Supporting Information

Water Sorption and Glass Transition of Pig Gastric Mucin Studied by QCM-D

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Figure S1. The dependence of dissipation changes on time at low RH. It presents a zoomed area of the dissipation changes at low RH.

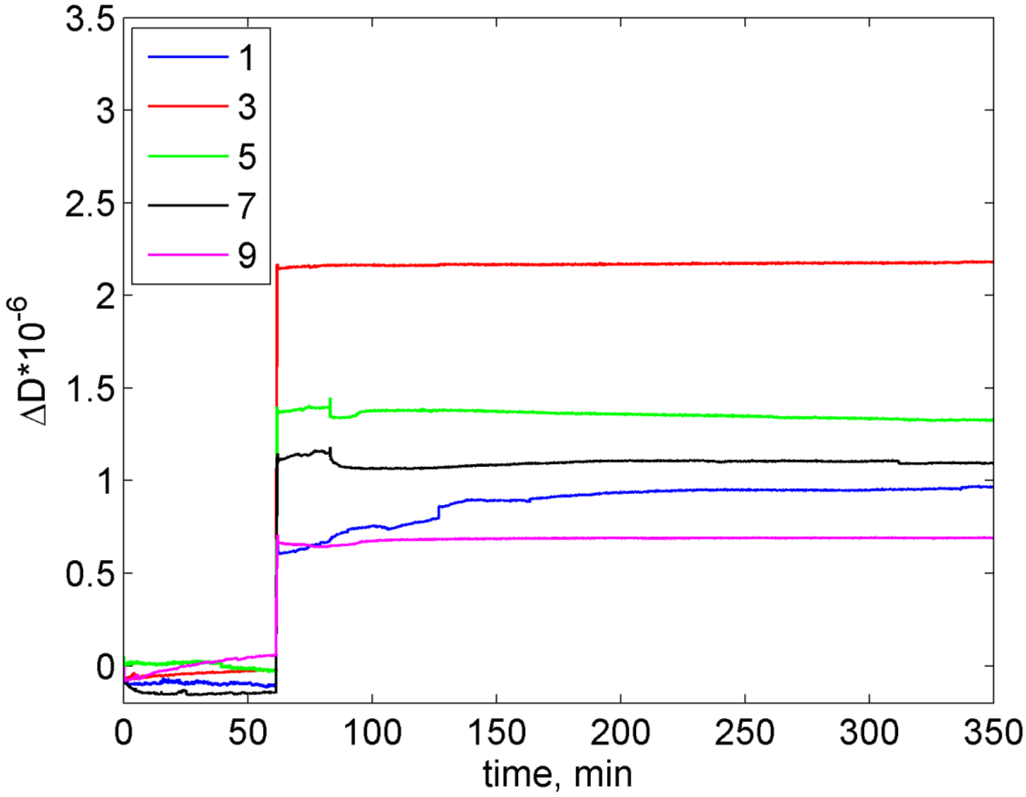


Figure S2. $\Delta f/n$ versus $n^{-\frac{1}{2}}$ at different PGM film thickness: 236 nm (red), 262 nm (blue)

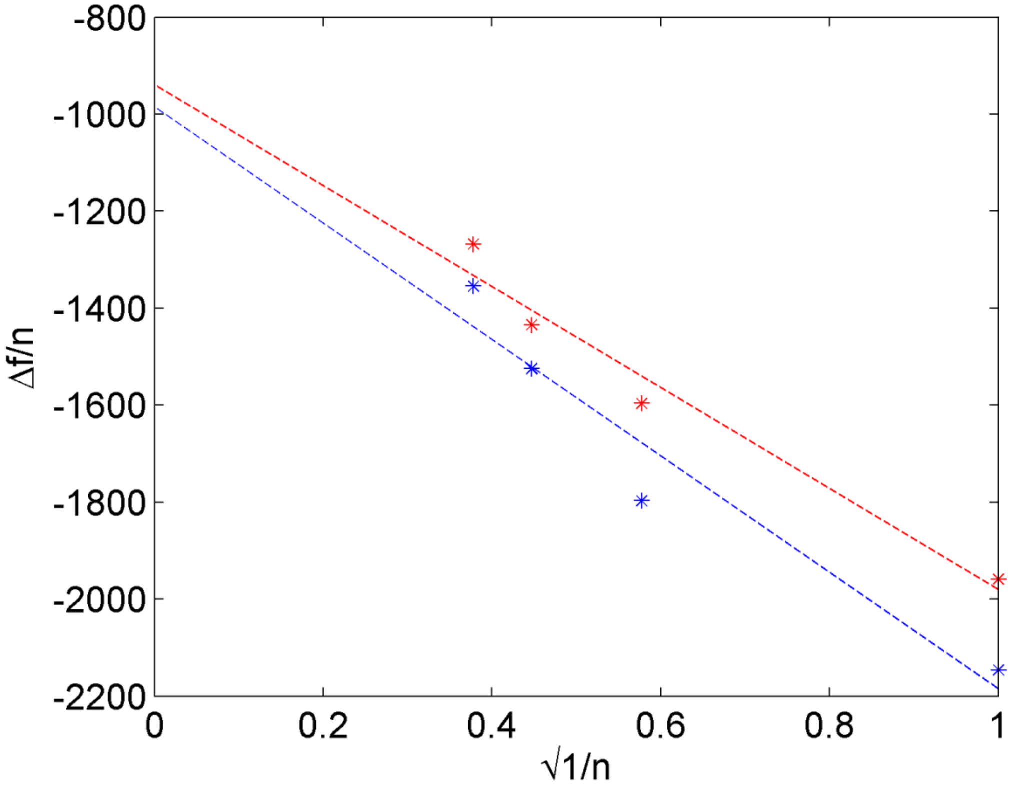


Figure S3. Sauerbrey masses of the water absorbed by the PGM film obtained by QCM-D and compared with water sorption isotherm studied by sorption calorimetry. Dashed line- sorption calorimetric data;[1] stars- QCM-D data, corresponding to different overtones (blue-1, red-3, green-5, black-7). The thickness of PGM film is 541 nm.

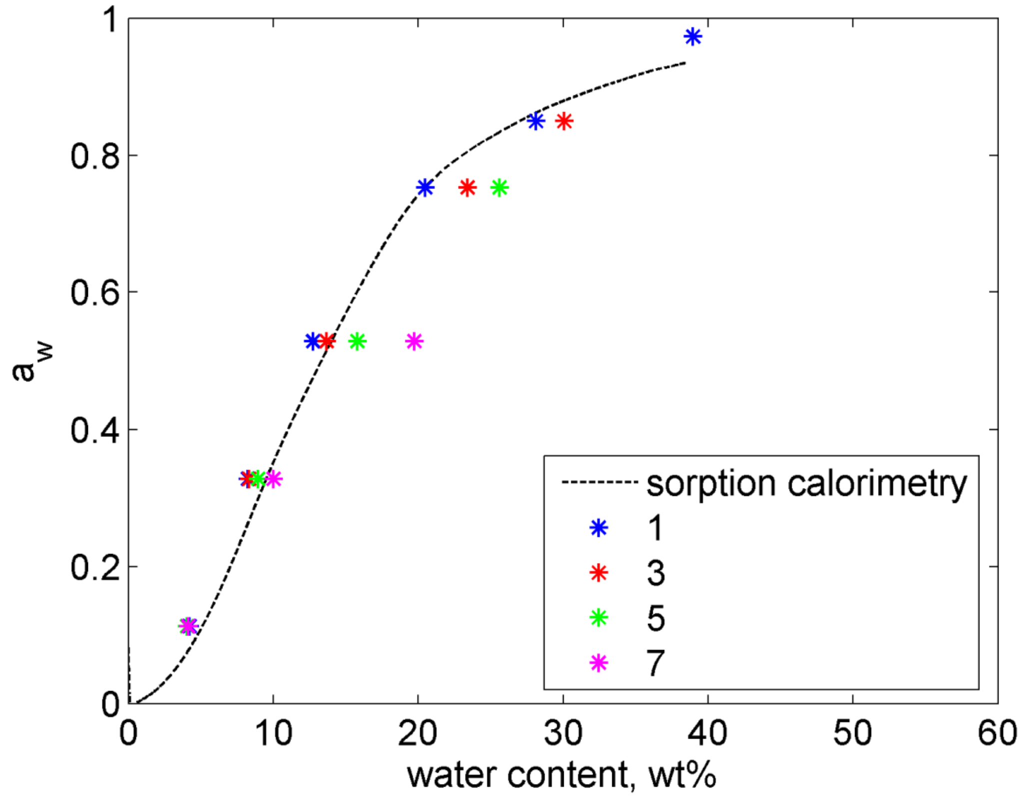
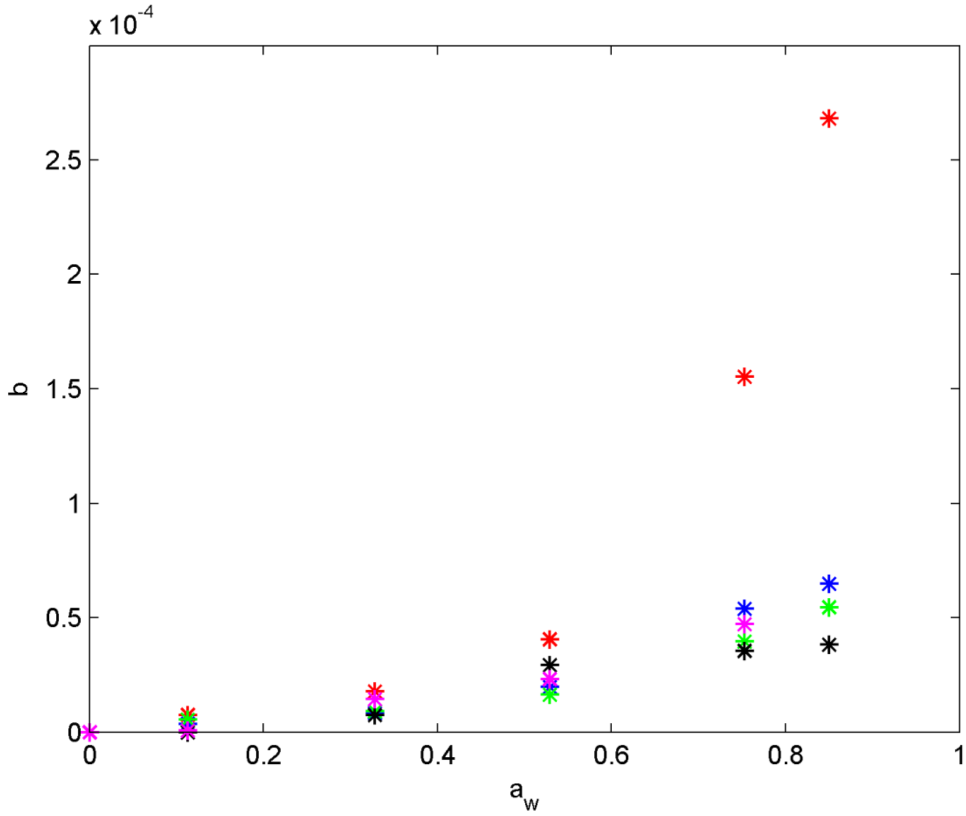


Figure S4. The parameter b (which defines the rheological properties of the PGM film) versus a_w for different PGM film thicknesses.



SI. Derivation of a formula for calculation of water content

The data on the frequency change normalized to overtone number of coated SiO_2 sensor with respect to uncoated sensor were analyzed using the equation for a single viscoelastic film[2] in air, where the frequency shift $\frac{\Delta f}{n}$ is proportional to square of the overtone order n^2:

$$\frac{\Delta f}{n} = \frac{-2f_0^2 m_f}{Z_q}\left(1 + \frac{1}{3}\frac{Z_q^2}{Z_f^2}\left(\frac{m_f}{m_q} n\pi\right)^2\right) \qquad \text{(S1)}$$

where $Z_q = 8.8*10^6 kg\, m^{-2} s^{-1}$ - the acoustic or mechanical impedance of quartz; $Z_f = \sqrt{\rho(G' + G'')}$ – the acoustic impedance of the film; f_0 – the fundamental frequency; m_f – the mass of the film per unit area; m_q – is the areal mass density of the crystal.

The eq S1 was simplified in the following way:

$$\frac{\Delta f}{n} = -a m_f (1 + b m_f^2 n^2) \qquad \text{(S2)}$$

where $a = \frac{2f_0^2}{z_q}$ and $b = \frac{1}{3}\frac{z_q^2 \pi^2}{z_f^2 m_q^2}$.

The frequency changes normalized to the overtone number is found as a frequency of each overtone at each RH for coated sensor with PGM film in respect to empty (uncoated) sensor:

$$\frac{\Delta f}{n} = \frac{f_f}{n} - \frac{f_e}{n} \qquad \text{(S3)}$$

The frequency change for the dry PGM film is found as a frequency of each overtone at each RH for coated sensor with dry PGM film in respect to empty (uncoated) sensor:

$$\frac{\Delta f_d}{n} = \frac{f_d}{n} - \frac{f_e}{n} \qquad \text{(S4)}$$

Combining eq S3 and S4, one gets:

$$\frac{\Delta f}{n} = \frac{f_f}{n} + \frac{\Delta f_d}{n} - \frac{f_e}{n} = \frac{\Delta f_w}{n} + \frac{\Delta f_d}{n} \qquad \text{(S5)}$$

Combining eq S2 and S5, one can write:

$$\frac{\Delta f_w}{n} + \frac{\Delta f_d}{n} = -am_f(1 + bm_f^2 n^2) \quad \text{(S6)}$$

The mass of the dry film was calculated using Sauerbrey[3] equation:

$$\frac{\Delta f_d}{n} = -am_d \quad \text{(S7)}$$

where $a = \frac{2f_0^2}{z_q}$ from the eq S1.

Then eq S6 will be:

$$\frac{\Delta f_w}{n} = -am_f\left(1 + bm_f^2 n^2\right) + am_d = -am_w - abm_f^3 n^2 \quad \text{(S8)}$$

Let us introduce the Sauerbrey mass of the water absorbed by PGM film:

$$\frac{\Delta f_w}{n} = -am_w^s \quad \text{(S9)}$$

Then eq S8 will be:

$$-am_w^s = -am_w - abm_f^3 n^2 \quad \text{(S10)}$$

After eq S10 was simplified and data on calculated mass of water absorbed by PGM film were normalized to the to the dry mass of PGM film, $\overline{m}_d$, the water content per dry mucin can be extrapolated to the zero overtone, using the following eq:

$$\frac{m_w^s}{\overline{m}_d} = \frac{m_w}{\overline{m}_d} + b\frac{m_f^3}{\overline{m}_d} n^2 \quad \text{(S11)}$$

SII. Derivation of a formula for calculation the ratio of the storage to the loss modulus G'/G''

Viscoelastic properties can be extracted from the equation for a single viscoelastic film in air:[2]

$$\Delta\tilde{f} = -\frac{f_0}{\pi Z_q} Z_f \tan(k_f d_f) \tag{S12}$$

where k_f is the wavenumber in the film; d_f is the film thickness. If $k_f d_f$ is much less than unity, the tangent in eq S13 can be Taylor-expanded as $\tan(x) \approx x + 1/3\ x^3$, resulting in the following:

$$\frac{\Delta\tilde{f}}{f_0} = -\frac{1}{\pi Z_q}\omega m_f \left(1 + \frac{1}{3}\frac{Z_q^2}{Z_f^2}\left(\frac{m_f}{m_d}n\pi\right)^2\right) \tag{S13}$$

$$-\frac{\Delta\tilde{f}\pi Z_q}{f_0 \omega m_f} = 1 + \frac{1}{3}\frac{Z_q^2}{Z_f^2}\left(\frac{m_f}{m_q}\right)^2 \tag{S14}$$

$$\frac{1}{Z_f^2} = \frac{1}{\rho_f G_f} = \frac{3}{Z_q^2\left(\frac{m_f}{m_q}n\pi\right)^2}\left(-\frac{\Delta\tilde{f}\pi Z_q}{f_0\omega m_f} - 1\right) \tag{S15}$$

Multiplying the numerator and denominator of $\frac{1}{G_f}$ by the complex conjugate of G_f,

$$\frac{1}{G_f} = \frac{\bar{G}}{|G|^2} = \frac{G' - iG''}{(G')^2 + (G'')^2} \tag{S16}$$

one can write:

$$G' - iG'' = \frac{3\rho\left((G')^2 + (G'')^2\right)}{Z_q^2\left(\frac{m_f}{m_q}n\pi\right)^2}\left(-\frac{\Delta\tilde{f}\pi Z_q}{f_0\omega m_f} - 1\right) \tag{S17}$$

Denoting k for the expression

$$k = \frac{3\rho\left((G')^2 + (G'')^2\right)}{Z_q^2\left(\frac{m_f}{m_q}n\pi\right)^2} \tag{S18}$$

we obtain:

$$G' - iG'' = k\left(-\frac{(\Delta f + i\Delta\Gamma)\pi Z_q}{f_0\omega m_f} - 1\right) \tag{S19}$$

$$G' - iG'' = -\frac{\Delta f \pi Z_q k}{f_0\omega m_f} - \frac{i\Delta\Gamma\pi Z_q k}{f_0\omega m_f} - k \tag{S20}$$

and

$$G' = -\frac{\Delta f \pi Z_q k}{f_0\omega m_f} - k \tag{S21}$$

$$-iG'' = -\frac{i\Delta\Gamma\pi Z_q k}{f_0\omega m_f} \tag{S22}$$

Thus, the ratio of the storage modulus to the loss modulus $\frac{G'}{G''}$, can be calculated as:

$$\frac{G'}{G''} = -\frac{\Delta f + \frac{2f_0 n m_f}{Z_q}}{\Delta\Gamma} = -\frac{\Delta f + \left(\frac{\Delta f}{n}\right)_{extrap} n}{\Delta\Gamma} \tag{S23}$$

- References

(1) Znamenskaya, Y.; Sotres, J.; Engblom, J.; Arnebrant, T.; Kocherbitov, V. Effect of Hydration on Structural and Thermodynamic Properties of Pig Gastric and Bovine Submaxillary Gland Mucins *J. Phys. Chem. B* **2012**, *116*, 5047-5055.
(2) Johannsmann, D. Viscoelastic Analysis of Organic Thin Films on Quartz Resonators *Macromol. Chem. Phys.* **1999**, *200*, 501-516.
(3) Sauerbrey, G. Verwendung Von Schwingquarzen Zur Wägung Dünner Schichten Und Zur Mikrowägung *Zeitschrift für Physik A Hadrons and Nuclei* **1959**, *155*, 206-222.