PLENARY REPORT

FROM FOAMED SUSPENSIONS TO FUNCTIONAL POROUS MATERIALS

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Abstract

Direct foaming of suspensions of solid particles, followed by drying of the obtained foams, is a highly efficient method for production of ultralight porous materials for various applications. Among the key factors in the application of this method is the appropriate choice of surfactant, as well as the optimization of its concentration. These two factors play a crucial role in the processes of suspension foaming and of foam stabilization upon drying. In this talk we summarize briefly our recent results in this area, published in a series of four preceding original papers, as explained below.

We established that there are several common macroscopic properties which control the suspension foaminess and the foam stability, independently of the specific mechanism of foam stabilization (via particle adsorption or via gelation of the continuous phase in the foam): (1) The foaminess is controlled exclusively by the suspension viscosity under shearing conditions which closely mimic the foaming process; (2) The stability of the wet foam is controlled exclusively by the suspension yield stress; (3)The foam stability upon drying is controlled by the homogeneous particle distribution (ensured by mild particle aggregation) and the related homogeneous propagation of the receding water front in the drying foam.

The above set principles allowed us to formulate optimal conditions for preparation of materials of various chemical compositions, such as silica, carbonate, alumina, gypsum, etc. These materials could incorporate different functionalities, including high performance thermal insulation, sound insulation, as catalysts support, tissue scaffolds, and others.

Keywords: functional porous materials, particle suspension, foaminess, foam stability, transport in porous media, thermal insulation.

1. INTRODUCTION

The studies of concentrated suspensions in presence of foaming agents have first been reported in mineral flotation industry [1]. Soon after, first attempts to prepare solid materials from surfactant-particle mixtures were made and patented [2]. Unfortunately, the latter materials never found real applications due to their complexity and to the lack of physicochemical control of their properties.

In the beginning of the 90's, the re-invention of particle containing foams started with the development of gel-casting method [3-4]. Protein- or monomer-containing suspensions were foamed and then settled via wet foam sintering or polymerization [3-5]. These processes provided opportunity for preparation of porous materials of various nature and complexity. However, the fine tuning of the materials' porosity and bubble size distribution was inaccessible at the time, as foams tended to coarsen fast in the wet state. Any optimization of the microstructure was based on trials-and-errors.

In 2006, the group of Ludwig Gauckler in ETH-Zurich re-discovered the particle surface modification using oppositely charged short-chain surfactants and started producing particle-stabilized foams [6-8]. The obtained wet foams were stable against coarsening, but for unknown at that time reasons most of them failed to dry into large-scale materials without cracking [9]. Therefore, these authors continued to study and to use the gel-casting modifications via proteins and enzymes [9,10].

Although their discovery allowed some optimization of the foam air content and pore-size distribution, based on the suspension properties, some of the observed phenomena lacked clear physicochemical explanations: 1) why should only oppositely charged short-chain surfactants be used; 2) which is the key factor to control the suspension foaminess; 3) what prevents the water drainage in these suspensions; 4) why do the materials crack upon drying; 5) what is the relation between the air content in the wet foams and the mass density of the final porous material, etc?

2. FOAMINESS OF SUSPENSIONS

To answer the above questions, we performed several related studies [11-15]. Thus, to clarify the role of surfactant type, we used two different types of surfactants for surface modification of negatively-charged silica particles [11-13]: a) the long-chain cationic surfactant *tetradecyl trimethyl ammonium bromide* (TTAB); and b) the amphoteric *cocamidopropyl betaine* (CAPB).

We found that the cationic TTAB adsorbs fully on the silica surface at low concentrations, whereas the CAPB adsorbs only partially, allowing most of the surfactant molecules to remain dissolved in the aqueous phase of the suspensions. As a result, during foaming with a kitchen mixer, the two surfactants provided two qualitatively different mechanisms of foam stabilization:

A) TTAB adsorbed on the particle surface, thus partially hydrophobizing it. Therefore, the particles adsorbed at the surface of the bubbles and stabilized the foam (see Fig. 1A);
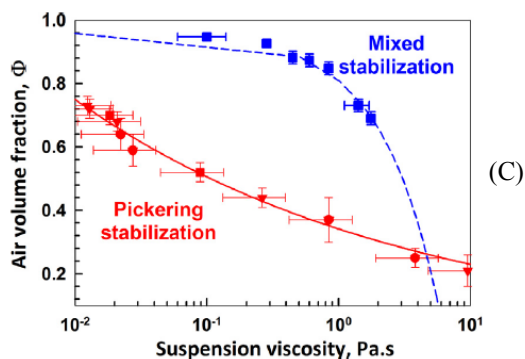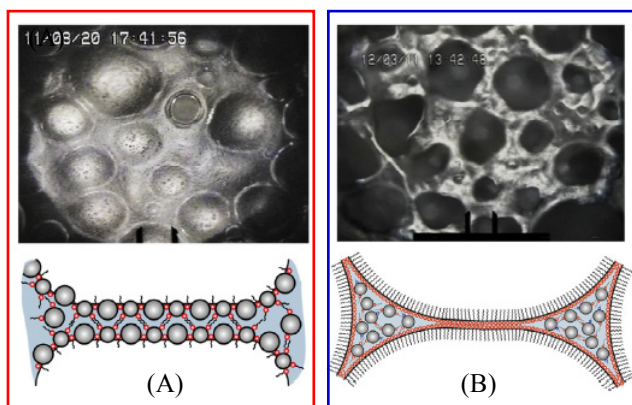

(A)   (B)

(C)

Fig. 1. Reflected light microscope image and illustrative scheme of the mechanism of stabilization of the foams, prepared from suspensions of silica particles and containing (A) cationic surfactant and (B) amphoteric surfactant. (C) Air volume fraction in foamed suspensions, as a function of the viscosity of the silica-surfactant mixtures for cationic surfactant (Pickering stabilization) and amphoteric surfactant (Mixed stabilization). This figure is adapted from Ref. [12].

B) CAPB molecules predominantly adsorbed on the surface of the bubbles, while the modified solid particles remained in a gelled state in the aqueous Plateau channels and nodes of the foams (Fig. 1B).

We found that the air content in the foamed suspensions decreased with the increase of suspension viscosity (Figure 1C). We observe two distinct master curves, depending on the mechanism of foam stabilization. The viscosity of the suspensions depended on the concentration of particles and surfactant, and generally increased with the increase of both ingredients.

3. STABLITY OF THE FOAMS

Besides the difference in the foaminess, these two types of surfactants showed significant differences in their wet foam stability and drying behavior. Based on their composition, i.e. concentration of particles and surfactant, most foams were unstable to coarsening and drying. Figure 2A shows illustrative results for silica particles in the presence of TTAB – foams at low concentration of surfactant and particles (θ is particles surface coverage by the surfactant) suffered from drainage of the liquid phase from the wet foam, whereas the high concentrations of surfactant and particles led to formation of severe cracks during drying.

Experimental results showed that the stability against drainage depended exclusively on the ratio between the yield stress of the particle suspensions and the bubble size in the foams:

$$\tau_0/R_b \geq 2\Delta\rho g \qquad (1)$$

Here τ_0 is yield stress, R_b is the mean radius of the bubbles, $\Delta\rho$ is the mass density difference between the suspension and the air, and g is the gravitational acceleration constant.

As the surfactant adsorbed on the surface of the particles, the latter attracted each other due to hydrophobic forces, created by the hydrophobic tails of the adsorbed surfactant molecules. This attraction manifested as a gradually increasing yield stress of the suspension. Once the yield stress became higher than the hydrostatic pressure at a bubble scale, the liquid drainage stopped and the foams could be dried to porous materials (see Fig. 2B).

The yield stress increased with the increase of surfactant and particle concentrations, which was a clear indication of the formation of larger number of hydrophobic bridges between the particles. Once we reached a threshold particle aggregation, the particles started forming large clusters inside the suspensions (see Fig 2C) which prevented the homogeneous drying of the foams and led to formation of cracks in the drying materials.
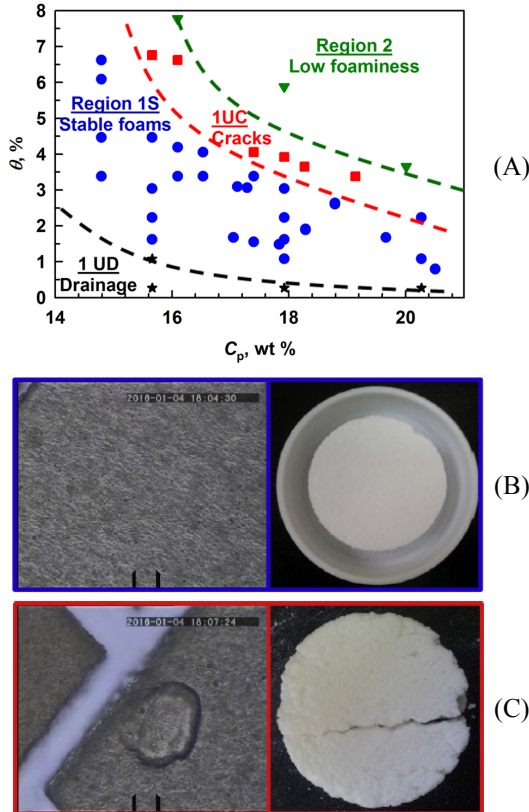

Fig. 2. (A) Foam formation and stability diagram of silica+TTAB mixtures. Diagram is plotted as surface coverage of the particles by surfactant vs concentration of particles. Different topological regions are color coded and noted. Microscope observation of suspension wetting film in reflected light and macroscopic material from region 1S are shown in Figure (B) and from region 1UC - in Figure (C). Figure is adapted from Ref. [12].

Similar results were obtained with CAPB, despite the differences in the mechanism of foam stabilization. Additional process of bubble Ostwald ripening was observed in the wet CAPB foams, which was also counteracted by the yield stress of the suspensions, once the yield stress became higher than the bubble capillary pressure:

$$\tau_0 > \sigma/R_b \qquad (2).$$

The formation of cracks in the drying foams could also occur as a result of particle migration during drying or inhomogeneous water distribution. Such is the case of carbonate foams in the presence of different anionic surfactants [13]. We found that weakly interacting particles, which do not aggregate, could migrate during drying. This migration leads to inhomogeneous distributions of the particles and to worse mechanical performance of the final materials (see Ref. 13 for details).

4. DRYING AND FOAM STRUCTURE

Along the drying process, the foams typically shrink which results in a significant decrease of their volume. We developed a theoretical model, allowing us to predict the shrinkage of the materials, their final mass density and the change in their bubble size (provided that there is no Ostwald ripening) [14]. This model requires single experimental parameter, ρ_{susp}, that could be determined by drying a non-foamed suspension and measuring its mass density:

$$\rho_{PM} = \rho_{susp}\left(1-\Phi\right) \qquad (3)$$

$$K = 1 - \frac{\rho_{SiO_2}}{\rho_{susp}} \frac{1}{\left(1 + \frac{\rho_{H_2O}}{\rho_{susp}}\left(\frac{1-\varphi_p}{\varphi_p}\right)\right)} \qquad (4)$$

Here ρ_{PM} and ρ_{susp} are the mass densities of the porous material and of the dry suspension, Φ is the air volume fraction of the wet foam, K is the shrinkage volumetric ratio, ρ_{SiO2} is the mass density of the particle material, and φ_P is the particle volume fraction in the suspension.
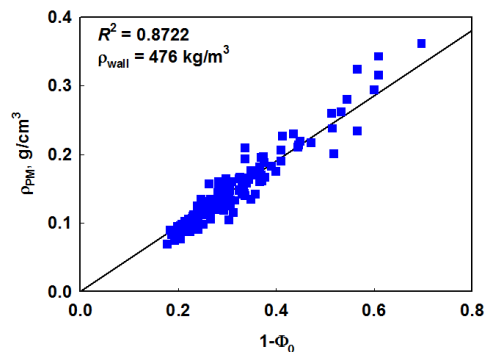

Fig. 3. Mass density of dried porous materials, obtained from wet Pickering foams, as a function of the bubble volume fraction in the wet foam. Figure is adapted from Ref. [14].

The experimental results showed very good agreement between the experiment and the model without using any adjustable parameters (Fig. 3). The experiment confirmed also the theoretical prediction for the bubble shrinkage along the drying process, which turned out to be proportional to the macroscopic shrinkage of the foam, determined by Eq. (4).

5. FUNCTIONAL MATERIALS

The final porous materials could be used as efficient thermal insulators, with desired mechanical properties and low thermal conductivity (see Fig 4A and B).

Non-sintered TTAB containing foams at 120 kg/m^3 outperform the commercial expanded polystyrene insulations by 5-10% in thermal resistance, while having similar mechanical strength (60-100 kPa). In addition, they provide the highest possible class of fire safety.
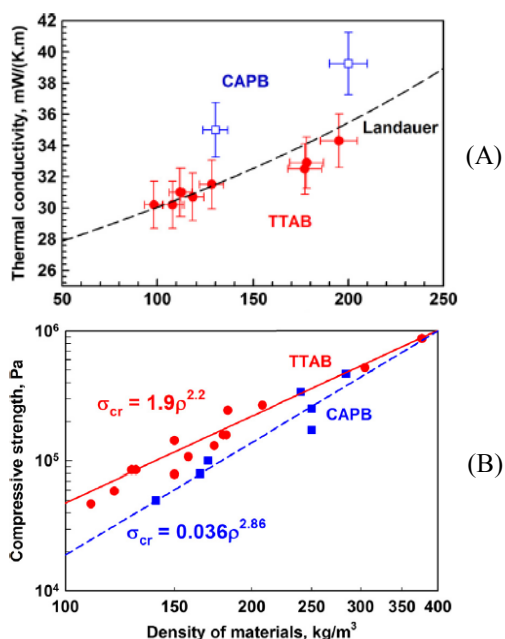

Fig. 4. *(A) Thermal conductivity and (B) Compressive strength of porous silica materials, as functions of the material density. Figure is adapted from Refs. 12 & 15.*

CONCLUSION

Suspension foaming is a highly efficient method for production of ultralight porous materials with various applications. Key factors for optimal application of this method are the appropriate choice of surfactant, as well as its concentration optimization.

We established [11-15] that there are common macroscopic properties which control the suspension foaminess and foam stability, independently of the specific mechanism of foam stabilization: (1) Foaminess is controlled exclusively by the suspension viscosity under shearing conditions, which closely mimic the foaming process; (2) Foam stability to bubble coarsening and foam drainage is controlled exclusively by the suspension yield stress; (3) Foam stability to drying is controlled by the homogeneous particles distribution (ensured via mild particle aggregation) and the related homogeneous propagation of the receding water front in the drying foams.

The above principles allowed us to formulate [11-14] optimal conditions for preparation of materials of various chemical nature, such as silica, carbonate, alumina, gypsum, etc. These materials could incorporate different functionalities, including high performance thermal insulation, noise insulation, as catalyst supports, tissue scaffolds, and others [15].

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