

A PEG-Based Co-Polymer for Protein-Resistant Surfaces Studied by Ellipsometry and Quartz Crystal Microbalance

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INTRODUCTION: Poly(ethylene glycol) (PEG) has been known as a biomaterial for several decades and is used in many biomedical applications [1]. When grafted onto a surface at a sufficiently high density, PEG chains have the ability to prevent the adsorption of proteins, i.e. to render the surface protein resistant [2]. A possible way to reach high PEG densities is to graft the chains covalently onto a polymeric backbone, as for example poly(L-lysine) (PLL). This graft copolymer, denoted PLL-g-PEG, adsorbs electrostatically on negatively charged surfaces (such as many metal oxide surfaces) from aqueous solution, due to the presence of protonated amine groups. A main advantage of this polymeric system is the possibility to tailor the architecture by varying the molecular weights of both components (PLL and PEG), as well as the grafting ratio (defined as the number of lysine units in the backbone per PEG chain). Pasche et al. [3] showed that the protein-resistance capability of the coating strongly depends on the polymer architecture, and that a high ethylene glycol density is required to withstand protein adsorption. Variable angle spectroscopic ellipsometry (VASE) is a highly sensitive technique that allows the determination of layer thicknesses of adsorbed polymers in the dry state. The quartz crystal microbalance with dissipation monitoring (QCM-D) on the other hand, gives information about *in situ* layer thicknesses as well as about the water content of the layers (when calibrated with an optical technique).

METHODS: PLL-g-PEG with different PEG molecular weights (1, 2 and 5 kDa) and grafting ratios (2, 3.5, 6.5, 15 and 30) were adsorbed on cleaned Nb₂O₅. HEPES (4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid, 10 mM, pH = 7.4) was used as a solvent. Ellipsometry measurements were carried out in the dry state, while QCM-D allows real-time monitoring of the adsorption process.

RESULTS: The dry layer thicknesses correlate linearly with adsorbed dry mass (data not shown). Figure 1 shows the direct comparison of dry and wet layer thicknesses. While dry layers have thicknesses between 1-3 nm, the wet thicknesses

are much larger (2-12 nm). These differences are attributed to coupled water in the layer that also gets measured by QCM-D.

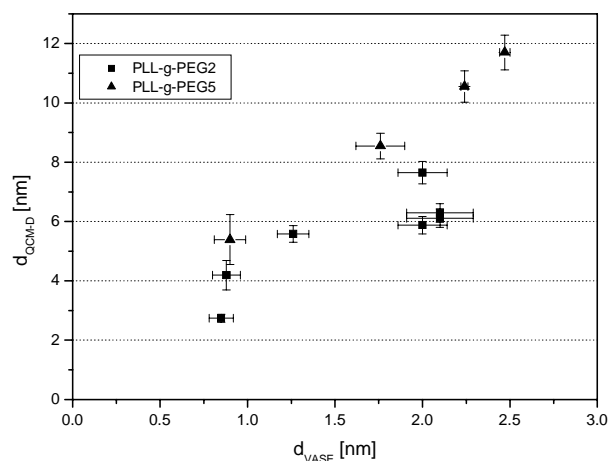


Fig. 1: Layer thickness comparison between dry (ellipsometry) and wet layers (QCM-D). Note the large differences due to hydration of the layers.

For surfaces with densely grafted PEG chains, the number of water molecules per EG monomer unit are lower (~8) than for surfaces with sparse grafting (~25).

DISCUSSION & CONCLUSIONS: The combination of optical and acoustic techniques allows the quantitative determination of the water content in adsorbed polymeric layers. The number of water molecules per EG unit determined for densely grafted PEG chains corresponds to structured water around PEG chains. These layers also gave the best results regarding protein resistance [3], showing the importance of structured water acting as a steric-entropic-osmotic barrier to approaching proteins.

REFERENCES: [1] Harris, J.M., Poly(ethylene glycol) Chemistry, Biotechnical and Biomedical Applications, (1992), New York and London: Plenum Press; [2] Jeon, S.I., et al., J Coll Interf Sci, (1991), 142, 149-158; [3] Pasche, S., et al., Langmuir, (2003), 19, 9216-9225.

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