Stability and Viscoelasticity of Magneto-Pickering Foams

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Supporting Information

ABSTRACT: We have developed a new class of bistable Pickering foams, which can remain intact for weeks at room temperature but can be destroyed rapidly and on-demand with the use of a magnetic field. Such responsive foam systems can find application in various industrial and environmental processes that require controlled defoaming. These foams are stabilized by particles of hypromellose phthalate (HP-55) and contain oleic acid-coated carbonyl iron particles embedded in the HP-55 matrix. The complex behavior of these foams arises from several factors: a robust anisotropic particle matrix, the capacity to retain a high amount of water, as well as an age-dependent response to an external field. We report how the structure and viscoelastic properties of the foams change with time and affect their collapse characteristics. The evolution of foam properties is quantified by measuring the rate of liquid drainage from the foam as well as



the rate of bubble growth in the foam with respect to time elapsed (in the absence of a magnetic field). We also evaluate the time necessary for foam collapse in magnetic fields as a function of magnetic particle content. A decreasing liquid volume fraction in the foam during aging leads to an increase in the elasticity and rigidity of the foam structure. These data allow us to identify a transition time separating two distinct stages of foam development in the absence of field. We propose different mechanisms which control foam collapse for each stage in a magnetic field. The stiffening of foam films between air bubbles with age plays a key role in distinguishing between the two destabilization regimes.

■ INTRODUCTION

Aqueous foams, which can be considered soft complex fluids, are amorphous materials composed of close-packed bubbles.¹ They are thermodynamically unstable systems, which are kinetically stabilized by the addition of surfactants and/or solid particles that can adsorb strongly at the air-liquid interface. The use of particles in foam and emulsion formulation is known as Pickering/Ramsden stabilization.^{2,3} Foams can be designed to possess tunable properties and variable functionalities through the inclusion of particles or surfactants with special properties.⁴ Kim et al. demonstrated that intense and selectively colored foams could be engineered through the incorporation of hydrophobic dye into the particle stabilizers of a Pickering foam.⁴ Salonen et al. developed a system which could be controllably foamed by varying its exposure to temperature and UV light,⁵ and Fameau et al. developed a smart foam system, which could be destabilized through a change in temperature.⁶

We are interested in systems, which are very stable on their own but can be manipulated using magnetic fields and herein investigate a class of magneto-Pickering (MP) foams with extraordinary stability. The use of partially hydrophobic particles in foam stabilization can result in the formation of foam films, which are remarkably stable against rupture. This superstabilization is achieved through the percolation of particles at the surface of the air bubbles, forming a shell which slows down the effects leading to foam destabilization.⁷⁻⁹ Magnetic responsivity, allowing for noncontact defoaming, is achieved through the incorporation of iron (Fe) particles into the foam network. Destabilization by magnetic field is a noninvasive and efficient approach to collapse persistent biphasic systems as an alternative to chemical and mechanical defoaming techniques. In addition, foams which are superstable and can maintain a high liquid fraction, like the ones presented here, are promising agents for water remediation processes and oil recovery. In the past, a number of researchers have explored the characteristics of emulsions and microbubbles stabilized by magnetically responsive particles.¹⁰⁻¹⁹ The use of external magnetic fields to manipulate the structure of ferrofluid foams was studied by Hutzler et al.^{20,21} Moulton et al. employed magnetizable nanoparticles to study liquid drainage in soap foams.²²

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Figure 1. (a) Optical micrograph of 2.7 wt % Fe foam bubble from a 5 day old foam sample. The image illustrates that bubbles are covered by HP-55 particles and that carbonyl iron particles decorate the HP-55 shell around the bubble. (b) SEM micrograph of dried magneto-Pickering foam. The dark gray matter remaining after foam bubble breakdown is the HP-55 matrix, and the white particles are carbonyl iron. Scale bar = 10 μ m.

However, to our knowledge, magnetic fields have not been exploited in the *destruction* of foams until our previous brief report of magneto-Pickering foams as a new functional system.²³ We now seek to understand how microscopic and macroscopic properties define the foam network and affect the dynamics of foam collapse in the presence of a magnetic field. To address this, we characterize key structure-related properties of the foam network (e.g., liquid fraction, bubble size distribution, collapse time in a magnetic field, and viscoelasticity) as a function of foam age.

EXPERIMENTAL METHODS

Sample Preparation. Hypromellose phthalate (HP-55, Shin-Etsu Chemical Company, Ltd.) stock solution was prepared as described previously.²⁴ HP-55 is a hydrophobically modified cellulose which has been shown to be an efficient foam stabilizer.²⁴ The magnetically responsive carbonyl iron (CI) microparticles (avg. diameter 4.5-5.2 μ m) were obtained from Sigma. Carbonyl iron is a form of elemental iron, derived from the decomposition of iron pentacarbonyl. It is ferromagnetic in nature but exhibits low magnetic hysteresis as a result of its "onion skin" structure.^{25,26} Since these particles are quite large and hydrophilic, they do not naturally adsorb at the air-water interface. To ensure that the CI particles would remain in the hydrophobic phase, we functionalized their surfaces with oleic acid. 17,27,28 To make the foams, we combined HP-55 (10 g, 10 wt % stock) with iron particles, added water (88 mL), and aerated the water/HP-55 solution for 1 min using a professional blender (Oster model 4242), while adjusting pH to ~2.5-3 with 1 M hydrochloric acid. Next, the foam was transferred into a cylindrical glass vessel and was left to evolve in the airtight container at room temperature (~23 °C) prior to testing. Aging foams in an airtight container at room temperature prevents evaporative loss of water from the foam.

The volume fraction of water in the foam samples was determined as follows. Foams were left to age in airtight containers for a predetermined period of time, after which the liquid drained out from the foam head was extracted using a syringe and needle. Water remaining in the foam head was removed by drying the sample in an oven at 90 °C. The fraction of liquid in the foam was then calculated through a mass balance.

Scanning Electron Microscope (SEM). Scanning electron micrographs were taken using a FEI Phenom (Phenom-World B.V., The Netherlands). SEM samples were prepared by air-drying on PELCO tabs (Ted Pella, Inc.) fixed to the SEM stub.

Optical Microscopy. Optical micrographs were obtained using an Olympus BX-61 microscope equipped with an Olympus DP-70 digital CCD camera. Micrographs of foam samples were processed to evaluate bubble size distribution. We measured the average bubble size

using ImageJ to determine the size distribution of the bubbles.²⁹ Examples of micrographs used for bubble size determination are included in Figures S2 and S3 of the Supporting Information.

Rheology. The rheological properties of the foam samples were measured using a TA Instruments AR2000 rheometer with parallel plate geometry, the top plate having a diameter of 40 mm. All experiments were conducted at a 3 mm gap. During the measurements, the temperature of the Peltier plate was held constant at 25 °C, and the sample was covered with a homemade solvent trap in order to prevent water evaporation. Serrated plates were used to minimize the effect of slip in our experiments. In addition, samples were tested at different gaps to ensure reproducibility and absence of wall slip.³ Dynamic oscillatory stress sweeps and frequency sweeps were performed at 25 °C. The dynamic viscoelastic moduli of the foam were measured between shear stresses of 0.01-100 Pa at a constant frequency of 6.28 rad/s to determine the boundaries of the linear viscoelastic region (LVR) of the foam samples. Frequency sweeps were performed from 0.1 to 300 rad/s at a constant shear stress of 3 Pa to observe the dependence of the elastic and viscous moduli of the foams on frequency. Using the data from frequency sweep experiments, the damping factors (tan δ) of all samples were evaluated at a frequency of 6.28 rad/s

Superconducting Quantum Interference Device (SQUID) Magnetometry. The magnetic response of Pickering foams containing carbonyl iron particles was measured using a SQUID magnetometer (Quantum Design MPMS-XL7). A small quantity of foam sample was placed into a holder and the samples were tested at 300 K. Magnetization curves, from which mass magnetization was obtained as a function of applied magnetic field, were measured for wet (newly prepared) and dry (aged) foams.

RESULTS AND DISCUSSION

Hypromellose phthalate is a type of hydrophobically modified cellulose, which is used for enteric coatings in the pharmaceutical industry. Previous work by Wege et al. demonstrated the ability of HP-55 particles to stabilize foams for months.²⁴ When precipitated under shear at pHs close to its isoelectric point, HP-55 forms anisotropically shaped particles, which adsorb at the air—water interface, forming an armor composed of cellulose particles at the bubble surface (Figure 1a). The first foam stabilization mechanism provided by the HP-55 particles is steric repulsion between the adsorbed particle layers, which helps maintain thick liquid films between the pressed bubbles. These thick particle layers prevent film breakage and suppress gas diffusion between the bubbles in the foam.^{31,32} The second mechanism of foam stabilization by HP-

55 is based on the mechanical rigidity resulting from the entanglement of anisotropic particles at the film surface. The MP foams are made magnetically responsive through the inclusion of functionalized iron particles into the HP-55 matrix (Figure 1). The SEM image in Figure 1b demonstrates the presence of CI particles in a continuous network of HP-55. In the absence of an external magnetic field, CI particles are randomly distributed in the HP-55 polymer matrix around the bubbles. Despite the large density difference between the magnetic particles (7.86 g cm⁻³) and anisotropic HP-55 particles (1.28 g cm⁻³), the former remain trapped within the matrix of the latter, and the system remains stable for more than one week, without significant iron particle sedimentation (Figure 2).



Figure 2. Normalized foam head volume as a function of time. After rapid initial drainage and compression, the foam remains stable for more than one week. Note that the graph has a break between 4000 and 12000 min.

We characterized the foam samples in terms of stability against aging, viscoelasticity, and dynamics of destruction in the presence of a magnetic field. In the following section of the paper, we examine the relationship between the physical and functional properties of MP foam with age. The experimental data are summed into a simple model explaining the connections between the intrinsic properties of MP foams and their destabilization pathways.

Foam Stability: Liquid Drainage, Bubble Coarsening, and Coalescence. The degree of deformation as well as packing density of the closely packed air bubbles in foam is a function of the volume fraction of liquid in the system. The fraction of liquid in the foam can be represented by the expression: $\varepsilon = V_{\text{liq}}/V_{\text{foam}}$, where V_{liq} is the volume of liquid dispersed in the foam, and V_{foam} represents the volume of foam.³³ Since foam liquid content is directly correlated to the evolution of average bubble size, bubble packing, and foam viscoelastic properties,³⁴ we report data for measurements of foam water fraction as a function of time (Figure 3a). The decay of the water fraction occurs rapidly in the initial stages of the foam aging process and slows down after one day for samples containing 2.7 wt % Fe. This behavior can be approximated by an exponential expression $\varepsilon {\sim} t^{-\beta}$, where ε represents the fraction of water in the foam phase, β is an exponent which correlates to the rate of liquid drainage from the foam, and t is time.³⁴ The value of β for surfactant foams is usually between 2/3 and 2. For the present MP system, the value of $\beta_{\rm max}$ is ~1/6, which tells us that our foams drain much



Figure 3. (a) Foam water fraction as a function of time at different carbonyl iron concentrations. All samples make a transition from "wet" to "dry" foams. (b) Average bubble diameter as a function of time for the MP foam. The carbonyl iron concentration is 2.7 wt %.

slower than conventional surfactant-stabilized foams. The magneto-Pickering foams contain a very high initial liquid fraction of \sim 0.5 for the samples containing 2.7 wt % Fe. This is common for particle stabilized foams but is on the high end of the standard classification used for the water content of surfactant-based foams, which is as follows: $\varepsilon > 0.35$ (bubbly liquid); $\varepsilon \sim 0.35$ (wet foam); and $\varepsilon < 0.05$ (dry foam).^{33–36} The much higher liquid retention capability of magneto-Pickering foams over that of conventional surfactant systems can be attributed to the thick films sustained by steric repulsion between the voluminous HP-55 particle layers at the surfaces of adjacent bubbles. These particles, which also reside in the thick liquid films of the foam, slow down the drainage of fluid from the air-rich phase of the system. Even for our "dry foam" cases, ε is >0.10, which differs from the conventional definition of dry surfactant foams. Since foams are metastable systems, their evolution also involves processes of coalescence and coarsening, which lead to a growth in the average bubble size over time. Our foams consist of polydisperse spherical bubbles that, at the time of formation, have an average bubble diameter of \sim 50 μ m and coarsen over a period of one week to a diameter of ~500 μm (Figure 3b).

Several authors have conducted experiments and simulations to evaluate the dependence of foam bubble sizes on time. It has been shown that in the limit of dry foams, growth of the average bubble size scales as $R(t) \propto t^{1/2} \cdot 3^{7-39}$ In the case of foams stabilized by surfactants or amphiphilic molecules,

drainage, coarsening, and coalescence occur in a matter of hours. In magneto-Pickering foams, drainage to establish a pseudostationary state under gravity occurs in about 30 min, followed by minor coalescence through the rupturing of liquid films between bubbles on a timescale of less than one day, and slow coarsening through gas diffusion from smaller bubbles to larger bubbles after a few days. Mathematical fits of our data show that the average size of bubbles in fresh foams scale as R $\sim t^{0.36}$, while the average size of bubbles in aged foams scale as $R \sim t^{0.12}$. Thus, the evolution of average bubble size in our system occurs at a slower rate than in surfactant stabilized foams.^{37,40} In addition, the mathematical fits for our data show that once the foam transitions from the rapid to slow evolution regime, the rate of bubble growth slows down by $\sim 1/3$. This is mostly likely due to the contribution of both coalescence and coarsening events to the increase in average bubble size in fresh foam samples. Once enough liquid drains out of the foam head $(\varepsilon < 0.36)$ and the HP-55 armored bubbles begin to form a close-packed network, coalescence events will become nonexistent and any increase in bubble size can only be attributed to interbubble gas diffusion. This transition between the two evolutionary regimes occurs when the foam is ~ 1 day old (Figure 3, panels a and b).

Rheology: Evolution of Viscoelastic Behavior. On a macroscopic scale, we can characterize the magnetic foam system by studying the response of the bulk foam to tangential deformation. We interpret the macroscopic behavior of these Pickering foams in the framework of their dynamic rheological behavior. MP foam samples were subjected to small-amplitude oscillatory shear, and their storage (G') and loss (G'') moduli were measured as a function of angular frequency, ω .^{41,42} These moduli are related to the complex modulus, G^* , through the expression $G^*(\omega) = G'(\omega) + iG''(\omega)$.⁴³

The relative magnitudes and shapes of these rheology functions in relation to frequency provide a signature of the state of a material in terms of its elastic and viscous nature.^{44–46} The results from the frequency sweep experiments plotted in Figure 4a show a weak dependence of the moduli (G' and G'') on ω . Figure 4a reveals the frequency spectrum of the storage (G') and loss (G'') moduli of two foams samples: fresh (1 h) and aged (3 days). The frequency sweep experiments were performed using a shear stress in the linear viscoelastic region $(\sigma_{\rm LVR} = 3 \text{ Pa})$ of the material. The storage modulus of the fresh sample is relatively flat with a slight dependence on frequency. More importantly, it is approximately 1 order of magnitude higher than G''. These results taken together suggest that our foams behave as an elastic, gel-like material.^{44–48} This finding is significant, because surfactant-based wet foams or emulsions with similar water fraction (~0.5) normally exhibit viscous behavior with the absence of any yield stress.⁴⁹ Foam elasticity results from the springlike nature of the foam films, which is dependent upon the extent of bubble packing as well as the composition of the continuous phase in the foam.⁵⁰ In wet foams, the films are highly hydrated and foam bubbles are loosely packed. This generally results in a viscous or viscoelastic behavior reminiscent of polymer melts and solutions, with G'and G'' strongly dependent on frequency.^{44,45} The fact that our sample is elastic and exhibits a yield stress (Figure S1 of the Supporting Information) indicates that the solid-particles at the gas/liquid interface dominate the rheological behavior of these foams by interacting with each other and forming a jammed network in the bulk phase of the foam.



Figure 4. (a) Storage, G', and loss, G'', moduli as a function of frequency for foams of different ages and at 2.7 wt % Fe. Filled symbols represent G' and hollow symbols represent G''. The shape of the G' and G'' curves show that when testing in the linear viscoelastic regime (LVR), the foam behaves as a gel-like material and has low frequency dependence. (b) Damping factor, G''/G', at 6.28 rad/s versus foam age. The carbonyl iron concentration is 2.7 wt %.

The slight increase and flattening of G' with age, particularly at low frequencies, indicates the formation of a stronger elastic network (Figure 4a). Interestingly at this stage, the water fraction of the sample has decreased to ~0.25. For a surfactantbased system, this would lead to a transition from a wet to a closed-packed foam structure with a significant change in rheology, including a sol to gel transition, and appearance of a yield stress. In our case, we observed a yield stress for all samples tested and only saw a moderate change in G' despite substantial liquid drainage. This provides further evidence that solid particle interactions dictate the G' of the MP foam system.

The relationship between damping factor (G''/G'), or tan δ , and the age of the foam is plotted in Figure 4b. The phase angle between applied deformation and system response, δ , can be used as a metric for how elastic or viscous a material is. A value of $\delta \sim 90^\circ$ corresponds to a perfectly viscous material, whereas $\delta \sim 0^\circ$ corresponds to a perfectly elastic material. A fresh magneto-Pickering foam has $\delta \sim 10^\circ$ (found from data in Figure 4b). This foam can already be considered a very elastic material. As it ages to 5 days, δ decreases to a value of $\sim 5^\circ$, which means that the degree of material elasticity has doubled over this period of time. This decrease in damping factor and phase angle can be attributed to the drainage of liquid from the

foam. As water drains out of the system, the air fraction in the foam rises, increasing its elastic modulus.

In summary, the physical properties and rheological behavior of the foam were found to be highly dependent upon its age. Comparing the data related to the stability of the foams (Figure 3, panels a and b) with its rheological properties in Figure 4b (damping factor), we see remarkable consistency in that the decay in tan δ also shows a transition point of ~1 day. The same critical one-day point was determined in the previous section to be the time at which bubble evolution in the foam transitions from the fast-evolving to slow-evolving regime. This transition time likely corresponds to the point at which HP-55 particles on the surface of neighboring bubbles interlock to form rigid lamellae.

Collapse: Foam Breakdown on Demand by Magnetic Field. We describe above the effect of the maturing process on the intrinsic properties of magneto-Pickering foams in the absence of fields. However, the most distinctive property of these foams is their ability to respond to the gradient force of magnetic fields. When exposed to a gradient magnetic field, the iron particles trapped in the HP-55 matrix are magnetized. The magnetically polarized particles are attracted toward areas of higher field strength, pulled by a lateral force in the direction of the field gradient. Magnetized iron particles acquire a dipole moment, $\vec{m} = V \chi \vec{H}$, proportional to the particle volume, V, and to their magnetic susceptibility, χ .⁵¹ The force on one particle inside a magnetic field depends on the volume of the particle, the difference in magnetic susceptibility between the particle and surrounding medium, $\Delta \chi$, and the strength and gradient of the applied magnetic field $(\vec{B} \text{ and } \nabla \vec{B}, \text{ respectively})^{S}$

$$\vec{F}_{\rm mag} = \frac{V\Delta\chi}{\mu_0} \vec{B} (\nabla \vec{B})$$

where μ_0 is the permeability of free space. The magnetizability of a system depends on its components. In our case, the foams are a mixture of diamagnetic materials ($\chi \cong -10^{-6}$ to -10^{-4} , see the Supporting Information), such as water and HP-55, and ferromagnetic carbonyl iron particles, which are strongly polarizable and attracted to areas of high magnetic field gradients.

The MP foams were destabilized and collapsed using a neodymium (NdFeB) magnet ($B_r = 1.43$ T). We demonstrated in our previous work that the mechanism of foam collapse is dependent on the foam age as well as on the concentration of magnetic particles in the foam.²³ In the range of magnetic field strengths used in the present study, we found that the iron particle concentration required to destabilize the HP-55 matrix is above 1.3 wt %; this correlates to a HP-55:Fe weight ratio of 1:1.3. The overall foam collapse trend showed that the length of time necessary for destruction decreased as the age of the foam increased (Figure 5). Subsequently, we identified that wet and dry foams collapse in a different manner and speculated as to the mechanisms responsible for foam destabilization in these two systems.

The magnetization behavior of the composite magneto-Pickering foams was characterized using a SQUID magnetometer. In Figure 6, we present magnetization, M (emu g⁻¹), curves for two magnetic foams, a fresh foam and an aged foam, as a function of the applied magnetic field, H(Oe), at 300 K. The mass magnetization of the foam increases with an increase in the magnitude of the applied field until saturation magnetization, M_{sr} is reached. This saturation value corre-



Figure 5. (a) Collapse time versus foam age. The carbonyl iron concentration is 2.7 wt %. (b) Collapse time versus age for foams of different Fe concentrations. These times are determined from collapse experiments performed on foams contained in sealed glass vials and are the times necessary for deformation of the entire foam head toward the magnet in the different foam samples.



Figure 6. Magnetization curves for magneto-Pickering foams. These curves represent the mass magnetization as a function of applied magnetic field for fresh and 1 day old foams at 300 K and 2.7 wt % Fe.

sponds to the alignment of all magnetic dipoles in the sample with the applied magnetic field and is a function of the number of particles in the sample. Conventional ferromagnetic particles retain a remnant magnetization in zero field that can only be switched by applying a reverse field exceeding the coercive field, H_c . Magneto-Pickering foams, however, behave as a material



Figure 7. (a) Snapshots of microscopic collapse process for wet foam (top row) and dry foam (bottom row). Exposure of dry foam to a magnetic field results in film stretching and bubble coalescence; such destabilization mechanisms are not experienced by wet foam in a magnetic field. (b) Mechanism of foam collapse as a function of age. Mechanism of collapse for wet foam—bubble ejection from particle matrix by magnetic field (top row). Mechanism of collapse for dry foam—film rupture via stretching by magnetic field (bottom row).

without magnetic hysteresis, which is characteristic of carbonyl iron powder.⁵³ Carbonyl iron can be considered a magnetically soft material, whose ferromagnetic nature results in a high saturation magnetization, $M_{\rm s} \cong 200$ emu g^{-1.53}

As seen in Figure 6, the M_s of aged foam is ~6 times larger in magnitude than the M_s of fresh foam. Both foams saturate in fields stronger than $H = 5 \times 10^3$ Oe but the saturation magnetization of the fresh foam sample is $M_s = 1.6$ emu g⁻¹, while that of the aged foam is $M_s = 9.8$ emu g⁻¹. The magnetic susceptibilities of the foams were calculated from the slope of a line fitted to the initial part of the magnetization curve and were found to be $\chi^{\text{fresh}} = 0.0005$ emu g⁻¹ Oe⁻¹ and $\chi^{\text{1day}} = 0.0022$ emu g⁻¹ Oe⁻¹. The difference in the saturation magnetization and magnetic susceptibility of these systems results mainly from the difference in water content and, therefore, the center-tocenter distance between carbonyl iron particles in the foam samples. These data reveal a correlation between foam liquid content and response to a magnetic field and explain why older foams are more susceptible to a magnetic field, which was observed during the collapse experiments shown in Figure 5.

The forces involved in the action of a static magnetic field on the foam are schematically illustrated in Figure 7. It is important to note that the bubble packing configuration evolves over time due to drainage and coarsening but that carbonyl iron particles remain in the foam throughout the aging process. Observation of wet and dry foams in a magnetic field using optical microscopy revealed a difference in the mechanisms responsible for their collapse (Figure 7a). The exposure of wet foam to a magnetic field resulted in the movement of the bulk foam system (bubbles, HP-55, water, carbonyl iron particles) as a plastic body flowing toward the source of the field. This step is followed by the macroscopic expulsion of air bubbles out of the foam matrix. Thus, the collapse of wet foam results from the discharge of air bubbles from the foam matrix. Dry foams also deform toward the source of the magnetic field, but this deformation is rapid and violent (Figure 7b). Although both foam systems contain the same initial concentration of iron particles, the magnetically responsive particles are spaced further apart in the wet foam system than in the dry foam system as a result of the difference in their water content. This is also seen in the slow deformation and collapse of the fresh foam; magnetic particles that are more spread out do not experience strong dipole-dipole interactions. In addition, the presence of water as a free liquid medium results in the ability of particles to migrate individually toward the source of the field or rearrange to form chains with other particles. In older foams, the proximity of the magnetically responsive particles to each other due to the reduction of water in the films results in a stronger collective response to the applied magnetic field. The close packing and trapping of particles in the thin, gel-like foam films allows them little room to rearrange or migrate freely toward the source of the field. As a result, CI particles collectively stretch the thin films between

bubbles, while pulled by the magnetic field, causing film rupture and bubble coalescence.

To further test the validity of the above hypothesis on the mechanism of destruction of fresh and old foams, we developed a model evaluating the number of particles necessary to induce breakdown in wet and dry foams using two different collapse mechanisms. The minimum number of particles needed to collapse the foam in each scenario was evaluated as follows:

$$N_{\rm p}^{\rm wet} \approx \frac{\Delta P \pi R_{\rm bubble}^2}{F_{\rm mag}}$$
 (2)

$$N_{\rm p}^{\rm dry} \approx \frac{\gamma l_{\rm stretch}}{F_{\rm mag}}$$
 (3)

In these expressions, F_{mag} is the magnetic force that the field exerts on one iron particle, N_p is number of particles, ΔP is the Laplace pressure inside an air bubble, R is the radius of the bubble, γ is the energy at the air–water interface, and l_{stretch} is the length over which the particles act to stretch the bubble. For the fresh foam system, we evaluate the force that leads to the expulsion of one air bubble from the foam matrix. The pressure inside a bubble of radius R exceeds that outside it by the Laplace pressure ($\Delta P = 2\gamma / R$). To squeeze a bubble out of the foam matrix, a force must be exerted to overcome the Laplace pressure distributed over the cross-sectional area of the bubble (πR^2) . The force on the bubble surfaces exerted in opposition to the Laplace pressure is the attraction between the CI particles around the bubble and the applied magnetic field $(N_{\rm p}^{\rm wet} \dot{F}_{\rm mag})$. In eq 2, we have equated the Laplace pressure of one air bubble to the total force of attraction between the CI particles around the bubble to the magnetic field. This equation can be used to estimate the number of CI particles necessary to induce collapse by air expulsion from a fresh foam sample.

As the foam ages (Figure 7b), magnetic and HP particles are compressed and immobilized in the less fluid films as water drains out by gravity. The particles in the thin gel-like films lose their mobility and exert collective stresses on the film when magnetized. In this model, the destruction of the dry foam is based on the rupture of thin films between adjacent bubbles. In eq 3, we have equated the force needed to rupture a thin film $(\gamma l_{\text{stretch}})$ to the total force exerted on the film by the attraction between CI and the magnetic field $(N_p^{dry} \vec{F}_{mag})$. In this model, the magnetic pull of the particles is opposed by the tension (γ) at the bubble surfaces. While there may also be a small tensile stress from the particle matrix opposing thin film rupture, this force is assumed to be negligible in the model. This is because the HP-55 particles stabilize the foam when compressed, but the particle network is expected to have poor tensile strength. In addition, once the tensile strength of the particle network is overcome and the new interface is generated during the stretching of the foam film, the main force opposing film rupture is the surface tension at the air-liquid interface.

We determined the minimum number of particles necessary to induce collapse of wet and dry foams using the above derived expressions and compared the values for the estimated number of particles needed to induce collapse to the actual number of particles in the foam head (Table 1). The number of magnetic particles loaded into a foam is evaluated as 2×10^{10} (considering a concentration of 2.7 wt % Fe). According to the expression above for N_p^{wet} , approximately 4000 iron particles are needed to squeeze one bubble out of the wet foam matrix (Table 1 and Figure 7b); and in the case of drier foams,

Table 1. Summary of Forces Needed for Destruction of Wet and Dry Foams a

	$F_{\rm mag} ({\rm pN})^b$	$N_p^{\ c}$	CI/bubble ^d
wet foam	≈3.3	≈4000	≈2000
dry foam	≈9.0	≈4800	≈30000

^{*a*}Parameters used to solve for these values can be found in Tables S1 and S2 of the Supporting Information. ^{*b*}F_{mag} is the force experienced by one carbonyl iron particle in the \vec{B} field. ^{*c*}N_p is the number of particles needed to displace a bubble from the particle matrix (wet foam) or to rupture all the films in a bubble (dry foam). ^{*d*}The number of carbonyl iron particles surrounding a wet and dry foam bubble was estimated from experimental values of water fraction, foam volume, bubble size, and iron concentration; it is denoted by CI/bubble.

approximately 600 iron particles are required to rupture a film. Again, in the case of the dry foam, we assume that rupturing one of the thin film facets of the bubble would be sufficient to destroy the entire bubble. The quantities reported in Table 1 are calculated per bubble rather than per film (Table 1 and Figure 7b). These values are consistent with the number of CI particles in the foam, validate our proposed collapse mechanisms, and give us a semiquantitative estimate of the magnitude of the forces necessary to induce foam collapse. They also explain the drastic increase in the foam responsiveness and rate of destruction with foam age, as the number of particles per bubble in the aged system becomes nearly an order of magnitude larger than the one needed to induce foam destruction.

CONCLUSIONS

The magneto-Pickering foams are responsive soft magnetic materials with remarkably high, yet tunable stability. We analyzed the evolution of the foam network in terms of stability, viscoelasticity, and response to applied magnetic fields. These three sets of experimental data are complementary and wellcorrelated. They present a consistent model of the interplay between two distinct physical mechanisms of foam stabilization and breakdown, controlled by time-dependent draining and aging processes in the foam. The most interesting insight is the strong dependence of the foam properties on the aging process even though all foams were very stable in the absence of a magnetic field. The magneto-Pickering foams exhibited a transition point of ~ 1 day, before which all foam properties undergo rapid evolution and after which the changes in their properties over time slow drastically. Dynamic viscoelastic measurements of our samples suggested that MP foams behave in a way that is similar to that of viscoelastic solids, where the elastic component becomes strongly dominant in the aged samples. This is possibly correlated to the formation of a robust gel-like network by the HP-55 and iron particles in the foam films and Plateau borders after some free water drains down during the initial settling process. This critical transition was also observed in the response of the foam to a magnetic field, where the aged systems were destroyed almost instantaneously.

Our hypothesis pertaining to the destruction of foams of differing age was confirmed by magnetometry measurements, an evaluation of the forces involved, and the estimated number of particles needed for foam breakdown by the two mechanisms of foam destruction proposed in this work. The predictions are in good agreement with the experimental data, and point out that the combination of macroscopic and microscopic techniques used allowed for good characterization and

understanding of magneto-Pickering foam behavior during their aging and destruction by the magnetic field. The ability to noninvasively apply a well-defined force to iron particles confined in a film, as demonstrated in this work, opens up the field for precise measurements that can help elucidate the fundamental mechanisms behind the stabilization of Pickering foams. In addition, similar types of responsive foams can find a range of practical applications where on-demand foam destruction and removal is needed.²⁷

ASSOCIATED CONTENT

S Supporting Information

Foam collapse movies. Parameters used in the models to explain the collapse of wet and dry foams. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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