Foams

DOI: 10.1002/anie.201105399

Smart Foams: New Perspectives Towards Responsive Composite Materials

*Adrian Carl and Regine von Klitzing**

fatty acids · foams · interfaces · self-assembly

Owing to their high surface/volume ratio, stable foams are well suited for the decontamination of surfaces, for example. At the end of the cleaning process, the foam should be destabilized in a controlled way in order to end up with a small volume of contaminated liquid which is easier to handle. While there are already several examples of ultrastable foams in literature, reports of foams with switchable stability are rare. In this context the work of Fameau et al.[1] presents a milestone in the triggering of foam stability by external stimuli.

In the production of foams the amount and stability depend on the complex interplay between the foamability at the beginning of the foaming process and the subsequent drainage, which is highly related to surface and bulk rheological properties. When the drainage is slow, the stability is governed by gas diffusion and surface forces across the lamellae which affect the coalescence (lamella rupture) and coarsening (gas exchange between bubbles as a result of differences in Laplace pressure). Hence, in order to gain full understanding of the system, information about the bulk structure, surface tension and surface viscoelasticity, foam lamella behavior, and the macroscopic foam is essential.[2]

To produce a large amount of stable foams two important conditions must be met: high foamability resulting from the fast adsorption of active compounds to the lamella surface, and high stability of the foam caused by the formation of an elastic surface layer by the strongly (irreversibly) adsorbed surface-active material. These are often counteracting features. Low-molecular-weight surfactants show good foamability and fast aging within one hour caused by fast adsorption/desorption kinetics. In contrast, partially hydrophobized particles in so-called Pickering foams have high adsorption barriers but a long lifetime (weeks, months). The particles are irreversibly adsorbed at the lamella surface, and the elastic dilatation modulus increases with increasing surface coverage, which prevents coarsening ($E > \gamma/2$, Gibbs stability criterion).[3] In general, high surface coverage is needed for high stability. In this context the aim of current research is to tailor surface-active compounds to obtain high foamability and long-living foams.

The energy required to remove a particle from the interface depends on the particle/fluid contact angle and the particle size.[4] Usually, the foamability shows a maximum at contact angles of around 90°. At the oil/water interface or oil/air interface the contact angle of the particles can be tuned by modifying the particles and by varying the polarity of the oil phase. It was found that particle-stabilized foams are formed for contact angles between 40 and 90°.[5] In contrast, it is much more challenging to control the adsorption of particles at the air/water interface. When the hydrophobicity of the particles is adjusted, partial clustering at the surface can be observed.[3,4] Usually, hydrophilic inorganic particles like silica, metal, and laponite particles are hydrophobized by silanization or by the physisorption of surfactants like cetyltrimethylammonium bromide ($C_{16}TAB$), sodium dodecylsulfate (SDS), and other short-chain amphiphiles.[3,6–8] Often, particles are used in combination with surfactants. Then, two relaxation mechanisms at the air/water interface can be identified: a low-frequency process associated with surfactant-decorated particles and another relaxation process at high frequency related to surfactant monomers.[6]

Another parameter for controlling the adsorption at the lamella surface is the particle charge. In a study with latex particles with a diameter of 700–900 nm, their charge was found to strongly affect the foam stability.[9] Positively charged latex particles adsorb well at the negatively charged air/water interface leading to stable foams; anionic latex particles are depleted from the air/water interface and present ineffective foam stabilizers.

In summary, foams stabilized with particles are "ultrastable" but the stability cannot be adjusted in situ by this strategy. In a recent study Rodrigues et al. used magnetic particles for to stabilize foams; bubbles were generated that were responsive to magnetic field gradients and could be heated up by an oscillating magnetic field.[10] Nevertheless, the foam stability was not controlled because of the low magnetic response probably originating from the small particle size (nanometer range). Velev and co-workers have showed that foams stabilized with larger magnetic particles can be destroyed instantaneously by applying a magnetic field.[11].

Besides particles, macromolecules and supramolecular aggregates offer new perspectives for the control of foam stability. For instance, polymers can be added to tune the stability of foam lamellas. Foam lamellas formed from aqueous solutions of charged surfactants and oppositely

---

[*] Dipl.-Chem. A. Carl, Prof.Dr. R. von Klitzing
Stranski-Laboratorium für Physikalische und Theoretische Chemie
Institut für Chemie, TU Berlin
Strasse des 17. Juni 124, 10623 Berlin (Germany)
E-mail: klitzing@chem.tu-berlin.de

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

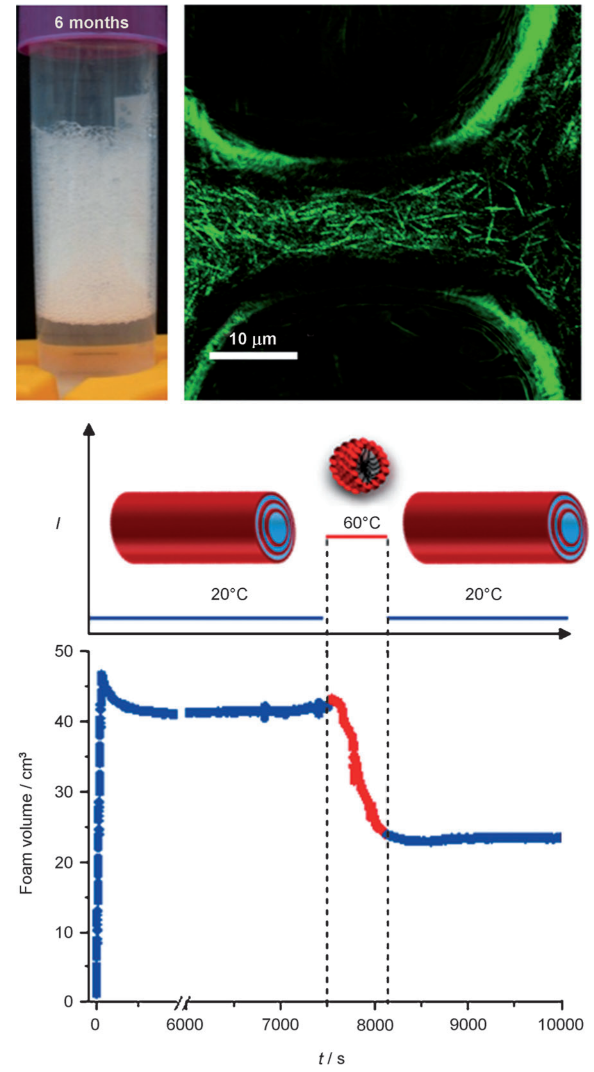

Figure 1. Left: Foam is still stable after six months. Center: Foam lamella containing 12-HSA tubes at 20 °C (confocal microscopy). Right: External triggering of foam stability by temperature changes; taken from Ref. [1].

charged polyelectrolytes show a stability minimum close to the isoelectric point (IEP), that is, for a 1:1 mixture of surfactant charges and polyelectrolytes charges.[12] A combination of surface tension and surface elasticity measurements showed a low compressibility (high *E*-modulus) of the surfaces at the IEP, which led to the conclusion that in this case surface forces dominate rather than mechanical properties.

Macromolecules such as proteins, which are sensitive to external parameters like pH and ionic strength, are of interest for producing foams with controlled stability.[13] So far, only one study has used macromolecules to trigger the foam stability. Salonen et al. designed "light and temperature bi-responsive emulsion foams".[14] The foams were generated from emulsions containing a temperature-sensitive surfactant and a light-responsive polymer (labeled with an azobenzene dye). The foamability decreases upon heating, is stopped by UV irradiation, and recovered upon cooling (Figure 1).

Taking into account the difficulties in triggering the stability of a foam by an external stimulus, the strength of the strategy described by Fameau et al. for "switching reversibly between ultrastable and unstable foams" is even more pronounced.[1] Their elegant approach relies on the temperature-dependent switching the polymorphism of amphiphile aggregates. They used 12-hydroxystearic acid (12-HSA), which has a low surface tension and forms elastic layers at the air/water interface. In order to disperse 12-HSA in water, they added a water-soluble organic counterion. The amphiphiles form self-assembled multilayer tubes with a length of 1 µm and a width of 600 nm, and an ultrastable foam is produced. The gas and the liquid are preserved within the foam, and the foam is quite wet (20 % average liquid fraction). There are three explanations for this behavior: Fatty acid monomers adsorb readily at the lamella surface (high foamability) and the tubes are expelled from the "bulk" of the lamellas into the plateau borders where they jam and prevent fast drainage and aging. In addition, the tubes are adsorbed at the lamella surface, leading to a high dilatational modulus (low compressiblity) and therefore halt coarsening.

Upon heating to 60 °C the self-assembled tubes metamorphose into micelles, and the foam decomposes immediately. A foam that was stable for months can be destroyed within minutes. The destruction process can be immediately stopped by cooling the foam to room temperature, which indicates a reversible change in polymorphism from micelles back to tubes. The (de)stabilization temperature can be tuned by the organic counterion.

To summarize, a series of experiments in the last decade showed that the Pickering concept for stabilizing emulsions by particles or aggregates can be also transferred to foams. Ultrastable foams can be generated by inorganic particles with an intermediate contact angle. On the other hand, not many studies exist on triggering the foam stability by external stimuli. In this context, the work of Fameau et al. on thermosensitive (de)stabilizing fatty acid aggregates is very innovative and timely. It offers new perspectives for responsive composite materials.

Received: July 31, 2011
Published online: October 28, 2011

---

[1] A. L. Fameau, A. Saint-Jalmes, F. Cousin, B. H. Houssou, B. Novales, L. Navailles, F. Nallet, C. Gaillard, F. Boué, J.-P. Douliez, *Angew. Chem.* **2011**, *123*, 8414; *Angew. Chem. Int. Ed.* **2011**, *50*, 8264.
[2] C. Stubenrauch, R. von Klitzing, *J. Phys. Condens. Matter* **2003**, *15*, R1197.
[3] A. Stocco, W. Drenckhan, E. Rio, D. Langevin, B. P. Binks, *Soft Matter* **2009**, *5*, 2215.
[4] B. P. Binks, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21.
[5] B. P. Binks, A. Rochera, M. Kirkland, *Soft Matter* **2011**, *7*, 1800.
[6] L. Liggieri, E. Santini, E. Guzman, A. Maestro F. Ravera, *Soft Matter* **2011**, *7*, 7699.
[7] R. M. Guillermic, A. Salonen, J. Emile, A. Saint-Jalmes, *Soft Matter* **2009**, *5*, 4975.
[8] U. T. Gonzenbach, A. R. Studart, E. Tervoort, L. J. Gauckler, *Angew. Chem.* **2006**, *118*, 3606; *Angew. Chem. Int. Ed.* **2006**, *45*, 3526.

[9] S. L. Kettlewell, A. Schmid, S. Fujii, D. Dupin, S. P. Armes, *Langmuir* **2007**, *23*, 11381.

[10] J. A. Rodrigues, E. Rio, J. Bobroff, D. Langevin, W. Drenckhan, *Colloids Surf. A* **2011**, *384*, 408.

[11] Unpublished results.

[12] N. Kristen, R. von Klitzing, *Soft Matter* **2010**, *6*, 849.

[13] A. P. Middelberg, M. Dimitrijev-Dwyer, *ChemPhysChem* **2011**, *12*, 1426.

[14] A. Salonen, D. Langevin, P. Perrin, *Soft Matter* **2010**, *6*, 5308.

ChemistryViews

Education & entertainment

Exciting news

Spot your favorite content

www.ChemistryViews.org

Unique articles

Multi-media

Free & easy access to new magazine

New online service brought to you by

ChemPubSoc Europe

WILEY-VCH

603701008

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim