Supporting Information

Magnetically Responsive Pickering Foams

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Contents

Description of the procedures by which the magneto-Pickering foams were formed and characterized. Movies illustrating the macroscopic collapse of fresh foam and microscopic response of wet and dry foams to a magnetic field. The movies demonstrate the slow deformation of wet foam and the rapid breakdown of dry foam by the action of the applied magnetic field. Figure with snapshots from the microscopy videos illustrating the mechanisms responsible for collapse of wet and dry foams with corresponding discussion. Rheology data describing the evolution of the viscous and elastic behavior of the magneto-Pickering foams as a function of age.

Procedures for Making Magneto-Pickering Foam & Measuring Foam Water Fraction

Typical foams were made by diluting a mixture containing 2.67 g of functionalized iron particles and 10 g of a stock solution containing 10 wt% hypromellose phthalate (HP-55, Shin-Etsu Chemical Co., Ltd.) in deionized water (obtained from a Millipore RiOs 16 RO system) to a total volume of 98 mL prior to foaming. The HP-55 stock solution was prepared as described in Wege et al.[3], and functionalized iron particles were prepared by mixing ~ 21 g carbonyl iron powder (avg. dia. 4.5-5.2 µm, Sigma) with 35 mL solution of 0.1 M oleic acid in methanol. The methanol and excess oleic acid were washed away prior to use. Hydrochloric acid (2.6 M) was added to induce the precipitation of HP-55 particles under shear, and to adjust the pH of the final system to a value between 2.5 and 3. The solution was sheared and aerated at 15000 rpm for 1 minute in a high-speed blender (Oster Model 4242), and the resulting foam was transferred into glass vials (12.37 mm ID) for testing. To determine the drainage behavior of the magneto-Pickering foam, samples were prepared and left to drain for a predetermined period of time in closed glass vials (12.37 mm ID). The initial pour volume of the samples tested was approximately 29 mL. After the allotted drain time, the water phase below the foam was extracted using a needle. The foam liquid fraction was then calculated using a weight balance subsequent to solvent evaporation.

Contents and Description of the Supplementary Movies

Movie 1: *Macroscopic Collapse of Wet Foam*
Movie 2: *Macroscopic Collapse of Dry Foam*
Movie 3: *Microscopic Response of Wet Foam to a Magnetic Field*
Movie 4: *Microscopic Response of Dry Foam to a Magnetic Field*

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[3] Wege, H. A.; Kim, S.; Paunov, V. N.; Zhong, Q.X.; Velev, O. D. *Langmuir* **2008**, 24, 9245-9253.

The contents and the processes visualized by these movies are as follows.

Movie 1: Macroscopic Collapse of Wet Foam

In this movie, one may observe that upon exposure to the applied field, the wetter foam slowly collects toward the side of the vial on which the magnet has been placed. This is a result of the existence of wet, elastic films in the foam, which allow loose iron particles to flow around the bubbles and through the foam. Once the foam body has collected at the source of the field, bubbles are pushed out of the foam as a result of particle aggregation toward the magnet. This happens because the push force of the particles is not large enough to pop the bubble, so the elastic bubble deforms and gets squeezed out of the particle mass. Movie 1 is in real time up until 23 seconds; after this, the movie is playing at 16x speed.

Movie 2: Macroscopic Collapse of Dry Foam

In this movie, one may observe that upon the application of the magnetic field, the aged foam sample is rapidly collapsed toward the magnet. The rapid breakdown of the foam is a result of the lower water content and tighter bubble packing associated with aged foam. The drainage of liquid from the foam during the aging process causes the liquid films in the foam to thin, making them weaker and more prone to rupture in response to an applied force. In addition, whereas loose iron particles were able to migrate through the foam structure in the wetter foam sample, they are more tightly packed into the foam structure in the dry sample. Thus, when the field is applied, instead of travelling toward the magnet by weaving through the liquid-filled films in the foam, the particles must push or pull on the bubbles around them.

Movie 3: Microscopic Response of Wet Foam to a Magnetic Field

In this movie at higher magnification one can observe how upon exposure of wet foam to the magnetic field, bubbles and iron particles all migrate in the direction of the applied field. The migration is slow - possibly as a result of the drag force from water since fresher foam samples have high water content. This process corresponds to the macroscopic collapse behavior of wet foam. As shown in Movie 1, the deformation of wet foam upon exposure to a magnetic field is slow and gradual. To prepare this movie, a small sample of fresh foam was placed under the microscope, and exposed to a magnetic field. The magnet used was placed so as to simulate the macroscopic collapse experiments.

Movie 4: Microscopic Response of Dry Foam to a Magnetic Field

In this movie, one may observe that in dryer foams the bubbles tend to be more tightly packed. Thus, upon the application of the magnetic field, there is less room available for the jammed bubbles to move and rearrange. In this case, the bubbles are prone to coalescence as well as popping. One may also observe that particles are “peeled” off the surface of the bubble facing the magnet while on the opposite side of the bubbles, the particles aggregate. It can be seen in this movie that dryer foams break as a result of bubble coalescence as well as film rupture upon exposure to the magnetic field. To prepare this movie, a small sample of aged foam was placed under the microscope, and exposed to a magnetic field. The magnet used was placed so as to simulate the macroscopic experiments.

Mechanism for Collapse of Wet and Dry Foam

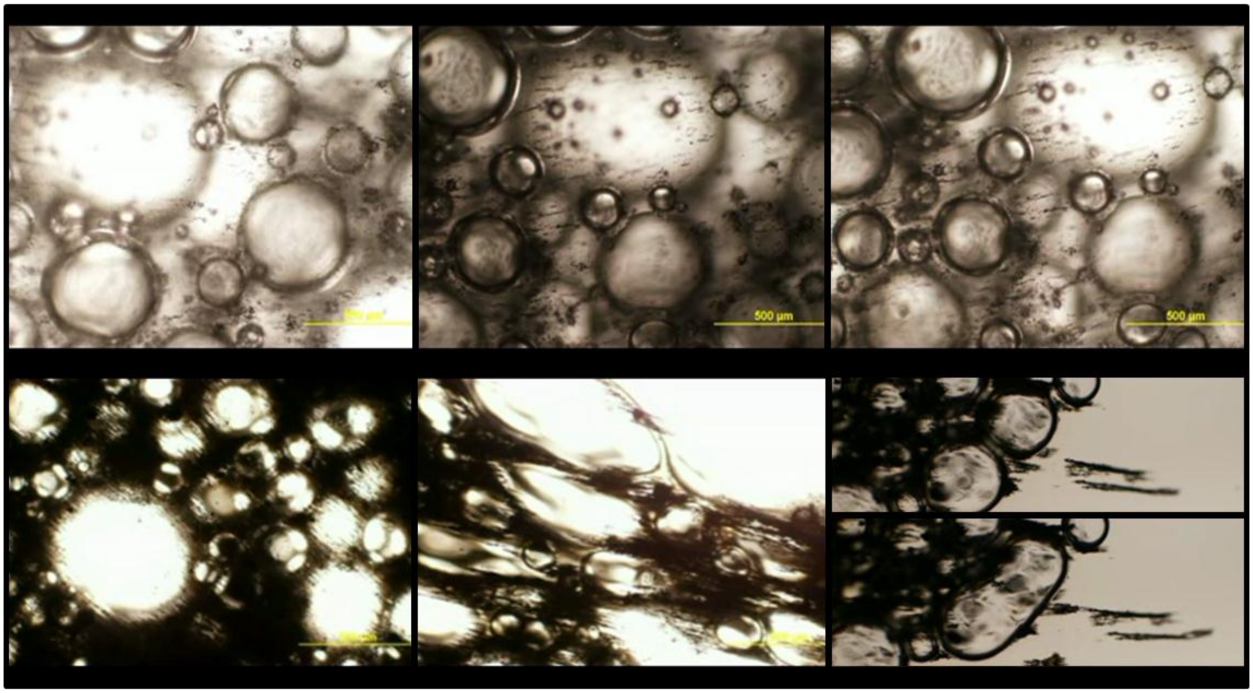

Figure S1. Snapshots of microscopic images illustrating the collapse process for wet foam (top row) and dry foam (bottom row). Exposure of dry foam to a magnetic field results in rapid film stretching and bubble coalescence; such destabilization mechanisms are not experienced by wet foam in a magnetic field.

Observations of wet and dry foams in a magnetic field using optical microscopy demonstrate the difference in the mechanisms responsible for their collapse (Fig. S1). Although both foam systems contain the same initial concentration of iron particles, the magnetically active particles are spaced further apart in the wet foam system than in the dry foam system as a result of the difference in water content. This results in the slow deformation and collapse of the fresh foam; magnetic particles that are more spread out do not experience strong dipole-dipole interactions with surrounding particles. In addition, the presence of water results in the necessity of the particles to overcome hydrodynamic drag forces when attempting to migrate toward the source of the field or form chains with other particles. We observed through optical microscopy that the exposure of wet foam to a magnetic field results in the movement of the foam system (bubbles, HP-55, water, CI particles) as a whole. In older foams, the proximity of the magnetically responsive particles to each other, as well as the decreased water fraction in the films results in a strong response from the particles when the sample is exposed to a magnetic field. The close packing of the bubbles in the foam also gives them little room to rearrange and migrate around the bubbles toward the source of the field. As a result, the particles stretch the thin films between the bubbles while migrating toward the magnetic field, causing film rupture and bubble coalescence.

Rheological Properties of Foam as a Function of Age

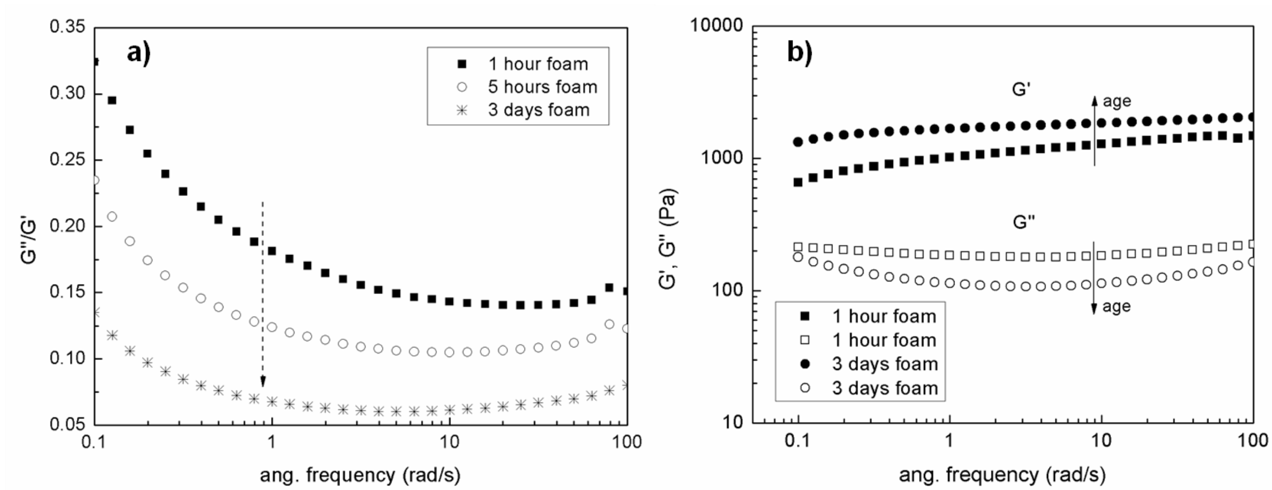

Figure S2. Rheological properties of magneto-Pickering foam as a function of age. (a) Damping factor, G''/G' as a function of angular frequency for foams tested at different time points of the aging process. (b) G' and G'' as a function of angular frequency for a fresh foam and an older foam.

The viscoelastic properties of foams were analyzed in a TA Instruments AR2000 rheometer with serrated parallel plates with a diameter of 40 mm. The experiments were conducted for a 3 mm gap. The data demonstrate that the viscoelasticity of the foam changes pronouncedly with age **(Fig. S2)**. As the foam ages, the moduli ratio G′′/G′, which is a measurement of material damping, decreases. This behavior results from the increase of the storage modulus, G′, and decrease of the loss modulus, G′′ with foam age. These rheological shifts are likely a result of the drainage of the water from the foam. Fresh foams contain a higher content of water, and when stress is applied, the bubbles may move in response to the applied force independent of each other. However, in older foams, the bubbles are more tightly packed in the foam as a result of the drainage of water. Thus, there is a more pronounced elastic response to an applied stress; in this case, all the bubbles in the foam respond as a whole. The shift to more elastic response, combined with the existence of a yield stress in the system, leads to rapid magnetically driven breakdown of the aged foams.