Polymer characterization using MP-SPR – Adsorption studies and layer thickness

Polymers are extensively studied and often their interactions with other molecules play a key role in the product functionality. Two separate polymer interaction studies were conducted using label-free real-time Multi-Parametric Surface Plasmon Resonance (MP-SPR). In the first case, functionalization of nanocellulose surfaces was performed by adsorption of block copolymers. Secondly, the efficacy of antifouling of the PEG-based polymer brushes was quantified by measuring adsorption of serum samples. Based on the MP-SPR measurements, polymers were further characterized in terms of thickness and adsorbed mass. Nanocellulose functionalization was confirmed to be successful and -OH terminated 10 kDa PEG was found to be the best anti-fouling coating, producing 99% resistance.

Introduction

Polymers are extensively studied in order to develop functional materials for various applications, such as anti-fouling or barrier coatings, organic solar cells, composites, drug delivery systems, biosensors or diagnostics. In the last decades especially renewable materials, such as nanocellulose, are studied to replace carbon-based materials in functional materials applications.

The unique MP-SPR Navi™ instruments can perform measurements in a wide angular range (40-78 degrees) and at more than one wavelength, making the instrument an excellent tool for polymer characterization. MP-SPR can measure molecule adsorption in real-time and the same measurement provides also layer thickness. For layers that do not absorb light, thickness can be measured from nanometers up to micrometers. Additionally, with MP-SPR the exclusive feature of PureKinetics™ reveals changes in liquid composition during the measurements, solving some challenges related to optical characterization methods.

Materials and methods

Cellulose nanofibrils (CNF) were spin coated on gold MP-SPR sensor slides after UV/ozone cleaning and pre-treatment with a polyethylenimine (PEI) anchoring layer. TEMPO-oxidation was done *in situ* on the CNF surfaces (TOCNF).

Block copolymers of poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA) and poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA) with varying block sizes were synthesized and adsorption on the TOCNF was measured (Figure 1, left). The block copolymer concentrations were 0.5 g/L in 2.5 mM phosphate buffer solution at pH 6.8. Measurements were performed at 20˚C with a MP-SPR Navi™ 200 OTSO instrument, using a flow rate of 100 µL/min. More detailed information can be found in the original publication of Vuoriluoto *et al*., 2015.

In a separate experiment, poly(ethylene glycol) (PEG) polymer was adsorbed on a cleaned gold sensor slide *in situ* using 0.9 M Na_2SO_2 as running buffer. A reference surface was coated with oligo(ethylene glycol) (OEG) using 99.7% ethanol as a running buffer. Thickness and the grafting densities of the polymers were determined from the MP-SPR measurements.

Serum sample (bovine serum albumin) was diluted in PBS to 10% by volume which still contained a high protein concentration of approximately 10 g/L. Serum interaction with unmodified gold, the OEG and the various PEG coated gold surfaces was measured. Measurement was performed with an MP-SPR Navi™ 220A-L NAALI instrument at 22˚C, using a flow rate of 5 µL/min. More detailed information can be found in the original publication of Emilsson *et al*. (2015).

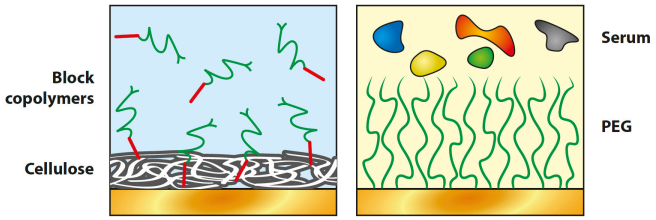

Figure 1. Schematic view of the adsorption of block copolymers onto nanocellulose surfaces (left) and of serum components onto the poly(ethylene glycol) polymer brushes (right), as studied using MP-SPR.

Results and discussion

The MP-SPR measurements confirmed that all the PDMAEMA-b-POEGMA copolymers adsorbed in significant extent onto the TEMPO-oxidated nanofibrillated cellulose surface (Figure 2). The adsorbed amount varied depending on the polymer segment length. Measured MP-SPR values were compared to Quartz Crystal Microbalance with Dissipation (QCM-D) measurement, however, the response in QCM-D is not only related to mass uptake, but it is also affected by charge neutralization and water expulsion from the surface (dehydration), causing negative responses with some of the copolymers (Figure 2). The MP-SPR technique does not suffer from the water-coupling limitation as QCM-D, hence the adsorbed mass and polymer adsorption kinetics can be directly determined.

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The same MP-SPR measurement was used to determine the thickness of the layer as well. As expected, longer copolymers formed thicker layers (Figure 2). In further studies, the antifouling properties of PDMAEMAb- POEGMA functionalized TOCNF surface against human IgG was quantified using MP-SPR (Vuoriluoto *et al*. 2016).

In the serum interaction studies, 2, 5, and 10 kDa PEG brushes provided good serum resistance and showed better resistance compared to the OEG monolayer (Figure 3). The best resistance, approximately 99%, was obtained with hydroxyl-terminated 10 kDa PEG resulting in only 4 ng/cm² bound mass. However, also the PEG brushes are highly inert (95-97% resistance) on time scales from hours up to at least 1 day, and were found suitable for biosensor applications.

Conclusions

MP-SPR is shown here as a great tool for soft material characterization in terms of degree of polymer layer functionalization through the adsorption of other molecules and the antifouling against serum. Uniquely, MP-SPR separates bound water from the real protein adsorption and therefore, provides high quality data also for hydrogels. Besides label-free, real-time measurements of binding kinetics, MP-SPR resolves also layer thickness, refractive index and adsorbed mass.

See how to measure thickness and refractive index using MP-SPR (AN#128) or how to monitor polymer swelling due to pH or electric

Original articles:

Emilsson *et al*., ACS Applied Materials & Interfaces, 7, 2015
Vuoriluoto et al., The Journal of Physical Chamistry B, 119, 2015

Reference:

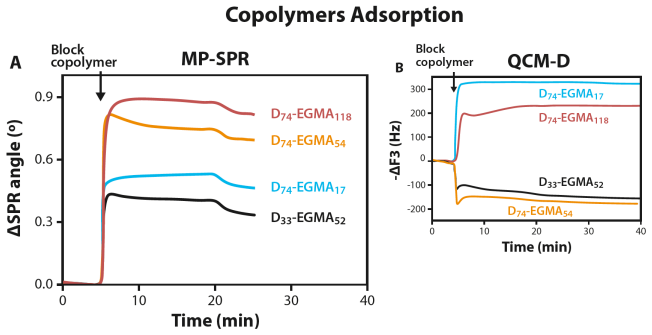
Vuoriluoto *et al*., ACS Applied Materials & Interfaces, 8, 2016

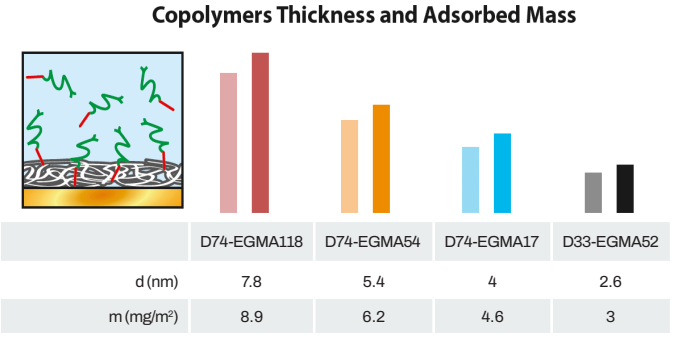
Recommended instrumentation for reference assay experiments

MP-SPR Navi™ 200 OTSO, 210A VASA or 220A NAALI with additional wavelength -L

Sensor surface: Au, other metal or inorganic coating

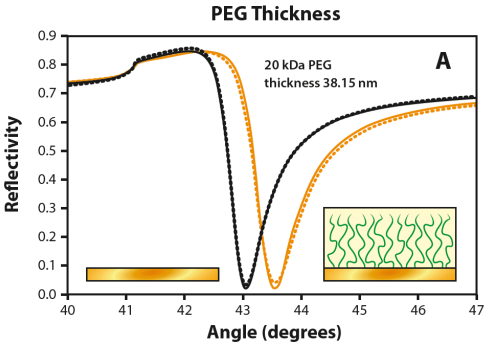
Software: MP-SPR Navi™ Controller, DataViewer, LayerSolver™ and TraceDrawer™ for MP-SPR Navi™





	D74-EGMA118	D74-EGMA54	D74-EGMA17	D33-EGMA52
d (nm)	7.8	5.4	4	2.6
m (mg/m²)	8.9	6.2	4.6	3

Figure 2. A) Adsorption of PDMAEMA-b-POEGMA copolymers with varying segment length onto a TOCNF surface, as measured by MP-SPR, and calculated thickness and mass values. B) QCM-D responses, suggesting that instead of polymer adsorption, there would be removal from the surface. However, the MP-SPR data confirms that polymer is adsorbed to all surfaces. The negative responses in QCM-D are caused by water expulsion, which cannot be separated from the measurement due to the working principle of the method.



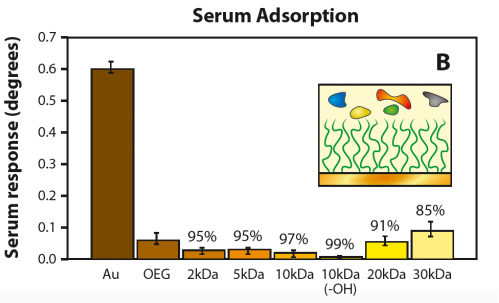


Figure 3. A) Full MP-SPR curve measured in air before and after PEG deposition for the fitting of the layer thickness. B) Adsorption of a serum sample onto various polymer surfaces

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