Application Note # 159

Material Swelling Studies using MP-SPR: Cellulose in Water Vapor and Polymer Barrier in Solvent Vapors

Multi-Parametric Surface Plasmon Resonance (MP-SPR) detects interaction of vapors with different materials in real-time and without help of any labels. As the method works with thin films and minute volumes, the measurements are fast and highly sensitive.

Swelling of nanocrystalline cellulose (NCC) in water vapors was measured using MP-SPR. Saturated saline solutions were utilized to form different water vapor contents to passing air flow. NCC layer swelled with increasing moisture content in the air and the thickness of the film changed from 34.5 nm to 36.1 nm.

In a separate study, the uptake of ethanol and toluene vapor by block copolymer films was studied using MP-SPR. The uptake showed linear increase when vapor concentration was changed from 0% to 100% using 10% steps, and barrier properties of the film were evaluated.

Introduction

Vapor-induced changes in material are an important field of research for barrier coatings in packaging, environmental monitoring, pharmaceuticals (drug storage), paper, polymer and corrosion research.

Surface Plasmon Resonance (SPR) is a well-established method to measure binding affinity and kinetics of molecular interactions. However, the physical phenomenon is also applicable to material characterization. Comprehensive Multi-Parametric Surface Plasmon Resonance (MP-SPR) instruments can perform measurements in an exceptionally wide angular range (40-78 degrees) and at more than one wavelength, thus making MP-SPR an outstanding tool also for material characterization.

MP-SPR measures adsorption of molecules in real-time, and the same measurement provides also layer thickness and refractive index. For layers that do not absorb light, thickness can be measured from nanometers up to micrometers. Additionally, layer characterization can be performed in liquid, in air and in various other gaseous environments, thus making MP-SPR a very versatile tool for barrier characterization.

Sensor slides can be easily coated *in situ* and *ex situ* by various methods, such as spin coating, dip coating, ALD, self-assembly and many others. The sensors with applied coatings are then simply placed in our easy-to-use sensor holder and inserted into the MP-SPR instrument. MP-SPR uses an elastomer-coated prism and thus allows oil-free operation, which in turn allows further characterization of the coatings. After MP-SPR vapor adsorption experiments, the sensors can be easily removed for measurements by AFM, SEM and other surface methods.

Gases and vapors can be applied to MP-SPR measurement using multiple methods (see Figure 2).

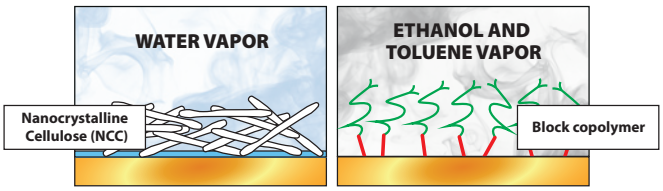

Figure 1. Swelling of nanocrystalline cellulose (NCC) in water vapors and the uptake of ethanol and toluene vapor by block copolymer films were measured using MP-SPR.

Materials and methods

Both experiments were performed using MP-SPR Navi™ 200 OTSO equipped with gas flow-cell, and performed in two individual measurement channels simultaneously on the surface.

Study 1

Nanocrystalline cellulose (NCC) was spin-coated on gold sensor slide functionalized with a poly(ethylenimine) (Figure 1). Water vapor was formed using a saturation bubbler and saturated salt solutions before guiding the controlled moist-air into the MP-SPR flow-cell (Figure 2A). NCC swelling was studied in various moisture concentrations. Moisture contents were created by passing ambient air through LiCl (11%), $MgCl_2$ (33%), $Mg(NO_3)2$ (53%), NaCl (75%), KNO_3 (95%) and water (100%). After application of the water vapours, the NCC film was exposed back to the ambient air at ambient temperature of 22 °C.

Thickness and refractive index of the cellulose film was calculated using a two wavelengths (670 nm and 785 nm) method and LayerSolver™ software.

Study 2

Commercially available block copolymer was spin coated on a gold sensor slide. Uptake of ethanol and toluene vapors by block copolymer was measured (Figure 1). Vapour gradient was formed using bubbler, mass flow controllers, and mixing unit before guiding the flow into the MP-SPR flow-cell (Figure 2C). The vapor concentration in the gas flow was controlled between 0% (no organic vapor) and 100% (fully saturated organic vapor from the bubbler). The concentration was increased in steps of 10%, while the polymer response was simultaneously monitored in real-time.

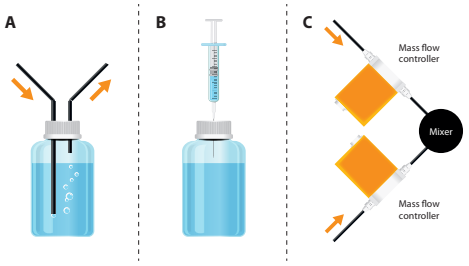

Figure 2. Examples of different configurations of MP-SPR vapor measurements. A) Saturation bubbler, B) Head space injection, C) Mass flow controller and injector.

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Results and discussion

The uptake of water vapor by NCC film and its subsequent swelling were observed as the water vapor content was increased in steps from 11% to 100% (Figure 3). Reaction of the film was similar in both measurement channels, however, small difference in response was detected. This difference is attributed to the spin coating, which resulted in different thickness of the NCC film in the two individual measurement areas, causing variation in the swelling and water uptake.

In both measurement areas, the 75% moisture caused smaller response than 53% moisture. In this preliminary experiment, the reason was not studied thoroughly. It is likely that the $Mg(NO_3)_2$ solution was not fully saturated, and thus the actual moisture content was less than the expected 75%.

Thickness and refractive index (RI) of the NCC film was determined by modelling full SPR curves in LayerSolver™ (Figure 4). NCC swelled slowly. Therefore, longer injections could have allowed the surface to swell even more. The increase of the RI of the layer in each step shows that the water from the moist air stays in the network, thus effectively changing the total optical density (RI) of the layer.

In the separate study, the vapor reached a steady state at each vapor concentration in less than 5 minutes (Figure 5). However, when returning to 0% concentration, the complete desorption took more than 85 minutes in both cases. The amount of vapor uptake increased linearly with increasing ethanol concentration, as well as with toluene (Figure 6). The high sensitivity of MP-SPR allows the use of thin polymer films for interaction studies. This is extremely useful when barrier properties are studied, as the time required for the measurement is reduced. PureKinetics™ measured by MP-SPR revealed that no change in bulk refractive index (due to change in ambient vapor concentration) was present during the measurement. This confirms that all the detected changes were caused by the changes in polymer film (See more information about unique PureKinetics™ feature of MP-SPR in Application Note #147).

Conclusions

MP-SPR allows measurement of gas induced changes in polymer films in real-time. Both, water moisture and organic solvent vapors, can be studied. Data from the experiment provide information on vapor uptake rates as well as on layer properties (thickness and refractive index) simultaneously. MP-SPR provides also valuable information about barrier properties of the films and coatings.

See also how polymers have been characterized in liquid using MP-SPR: mass and thickness of block-co-polymers adsorbed on cellulose nanofibrils (CNF), and adsorption of serum components onto the poly(ethylene glycol) polymer brushes Application Note #149.

Acknowledgement:

We thank Dr. Tekla Tammelin from the Technical Research Center of Finland (VTT) and Dr. Thomas Schäfer from POLYMAT, University of the Basque Country, Spain for their co-operation in this work.

Recommended instrumentation for reference assay experiments

MP-SPR Navi™ 200 OTSO or 210A VASA with additional wavelength (-L) and gas flow-cell.

Sensor surfaces: Au, other metal, or inorganic coating

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

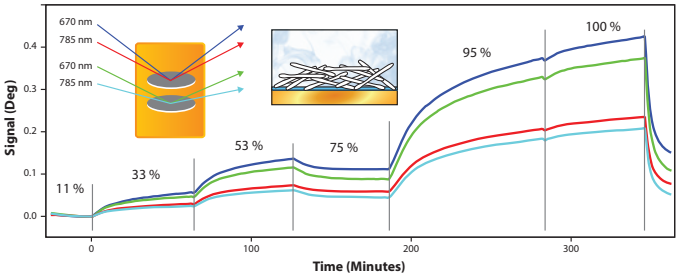

Figure 3. Real-time swelling of nanocrystalline cellulose (NCC) film under different vapor water contents. Air moisture contents: LiCl (11%), $MgCl_2$ (33%), $Mg(NO_3)_2$ (53%), NaCl (75%), KNO_3 (95%) and water (100%). Swelling was measured simultaneously using two different wavelengths (670 nm and 785 nm) on each measurement channels.

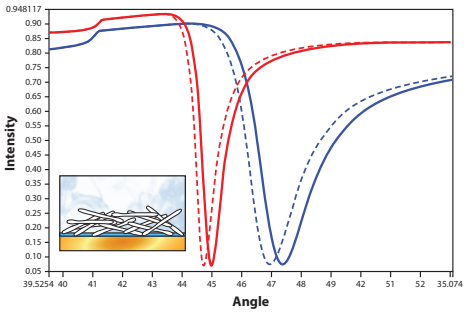

Figure 4. Full SPR curves of nanocrystalline cellulose film in ambient air (dashed line) and in water vapor (solid line). SPR curve is shifted to the right due to NCC film swelling. Thickness and refractive index of the films were calculated (table under this figure) under different vapor concentrations and based on two wavelength data (670nm and 785nm).

Moisture	d (nm)	n@670nm
11 %	34.5	1.379
33 %	34.7	1.381
53 %	34.6	1.388
100 %	36.1	1.394

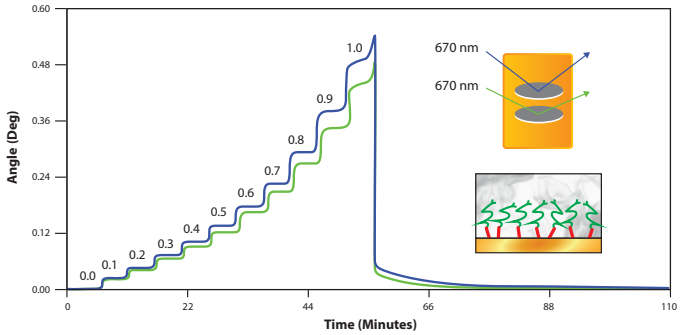

Figure 5. The uptake of ethanol vapor in block copolymer film measured in real-time using MP-SPR. Ethanol vapor content was increased from 0 % to 100 %, using steps of 0.1. The measurement was performed simultaneously in two individual channels. Small differences in the responses were caused by different thickness of the film caused by spin coating.

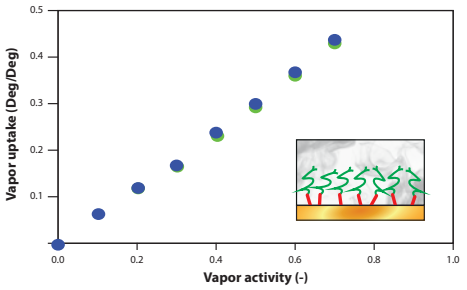

Figure 6. Uptake of toluene vapor in block copolymer film was equal in two measurements performed simultaneously using MP-SPR (blue and green).

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