

Determining the Amount of Bound Water in Polymer Layer Combining MP-SPR and QCM Data.

A triblock copolymer Pluronic P-105 adsorption on polypropylene (PP), polyethylene terephthalate (PET), nylon and cellulose surfaces was measured with Multi-Parametric Surface Plasmon Resonance (MP-SPR) and Quartz Crystal Microbalance (QCM). Wet mass (QCM) and dry mass (MP-SPR) of polymer layer was calculated and compared to determine the amount of coupled water in the layer. Polymer adsorption kinetic to different surfaces was also determined. Adsorbed mass and the amount of coupled water was depending on the hydrophilicity of the surface.

Introduction

Amphiphilic polymers have a tendency to self-assemble and create organized structures on surfaces, especially in the case of block copolymers where the blocks are of different solution properties. This can be used to tailor the surface properties, such as wetting, lubrication and colloidal stability, which are of great interest for many high performance applications such as drug delivery vehicles, improved emulsifiers in paints and paper industries, and so on. Liu et al. [1] studied relationship between bulk polymer solution and self-assembled layers with many materials relevant to textile and paper industries.

Multi-Parametric Surface Plasmon resonance (MP-SPR) and Quartz Crystal Microbalance (QCM) are both label free and real-time measurement techniques which can be utilized to characterize molecule interactions and layer properties. MP-SPR is an optical measuring technique to determine extremely small changes in refractive index near SPR sensor surface. The refractive index is directly proportional to mass at the sensor surface, so changes in SPR angle can be directly related to change in mass. In water medium the hydration of molecules does not contribute to the SPR signal, because there is no refractive index difference between water as the medium and water as a part of the hydrated molecule. Thus, it is possible to measure the hydration free mass of molecules, so-called "dry mass", with SPR. The QCM method measures mass connected mechanically to the sensor surface from the changes in oscillation frequency of a quartz crystal. The mechanical mass measured by QCM also includes water bound in the material.

By combining these two surface sensitive measuring techniques, it is possible to estimate the mass percentage of bound water in thin layers close to the sensor surface. The combination is natural, as both instruments use gold coated sensors as standard for measurements, and therefore the sensor preparation can be performed in exactly the same manner to minimize systematic error in the experiment.

Materials and Methods

The adsorption of nonionic, symmetric triblock copolymer of ethylene oxide and propylene oxide (Pluronic P-105) was studied with polypropylene (PP), polyethylene terephthalate (PET), nylon and cellulose surfaces (Fig.1). The surfaces were prepared *ex situ* by spin coating. The details of the preparation are described in the original publication [1].

BioNavis SPR Navi 200 instrument was used in the SPR experiments and Q-Sense E-4 in the QCM experiments. All the experiments were performed with Milli-Q grade water and temperature of 25 °C, with Pluronic concentration ranging from 1×10^{-4} to 10 w/v %. To correlate the SPR response to real mass, instead of the commonly used response unit approximation applied for proteins ($1 \text{ RU} = 0.0001^\circ = 0.1 \text{ ng/cm}^2$), the refractive index increment dn/dc of Pluronic P-105 was measured and used to calculate conversion coefficient for the SPR signal. The coefficient was $0.14 \text{ ng/cm}^2 / \text{RIU}$. The amount of coupled water was calculated using the formula:

$$\% \text{coupled water} = \left(\frac{\Delta m_{QCM} - \Delta m_{SPR}}{\Delta m_{QCM}} \right) \times 100\%$$

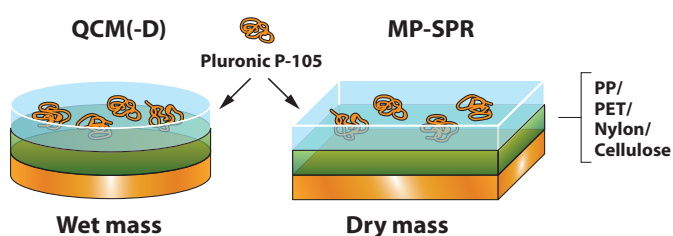


Figure 1. Pluronic-P interaction to polypropylene (PP), polyethylene terephthalate (PET), nylon and cellulose surfaces was measured with Multi-Parametric Surface Plasmon Resonance (MP-SPR) and Quartz Crystal Microbalance (QCM). With mechanical QCM technique wet mass is get whereas optical MP-SPR technique senses dry mass even if measurement is done in liquid.

Results and Discussion

MP-SPR responses against time when different concentrations of Pluronic were injected to PP surface can be seen in Figure 2. The other surfaces gave similar behaviour, as well as the QCM frequency [1].

The adsorption kinetics were found to be Langmuir type adsorption and follow the empirical kinetic equation:

$$\frac{\Gamma(t)}{\Gamma_{\max}} = K' - e^{-k_{\text{obs}} t}$$

Where $K' = (C/(C + kd/ka))$, Γ = mass/area Γ_{\max} = maximum mass/area and C , ka and kd are concentration, association and dissociation constants, respectively. An example of the kinetic fit is shown in Figure 2.

Adsorbed polymer MP-SPR response as a function of concentration to all studied surfaces is compared in Figure 3 showing clear difference between surfaces.

The adsorbed mass from both QCM and MP-SPR measurements was calculated (Fig.4). The adsorbed mass from the MP-SPR measurement was smaller than from the QCM-D measurement as expected due to coupled water included in QCM-D response (Fig.4). The adsorbed mass was found to decrease with increasing substrate hydrophilicity, and the amount of coupled water in the layer increased with increasing hydrophilicity of the substrate (Fig.4). Atomic force microscopy (AFM) showed that the polymer forms micelles when adsorbing on hydrophilic substrate, which explains the trend in the adsorbed mass and water content measured [1].

In this experiment the same flow rate, 0.1mL/min, was used in both MP-SPR and QCM-D experiments. However, in MP-SPR the flow-cell volume is only 1 μ L whereas in QCM-D the flow-cell volume is 40 μ L. To ensure the same mass transfer in both measurements the flow rate should be adjusted. Flow rate 10 μ L/min in MP-SPR corresponds 73 μ L/min in QCM [2]. For more details, see BioNavis Application Note 129

Conclusions

Combining the two methods, MP-SPR and QCM, it is possible to measure the amount of bound water in interfacial layers with simple experiments. The same experiments can also be used to determine the kinetics of adsorption. The understanding of the hydration of interfacial layers helps to understand the structure-property relationship of the layers, and can lead to future improvements in nanofabrication methods and nanofabricated coatings.

Additionally to adsorption kinetic and dry mass, MP-SPR can be also used to further characterize the deposited film. E.g. the thickness and refractive index of the layer can be determined (for more information see BioNavis Application Note 128).

References:

- [1] Liu et al. Langmuir 2010, 26(12), 9565–9574
 [2] Viitala et al. Journal of colloid and interface science 2012, 378, 251-259

Recommended instrumentation for reference assay experiments

SPR Navi™ 200, 210A or 220A with additional wavelength (L)

Sensor surfaces: Au, other metal or inorganic coating

Software: SPR Navi™ Control, SPR Navi™ DataViewer, SPR Navi™ Layer Solver, Trace Drawer™ for SPR Navi™

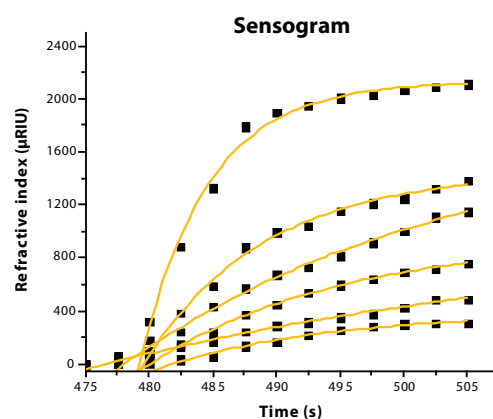


Figure 2. MP-SPR data from Pluronic P interaction with polypropylene (PP) surface. Change in refractive index as a function of time for different concentrations (15400 – 0.154 μ M from top to bottom) of the copolymer. Injection starting point is zoomed to show kinetic of the binding. Kinetic fit shown is based on Langmuir adsorption model.

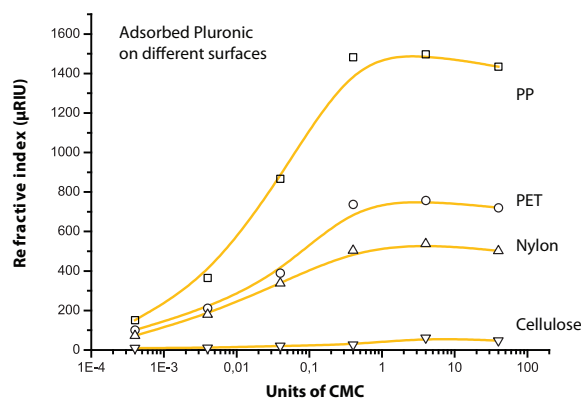


Figure 3. The refractive index of the layer created by the Pluronic P copolymer sample to different surfaces during MP-SPR measurement as a function of CMC concentration (CMC = 381 μ M). The lines are visual guides for viewing the trend.

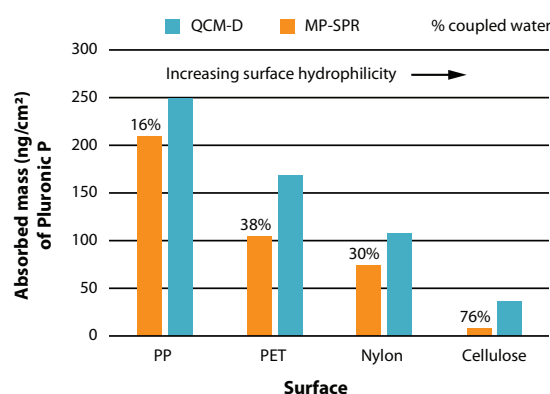


Figure 4. Absorbed mass of Pluronic P (1.54mM) to different surfaces after rinsing with water and % of coupled water.