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Magnetically Responsive Pickering Foams

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S *Supporting Information*

ABSTRACT: We introduce a new class of Pickering foams which can be manipulated using a magnetic field. These foams are stabilized by a mixture of magnetic and nonmagnetic particles. They exhibit excellent stability in the absence of a magnetic field, but can be rapidly destroyed on demand with the application of a threshold field. We characterize their stability in the absence of a magnetic field by measuring the rate of water drainage from the foam as a function of time. We also correlate their collapse behavior under a magnetic field to the foam liquid fraction, as well as the concentration of magnetic particles in the foam. This novel system can be used to study the properties of Pickering foams, and has potential applications in noncontact defoaming processes.

Most conventional foams are stabilized by surfactants or proteins. Particle-stabilized foams, or Pickering foams, have been a topic of study as a result of their remarkable stability.[1−9] Although a number of researchers have evaluated the effectiveness of different types of particles in foam stability, there is still paucity of data on the fundamental properties of these foams, such as the time-evolution of foam liquid fraction. In addition to stabilizing bubbles and thin films, the particles employed in the system can also be used to impart functional characteristics, such as color, onto the foam.[8] These particle stabilizers in effect turn the foams into responsive materials, a topic of expanding scientific interest.[10−14] Materials which can be manipulated using magnetic fields are one of the simplest type of such structures. The use of external magnetic fields to manipulate the structure of ferrofluid foams was studied by Hutzler et al.[15,16] Moulton and Pelesko employed magnetizable nanoparticles to study liquid drainage in soap foams.[17] To our knowledge, however, the use of magnetic particles to induce on-demand destruction in foams has not been reported until now.

We describe a new class of "magneto-Pickering" foams, which are stable in ambient conditions, but rapidly collapse in magnetic fields. These foams are stabilized by hypromellose phthalate (HP-55) particles and contain oleic acid coated carbonyl iron particles (4.5−5.2 μm average diameter) embedded in the HP-55 matrix. The use of HP-55 for foam stabilization is based on previous work by Wege et al., which demonstrated that irregularly shaped HP-55 particles formed using a liquid−liquid dispersion shear method can stabilize foams for periods as long as months.[9,18] The intermediate hydrophobicity and anisotropic shape of the HP-55 particles allow them to interlock and form stable structures around the bubbles, thus, stabilizing the foam. The magneto-Pickering foams were made by diluting a mixture of functionalized iron particles and HP-55 stock solution in deionized water followed by aeration in a blender (the details of the procedures are provided in the Supporting Information). During blending, hydrochloric acid was added to induce the precipitation of the HP-55 particles under shear, and to adjust the final pH of the system to a value between 2.5 and 3 (Figure 1a). The major stabilizing component in the resulting foams is the particles of modified cellulose, which occupy approximately 2.3× to 4.6× larger volume fraction than the iron particles. The magnetically responsive Fe spheres are permanently trapped inside the gel-like matrix of percolated HP-55 particles adsorbed at the interfaces and captured in the foam films and menisci (Figure 1b). The foams were poured into glass cylinders immediately after blending, and their volume and phase composition were monitored over time.

In the absence of a magnetic field, the foams contained in the glass cylinders were stable for more than a week. This finding is consistent with earlier studies conducted on foams containing just HP-55 particles.[8,9] The magneto-Pickering foams, however, were destroyed in a matter of seconds when an external magnetic field was applied. This was done by placing a rectangular magnet (1 in.× 2 in.× 0.75 in.), with poles oriented along the 0.75 in. direction ($B_r = 1.43$ T), on a stand at the height of the foam level, and in contact with the outside of the foam-containing cylinder. This process and subsequent foam collapse were captured in digital video using a Canon EOS 5D camera with a 100 mm macro lens. Foams at different stages of the aging process were collapsed to determine the effect of water drainage on their breakdown behavior. The rate and mechanism of foam collapse were found to be dependent upon the age of the foam, as well as the concentration of magnetic particles in the system (see Supplementary Movies). The dependence of collapse time on the age of the foam, as well as on the concentration of magnetizable particles in the system, is illustrated in Figure 2a. The data point out that the time necessary for foam collapse rapidly decays with the age of the foam. When a magnetic field is applied to a freshly made sample, the foam slowly deforms as a plastic material and collects toward the source of the field within ~15 s. The foam body then begins "oozing" air phase and becomes largely defoamed in another 5−10 min. In contrast, when a magnetic field is applied to foams aged for more than 3 days, the foam rapidly breaks down in 1−3 s, the collapse proceeds without structural rearrangement, and the particles are

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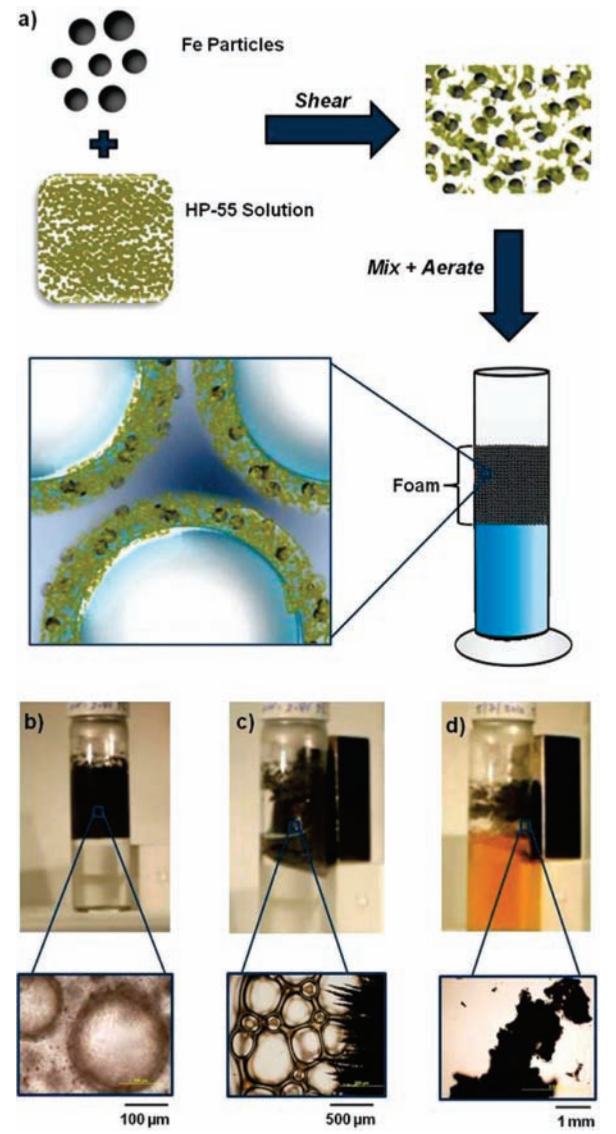

Figure 1. Formation and structure of magneto-Pickering foams. (a) Schematic of the procedure for making these foams. It involves combining functionalized iron particles with HP-55 stock, followed by HP-55 particle formation under shear and foam build-up through whipping air into the liquid during mixing. The components are not drawn to scale. (b) Wet foam prior to exposure to a magnetic field. The optical microscope image below shows that the foam bubbles are surrounded by iron particles. (c) Collection of fresh foam (age = 5 h) in the direction of the magnet upon exposure to the field. The microscope picture shows withdrawal and alignment of the magnetic particles. The bubbles are squeezed out of the particle mass and will undergo coalescence and popping. (d) Breakdown of dry foam (age = 11 days) in the direction of the magnet upon exposure to the field. The micrograph shows the collection of the cellulose and iron particle mass as a whole.

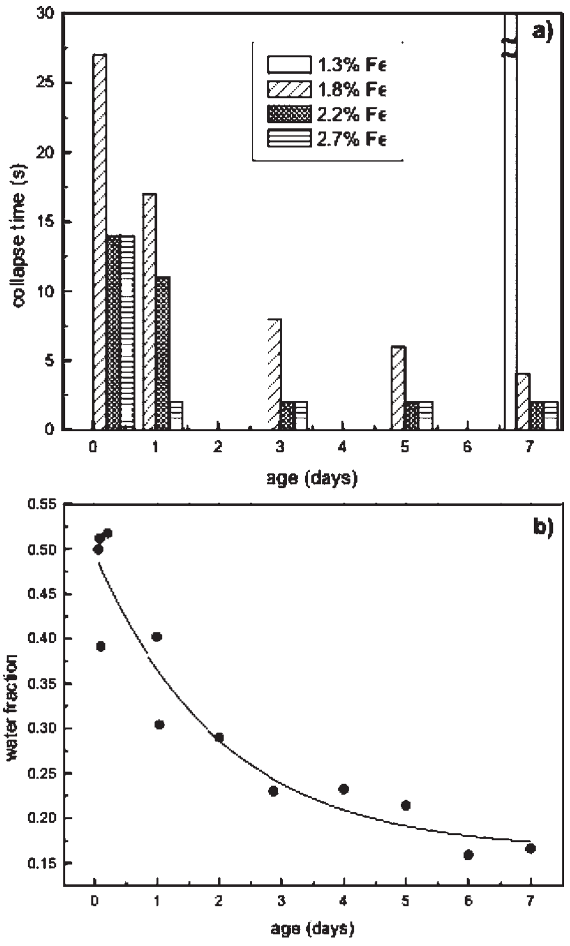

Figure 2. (a) Collapse time vs age for foams of varying Fe particle concentration. The collapse time decreases as the age of the foam increases. The amount of the time required for collapse also decreases as the concentration of carbonyl iron in the foam sample increases. Foams made with ≤1.30 wt % carbonyl iron show little response to the magnetic field even after 7 days of aging, so only the last bar indicating collapse time values greater than 60 s is included in the figure. All foams were formed from suspensions containing 1 wt% HP-55. (b) Water fraction in foam containing 2.7 wt % Fe particles as a function of time. The dots (•) represent experimental data and the line represents the least-squares exponential decay fit.

rapidly collected toward the source of the field (see Figure 1c,d and Supplementary Movies). Our hypothesis is that the films between bubbles in fresher foams are thicker, and upon the application of a magnetic field, the particles are able to move around in the "wet" foam film; in this scenario the bubbles may rearrange with respect to each other, which is also observed experimentally. In aged foams, the films between the bubbles contain a lower fraction of water and are thinner. The particles as well as the bubbles in the drier foam are jammed and have little room to rearrange upon exposure to a magnetic field. As the particles in these foams are attracted toward the magnet, they pull on the thin rigid films between the bubbles, resulting in film rupture and rapid defoaming.

The age-dependent resistance of the foams to magnetic field breakdown can be correlated to the lower water volume fraction in older foams in comparison to fresher foams. The stability of any foam is a function of its liquid content, which changes here as the water drains down the film and Plateau three-phase borders. Over time, foams undergo natural aging processes, such as coarsening and drainage.[19] To our knowledge, the time course of liquid drainage in Pickering foams over extended periods of time has not been reported. Since the long-term draining process strongly affects the response of our foam to magnetic fields, we measured the evolution of the water volume fraction in magneto-Pickering foams over time (Figure 2b). The data confirm that the liquid fraction in the foam exhibits an exponential-like decay on time scales comparable to the transition from plastic to elastic foam response in magnetic fields. According to the literature, our foams can be classified as "very wet" since the starting liquid fraction, ε, is greater than 0.35.[20] They maintain a high liquid fraction for long periods of time, likely due to the arrest of bubble coarsening by the protective particle shells around the bubbles, as well as a decrease in the rate of liquid drainage from the foam as a result of the formation of particle networks inside the films.[4−7]

We also confirmed the hypothesis about the age-dependent mechanism of magnetic defoaming by directly observing the response of wet and dry foams to magnetic fields at the level of single bubbles by optical video microscopy. The Fe spheres do not interact before the application of a field as they lack permanent magnetic moment. In wet foams, when the field is applied, loose particles assembled in short chains as well as bubbles surrounded by iron particles migrate slowly as a whole toward the magnet (Figure 1c). In drier foam samples, several mechanisms leading to foam breakdown were observed. These mechanisms include bubble popping and coalescence, which seem to be caused by film rupture as a result of the stretching of the interface between bubbles (for an illustration of these processes, see the Supplementary Movies and Figure S1). More evidence that the defoaming is a result of the forces applied by the particles on the thin water films can be found in the collapse experiments performed as a function of magnetic particle concentration. They demonstrate that the response of the foam to the magnetic field was critically influenced by the concentration of iron particles in the air-rich phase (Figure 2a). Below an iron concentration of 1.30 wt % in the pre-aerated suspension, the foams showed negligible response and no breakdown when the field was applied. We believe this indicates that a critical number of particles are needed to break the films between the bubbles by collectively applying force stretching the liquid membrane. At lower than critical particle loading, the magnetic force acting on the films is insufficient for their stretching and breakdown (Figure 2a).

In summary, a new class of responsive "magneto-Pickering" foams was developed and characterized. They can serve as a model system for studying properties of Pickering foams, such as drainage, and their response to external fields. The breakdown of these foams in response to an applied magnetic field is affected by the age of the system as well as the concentration of magnetic particles in the dispersion. A pronounced difference between the response of wet foams and dry foams to a magnetic field was observed both macroscopically and microscopically. This difference can be attributed to the decreasing water fraction in the foams due to gravitational drainage, leading to particle interlocking and shifting of the film and composite foam response from viscous to elastic. Preliminary results on the rheology of these foams as a function of age presented in the Supporting Information confirm the transition from plastic to elastic response within this time interval.

The magnetically controlled systems can find application in a wide range of new industrial defoaming processes. Foam is an undesirable byproduct in many processes, including fermentation, wood pulp production, and detergent manufacture. Traditionally, interfacially active defoamers (i.e., alcohols, silicone oils) have been used to destabilize and destroy unwanted foam in such processes.[21,22] However, defoaming by chemical compounds can be expensive, invasive, and can result in contamination of the product or the environment. Mechanical defoaming is less invasive and can be used regardless of the foam composition; however, existing mechanical defoaming methods are not effective at destroying highly viscoelastic foams, and require special equipment and high energy input.[23] Magneto-Pickering systems may be applied in rapid and inexpensive processes to break down or collect unwanted foam. In addition, the particles employed may be easily collected magnetically after use and recycled, reducing the environmental impact of the defoaming process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. 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. This material is available free of charge via the Internet at http://pubs.acs.org.

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