would potentially restrict the cell adhesion desirable for tissue engineering applications. There is some evidence that hydrophilic surfaces are preferable for cell adhesion and growth. Previous studies display the promise of utilizing radio-frequency nitrogen plasma treatment in increasing the surface hydrophilicity of PLA and CS. In addition, nitrogen plasma treatment polymers have been shown to exhibit improved surface cell adhesion properties. Many plasma treated polymers, including PLA and CS exhibit a phenomenon known as hydrophobic recovery, where the polymers partially retain their original hydrophobic properties with age. Hydrophilicity loss in treated PLA and CS is detrimental, especially in applications that require cell adhesion. Methods of preventing this phenomenon in PLA and CS are widely unexplored.

This work explored the impact of various aging conditions (storage in vacuum, cold temperature, and air) on the surface hydrophilicity of nitrogen-plasma-treated PLA and CS following treatment. Films were prepared as model substrates using the solvent-casting method. The films were treated in a RF plasma reactor under optimized parameters (power, pressure, and treatment time). After treatment, the films were aged in the different aging environments for two weeks. Throughout the aging period, multiple surface analyses were conducted on samples exposed to the various preservation environments, including untreated samples as controls. Surface wettability analysis utilizing water contact angle goniometry displayed that vacuum aged samples possess the least hydrophobic recovery in comparison to the other aging conditions. Additionally, surface chemical composition was examined using x-ray photoelectron spectroscopy. Expanding these treatment preservation methods to PLA and CS has potential to positively impact their use as scaffolds in the biomedical field.

11:15am **BI2-MoM-13 3-D Atomic Layer Infiltrated Metal Oxide Barriers for Thin-Film Active Microelectrode Arrays***, **Martin Niemiec**, K. Kim,* University of Connecticut

A recent trend in neural interfaces is a shift away from rigid devices comprised of materials such as silicon and metals toward thin and flexible material classes such as polymers. While such devices show more favorable biointegration over chronic timescales, they are often plagued by issues of reliability, stemming from poorer resistance to the permeation of moisture and ions as compared to traditional materials. As such, the incorporation of ultrathin barrier layers of inorganic materials deposited by atomic layer deposition (ALD) or chemical vapor deposition (CVD) is an area of interest. Most ALD and CVD processes incorporate wafer-grown inorganic barriers, depositing metal oxides above and below the polymeric layers, followed by via opening using established microfabrication techniques. However, the etching step can leave unprotected polymer sidewalls, leaving a significant path for permeation, and the high stiffness mismatch between the polymer and inorganic film often leads to interfacial delamination. Herein, we describe a technique and its advantages for the fabrication of mechanically reliable thin-film barrier encapsulated polymeric active microelectrode arrays with three-dimensional all-side atomic layer infiltration using a modified liftoff process. Unlike barriers grown on-wafer, the metal oxides infiltrate all sides of the polymer array at once and leave no exposed sidewalls vulnerable to moisture. Secondly, the gradual stiffness transition at the polymer-inorganic barrier interface can reduce delamination and improve flexibility. Finally, the modified liftoff process allows ALD via opening on freestanding devices. We have demonstrated such devices previously in a completely encapsulated form, without active microelectrodes. Here, the combination of active electrodes with our three-dimensional coating is achieved via a modified liftoff process utilizing ultrasonication to remove the metal oxide over the microelectrodes, without removing it elsewhere. Because the inorganic barrier is deposited after insulation via opening, our devices feature the additional benefit of via sidewall encapsulation with a protective barrier, thereby decreasing the chances of side-permeation and delamination initiation at the microelectrode. The encapsulation (~10nm Al2O3, ~25nmTiO2) can provide water vapor transmission rates less than 1 mg m-2day-1 at 85% RH (see supplement). Ongoing accelerated aging tests will offer insights as to the effectiveness of our encapsulation on preserving functionality under implanted conditions, with initial trials showing functionality up to ~20 days at 87°C (roughly 640 days at 37°C).

11:30am **BI2-MoM-14 Injectable Siloxane Sponges for on-Site Treatment and Rapid Hemostasis**, *P. Sarkar,* ***Kausik Mukhopadhyay,*** University of Central Florida

Hemorrhage is one of the main causes of preventable civilian death and on the battlefield. According to a report by the USAMRDC in 2022, nearly 50% of combat deaths have been due to exsanguinating hemorrhage. Of those, about half could have been saved if timely, appropriate care had been available. This underscores the need to develop appropriate FDA-approved hemostatic treatments. While external wound injury can be treated mostly by visual inspection, internal hemorrhages are often much more intractable. The need to treat trauma wounds requires an immediate solution that can be applied by individual soldiers in the field swiftly and efficiently. In our current study, we report a silicone-based hemostatic bandage system that is both antibacterial and self-expanding. The two-component hemostatic system chemically reacts in situ to form a stretchable foam that generates autogenous pressure on the wound to control bleeding. It can be easily administered with a dual-syringe device, and when the components interact on delivery, hydrogen peroxide decomposition is catalyzed by silver oxide, releasing oxygen to expand the siloxane matrix into a rigid ‘foam’ within seconds. This foam or sponge then acts as a 'tamponade' arresting further bleeding. The adhesive properties of the foam render them optimal for wound-dressing applications and the presence of silver oxide imparts antibacterial effects against both Gram-positive and Gram-negative strains of bacteria. Optimization of the constituents allows control over system temperature and porosity. Support data include studies on rheology, adhesion, and in-vitro assays. To further assess the efficacy of the foam, a unique mannequin system capable of simulating a deep abdominal wound has been employed. The objective of this novel hemostatic agent is to provide the injured party with a means to rapidly stagnate or arrest bleeding from external and internal wounds in a manner superior to those currently available. This unique formulation presents an easy and economical approach to a hemostatic bandage system with spontaneous self-expanding properties, capable of remaining functional in inclement weather conditions.

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