

Functional porous ceramics using amphiphilic molecule

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Inorganic particles (Al_2O_3 , SiO_2 , etc) are in situ hydrophobized upon adsorption of short-chain amphiphilic molecules, can be used as porous foam stabilizers. We tailor the microstructure of particle-stabilized wet foams; the foam air content, average bubble size, and bubble size distribution by changing the composition of the initial colloidal suspension. Wet foams featuring average bubble sizes between 30 and 300 μm and air contents between 45% and 90% were obtained by adjusting the amphiphile and particle concentration, and particle size in the initial suspension. The influence of these parameters on the porosity was satisfactorily described in terms of the combined effects of the contact angle and surface tension of the initial suspensions, directly affected by the amphiphile concentration.

Key words: Porosity, Porous ceramics, Amphiphile concentration, Contact angle & Surface tension.

Introduction

Porous ceramics are of interest due to their potential applicability in catalysis, adsorption and separation, filtration of molten metals or hot gases, refractory insulation of furnaces, and tissue repairs and engineering. Ceramic foams produced by direct foaming have shown unprecedented stability in the wet state and elevated mechanical properties when sintered. These wet foams were stable over several days and showed no bubble coarsening, drainage, or creaming [1-3]. Their stability was attributable to the irreversible adsorption at the air-water interface of colloidal particles that were rendered partially hydrophobic by short-chain amphiphiles. The amphiphiles modified *in situ* the wetting behavior of the particle surface. Control of the particle wetting allows the preparation of suspensions containing high concentrations of such partially hydrophobic particles [4-6].

Adsorptions at fluid interfaces occurs when particles are not completely wetted by any of the fluids, thus exhibiting a final equilibrium contact angle at the triple phase boundary. The equilibrium contact angle (θ) is determined by a balance between the interfacial tensions involved. Similar to the hydrophile-lipophile balance (HLB) used for surfactant-stabilized systems, the contact angle determines the type of mixtures to be formed. Oil in water emulsions and foams are obtained for contact angles lower than 90°, whereas water in oil emulsions and mists (aerosols) are produced for contact angles varying from 90° to 180° [7, 8]. The stability

towards Ostwald ripening, on the other hand, has been explained by the mechanical resistance of the outer particle layer against the shrinkage and/or expansion of droplets and gas bubbles. The degree of particle hydrophobization achieved through the surface adsorption of amphiphiles was investigated with the help of surface tension measurements. A decrease in surface tension upon increasing the initial amphiphile concentration in solution is observed for all the evaluated suspensions. However, above a critical amphiphile concentration, a relatively strong decrease in surface tension is observed. Above this critical amphiphile concentration, the particles are sufficiently hydrophobic to attach to the air-water interface, leading to a decrease in surface tension more pronounced than that expected from the free amphiphiles alone. This significant reduction in surface tension upon particle adsorption is caused by a decrease of the total area of the highly energetic air-water interface [9, 10]. Direct foaming is of particular interest due to its simplicity, low cost, and versatility [2, 11, 12]. The irreversible adsorption of particles to the interface resulted in a percolating interfacial armor that mechanically impeded bubble growth, shrinkage, and coalescence [13, 14]. Suspensions could be foamed homogeneously throughout their entire volume, with porous bulk materials obtained upon drying and sintering. Such materials comprise mostly closed-porous microstructures with enhanced mechanical properties. In this study, the stabilization of wet foams with colloidal and final tailored microstructures was characterized through measurements of amphiphile concentration, bubble size, contact angle, surface tension, and porosity. The stabilities of the foams obtained here were due to different stabilization mechanisms of the air-water interface from those

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applied in conventional shaving foam. Unmodified silica particles were added which were expected to form networks throughout the foam lamellae, to aid the prevention of bubble coarsening and also produce efficient mechanical strength.

Materials and Methods

Materials

High-purity alumina (α - Al_2O_3 , $d_{50} \sim 500$ nm, Showa Chemical, Tokyo, Japan) and silica (SiO_2 , $d_{50} \sim 300$ nm, Junsei Chemicals, Japan), deionized water, hydrochloric acid (35% Yakuri Pure Chemicals, Osaka, Japan), sodium hydroxide powder (Yakuri Pure Chemicals, Kyoto, Japan) and propyl gallate (Fluka, China) were used.

Suspension preparation

The suspensions were prepared using propyl gallate as an amphiphile through the stepwise addition of alumina powder to an aqueous mixture of 0.01 M NaOH and 0.1 M propyl gallate. The solid loadings and pH of the suspensions were initially fixed at 50 vol% and 9.9, respectively. Homogenization and de-agglomeration were performed via ball milling for at least 24 hours using polyethylene milling pots and alumina balls (10 mm in diameter-2 : 1 ratio of balls to powder). The propyl gallate was adjusted to the required concentration in the final suspension (1-2 wt % to Al_2O_3). This was dissolved in NaOH ($\text{pH} > 10$) and added dropwise to the ball milled suspension under slight stirring in order to avoid local particle agglomeration. Finally, the pH was set at 9.9 and water was added until the solid contents were 30 vol%. In other experiments, suspensions under various pHs were also tested.

The SiO_2 suspensions were prepared through the addition of dry silica powder to water to achieve solid loadings of 45 vol%. The silica was unmodified and no further pH modification was required. Various blends of modified and unmodified particles were prepared and tested with a total solid content of 30 vol% under varying pH conditions.

Contact angle and surface tension

The contact angles and surface tensions of the suspensions were measured using the pendant drop method (KSV Instruments Ltd, Helsinki, Finland). Alumina suspensions were prepared through the dropwise addition of propyl gallate to generate solid loadings of 30 vol% alumina. The drop volume was varied between 5 and 10 μl depending on the nature of the suspension.

Foaming, drying, and sintering

The foaming of 150 ml suspensions was performed using a household mixer (150 watt, Super Mix, France) at full power for 3 to 5 minutes. The bubble size distributions of the foam were evaluated via optical microscopy in the transmission mode (Somtech Vision,

South Korea) with a connected digital camera. The bubbles sizes were measured using linear intercepts. The average sizes were determined from analyses of particular areas. Wet samples were shaped into cylinders by hand and subsequently dried in air at 20-25 $^{\circ}\text{C}$ for 24-48 h. The dried foams were sintered in an electric muffle furnace at 1200 $^{\circ}\text{C}$ for 2 h. The heating rate was 1 $^{\circ}\text{Cmin}^{-1}$ and the cooling rate was 3 $^{\circ}\text{Cmin}^{-1}$.

Results and Discussions

Initial particle and amphiphile concentration

The microstructures of wet foams can be tailored by the concentration of particles in the suspension. The influence of particle concentration on the microstructure of wet foams was determined by varying the solids content in an alumina suspension containing particles at a propyl gallate concentration. Also the amphiphile concentration of the initial suspension directly affects the colloidal particles' hydrophobicity; varying the particle concentration with constant amphiphile addition also affects the particles' hydrophobicity. Increasing the initial amphiphile concentration increased adsorption onto the particles, enhancing their surface hydrophobicity. Above a critical concentration of adsorbed amphiphiles, particles became sufficiently hydrophobic to adsorb to the air-water interfaces, stabilizing freshly introduced air bubbles. Therefore, foam formation and the resulting microstructures depended strongly on the suspensions' initial particle and amphiphile concentrations [13].

Fig. 1 shows wet foam stability decreased with increasing solid content from 10 to 50 vol% alumina. The foams' air contents also decreased from 82% to 60% over this range of solid concentrations. The decrease of air contents with solids contents over 50 vol% greatly increased the initial suspensions' viscosities. Additional increases of particle concentration greatly increased the suspension's viscosity, hindering the incorporation of air for foam formation. The effects of amphiphile strength on contact angle and wet foam stability were assessed

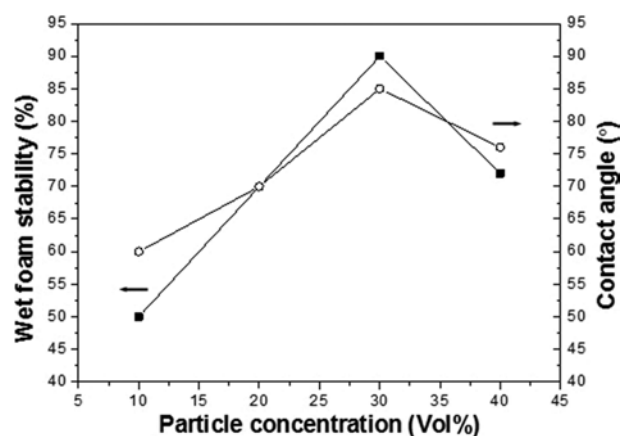


Fig. 1. Wet foam stability and contact angle with respect to the particle concentration of the initial suspension.

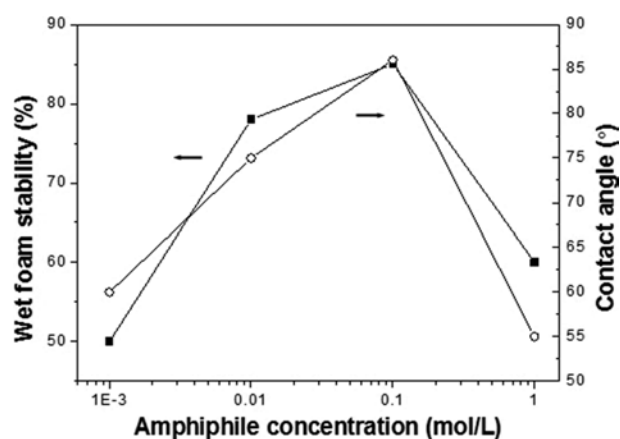


Fig. 2. Wet foam stability and contact angle with respect to the amphiphile concentration of the initial suspension.

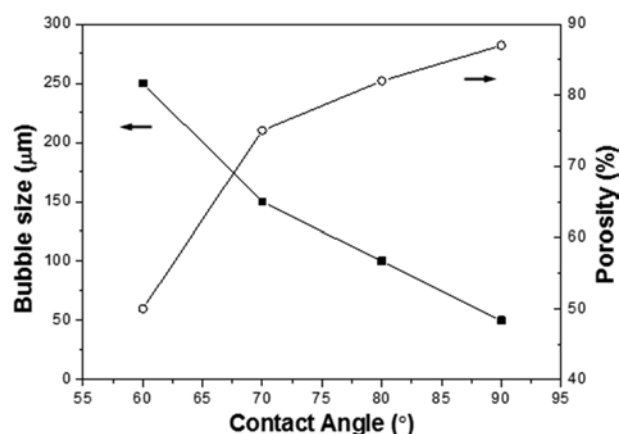


Fig. 3. Bubble size and porosity with respect to the contact angle of the initial suspension.

and are shown below in (Fig. 2). There was a change in the foam stability and its corresponding contact angles too. Higher the contact angle corresponding to the certain concentration of the amphiphile gave higher stability as shown in the figure. Despite the wet foams having nearly similar 70% air contents, their average bubble sizes decreased from 250-50 μm as propyl gallate concentration increased from 0.001 M to 1 M which can be seen from their respective contact angle datas in fig. 3. Foams with lower average bubble sizes also exhibited narrower bubble size distributions. The mixture of modified and unmodified particles showed similar properties with increasing particle concentration, with the only exception being the destabilization of suspensions with high silica contents. Ratios of alumina to silica of 0.1-0.3 resulted in stable foams with high porosity.

Contact angle and surface tension

The contact angle of particles in suspension can also be tailored with surface chemistry by adjusting the composition of the fluids. Adsorption at fluid interfaces occurs when particles are not completely wetted and exhibit finite equilibrium contact angles at the triple phase boundary. Stabilization has been reported to be

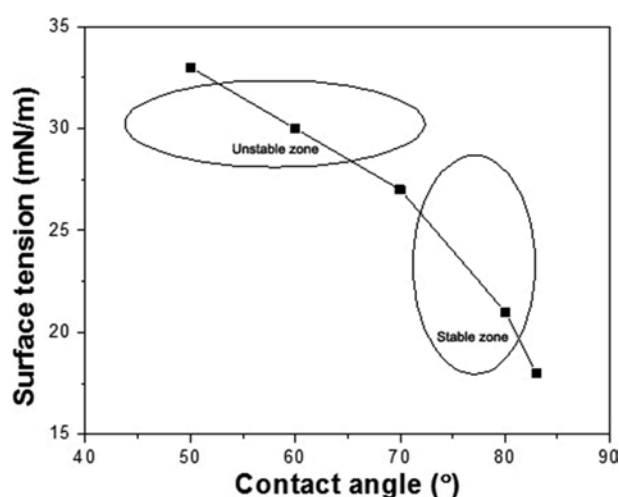


Fig. 4. Surface tension with respect to the contact angle of the initial suspension.

achieved at intermediate contact angles of 40 °~86 ° in oil (air)-in-water emulsions and foams. Besides the concentration of amphiphile, the suspension's pH also affected the wet foam microstructure. Highly aerated foams with small, narrowly distributed bubbles were achieved at pH (4 - 6). Higher pH (8 -10) resulted in foams with larger bubble and wider size distributions [13]. Fig. 3 and 4 shows that the bubble size of the wet foams and the porosity of the sintered ceramics. Bubble size decreased with the increase in the contact angle until it had average and uniform distributions as demonstrated in the fig. 3. It was also proved before that suspension contact angle of around 80 °~85 ° leads to higher stable foams which further increased by some other process can give mist or emulsions rather than foams. The required partial hydrophobization of the particles occurs at this point which leads to the porous ceramics with higher porosity. These foams had linear shrinkage of less than 25% after sintering and larger surface areas, and gained a porosity of about 80% after sintering. Fig. 3 and 4 also explains that the increase in contact angle and decrease in surface tension leads to average bubbles of less than 100 μm with higher porosity and mechanical strength. These are only the result of our experiments with certain parameters which may vary with use of different stabilizers giving different level of particles hydrophobization and shows the areas of stable and unstable zones.

Microstructure

The high stability of the wet foams allowed their direct drying in air at room temperature. However, to avoid cracking, the wet foams had to be slightly strengthened to overcome capillary stresses and to avoid differential shrinkage within the drying foam [11]. The subsequent drying and sintering with different heat treatment resulted in closed cells. Compared with surfactant-stabilized foams, these foams achieved

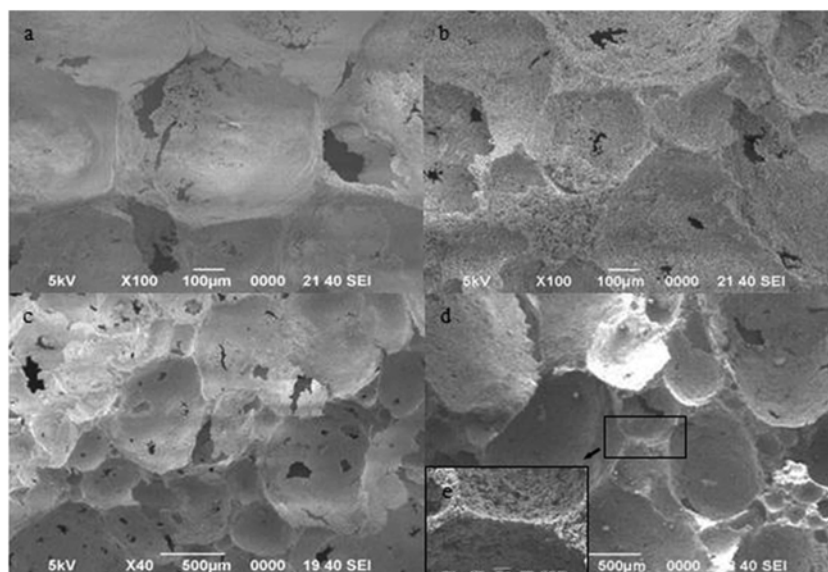


Fig. 5. Microstructures of the foams sintered at 1200 °C and 1300 °C, with 30 vol% of the total solid content, a. 0.001 M, b. 0.01 M, c. 0.1 M (at 1200 °C), d. 0.1 M (at 1300 °C), e. 0.1 M (showing inner cell separations).

smaller average cell sizes and exhibited either open or closed cells, even at high porosities [2]. It also shows the effect of particle and amphiphile concentration on the porosity of the sintered foams. Increase in both the components until the elevated point increases the porosity whereas further increase decreases it. Also the microstructural images of porous ceramics under different amphiphile conditions showed different bubble size, distribution and hierarchy, microstructures with an amphiphile of strength of 0.01 M showed larger bubbles size and wide distribution whereas with an amphiphile concentration of 0.1 M showed smaller average bubbles with narrow distribution [13]. Fig. 5 shows the microstructure of sintered foam at 15 kV resolutions which shows the pore distribution at different magnifications. Cells were both closed and open with an average size of *ca.* 100 - 300 µm. Single cells were separated by walls with minimum thicknesses of 1 - 3 µm. Comparative porosity analysis data (measured by Micromeritics) of the samples showed a higher porosity upto 82%. These data's also prove the analysis that the porosity of the samples are higher at a certain critical point which on our experiment were at 30 vol% particle concentration, with 0.1 M strength of amphiphile showing a contact angle of 82 °, surface tension of 21 mN/m and average bubble size of 100-200 µm.

Conclusions

Concentrated colloidal alumina particles were rendered hydrophobic *in situ* by propyl gallate, facilitating the preparation of high-volume wet foams with air contents of up to 82% and bubble sizes of 50 to 300 µm. The foams show neither bubble growth nor drainage over days. The degree of induced hydrophobicity was adjusted

through varying the concentrations of the particles and amphiphiles in the initial suspension. The remarkable resistance of the particle-stabilized foams against coarsening has been attributed to the irreversible adsorption of the partially hydrophobic particles at the air-water interface. The resulting highly stable wet foams could be dried in air without bubble coarsening or cracking. According to this model, the final bubble size could be controlled by changing the suspension contact angle, surface tension and scaling number containing these two variables was successfully employed to explain the effect of the suspension initial composition on the average bubble size and porosity of sintered foams. An increase in amphiphile concentration upto the critical point of 0.1 M leads to a decrease in surface tension and an increase in contact angle which led to foams with smaller average bubbles and higher porosity.

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