

# Polymer characterization using MP-SPR – Adsorption Studies and Layer Thickness

Polymers are extensively studied and often interactions 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). Functionalization of nanocellulose surfaces was performed by adsorption of block copolymers. The efficacy of anti-fouling 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

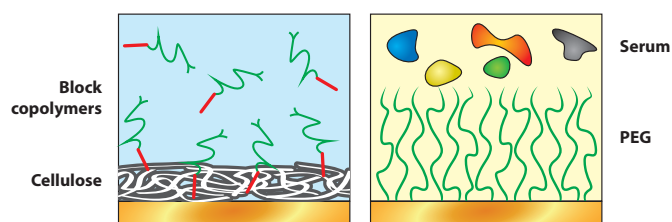
Cellulose nanofibrils (CNF) were spin coated on gold MP-SPR sensor slides after UV/ozone cleaning and pre-treatment with a polyethylenimine (PEI) anchoring layer. TEMPO-oxidation was done *in situ* on the CNF surfaces (TOCNF).

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). 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<sub>2</sub>SO<sub>2</sub> 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 adult) was diluted in PBS to 10% by volume which still contained a high protein concentration of approximately 10g/L. Serum interaction onto unmodified gold, the OEG and the various PEG 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 and of serum components onto the poly(ethylene glycol) polymer brushes, 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 separates water from the adsorbed mass of polymer and therefore, the results provide a real insight into the polymer adsorption kinetics and mass.

From the same MP-SPR measurement also layer thickness can be determined. As expected, longer copolymers formed thicker layers (Figure 2). In further studies, the anti-fouling properties of PDMAEMA-b-POEGMA functionalized TOCNF surface towards human IgG adsorption were 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/cm<sup>2</sup> 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 such as polymer layer functionalization and quantification of anti-fouling coatings. 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 also how to measure thickness and refractive index using MP-SPR (AN#128) or how to monitor polymer swelling due to pH or electric potential changes (AN#136).

## References:

### Original articles:

Emilsson et al. ACS Applied Materials & Interfaces 2015, 7, 7505-7515

Vuoriluoto et al. The Journal of Physical Chemistry B, 2015, 119, 15275-15286

### Other references:

Vuoriluoto et al. ACS Applied Materials & Interfaces 2016, 8, 5668-5678

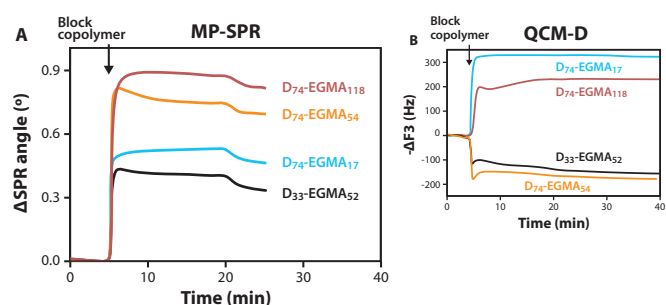
### Recommended instrumentation for reference assay experiments

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

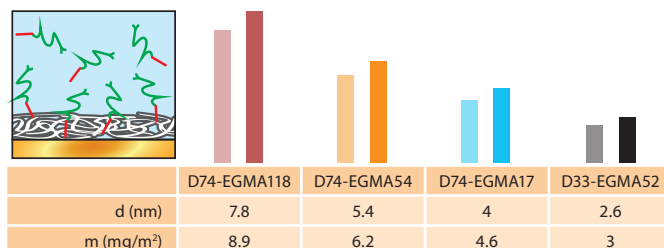
Sensor surfaces: Au, other metal or inorganic coating

Software: MP-SPR Navi™ Control, DataViewer, LayerSolver™, and Trace Drawer™ for MP-SPR Navi™

## Copolymers Adsorption

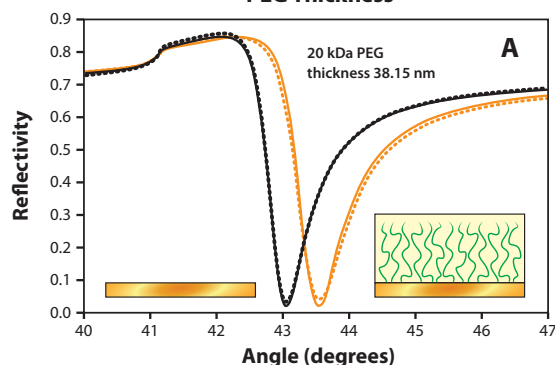


## Copolymers Thickness and Adsorbed Mass

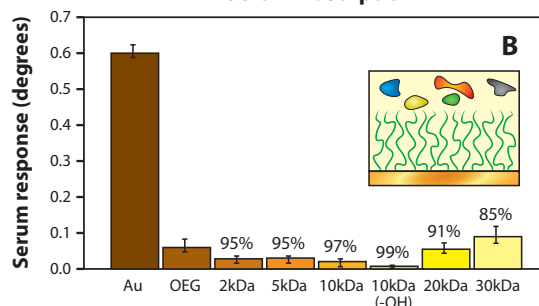


**Figure 2.** A) Adsorption of PDMAEMA-b-POEGMA copolymers with varying segment length onto a TOCNF surface, as measured by MP-SPR, and calculated thickness and mass values. B) QCM-D responses, suggesting that instead of polymer adsorption, there would be removal from the surface. However, the MP-SPR 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.

## PEG Thickness



## Serum Adsorption



**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.