Biomaterial Interfaces
Room 312 - Session BI2-TuA

Surface Modification
Moderator: A. Chilkoti, Duke University

2:00pm **BI2-TuA1 Dynamic Ellipsometric Studies of Protein Adsorption to Modified Chitosan Surfaces**, ***S. Sarkar***, *L.G. Castro, D.W. Thompson, J.A. Woollam, A. Subramanian,* University of Nebraska, Lincoln

Protein adsorption is a ubiquitous phenomenon whose effects are widespread and observable in fields as diverse as biofouling, molecular recognition and metabolic pathway activation (biocompatibility) and even qualitative and quantitative detection methods (ELISA). Protein interaction with materials and at interfaces is an area of ongoing study; however, little is understood of the immediate response of proteins to an exposed surface. Chemically modified chitosan films were used to investigate the adsorption of human serum albumin (HSA), immunoglobulin G, and fibrinogen. Diepoxides were reacted with amine groups present on chitosan and then five atomic geometries (n-butyl amine, 2-(t-Butylamino)ethanol, n-octyl amine, 2,4,6 Tris(dimthylaminomethyl) and t-butyl amine) and an anti-HSA molecule were attached to free epoxide ends to create surfaces preferential to albumin adsorption. Dynamic ellipsometric studies were carried out on the resulting surfaces to investigate protein adsorption phenomena. We have been successful in observing real time protein adsorption. In most cases protein adsorption had reached a saturation point after one-hour with the highest rate of adsorption occurring in the first ten minutes.

2:40pm **BI2-TuA3 The Generation of Protonated Amine Groups in Plasma Co-Polymers of Acrylic Acid and Allylamine for the Co-Culture of Keratinocytes and Melanocytes**, ***A.J. Beck***, *P. Eves,* University of Sheffield, UK*; J.D. Whittle,* Plasso Technology Ltd, UK*; N.A. Bullett,* Celltran Ltd, UK*; S. Mac Neil, S.L. McArthur, A.G. Shard,* University of Sheffield, UK

Plasma polymers prepared from acrylic acid, allylamine and mixtures of the two strongly interacting vapors were characterized using X-ray photoelectron spectroscopy (XPS) and near edge X-ray fine structure (NEXAFS). Plasma polymers prepared from pure acrylic acid and allylamine contained groups retained from the monomer with additional groups formed in the plasma. For the plasma copolymers, the XPS N 1s data and NEXAFS N k-edge provided evidence of protonated amines. The mixture of monomer vapors, in the absence of a plasma, consists of acrylic acid, allylamine and the product of their reaction: allylammonium acrylate salt. More protonated amines were detected in plasma copolymers prepared at low powers suggesting that they were largely retained from the monomer mixture rather than being formed in the plasma. The protonated amines in the monomer mixture undergo less dehydrogenation to nitrile groups in the plasma than the amines from the pure allylamine. This novel use of protecting groups for amines in low power plasmas has the potential to be extended to other desirable groups which tend to be diminished due to fragmentation even in very low power systems. We have demonstrated that plasma co-polymers of acrylic acid and allylamine contain protonated amine groups with carboxylates as the counter anion. It is postulated that such zwitterionic plasma polymers will have interesting surface charge properties in aqueous solution and it may be possible to control the isoelectric point of the surface by varying the plasma conditions and ratio of allylamine to acrylic acid vapors. These surfaces have been shown to facilitate co-culture of keratinocytes and melanocytes.

3:00pm **BI2-TuA4 Pulsed RF Plasma Polymerisation of N-isopropylacrylamide (NIPAAm)**, ***R. Talib***, *A.G. Shard, S.L. McArthur,* University of Sheffield, UK

There is a growing interest in the development of responsive polymer coatings for applications as diverse as tissue engineering and microfluidic devices. Plasma polymerization affords a convenient, one step route to generate such coatings. Previous studies have shown that continuous wave (CW) plasma polymerization of N-isopropylacrylamide (NIPAAm) is able to produce thermally responsive coatings on a variety of substrates. These CW studies have demonstrated that control of the deposition power and temperature is critical for the retention of functionality, but that too little power or too lower temperature will result in unstable coatings. In this study we investigate the use of pulsed power cycles as a means for both improving coating stability and controlling the thermal response of the coatings. We have investigated the influence of power, on- and off-times and reactor temperature on the coating chemistry, stability and thermal response. The role of the plasma parameters has been monitored using a capacitive probe. The probe enables accurate measurement of the duty cycle and clearly demonstrates that in certain regimes both the power and ratio of on/off time set by the pulse generator can result in significant delays in the striking of the plasma. In some instances, we demonstrate that the plasma actually fails to ignite during the majority of individual pulses. Accurate measurement of duty cycles enables direct comparison of coatings produced under pulsed power with those produces with equivalent CW powers. X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS) and captive bubble have been used to measure the resulting coating properties and compare the mechanisms of NIPAAm polymerization under CW and pulsed plasma conditions.

3:20pm **BI2-TuA5 Using Plasma Deposits to Promote Cell Population of the Porous Interior of 3D Tissue Engineering Scaffolds**, *J.J.A. Barry, M.M.C.G. Silva, K.M. Shakesheff, S.M. Howdle,* ***M.R. Alexander***, University of Nottingham, UK

Cell attachment and proliferation on poly(D,L-lactic acid) (PLA) tissue engineering scaffolds is low, this is generally regarded to be due to the hydrophobicity of the polymer surface. This study reports the first successful deposition of allyl amine plasma polymer throughout the porous network of a 3D scaffold to improve cell adhesion. This is compared and contrasted with the plasma grafting of allyl amine to the PLA. XPS analysis of sectioned scaffolds is used to demonstrate the penetration of nitrogen species to the inner surfaces. The nitrogen concentration at the exterior and interior scaffold surface was greater for the plasma deposits than the grafted surfaces. The variation in nitrogen concentration indicated a variation in thickness through the scaffold due to diffusion limited deposition in the interior pores. The chemistry was characterised using high resolution C1s and N1s core level with reference to literature NEXAFS and derivatisation studies. In vitro evaluation of biocompatibility was carried out by studying 3T3 fibroblast attachment, morphology and metabolic activity on the scaffolds. Cell activity and attachment was found to be greater for the plasma deposits than the plasma grafted PLA scaffolds and greater for both than the as-fabricated PDLLA scaffolds. It is concluded that plasma deposition is a viable method of increasing cell attachment throughout porous PLA and other scaffolds without changing the bulk characteristics of the polymer.

3:40pm **BI2-TuA6 Designing Interfaces for Biomolecular Interactions using Plasma Polymerization Techniques**, ***R. Foerch***, Max Planck Institute for Polymer Research, Germany

Recent advances in the synthesis and characterisation of plasma polymerized thin organic coatings has enabled new insights into the design of interfaces for specific interactions with biological molecules. Optical techniques such as surface plasmon resonance and waveguide mode spectroscopy have been used to monitor in real-time the reactions of proteins, antibodies and DNA at the interface of different plasma polymerised films. Combining these techniques with AFM, FTIR and XPS analysis has demonstrated a tremendous flexibility in surface design, plasma polymer structure and surface reactivity. The chemical composition, the macromolecular structure and the ability to form a 3-dimensional interface open up new concepts for the design of biomaterial surfaces. The interactions of proteins, antibodies and DNA can be correlated to plasma deposition conditions and subsequently the chemical and physical properties of the deposited layers.

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