Use of Torsional Acoustic Resonators for Microweighing, Polymer Rheology, and Monitoring of Biofilm Formation

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Abstract— **The work describes the use of readily available and economical quartz crystal torsional resonators for microweighing. The resonance behavior was probed by impedance analysis. Torsional resonators are straight-forwardly adapted to the detection electronics usually employed for driving a quartz crystal microbalance. The analysis proceeds as with quartz crystal resonators.**

The measurement of the viscoelastic parameters of a silicone oil gave results consistent with the corresponding low-frequency data. Thickness determinations on a film formed from a polymer dispersion have confirmed that torsional resonators indeed function as microbalances when the sample is thin enough. Biofilm formation is easily monitored, as well.

I. Introduction

The quartz crystal microbalance (QCM) enjoys widespread use as a simple tool to monitor processes at interfaces (and the deposition of thin films, in particular) with a rather outstanding sensitivity.[1,2] However, the QCM suffers problems when the films under investigation are thicker than a few microns.[3] The frequency shift, Δf, can only be converted to a film thickness, d_f, as long as the film is acoustically thin, where "acoustically thin" implies a thickness of less than about 10 % of the wavelength of sound.[4] Given that both polymer coatings and biofilms are often soft materials, the maximum film thickness is in the range of a few microns for 5 MHz crystals. Viscoelastic effects can be accounted for – and can even be an interesting piece of information – as long as they are small.[5] However, the situation becomes quite intractable when the film thickness reaches a quarter of the wavelength of sound. At $d_f = \lambda/4$ one encounters the "film resonance".[6,7,3] At this frequency, the film itself forms an acoustic resonator which is in tune with the quartz crystal resonator. The situation is analogous to the "vibrating reed" in beam bending. While equations describing the film resonance exist, they do not match the experiment very well. To the practitioner, a film resonance usually is bad news.

When the QCM is used to monitor biofouling,[8,9,10,11] the thickness of the biofilm often is at the upper limit of the dynamic range of the standard QCM (if not above). The size of a typical bacterial cell is of the order of many microns. Biofilms containing entire cell sheets are therefore many microns thick. The depth of penetration of the acoustic shear wave is much less than the thickness and the QCM only senses the bottom part of the cell sheet. The Sauerbrey relation cannot be applied.

II. Modeling

Torsional resonators have been around for many decades.[12,13] They have mostly been used to determine the viscosity of complex media at high frequencies.[14,15,16,17] We describe the application of torsional resonators for measurements of film thickness and for the monitoring of biofouling. Details of the modeling are provided in Ref. [18]. Essentially, the knowledge of the interaction of acoustic resonators with their environment, which was gained with thickness shear resonators, can be transferred to torsional resonators in a straight-forward way. If the frequency shift, Δf, is much less than the frequency, f, the small-load approximation holds and one has

$$\Delta f^* = \frac{\mathrm{i}}{2\pi M_q} \int_{Surface} \frac{u^2(r)}{\langle u^2 \rangle} Z_L(r)\,\mathrm{d}A \qquad \text{Eq. 1}$$

Here, $\Delta f^* = \Delta f + \mathrm{i}\,\Delta\Gamma$ is the complex frequency shift, $\Delta\Gamma$ is the shift of the half-band-half-width (bandwidth, for short), M_q is the mass of the crystal, r is some location on the surface of the crystal, $u(r)$ is the amplitude of oscillation at this location, $\langle u \rangle$ is the average amplitude, A is the area, and Z_L is

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TABLE I: RESONATOR CHARACTERISTICS

	TQ 56	TQ 78
Length [mm]	35 mm	25 mm
Diameter [mm]	12 mm	6 mm
Mounting	Pin and O-ring	2 Pins
Fundamental [kHz]	56.1	78.5
Bandwidth on Fundamental [Hz]	~ 1	~ 10
Mass M_q	10.4 g	2 g

the load impedance, that is, the ratio of stress and speed at the respective location. For inertial loading one has $Z_L = i\omega m_f$ with m_f the mass per unit area of the film. For viscous loading, Z_L is equal to $(i\omega\rho\eta)^{1/2}$ with ρ the density and η the viscosity. As with the conventional QCM, the sensitivity to loading varies with the location where the load is applied. The sensitivity scales with the square of the local amplitude.

III. EXPERIMENTAL

Fig. 1 shows the geometry of the resonators and two types of mounting. The electrodes are arranged in quadrupolar geometry (Fig 1c). Two-pin mounting (Fig. 1a) is relatively easy, but in this case the electrodes are exposed to the ambient medium. If the crystal is mounted by one pin and an O-ring around the waist (Fig. 1b), the access of the liquid can be limited to the lower half of the crystal, while the electrodes are applied on the upper half. The resonators used in this study were supplied by Flucon Fluid Control GmbH, Clausthal, Germany. To date, they are employed as viscosity sensors. Two types of resonators with fundamental resonance frequencies of 56 kHz ("TQ56") and 78 kHz ("TQ78") are available. Device parameters are collected in Table I. The resonance parameters were acquired by means of impedance analysis, using the unit SA250B (Saunders, Phoenix, Arizona). For the low-frequency rheology measurements, a conventional rheometer (Bohlin Instruments, Malvern, UK) in the oscillating mode was used.

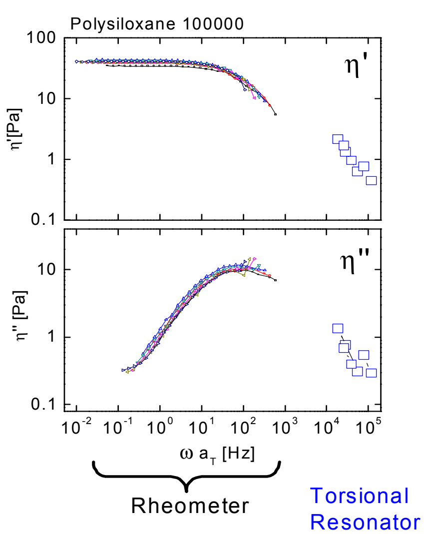

Figure 2: Master curves of the real and the complex part of the viscosity of silicon oil 100000. The data were recorded by a conventional rheometer and with torsional resonators. Time-temperature superposition was applied.

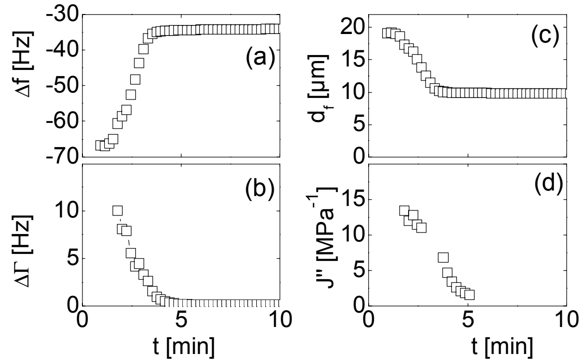

Figure 3: Drying kinetics of a film formed from a polymer dispersion. The bandwidth has been converted to a viscous compliance, J''.

IV. RESULTS AND DISCUSSION

In Fig. 2 we show a check, where we compare the viscoelastic parameters measured on a silicon oil (silicon oil 100000, Elbe Silikone, L Böwing GmbH, Hofheim, Germany) with the corresponding parameters as determined with conventional rheology. This material has a zero-shear viscosity of 100 Pa s. The measurements with the conventional rheometer were performed between 0°C and 100°C in steps of 10°C. The frequency was varied between 0.1 and 100 Hz. The measurements with the torsional resonator were carried out both with the TQ56 at 20, 50, and 100°C as well as the TQ78 at 20 and 50°C. Fig. 2 shoes a master curve obtained by time-temperature superposition. The data match reasonably well.

Fig. 3 shows results from a film drying experiment. The experiment was carried out with a polymer dispersion termed UPV3, kindly provided by María J. Barandiaran, University of the Basque Country. Details of the preparation are unessential. UPV3 was prepared via miniemulsion polymerization. It mostly contains acrylic polymers and some alkyd resin. The solids content is 55 %. The sphere diameter is in the range of 180 nm and the T_g of the spheres is about 5°C. Film formation from this dispersion readily occurs at room temperature. One can clearly follow the drying kinetics. The shift of the bandwidth, ΔΓ, has been converted to the viscous compliance of the film as described in Ref. 18.

For the biofouling experiments (Fig. 4) a cell line of pseudomonas fluorescens (DSMZ 147, provided by German Collection of Microorganisms and Cell Cultures) was used. The bacteria were cultivated in a medium containing 10g/L glucose and 1g/L yeast extract at 33°C.

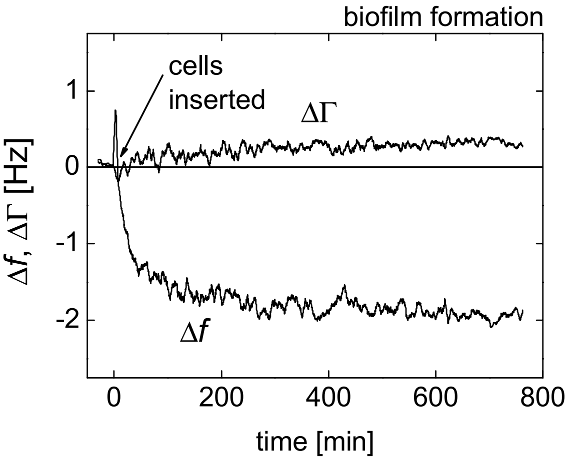

Figure 4: Results of a biofouling experiment. The resonator was exposed to a dispersion of pseudomonias fluorescens cells (DSMZ 147). The decrease in frequency corresponds to an equivalent Sauerbrey thickness of 0.5 µm. The Sauerbrey thickness is not necessarily equal to the geometric thickness because of roughness and softness. Note, however, that the increase in bandwidth is much less than the decrease in frequency. Accordingly, the resonator operates in the Sauerbrey regime and is expected to sense the entire cell. This contrasts to thickness-shear resonators, which would only sense the bottom part of the cell layer.

In order to facilitate cell attachment, the resonator was first coated with poly-L-lysine by dip-coating. Cell attachment did not occur on the untreated resonator surface. The poly(L-lysine) coated crystal was immersed in the buffer solution and left for about 1 hour to allow for thermal equilibration and acquisition of the base line. At $t = 0$, the cells were added to the solution. More details on the cell culture and biofouling experiments with this culture are given in Ref. [19]. After insertion into the culture medium, the cells start to proliferate, as indicated by the increasing turbidity of the suspension. At the same time, the frequency decreases due to the formation of a biofilm on the resonator surface. Note that the change is not caused by an increase of the viscosity of the solution: such in increase would have changed the frequency and the bandwidth by the same amount. The frequency shift of –2 Hz corresponds to a thickness of about 0.5 µm. Given that the cells themselves are thicker than a micron, one concludes that full coverage has not been achieved. In principle, softness also leads to a Sauerbrey thickness smaller than the geometric thickness.

However, soft layers usually induce a large shift in bandwidth, which is not the case here. More experiments on the formation of biofilms are in progress. At this point, we only demonstrate the usefulness of torsional resonators for this purpose.

V. CONCLUSION

Our work describes the use of readily available and economical quartz crystal torsional resonators for microweighing. The resonance behavior was probed by impedance analysis. Torsional resonators are straight-forwardly adapted to the detection electronics usually employed for driving a quartz crystal microbalance. The analysis proceeds as with quartz crystal resonators.

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REFERENC

1 C. Lu, A. W. Czanderna (edts.), *Applications of Piezoelectric Quartz Crystal Microbalances*, Elsevier, Amsterdam 1984.
2 A. Arnau (Edt.), *Piezoelectric Transducers and Applications*, Springer, Heidelberg 2004.
3 C.S. Lu, O. Lewis, *J. Appl. Phys.* **43**, 4385 (1972).
4 G. Sauerbrey, *Z. Phys.* **155**, 206 (1959).
5 D. Johannsmann*, Macromol. Chem. Phys.* **200**, 501 (1999), eq. 13.
6 V.E. Granstaff, S.J. Martin, *J. Appl. Phys.* **75**, 1319 (1994).
7 D. Johannsmann, K. Mathauer, G. Wegner, and W. Knoll, *Phys. Rev. B* **46**, 7808 (1992).
8 J. Wegener, A. Janshoff, and H. J. Galla, European Biophysics Journal with Biophysics Letters **28**, 26 (1998).
9 J. Li, C. Thielemann, U. Reuning, and D. Johannsmann, Biosensors & Bioelectronics **20**, 1333 (2005).
10 K. A. Marx, T. Zhou, A. Montrone, D. McIntosh, and S. J. Braunhut, Analytical Biochemistry **361**, 77 (2007).
11 R. Knerr, B. Weiser, S. Drotleff, C. Steinem, and A. Gopferich, Macromolecular Bioscience **6**, 827 (2006).
12 H.J. McSkimin, Journal of the Acoustical Society of America **24**, 355 (1952).
13 B. Bode, PhD thesis, Clausthal University of Technology 1984.
14 T. M. Stokich, D. R. Radtke, C. C. White, and J. L. Schrag, Journal of Rheology **38**, 1195 (1994).
15 L. Kirschenmann and W. Pechhold, Rheologica Acta **41**, 362 (2002).
16 G. Fritz, W. Pechhold, N. Willenbacher, and N. J. Wagner, Journal of Rheology **47**, 303 (2003).
17 M. Eugster, K. Hausler, and W. H. Reinhart, Clinical Hemorheology and Microcirculation **36**, 195 (2007).
18 W. Bücking, B. Du, A. Turshatov, A. M. König, I. Reviakine, B. Bode, and D. Johannsmann, submitted.
19 J. Hillerich, PhD thesis, TU-Darmstadt 2007.