

## SWELLING KINETICS OF A CELLULOSE MODEL FILM

### INTRODUCTION

A model system for studying swelling of cellulose fibres in real time was evaluated by spin coating a thin cellulose layer onto a quartz crystal, which was subsequently exposed to various salt and pH variations. The thin (30-90 nm) cellulose layer, considered being of paracrystalline cellulose type II, was prepared by dissolving cellulose fibres in NMMO and applying them to a SiO<sub>2</sub> coated quartz crystal. Salt concentration and pH were varied and the frequency and dissipation output recorded over several hours following each such variation.

### Surface preparation

Pulp was dissolved in NMMO (N-methylmorpholine-N-oxide), diluted to a specific concentration with DMSO (dimethyl sulfoxide) and spin-coated onto a SiO<sub>2</sub> coated quartz crystal pre-covered by a cationic polymer. The quartz crystal was spun at 2000 rpm for 20s, which produced a highly reproducible layer about 30-90nm thick (depending on cellulose concentration). Differently charged cellulose fibres were used to produce surfaces with both uncharged, and high charge, densities. The swelling kinetics of both surfaces were then compared.

### RESULTS

The swelling kinetics was studied by changing liquids from EtOH to solutions of different NaCl concentrations and/or different pH. In **Figure 1** the results for two differently charged surfaces are compared.

With the information provided by the dissipation factor the cellulose film was considered to be close enough to the valid region of the Sauerbrey relation and a first order exponential function could be fitted to the frequency data to model the kinetics of the swelling\*. For thicker films, viscoelastic modelling of frequency and dissipation data would have been required for accurate estimation of thickness changes. The initial buffer effect was disregarded and the fitting started 2 minutes after the change of liquid. The fitting was reproduced for different NaCl concentrations. The decay constant from the fit and frequency shift data was used to compare the results from the model system with fibre swelling experiments performed by swelling fibres in water and removing water not associated with the fibre wall (**Figure 2**). The Water Retention Value (WRV, standard method SCAN C 102X) was in this respect used as a measure of the

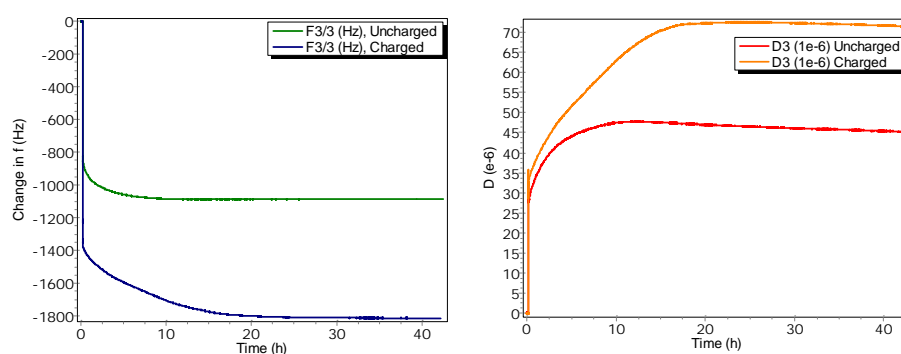
amount of water bound to the cellulose fibre.

The cellulose model surface showed similar swelling behaviour as to bulk experiments performed on fibres, which introduces the QCM-D approach as a real time method for the study of swelling kinetics.

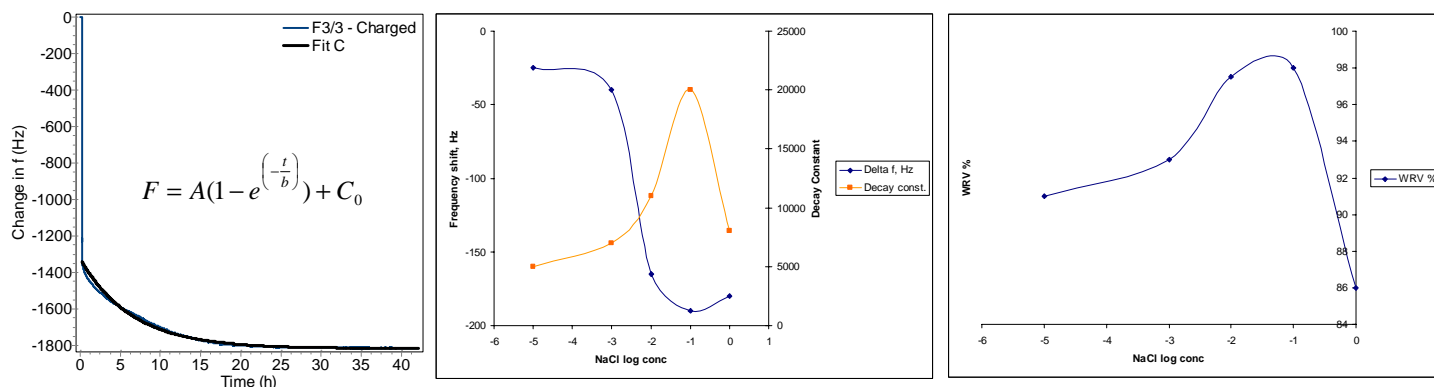
\* *Viscoelastic modelling and kinetic fitting are included in the evaluation software, QTools, provided by Q-Sense.*

### CONCLUSIONS

QCM-D detects water absorption in thin (nm) polymer films with great sensitivity. In combination with real time monitoring QCM-D can be used to monitor swelling kinetics in e.g. cellulose model films. In this application note it is also shown that the cellulose model film shows similar swelling kinetics as the true fibre wall.



**Figure 1** – Swelling kinetics for the uncharged and the charged model surface. The charged surface shows more swelling than the uncharged. The initial large shift can be explained by buffer effects and released stresses within the film. Frequency change (left), Dissipation change (right).



**Figure 2.** Fitting of a first order exponential function to the frequency data for model films (left). Decay constant (b) and frequency shift at different NaCl concentrations (centre). Water Retention Value (WRV) of fibres at the different NaCl concentrations (right). The decay constant, extracted from the fitting of QCM-D data to a first order exponential function, has a similar shape as the WRV value measured with standard SCAN C 102 X.

**REFERENCES**

Swelling of Model Films of Cellulose Having Different Charge Densities and Comparison to the Swelling Behavior of Corresponding Fibers  
 Langmuir 2003, 19, 7895-7903  
 Susanna Fält, Lars Wågberg, and Eva-Lotta Vesterlind

