Humidity can induce phase transitions of surfactants embedded in latex coatings which can drastically decrease their performance

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Wood, a material for the future

Wood: a renewable and widely applied building material

- Good mechanical properties
- Insulation
- Easily machinable

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But weathering (especially humid environments) can severely decrease the performance of wood as a building material.

Wood, a material for the future

Solution: Wood coatings/finishes

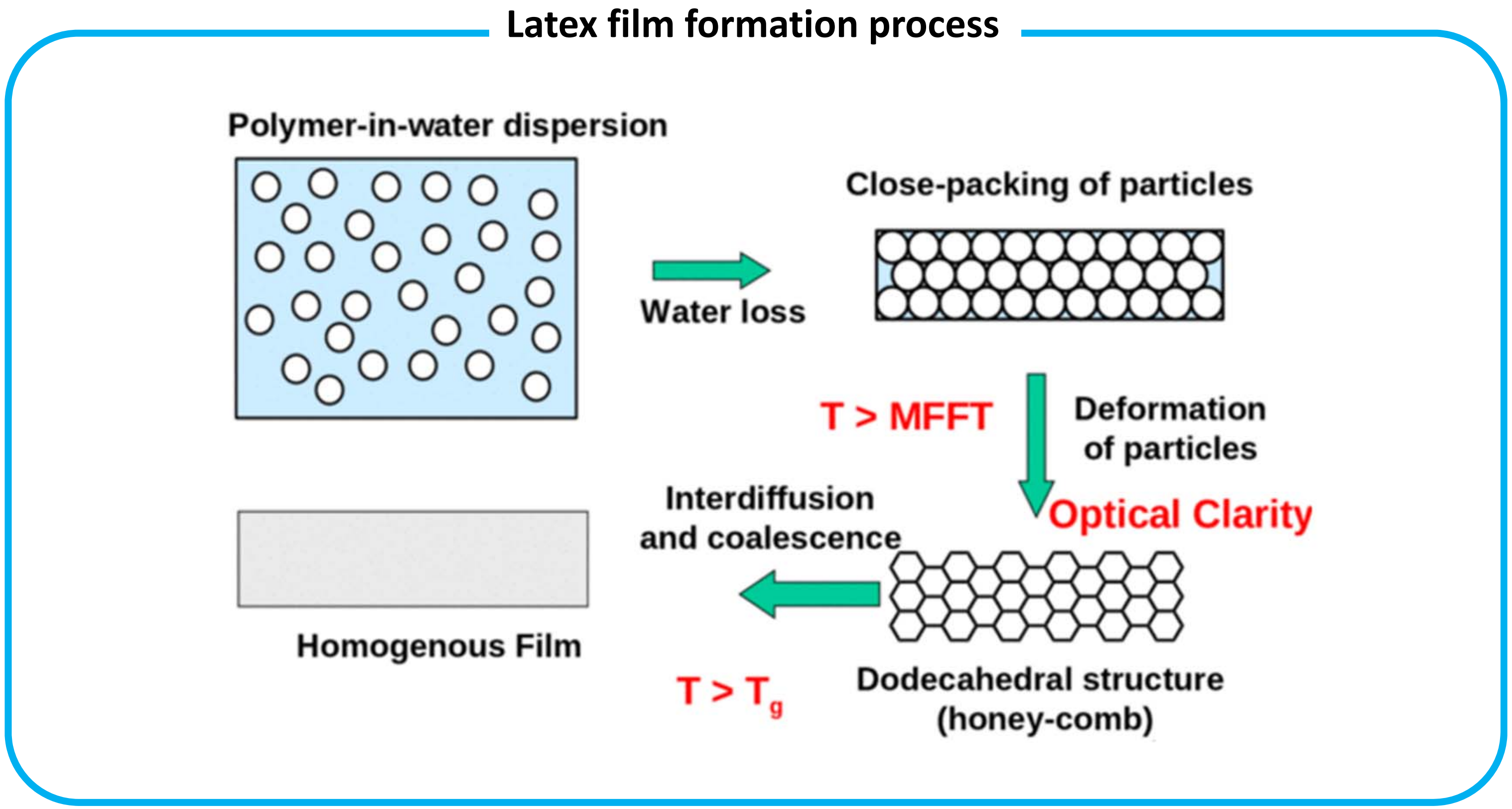
Typically with hydrophobic films/polymers in order to protect wood from humidity/water

Environmental concerns/legislations

Need to use **waterborne coatings** rather than solventborne coatings

What are waterborne coatings?

- Waterborne coatings are coatings formed by casting on a surface an aqueous dispersion of (mostly) hydrophobic polymer particles.



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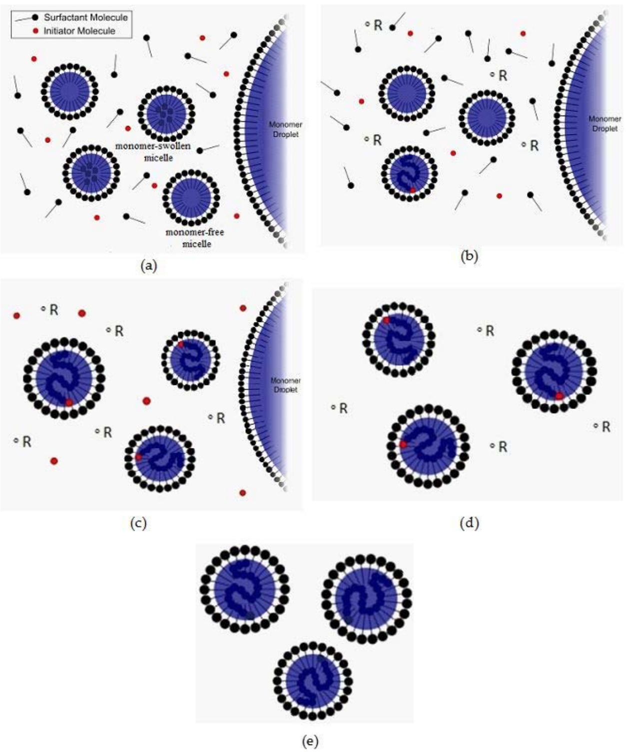
What type of aqueous dispersions are used for (wood) waterborne coatings?

Many waterborne coatings (mostly those based on acrylic polymers) are formed from aqueous dispersions of polymer particles stabilized with surfactants



Yamak, Emulsion Polymerization, DOI: 10.5772/51498

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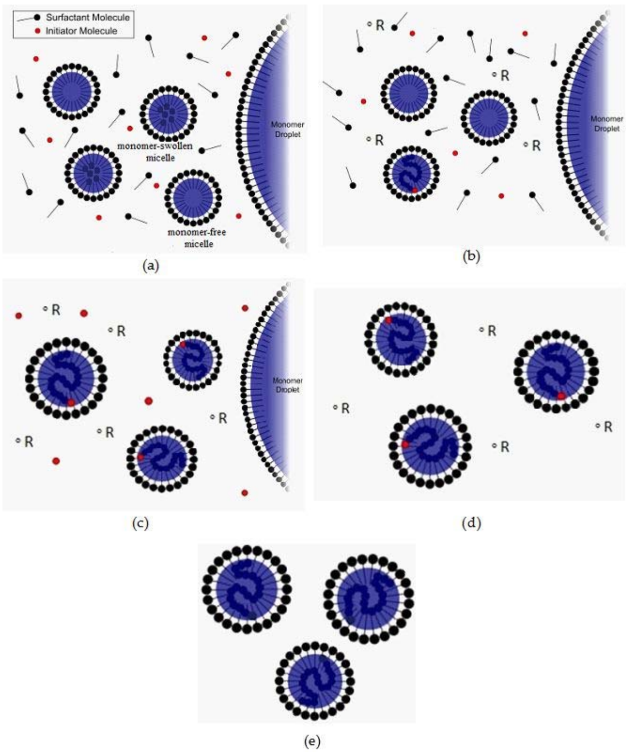

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What happens with surfactants after the coating is formed?

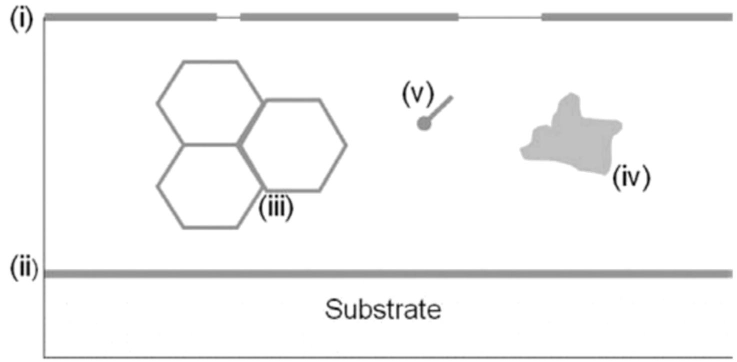

Fig. 6.2 Possible locations of surfactant in a *dry* latex film. Segregated at interfaces with (i) air or (ii) the substrate as either continuous or discontinuous layers; (iii) adsorbed along particle-particle boundaries. (iv) Surfactant can aggregate into pockets. Finally, some surfactants are partially miscible with the polymer phase and are (v) dissolved within the film matrix.

Keddie et al, Fundamentals of Latex Film Formation, Springer

Has an influence on the mechanical performance and the aesthetics of the coatings.

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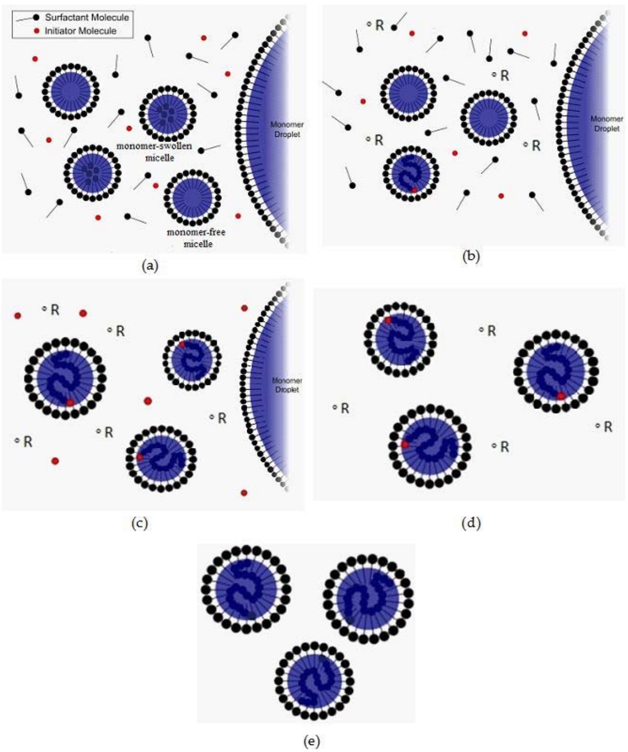

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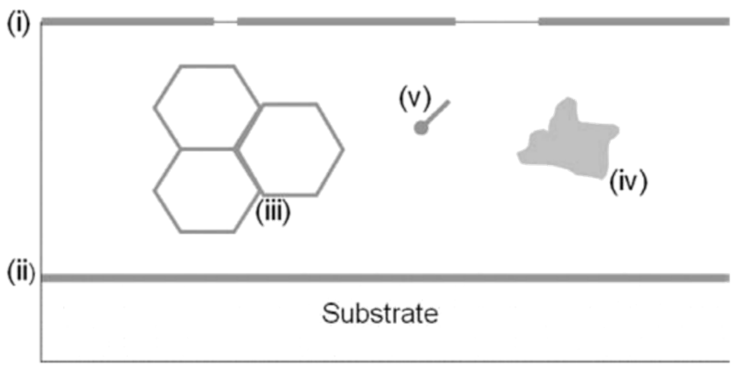

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↓

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Surfactants: extremely sensitive to the presence of water!

The influence of surfactants on waterborne coatings exposed to liquid water has been thoroughly studied

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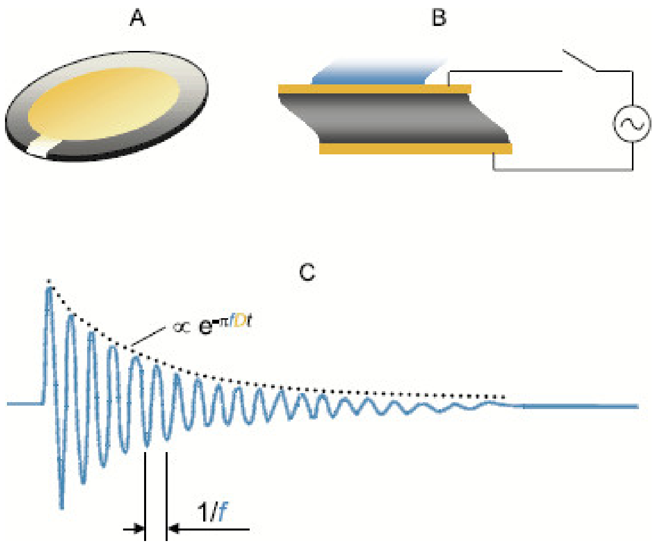
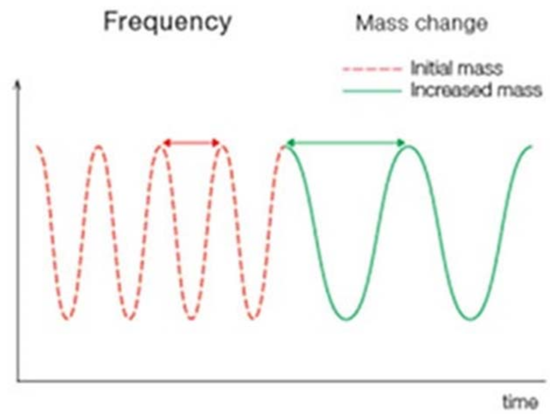
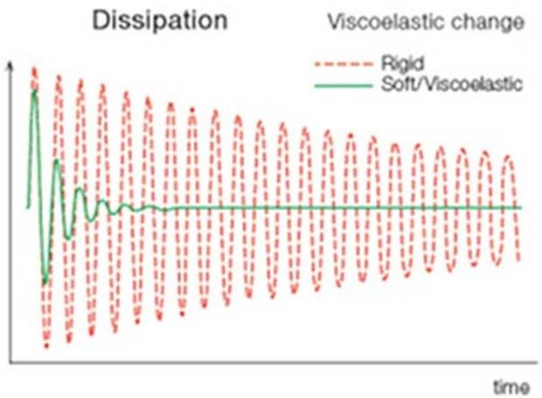
But do they influence the performance of the coatings just exposed to humid environments (RH<100%)?

Monitoring coating formation by means of QCM-D

Acoustic sensor







Mass variation

$$\Delta f \propto \Delta m$$

Viscoelasticity

$$D = \frac{1}{\pi\, f\, \tau} = \frac{1}{Q} = \frac{E_{dis}}{2\,\pi\, E_{stor}}$$

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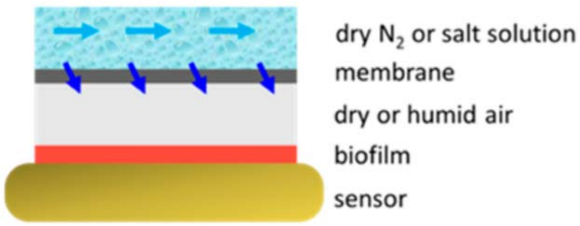
Monitoring coating formation by means of QCM-D

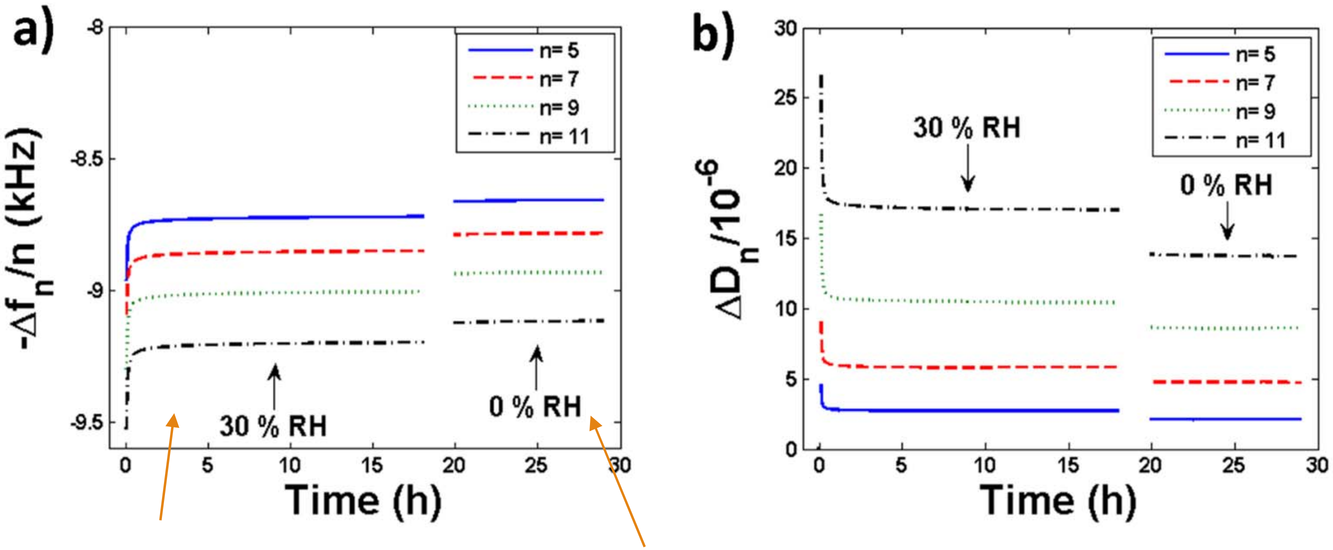


Common setup for QCM-D experiments

Acrylic coating where the original aqueous dispersion was stabilized with the surfactant Rhodacal ® DSB (Sodium Alkyl Diphenyl Oxide Sulfonate)

Experiments with controlled humidity

- Drying at RH = 30 %
- Test at RH = 0%



Related to initial mass of water evaporated

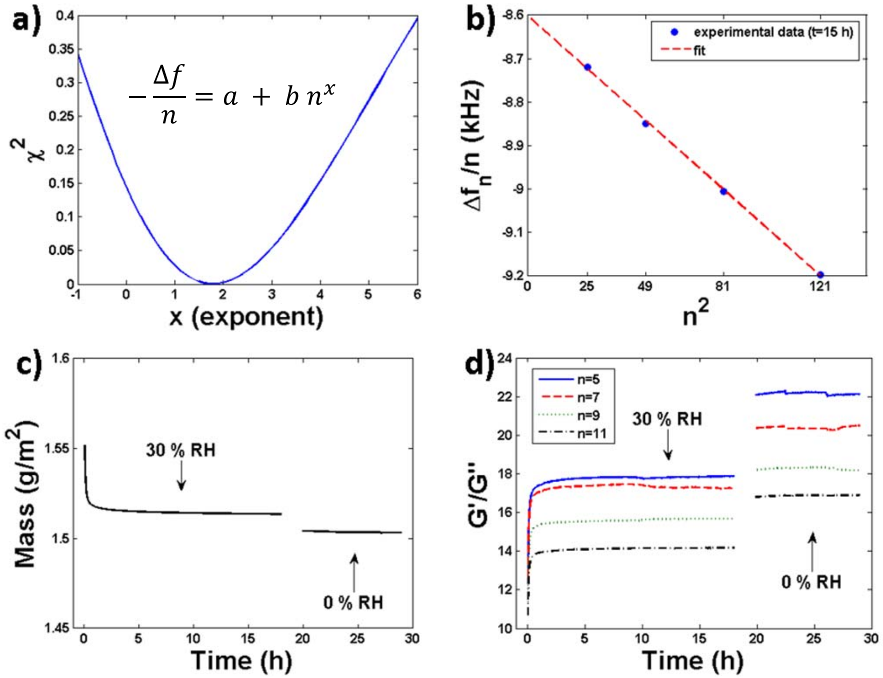
Related to humidity

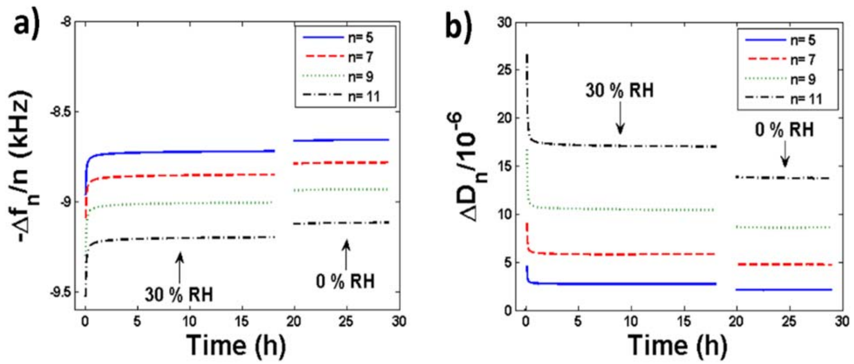
Modelling: Waterborne coatings have a viscoelastic character

For a viscoelastic film in air, the normalized frequency shifts are scaled by the overtone number to the square [1]

$$\frac{\Delta f}{n} = \frac{-2f_0^2 m_f}{Z_q}\left(1 + \frac{1}{3}\frac{Z_q^2}{Z_f^2}\left(\frac{m_f}{m_q}n\pi\right)^2\right)$$

In other words… $-\frac{\Delta f}{n} = a + b\,n^2$ → $a \propto m_f$





G' = Shear storage modulus
G'' = Shear loss modulus

$$\frac{G'}{G''} = \frac{-\Delta f_n + n\left(\frac{\Delta f_n}{n}\right)_{n\to 0}}{\Delta\Gamma_n}$$

[1] Johannsmann, D. Viscoelastic Analysis of Organic Thin Films on Quartz Resonators. Macromol. Chem. Phys. 1999, 200, 501−516.

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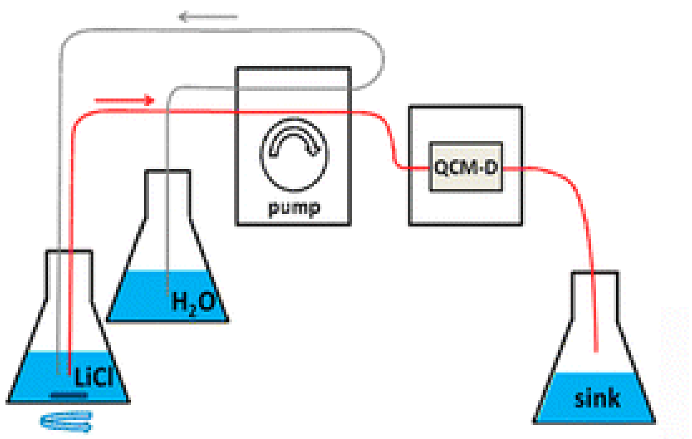
Sorption isotherms: QCM-D

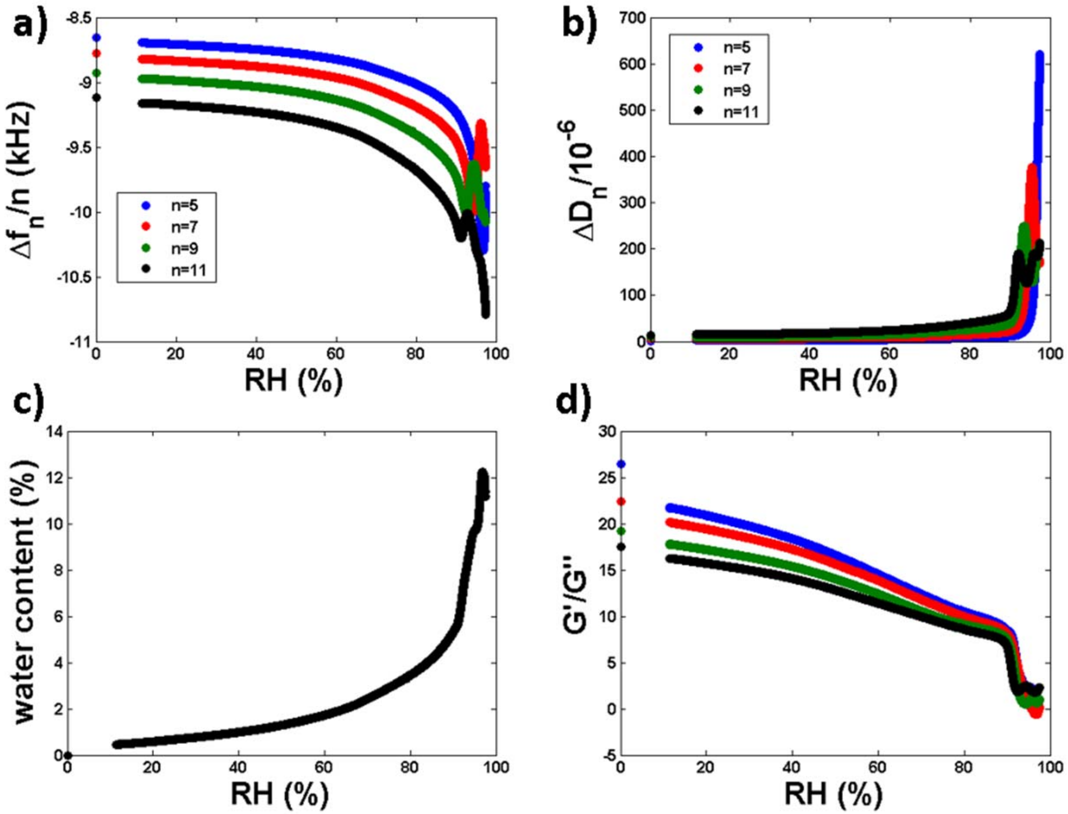
Acrylic coating where the original aqueous dispersion was stabilized with the surfactant Rhodacal ® DSB (Sodium Alkyl Diphenyl Oxide Sulfonate)

QCM-D experiments, increasing humidity continuously [2].



LiCl, RH = 11.31± 0.31 %

m_{LiCl}, m_{H_2O} and m_{sink} are known or measured.



Great change at RH > 90%

What is the responsible of this change?

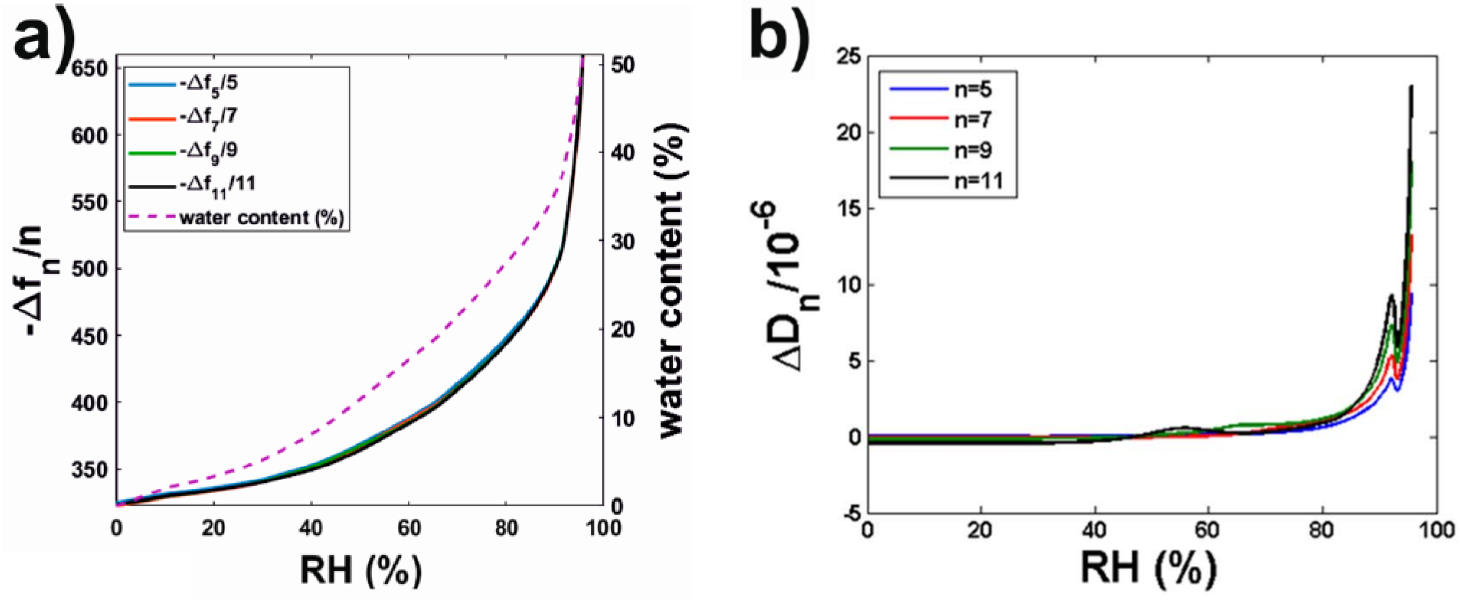
[2] Björklund, S., & Kocherbitov, V. (2015). Humidity scanning quartz crystal microbalance with dissipation monitoring setup for determination of sorption-desorption isotherms and rheological changes. *Review of Scientific Instruments*, *86*(5), 055105.

Sorption isotherms: QCM-D

Spin-coated layers of Rhodacal ® DSB (Sodium Alkyl Diphenyl Oxide Sulfonate)

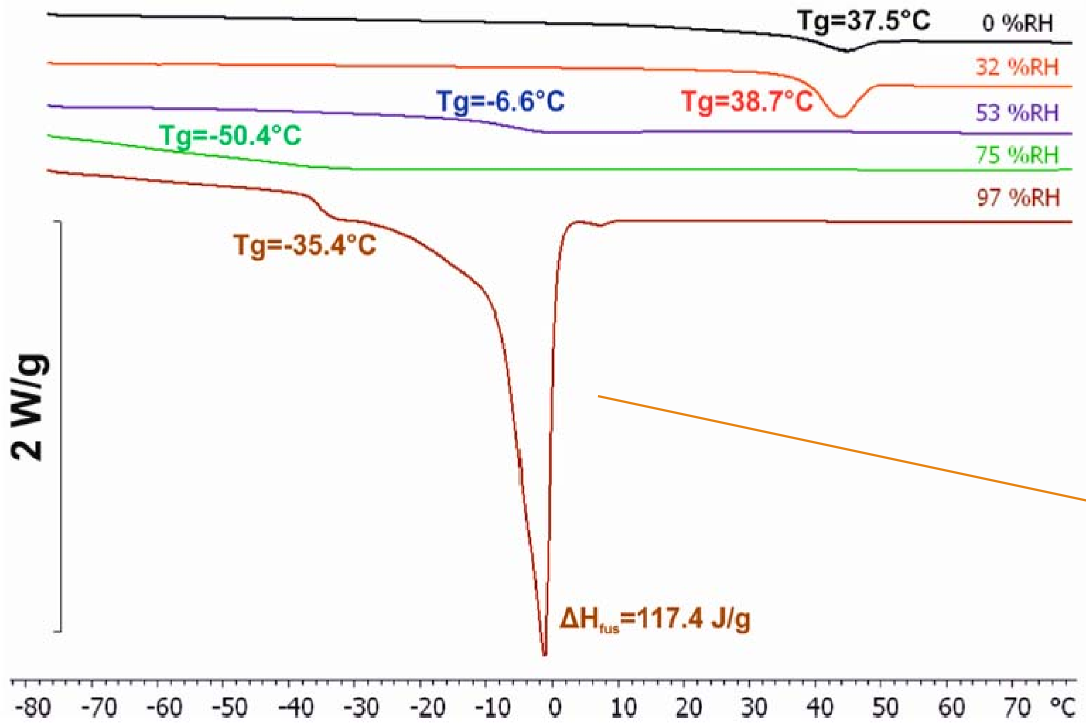
Same experiment with surfactant only.

The change at RH > 90% is also observed.



Differential Scanning Calorimetry

DSC scans of of Rhodacal ® DSB (Sodium Alkyl Diphenyl Oxide Sulfonate)

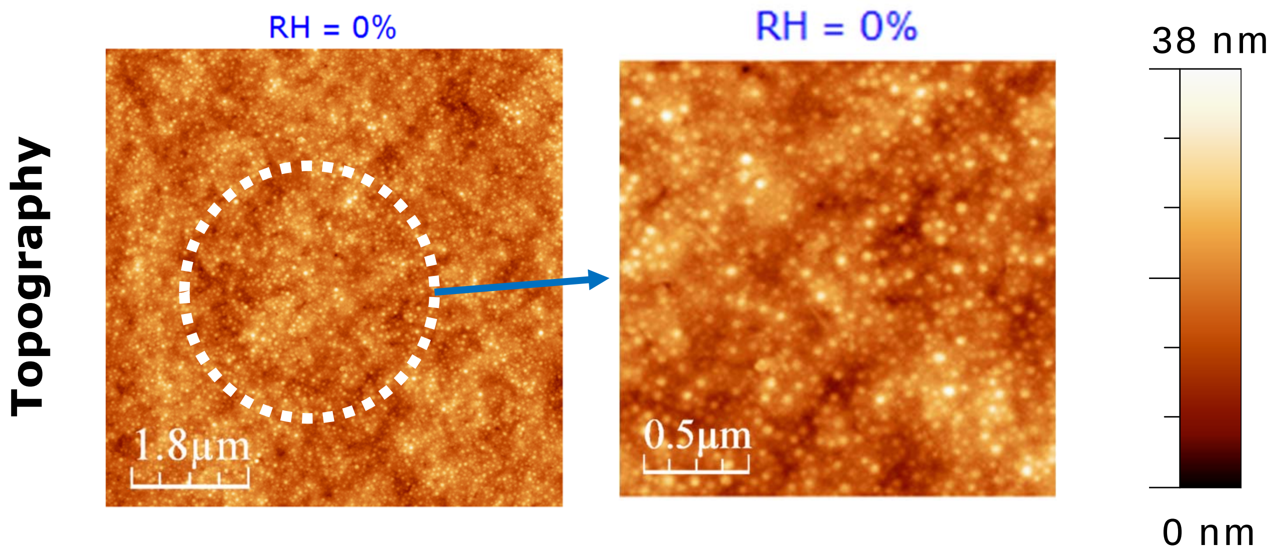


- Endothermic steps can be observed for all DSC scans.
- Steps for RH=0% and RH=32% correspond to a glass transition followed by a structural relaxation.
- Increasing of RH from 0% to 32% does not change significantly the glass transition temperature T_g.
- Further increase of RH leads to a decrease of T_g that could be explaining by plasticization effects.

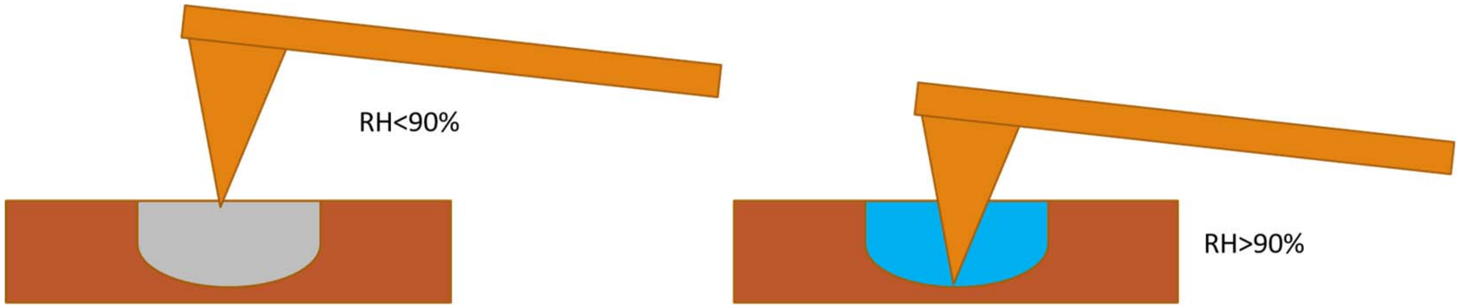
An increase of Tg for RH higher that 97% is observed, with a large peak characteristic of ice melting. In fact, the experiments shows that Rhodacal at 97% contains 35% of freezing water. This indicates that the surfactant for high values of RH undergoes a phase transition.

Studying mechanical properties as a function of relative humidity with AFM

Exposition to different relative humidity values:



Presence of artefacts (holes) where the film is softer due to water absorption.



Gonzalez-Martinez, J. F., Znamenskaya Falk, Y., Björklund, S., Erkselius, S., Rehnberg, N., & Sotres, J. (2018). Humidity-Induced Phase Transitions of Surfactants Embedded in Latex Coatings Can Drastically Alter Their Water Barrier and Mechanical Properties. Polymers, 10(3), 284.

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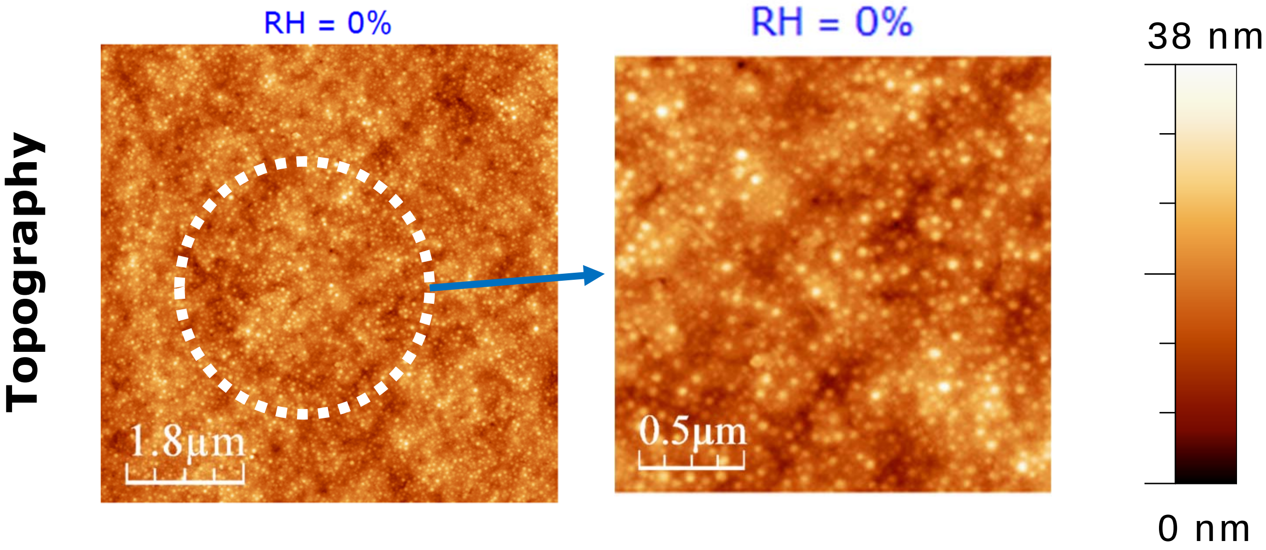

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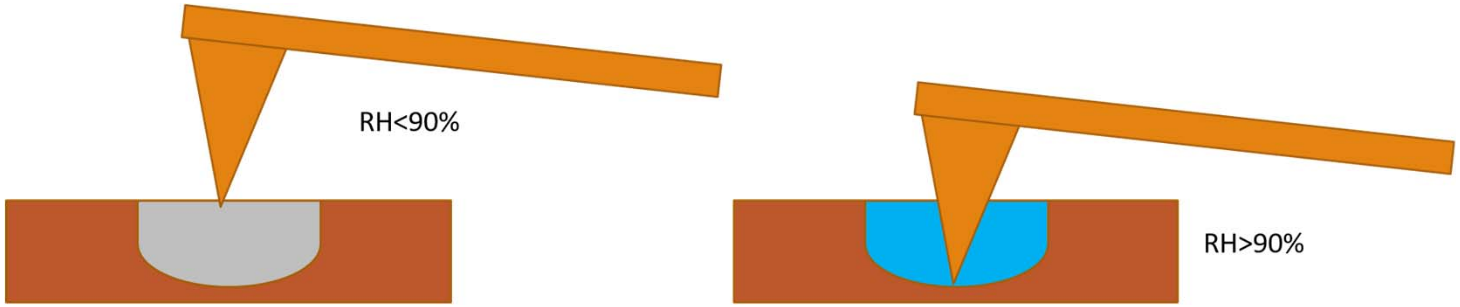

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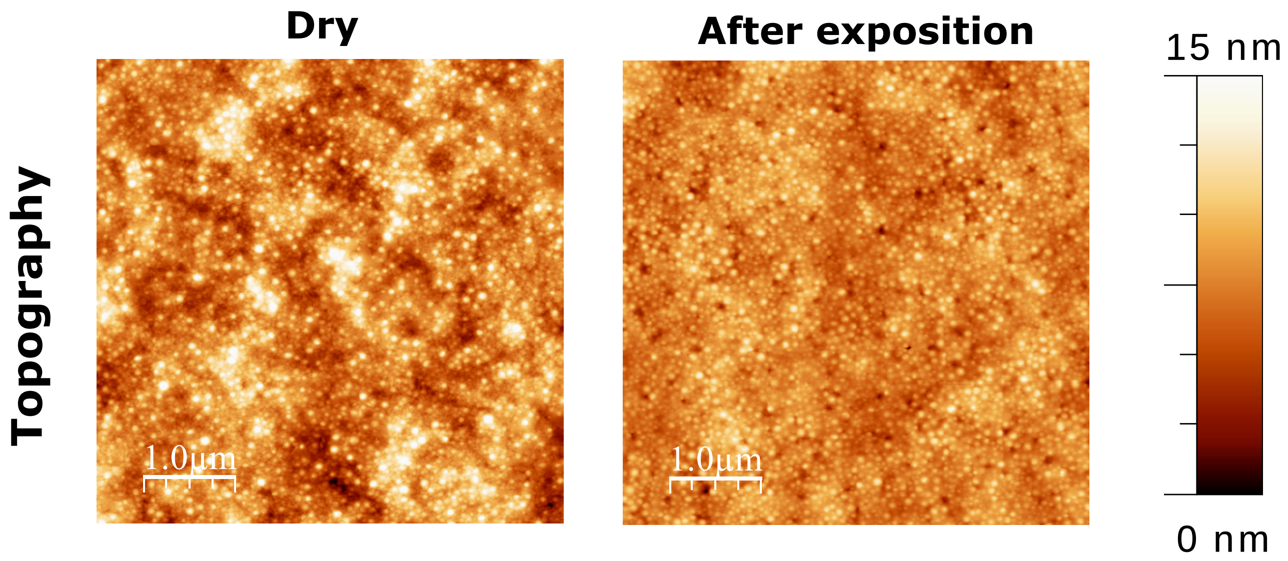
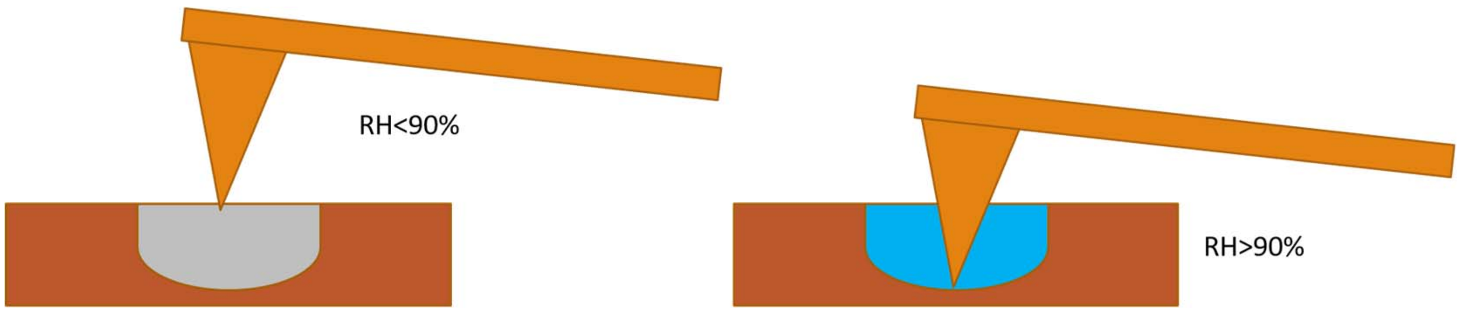
Exposition to liquid water:



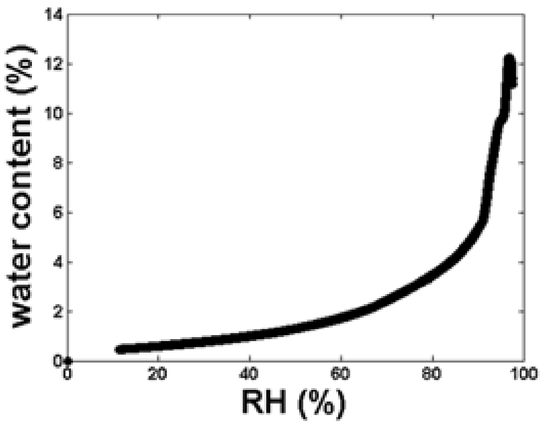
Presence of artefacts (holes) where the film is softer due to water absorption.

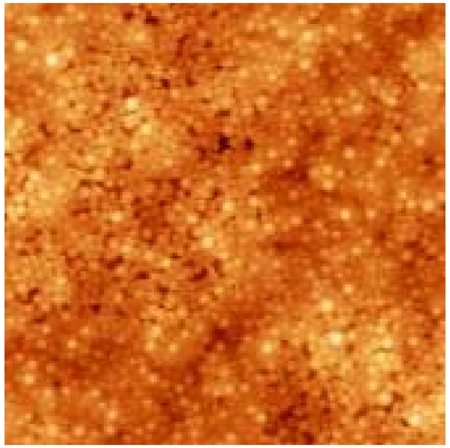
Same behaviour after exposition to liquid water.

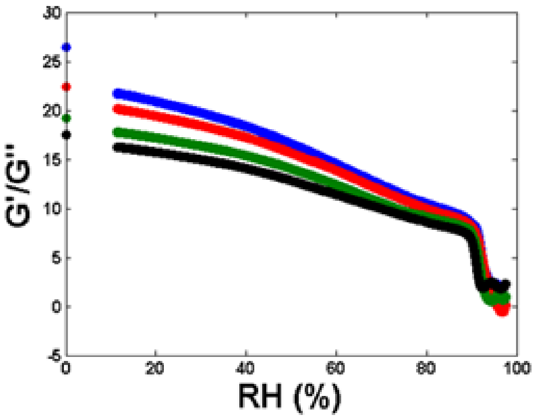


Take home messages

- The combination of QCM-D, DSC and AFM is a powerful strategy to investigate the response of coatings to changes in relative humidity.
- The presence of surfactant domains within the coatings can drastically lower their performance at high ambient humidities







Funding:

KK·stiftelsen

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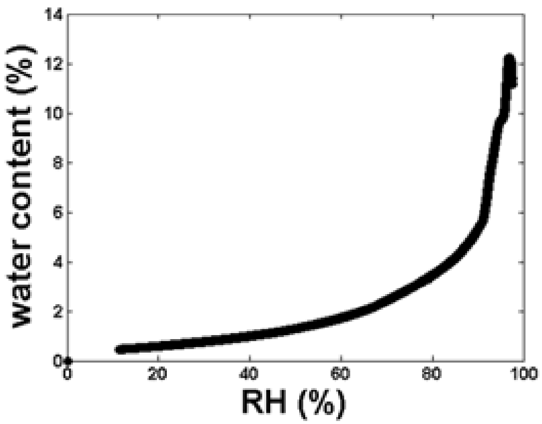

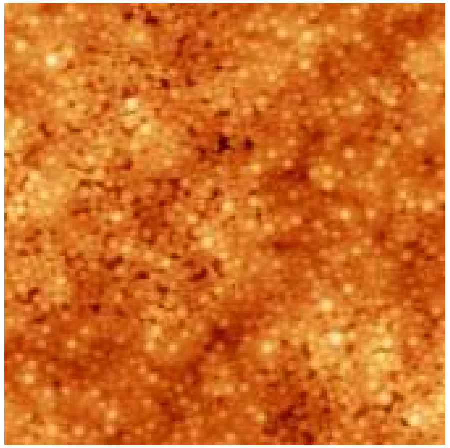

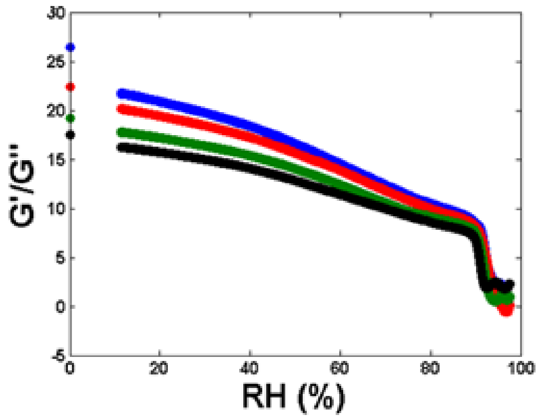

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Thank you for your attention!

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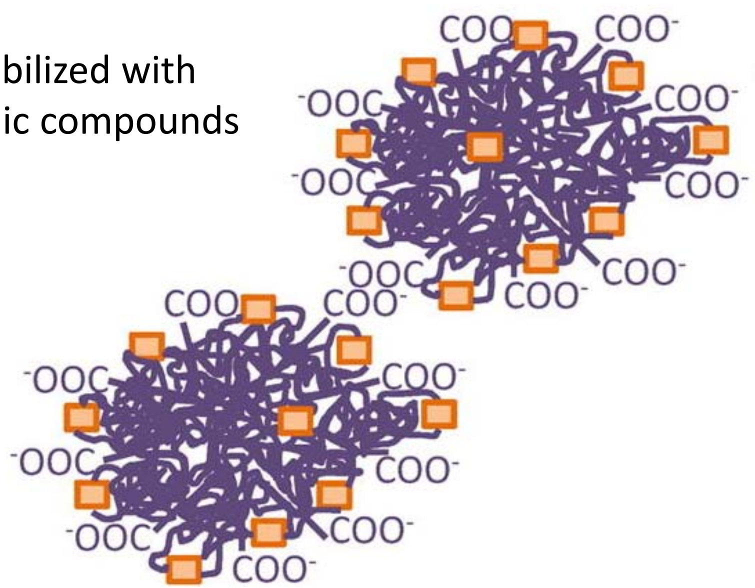
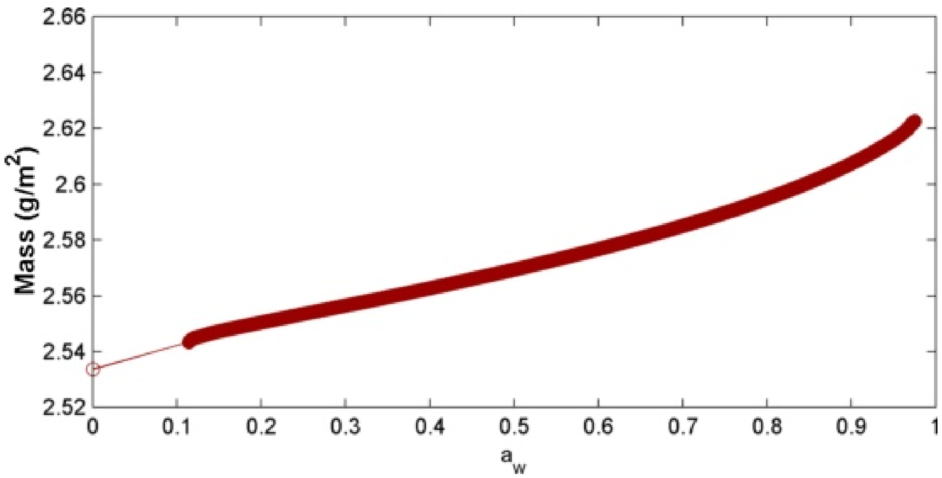
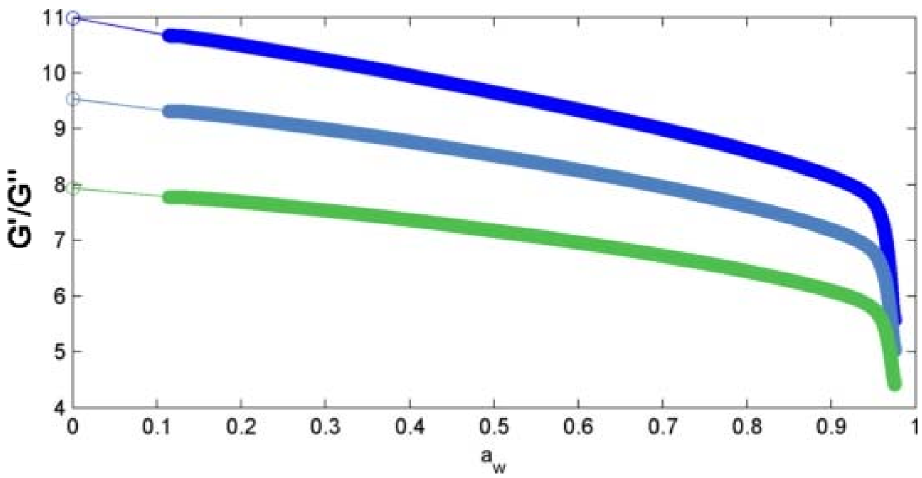
What if we use waterborne coatings that do not make use of surfactants? (e.g. polyurethane coatings)

Stabilized with ionic compounds







Again, a change in viscoelastic properties is seen at RH > 90%

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Apendix

- The mass of the water film was calculated using the Sauerbrey equation, where the linear relationship between mass addition and frequency shift is described

$$\Delta f / n = -2\, m\, f_0^2 / \mathrm{z_q}$$

- Where $\Delta f / n$ is the frequency change normalized to the overtone number n, $\mathrm{z_q} = 8.8 \cdot 10^6\ kg\, m^{-2}\, s^{-1}$ is the acoustic or mechanical impedance of quartz, f_0 is the fundamental frequency and m is the mass in $kg\, m^{-2}$.