Measuring Degradation Processes of Model Coatings Potentially Related to Bioenergy Applications

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ABSTRACT

Degradation mechanisms are relevant to a wide variety of applications including the bioenergy, biomaterial, semiconductor, and detergent industries. Therefore, it is of interest to study these mechanisms, for example, to better tailor formulations for enzymatic degradation efficiency. Studying real-time degradation processes is often not a trivial task. In this light, we present a procedure for developing model coatings to test degradation processes and then we monitor the degradation of these coatings with a quartz crystal microbalance with dissipation (QCM-D) instrument to fundamentally better understand the process. The results suggest a potential degradation mechanism that may be common to a wide variety of different coatings from a number of different industries.

Keywords: QCM-D, degradation, cellulose, biofuel .

INTRODUCTION

Enzymatic degradation of cellulose to form ethanol has received much attention recently due to the fact that ethanol can be considered a renewable energy. To maximize the effectiveness of biofuel conversion to energy sources and particularly ethanol it is necessary to better understand the mechanism by which biofuels are breaking down. There are not many analytical techniques currently available that allow monitoring fundamental degradation processes in real time. In order to better understand degradation processes in general (including enzymatic degradation of cellulose based materials) we developed a procedure to monitor the removal of a model coating in real time. This approach is powerful as it allows a variety of different types of coatings to be tested as well as different degradation formulations and different process conditions (such as concentration, temperature, pH, etc.).

Typically, coatings can be degraded from a surface by several processes occurring simultaneously or sequentially affecting the overall amount of material removed and the speed or efficiency of degradation. The efficiency, can for example, be defined by a formulation's ability to form aggregates effective in dissolving a coating and suspending it in solution that for surfactants occurs at the critical micelle concentration (CMC). Efficiency might also be dictated by a surfactant's capability to partition into a coating enabling absorption of water, which typically results in film swelling and decreased film viscosity.

Here we examine both degradation speed and efficiency using quartz crystal microbalance with dissipation (QCM-D). Example model coatings were formed on QCM-D sensor surfaces and the subsequent removal of these coatings was followed in real-time. The coatings consisted of a model lipid, triolein, and the degradation formulation consisted of the simple non-ionic surfactant, TritonX-100. Triolein thickness and viscosity was monitored as TritonX-100 was flowed across the surface of the coating allowing a more fundamental understanding of the degradation process beginning with an initial swelling stage and continuing with subsequent mass ejection as the coating continually became degraded. Concentration and temperature effects on the rate and efficiency of degradation were also measured and found to affect the overall process.

QCM-D BACKGROUND

Ever since the work of Sauerbrey in 1959[1] quartz crystal microbalances (QCMs) have been used to monitor the uptake of mass in vacuum. Commonly, QCMs are used in semiconductor metal plating applications to measure the thickness of deposited thin films in real-time. More recently, application of QCMs to liquid mediums has opened up numerous possibilities of applying this technique to the fields of nanotechnology, biotechnology, biology, drug delivery, etc., where real-time, *in situ* analysis of interactions of nanoscale molecules/particles at various surfaces, in the liquid medium is of critical importance.

A QCM consists of a thin quartz disc sandwiched between a pair of electrodes. Due to the piezoelectric properties of quartz, these crystals can be excited to oscillate at their resonance frequency (f) by applying an AC voltage across the electrodes. In the event of adsorption onto the surface of an oscillating quartz crystal, the resonant frequency will decrease. The resonance frequency

of the crystal depends on the total oscillating mass, including water coupled to the oscillation. For a thin and rigid film the decrease in frequency is linearly proportional to the adsorbed mass which is defined by the Sauerbrey relation.[1]

$$\Delta m = -\frac{C \cdot \Delta f}{n} \qquad \begin{array}{l} C = 17.7 \text{ ng Hz}^{-1} \text{ cm}^{-2} \\ n = 1,3,5, \text{ etc. is the overtone number.} \end{array}$$

In many situations the adsorbed film is not rigid and the Sauerbrey relation becomes invalid. By measuring the energy loss of the oscillator or dissipation (D) it can be possible to more fully characterize floppy or viscoelastic films. The dissipation parameter in combination with several frequencies and appropriate models allow determining whether the adsorbed film is rigid or viscoelastic (soft). In contrast, conventional QCMs only measure changes in frequency and fail to fully characterize a soft film.

With QCM-D, simultaneous measurement of resonance frequency change (Δf) and energy dissipation change (ΔD) is performed by periodically switching off the driving power of oscillation of the sensor crystal and recording the decay of damped oscillation as the adsorption and/or structural changes take place at the sensor crystal surface (Figure 1). While change in frequency provides information about mass changes (and thickness if the adsorbate's density is known), changes in dissipation (D) provide structural information about the viscoelastic properties of adsorbed films in real time.
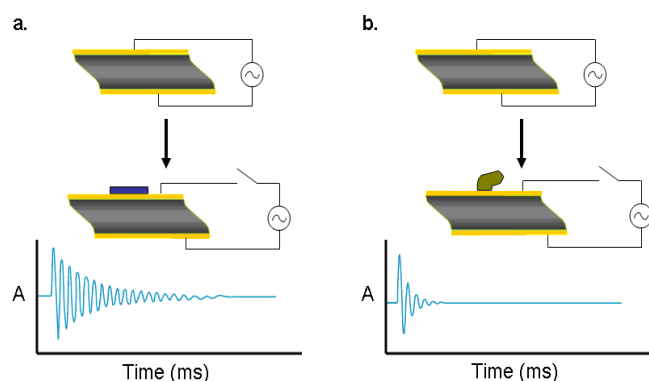

Figure 1. Schematic depicting the viscoelastic differences between (a) a rigid material and (b) a soft viscoelastic material. In each case (a and b), changes in frequency (change in mass or thickness if density is known) and dissipation (change in viscoelasticity) are monitored simultaneously.

EXPERIMENTAL

Materials:

Water was deionized (resistivity > 18 MΩ cm) and purified (Milli-Q plus, Millipore, France). Triolein (Sigma, T7140) and TritonX-100 (Sigma, T9284) were obtained from commercial sources and used without further purification.

Procedure:

Silicon dioxide (SiO_2) and stainless steel (SS) QCM-D sensors were rinsed with water, dried with nitrogen and cleaned in UV/O_3 for 10 minutes. Gold sensors were immersed in 5:1:1 solution of water:amonia:hydrogen peroxide for 10 minutes at ~80°C, rinsed with water and dried with nitrogen. The clean sensors were placed in the QCM-D instrument and a base line was acquired first in air and then in water to fully characterize the bare sensors. Then the sensors were coated with triolein. A few drops of 10 mg/ml triolein dissolved in toluene was spin-coated on either the SiO_2, SS or Au surfaces for 30 seconds at 2000 rpm. All triolein coatings were used within 1 hour. Thicknesses of the triolein coatings were measured based on the differences of the bare and coated sensors.

All degradation experiments were performed at 200 μl/min flow with four parallel experiments. For each experiment a base line was acquired in water, followed by addition of sample solutions and subsequent water rinse. Three concentrations of TritonX-100 were compared on the triolein coatings: 0.023 mM (~0.1 x CMC), 0.21 mM (~0.9 x CMC) and 23 mM (~10 x CMC). Measurements were done in duplicates and representative data is presented. All data was evaluated in QTools to extract thickness, viscosity and elasticity of the films as they were being degraded.

RESULTS AND DISCUSSION

Preparation of Coatings:

Spin coating triolein on silicon dioxide or stainless steel resulted in a network of drops rather than a uniform lipid coating. The same result was observed on freshly cleaned gold sensors. These surfaces were most probably too hydrophilic for the triolein solution to be able to wet sufficiently. However, clean gold sensors subsequently rinsed with ethanol could be covered with an even coating of triolein. Several protocols with varying triolein concentrations, amounts and incubation times prior to spin coating were evaluated producing the following thicknesses (assuming a triolein density of 910 kg/m3):

> 10 mg/ml, 10-20 μl, 30 s incubation, 40 nm
> 20 mg/ml, 18 μl, 30 s incubation, 150 nm
> 20 mg/ml, 15 μl, 5 s incubation, 95 nm

Measurements on the thicker films showed that the QCM-D signal was not able to penetrate through the entire coating. During the air-to-water transition the frequency is expected to decrease for all harmonics. However, as presented in Figure 1 (left), a 150 nm lipid layer is only sensed by the fundamental frequency, and none of the overtones, which increase upon water addition. In contrast, Figure 1 (right) shows a typical air-to-water transition for

the 40 nm lipid layer, which is thin enough for all harmonics to penetrate. It is important to point out that the coatings are of different thickness and viscosity and therefore the base lines are not on the same level in absolute numbers. Nevertheless, the relative increase or decrease in each frequency shows how the air to water transition was sensed differently on the two surfaces.
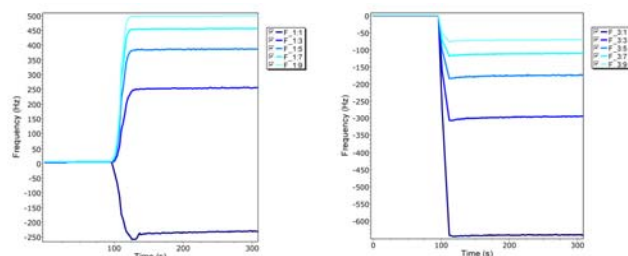

Figure 2. Air-to-water transition of a 150 nm triolein coating (left) and a 40 nm triolein coating (right). The baseline is in air and water was added at 100 s.

Surfactant Induced Degradation:

The TritonX-100 surfactant affected the lipid film at all concentrations (Figure 3). A near instantaneous swelling was observed after surfactant injection, most likely due to surfactant penetration into the film and thus absorption of water. In QCM-D, this process could be observed both as increased thickness of the coating (Figure 3 and Figure 4 left) and reduced viscosity (Figure 4 right) at 750 s. Subsequent removal of the coating was concentration dependent. Figure 3 shows that the highest concentration, 10 x CMC, removed ~ 92% of the coating. At the lowest concentration, 0.1 x CMC, the film swelled slowly throughout the measurement and the final film was ~3% thicker compared to the original coating. This
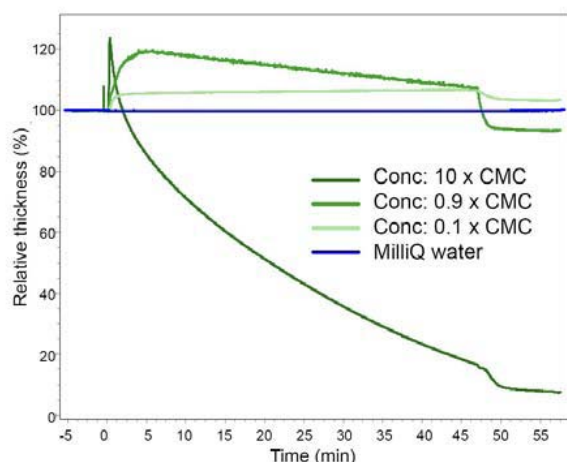

Figure 3. Changes in thickness of triolein upon addition of TritonX-100 (0 min) at three different concentrations and subsequent rinse with water (47 min). The temperature was held constant at 40 °C.

indicates irreversible addition of surfactant and water to the lipid film, which was consistent with a net decrease in viscosity of the lipid film. Swelling behavior was also observed at surfactant concentrations close to the CMC (0.9 x CMC), however it was followed by a ~7% thickness decrease upon rinsing. The above trend indicates that TritonX-100 is able to penetrate the triolein coating at low concentrations, begin to remove the coatings at surfactant concentrations close to the CMC and effectively degrade and remove the coatings at concentrations well above the CMC.

Viscosity analysis could also be used as a first indication of coating behavior during rinsing with water. A decrease in thickness upon rinsing the surfactant can be interpreted as coating degradation (i.e. removal of lipid material) or coating collapse (i.e. release of surfactant and/or water from the lipid coating), with the latter being associated with increased viscosity upon rinsing. Thus, as exemplified in Figure 4 upon rinsing with water at 3500 s the total decrease in thickness of triolein film is a combination of both processes: viscosity increase indicating partial coating collapse, and a net thickness decrease indicating partial coating removal.
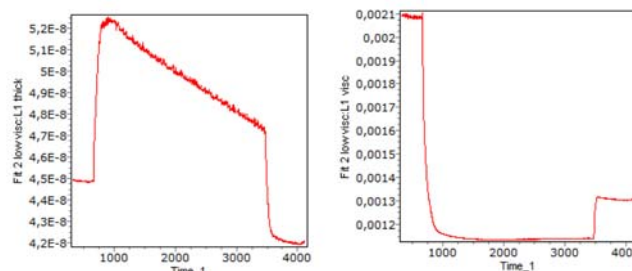

Figure 4. Thickness (left) and viscosity (right) of triolein upon addition of 0.9 x CMC TritonX-100 at 750 s and rinsing at 3500 s. Data acquired at 40 °C.

The degradation of triolein was also evaluated as a function of temperature by comparing the thickness response as a result of injecting concentrated TritonX-100 (10 x CMC) at 25 and 40 °C (Figure 5). Initial film swelling could be observed upon addition of the surfactant solution, however, the efficiency of coating removal was much higher at 40 °C compared with 25 °C. TritonX-100 is a non-ionic surfactant and it's behavior in water is therefore influenced by temperature. The most efficient detergency is expected close to the surfactant cloud point, around 65 °C. The increased removal of the coating at 40 °C compared to 25 °C may very well be governed by the fact that the temperature is closer to the cloud point. However, the exact behavior and thus optimal detergency of TritonX-100 in the water – triolein – TritonX-100 mixture is not known since during these studies only two temperatures were tested.
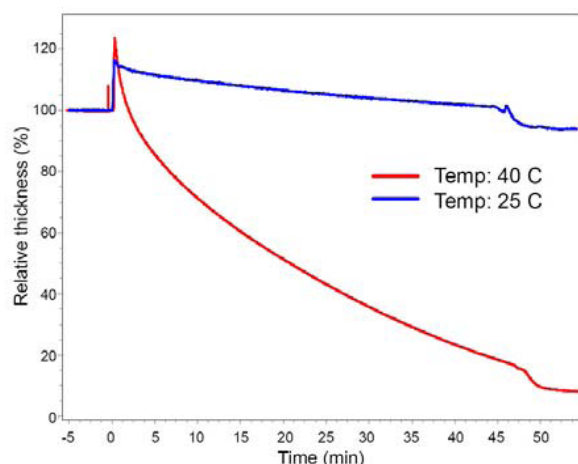
Figure 5. Thickness of triolein upon addition of 10 x CMC TritonX-100 at 25 and 40 °C. The coating was rinsed with water at 47 min.

CONCLUSION

Model coatings were prepared on QCM-D sensor surfaces and their degradation mechanisms were investigated. Optimal coating thicknesses were found to be ~40 nm. Initial swelling of all coatings was evident by a rapid thickness increase. Subsequent degradation of the coatings depended on the surfactant concentration and temperature at which the experiment was held. The results suggest a degradation mechanism by which the coating initially swells, then proceeds to degrade as time elapses depending on the concentration of surfactant and temperature of the process. The conditions giving maximum degradation in this study included a concentration 10 x the CMC and a temperature of 40 °C.

These experiments were designed to highlight the potential of this analytical approach to investigate the degradation mechanism of a particular coating and formulation combination. This same approach should be useful in monitoring a wide variety of different degradation processes relevant to a number of different industries. The main feature of this approach relates to the flexibility in the number of variables that can potentially be investigated including coating composition, coating thickness, composition of degradation reagents, and experimental conditions (such as concentration, temperature, pH or even salt). This same approach should be relevant to studying coating degradation mechanisms for a wide variety of different coatings from a number of different potential applications including monitoring cellulose based degradation processes.

REFERENCES

1. Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.