European Cells and Materials Vol. 6. Suppl. 1, 2003 (page 44) ISSN 1473-2262
Poster ID: 118

COMPRESSION OF ADSORBED POLY(L-LYSINE)–*G*–POLY(ETHYLENE GLYCOL) MEASURED BY AFM

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INTRODUCTION: Poly(L-lysine) grafted with poly(ethylene glycol) (PLL-*g*-PEG), a polycationic co-polymer positively charged at neutral pH, has been shown to spontaneously adsorb onto negatively charged surfaces, resulting in grafted PEG layers of controllable architectures, in terms of PEG molecular weight and density.[1] An *in situ* optical waveguide study of polymer and protein adsorption has demonstrated that the amount of protein adsorbed on the PLL-*g*-PEG-coated surfaces is strongly correlated with the EG monomer surface density, in turn determined by the polymer architecture.[2]

PLL-*g*-PEG coatings offer the possibility of varying both the polymer architecture and the degree of biointeraction in a controlled way. This characteristic of tuning the system's properties makes it attractive for a systematic study of the mechanical properties of PEG grafted layers. A colloid-modified AFM technique was used to probe the response of the various PEG layers under compression by a 5µm-SiO_2 sphere, demonstrating the influence of PEG chain length and density at different ionic strengths. Polymer-polymer interactions were investigated after coating both sphere and substrate with the co-polymer.

METHODS: A conventional atomic force microscope (AFM Nanoscope IIIa, DI) was modified by using a 5µ-SiO_2 sphere as a tip, and used to measure the resulting force from the compression between the sphere and PLL-*g*-PEG-modified Nb_2O_5 surfaces *in situ* as a function of the separation distance.[3] PEG molecular weights of 1, 2 and 5 kDa were analyzed, with PEG densities varying from 0 to 0.9 nm^{-2}, in HEPES buffer at pH 7.4, with salt concentrations from 1 to 150 mM.

RESULTS: AFM force measurements show the response to compression of the PEG layer between the underlying metal oxide surface and the microsphere, expressed as an interaction force varying with the separation distance. The measured force is dependent on the co-polymer architecture, PEG length and density. Figure 1 shows different force versus distance curves for adsorbed co-polymers with increasing PEG density.

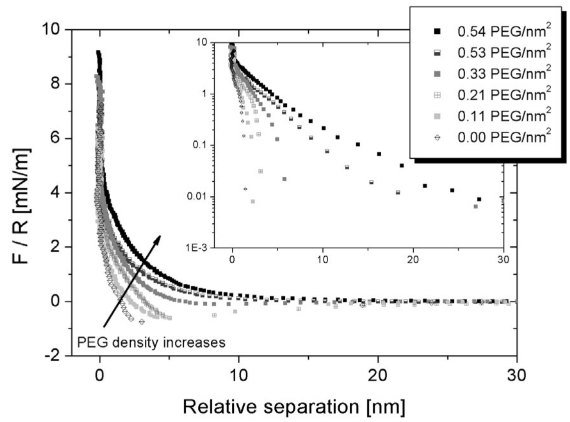

Fig. 1: Forces between a 5µm-SiO_2 probe and PLL-g-PEG-modified Nb_2O_5 substrates with MW 2000 PEG, and varying PEG densities (0 – 0.54 PEG chains/nm^2), in 10 mM HEPES pH 7.4, on a linear and on a log scale.

Performing the AFM measurements at different ionic strengths allowed for the discrimination between the steric repulsive force from the PEG chains and the electrostatic contribution from either the positively charged PLL backbone (attraction) or the negatively charged underlying substrate (repulsion). Polymer-polymer interactions showed additivity of the steric repulsive force.

DISCUSSION & CONCLUSIONS: PLL-*g*-PEG presents a controlled system in terms of interface architecture and protein adsorption. AFM force measurements on these well-defined PEG layers demonstrate the dependence of the surface forces on the PEG interface architecture, and their relationship to protein adsorption. The colloidal AFM is shown to have a high potential to elucidate the mechanisms of protein interaction with PEG layers.

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ACKNOWLEDGEMENTS: G. Gillies, K. Bremmel, F. Assi and S. Lee are thanked for their help with the AFM, J. Vörös and O. Borisov for helpful discussions. This work is financially supported by EPFL and ETHZ (TH-33./01-3).