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Electronic Supplementary Information to: Gravity-driven syneresis in model low fat mayonnaise

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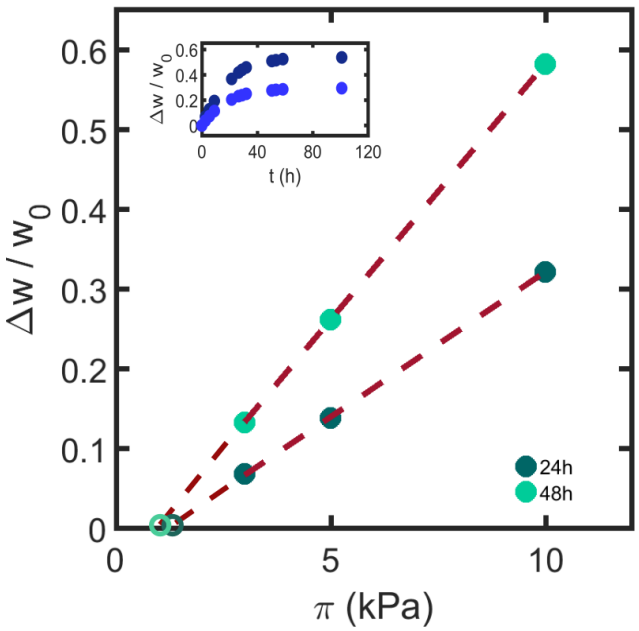

Fig. S1 Weight change of 0.55 wt% PEG (M_w 20,000 g/mol) solution normalized by initial weight as a function of osmotic pressure of dialysis solution. Extrapolated points represent the equilibrium pressure, as shown in open symbols. Inset: Evolution of weight change of PEG (M_w 20,000 g/mol) solution normalized by initial weight.

1 Osmotic pressure methods validation

To validate determining osmotic pressure under non-equilibrium conditions by dialysis, measurements are first performed with PEG, a polymer of which osmotic pressure in solution is stable over time. We use a PEG of 20,000 g/mol, which is of the same order of magnitude as the molecular weight of soluble starch[1]. A 0.55 wt% PEG solution in the cassette is dialyzed against solutions of known osmotic pressure of 3 kPa, 5 kPa and 10 kPa. The weight change of the cassette normalized by initial weight as a function of the osmotic pressure of the dialysis solution is shown in Figure S1. These pressures are used to limit the volume change of the cassette, which may cause error in determining the weight change. Additionally, dialysis for 24h and 48h represent before and after dialysis equilibrium (Figure S1 inset). The osmotic pressure of the solution inside the cassette can be found by linear extrapolation to the point where there is no weight change during the dialysis. At this point, the osmotic pressures inside and outside the cassette are equal. As depicted by the open symbols in Figure S1, the extrapolated osmotic pressure of 0.55 wt% PEG solution inside the cassette is approximately 1 kPa, which is in agreement with the previous calibration[2]. Weight change of 0.55wt% PEG (M_w 20,000 g/mol) solution normalized by initial weight as a function of dialysis time for dialysis solution with osmotic pressure 5kPa and 10kPa is shown in Figure S1 inset. Moreover, approximately the same osmotic pressure of 0.55 wt% PEG solution is obtained from the weight change data of 24h and 48h dialysis, as shown in Figure S1. This allows us to determine the osmotic pressure of starch suspension by the weight change data before dialysis equilibrium is reached, which reduces the possible change in osmotic pressure caused by starch retrogradation. This establishes a method for osmotic pressure measurements of slurry-like material, which cannot be measured with a membrane osmometer.

2 Composition analysis of expelled fluid from scoop syneresis

2.1 Starch test

A potassium triiodide solution of 0.1 M is prepared; 500 μl of the potassium triiodide solution is added into both 1 ml of the expelled fluid from the scoop syneresis experiment and Milli-Q water. The color change of the solutions is recorded and visually inspected to test for the presence of starch, see Figure S2a and S2b. The purple color in Figure S2b suggests the presence of starch in the expelled fluid.

2.2 Thermogravimetric analysis

Thermogravimetric analysis is conducted with a Simultaneous Thermal Analyzer (STA) 6000 and Pyris software (Perkin Elmer, United Kingdom). A 4 wt% native rice starch suspension is prepared as stated in section 2.1. For both soluble starch and an expelled fluid sample, 20 mg is added into the sample holder and placed inside the STA. Samples are first held at 30 °C for 1 min and nitrogen

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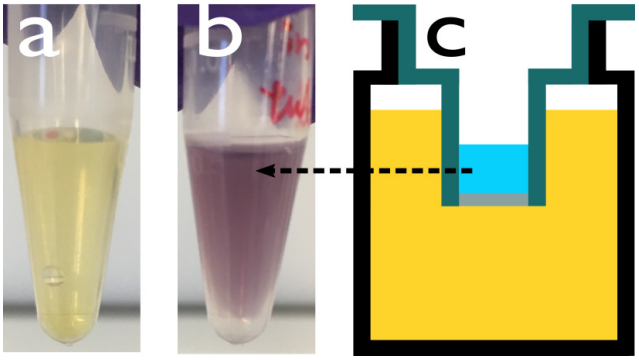

Fig. S2 (a, b) Iodine test of control and expelled liquid from the scoop syneresis experiment, as shown in blue in (c).

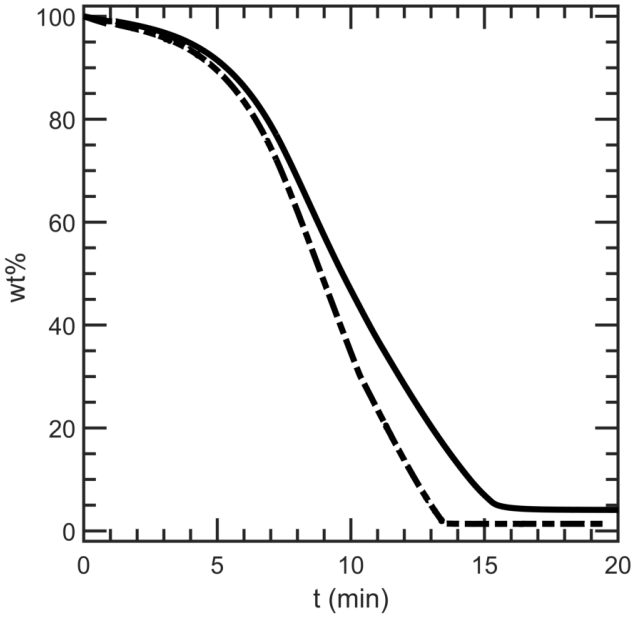

Fig. S3 Weight percentage of expelled fluid (-) and soluble fraction of 4 wt% starch suspension (-.) as a function of time.

is switched on at a flow rate of 30 ml/min. Next, a temperature ramp from 30 °C to 90 °C is applied at a rate of 10 °C/min, and finally the temperature is held at 90 °C for 15 min for complete evaporation of water. The sample weight is monitored and the solid content of the sample is calculated as the final weight divided by the initial weight. Weight percentage of expelled fluid and soluble fraction of 4 wt% starch suspension as a function of time is shown in Figure S3. To calculate starch content in the expelled fluid, weight of NaCl is substracted from the TGA data.

2.3 Gel permeation chromatography

A 4 wt% native rice starch suspension is prepared by bringing 0.4 g of starch to a volume of 10 ml Milli-Q water. The suspension is heated at 90 °C for 5 min under gentle stirring. After the suspension is cooled and equilibrated to 50 °C, it is centrifuged for 20 min at 10,000 g, and the supernatant is filtered through a 0.45μm filter to prevent clogging of the column. The sample of expelled fluid from the scoop syneresis experiment is centrifuged and filtered with the same procedure. The filtered expelled fluid and starch solution (25 μl) are injected into a PL aquagel-OH mixed 8 μ m 250 $\times$ 4.6 mm, PL1549-5801 column. The mobile phase is H_2O containing 0.05 wt% NaN_3 with a flow rate of 0.4 ml/min. A calibration curve relating the molecular weight to the retention time is obtained by using PEG solutions of known molecular weight. Apparent molecular weight of starch in expelled fluid and soluble fraction of 4 wt% starch suspension is shown in Figure S4.

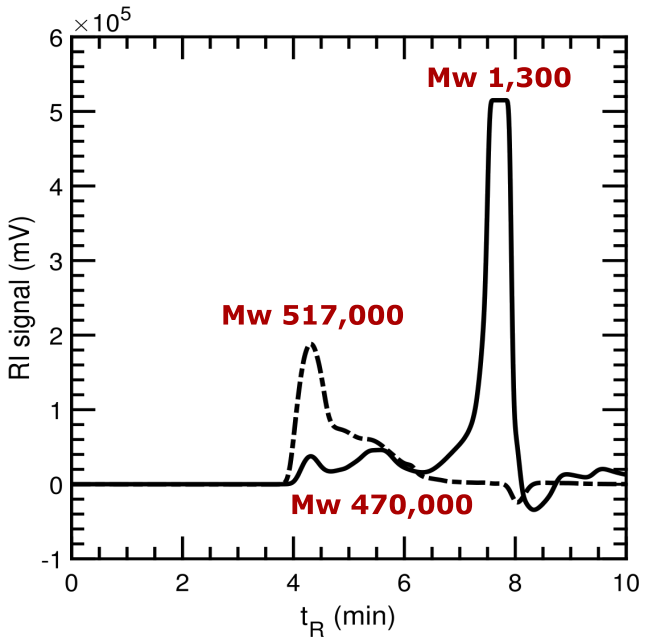

Fig. S4 Apparent molecular weight from gel permeation chromatography for expelled fluid (-) and soluble fraction of 4 wt% starch suspension (-.).

3 Krieger-Dougherty relation

The higher storage modulus in model low fat mayonnaise compared to 4 wt% starch (Figure 5) could be a rigid filler effect for composite suspensions and gels due to the small size and resultant high Laplace pressure of the oil droplets[3]. In this scenario, the relative complex modulus of composite suspensions/gels with solid viscoelastic particles ($G_f^* \gg G_m^*$)

$$G_r^* = \frac{(G_r^* - G_f^*/G_m^*)^{2.5}}{(1 - G_f^*/G_m^*)} \cdot (1 - \frac{\phi}{\phi_m})^{-2.5\cdot\phi_m} \qquad (1)$$

where G_r^* is defined as $G_r^* = G_c^*/G_m^*$ (G_c^*, G_m^* are the complex shear moduli of the composite suspension/gel and the matrix, respectively), G_f^* is the complex modulus of the filler particles. Equation 1 is analogous to the Krieger-Dougherty relation. Since the filler can be considered as a rigid particle, $G_f^* \to \infty$, and the first term of equation 1 is reduced to one[4]. As shown in Figure S5, the fitted G_r^* could not describe our experimental data.

4 Filter papper clogging test

To test whether oil droplets clog the filter paper in the scoop syneresis experiment, several additional experiments were conducted. The model low fat mayonnaise and starch suspension

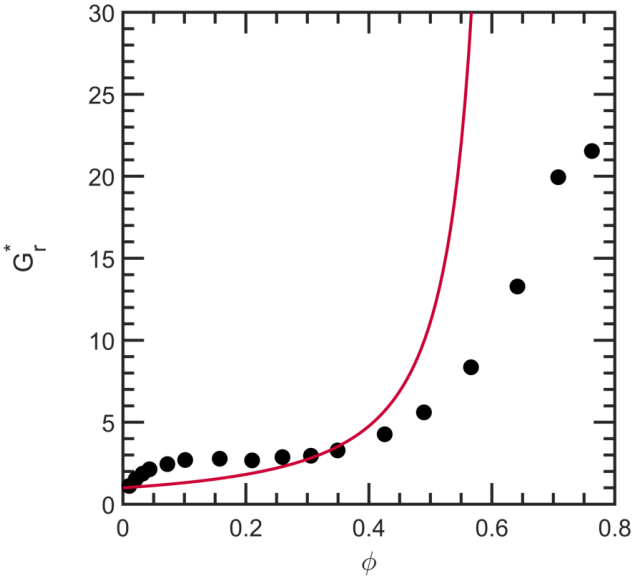

Fig. S5 Relative complex modulus of 4wt% starch model low fat mayonnaise as a function of disperse phase volume fraction. The red line represents the fit to the data by Equation 1 wtih ϕ_m = 0.64.

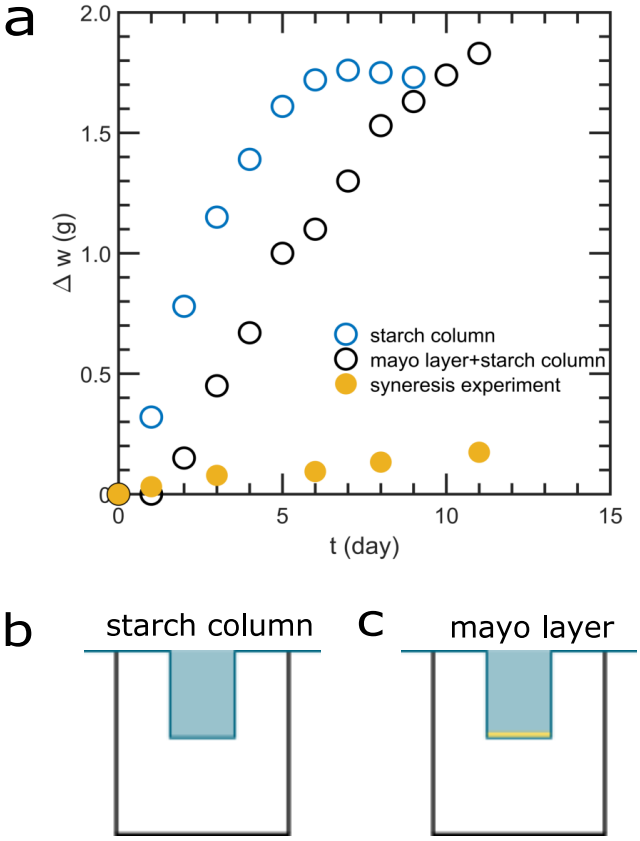

Fig. S6 Schematic (**b** and **c**) and results (**a**) of the mayonnaise layer experiment to test whether clogging of the filter paper is significant. (**b**) The inner tube, of height $h = 2\,\mathrm{cm}$, is filled with starch suspension. (**c**) The tube is filled with starch suspension with a small layer of model low fat mayonnaise in between the starch suspension and the filter paper. (**a**) Weight of expelled fluid from the tube into the jar as a function of time t. The expelled fluid weight in syneresis experiment ($h = 2\,\mathrm{cm}$) from Figure 1d is given for reference.

used in the current experiments are prepared as mentioned in section 2.1 in the manuscript. The starch suspension is added into the inner tube which is inserted into the jar and the weight of the expelled fluid is monitored. All the inner tubes are of the same height, $h = 2\,\mathrm{cm}$.

As a reference experiment, the inner tube is filled with starch suspension while leaving the jar empty, see Figure S6b, and the expulsion of fluid into the jar is measured. Next, we filled the inner tube with starch suspension, but with a small, yet macroscopic, layer of model low fat mayonnaise in between the starch suspension and the filter paper, see Figure S6c. We measured as a function of time the weight of expelled fluid in the jar, see Figure S6a. If oil droplets indeed clog the filter paper, the expelled fluid is expected, at least initially, to be similar to the scoop syneresis experiment in Figure 1d where model low fat mayonnaise column has the same height $h = 2\,\mathrm{cm}$ as the starch suspension column. However, we observed that the experiment with model low fat mayonnaise layer exhibits similar fluid expulsion as the experiment without, see Figure S6a. As both the reference and the model low fat mayonnaise layer experiment have a fluid expulsion rate of approximately an order of magnitude larger than the scoop syneresis experiment in the manuscript, these results suggest that the filter paper is not clogged by oil droplets.

In the scoop syneresis experiment mentioned in section 2.1 in the manuscript, model low fat mayonnaise is aspirated from the inner tubes as to mimic the formation of a scoop. In principle, this aspiration may cause clogging by sucking droplets from beneath the filter paper through the filter paper. To test this we conducted the following experiments. In an empty jar, model low fat mayonnaise is added into the inner tube and is aspirated after a week and then replaced by starch suspension, see Figure S7c. The same experiment is performed in a jar filled with model low fat mayonnaise, see Figure S7d. The expulsion characteristics of two experiments above are compared to the control experiment in which the inner tube is filled with starch suspension to start with, see Figure S7b. As the difference in the fluid expulsion rates between the three experiments is negligible, see Figure S7a, aspiration does not appear to clog the filter paper.

5 Cryo Scanning electron microscopy

Model low fat mayonnaise is prepared as described in section 2.1 and pipetted into small brass sample holders. The samples are frozen by plunging the sample holders into liquid nitrogen. Subsequently the samples are transferred to a cryo-preparation chamber (Leica) under vacuum where they are fractured at -90 °C and kept for 3 min to remove ice from the surface. Still under vacuum the samples are coated with 12 nm of tungsten by sputter coating and transferred under vacuum using a VCT100 shuttle (Leica) to a field emission scanning electron microscope (Magellan 400 from FEI). Samples are analysed at 2 KV, 6 pA at -120 °C.

References

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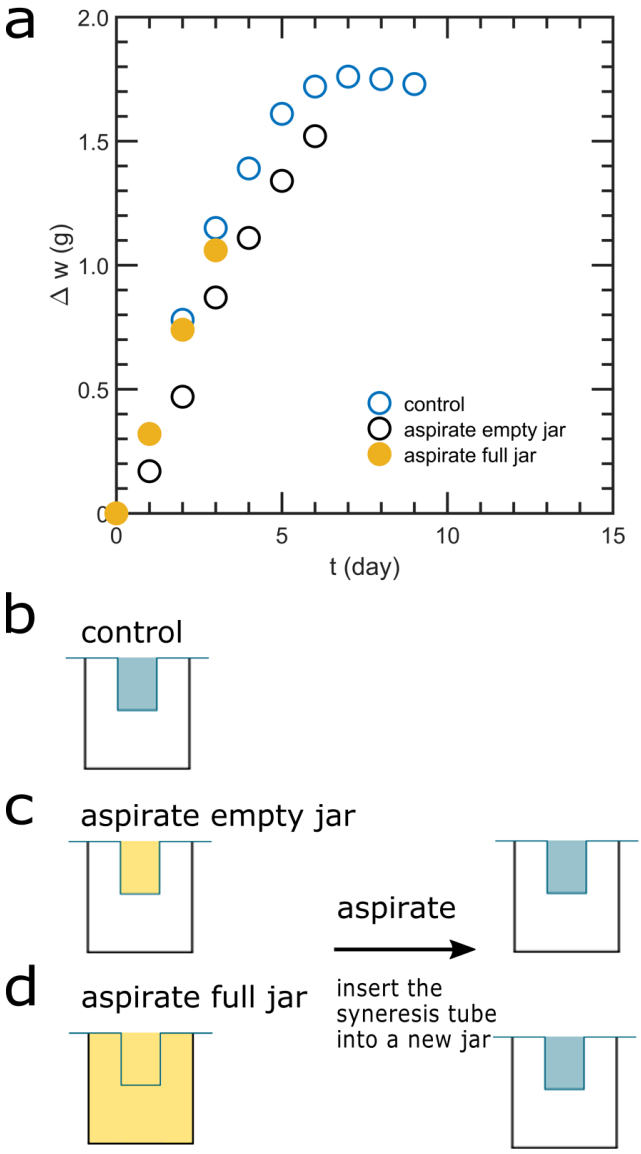

Fig. S7 Schematics (**b**, **c** and **d**) and results (**a**) of the experiments to test whether aspiration of model low fat mayonnaise causes clogging of the filter paper. (**b**) In the control experiment the inner tube is filled with starch suspension. (**c**) The inner tube is first filled with model low fat mayonnaise and left for one week. Afterwards, the mayonnaise is aspirated and replaced by starch suspension. (**d**) Same as **c** but both the inner tube and the jar are filled with mayonnaise. (**a**)Weight of expelled fluid from the tube into the jar as a function of time.

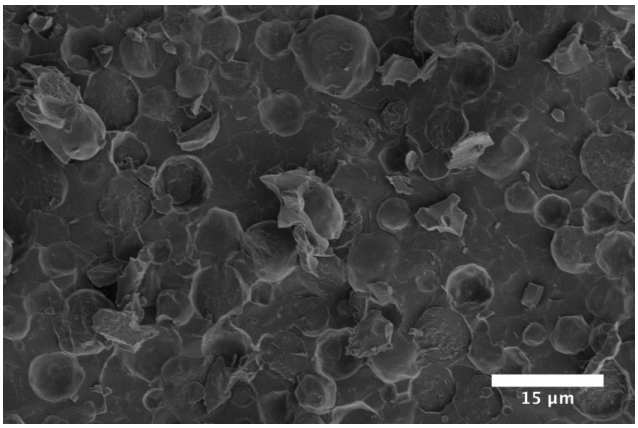

Fig. S8 Scanning electron microscopy image of 4 wt% native rice starch model low fat mayonnaise, 52 vol% dispersed phase.

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