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Macroporous gibbsite foams prepared from particle-stabilized emulsions using corn starch and agar as binders

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Abstract

Corn starch and agar were used independently as a water-uptake binder in combination with anionic sodium dodecul sulfate (SDS) which modifies the hydrophobicity of cationic gibbsite platelets for preparation of air-in-water (*a/w*) gibbsite foams via a simple mechanical frothing. Contact-angle (θ) measurements revealed that the apparent θ decreased from partially hydrophobic ($\theta \sim 62^\circ$) to more hydrophilic ($\theta \sim 47^\circ$) when the corn starch was first added, leading to foams with a reduced stability. As the concentration of corn starch reached above ~8 vol.%, θ returned back to greater than 60°, rendering then a stable foam. On the other hand, θ was found to decrease from 57° to 50° when the agar concentration increased above a mere 0.16 vol.%. This gave rise to a pronounced drainage and coalescence of the foam, and a further increase of the agar concentration only led to a quick disappearance of the *a/w* bubbles. By tailoring the binder concentration, macroporous gibbsite foams were produced from the air- or freeze-dried wet foams, which typically consisted of packing void cells over a cell-size distribution of 50–400 μm, a porosity ranging from 77% to 86%, and a three-point (green) rupture strength of up to 240 kPa.

Keywords: Porous material; Gibbsite; Emulsion; Corn starch; Agar

1. Introduction

Macroporous ceramics with a tailored pore structure has attracted much attention owing to its diverse applications in heterogeneous catalysis, separation, filtration, and thermal insulation [1]. For the successful preparation of the porous ceramics via suspension routes, natural polymers such as starch and agar have been used as a gelling agent upon shaping consolidation and a fugitive pore former when the shaped product is subjected to thermal burnout [2–14]. By carefully tuning the polymeric concentration, solids loading, and chemical composition of the natural polymers, the macroporous ceramics with a well-defined pore size, pore-size distribution, thermal/insulation property, and complex shape can be prepared by simple and cost-effective forming methods directly from suspensions in any nonporous mold. The starch consolidation casting (SCC), for example, has been developed for near-net-shaping of various porous ceramics with a controlled porosity over a range of 25–50 vol.% [2–10]. This method is yet difficult to fabricate porous materials with a porosity exceeding the above range [6], mainly because of the mechanical robustness required for the shaped product during binder burnout together with the inability of precise control over pore size stemming from the broad size distribution of the natural starch with grain shape largely depending on biological source and plant genotype. On the other hand, agar has been employed in ceramic gelcasting as a gelling binder for cordierite that showed a porosity up to 76 vol.% [13]. The agar facilitated formation of three-dimensional porous networks, in which OH bonding was formed with water molecules during the gelation process.

In view of the literature, Pickering emulsion [15,16] which stabilizes wet foams by the presence of well-anchored solid particles at the water–air or oil–water interface has received increasing attention for the preparation of porous ceramics via the suspension routes. The functional particles enable to provide elastic, mechanically robust, and functionally tailored shell textures that are vital to various emerging applications involving use of the hierarchically structured porous ceramics [17–19]. A suitable wettability is critically important for the

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particles to reside at the interface preferentially so that the overall interfacial energy can be replaced by the lower solid–liquid or solid–vapor surface energy [18,20]. Stable wet foams become attainable when coalescence, drainage (i.e., creaming), and disproportionation (i.e., Ostwald ripening) between neighboring bubbles can be hindered. Use of short-chain surfactant molecule in water that imparts the hydrophobicity of originally hydrophilic ceramic surface has been developed for the preparation of ultrastable oxide foams with a tailored pore structure [21–23]. In particular, stable alumina foams that can self-set at room temperature have been made possible by addition of calcium aluminate cement into the surface-modified alumina suspensions. This enables fabrication of mechanically robust alumina foam without the need of drying and sintering at elevated temperatures [24,25]. In addition, alumina foams with an aligned microporous wall have also been demonstrated from unidirectional freezing of alumina suspensions stabilized by adsorption of polyvinyl alcohol polymers on the particle surface, in which the polymers act as a binder and an emulsifier as well [26].

Gibbsite platelets, instead of spherical alumina particles, were used as a stabilizer for the preparation of stable air-in-water (*a/w*) foams in our earlier study [27]. The well-dispersed gibbsite platelets with a suitable hydrophobicity were found to reside and accumulate preferentially at the air–water interface with their major axis oriented in parallel with the interface. This produced well ‘‘armored’’ foams with a mechanical barrier sufficiently strong to resist the bubbles from coalescence and creaming in a much reduced solids loading, enabling then a facile fabrication of macroporous alumina with a relative porosity greater than 90% after sintering. Based upon the above findings, corn starch and agar were used independently as a water-uptake binder, together with anionic sodium dodecul sulfate (SDS) that modifies the hydrophobicity of the cationic gibbsite platelets in this study, for the preparation of stable *a/w* gibbsite foams via a simple mechanical agitation followed then by shaping in a non-porous mold. The as-prepared foams were air- or freeze-dried to form macroporous gibbsite compacts with a reasonable mechanical strength and pore structure before sintering.

2. Experimental procedure

2.1. Materials

The gibbsite particles were kindly provided by Prof. Fu-Su Yen (National Cheng Kung University, Taiwan) and were of platelet morphology with the length in major axis of about 500 nm. The particles bear a positive surface charge when dispersed in water at an acidic pH. Detailed physical characteristics and surface properties of the gibbsite platelets were reported elsewhere [27]. Corn starch (S-4126, mean particle size about 10 μm, Aldrich, Japan), agar (Aldrich, Portugal) and silica beads (Aldrich, Japan, mean particle size of 0.6 μm) were used as-received without any treatment. De-ionized water (18.2 Ω cm) was prepared from Millipore Super-Q Plus (U.S.A.). Reagent-grade sodium dodecul sulfate (SDS, $NaC_{12}H_{25}SO_4$, 99%, Aldrich, Japan), 1-dodecanol ($CH_3(CH_2)_{11}OH$, 98.6%, Tedia, U.S.A.), and hydrochloric acid (HCl, 37%, Aldrich, Germany) were used for surface modification and dispersion of the gibbsite particles in D.I. water.

2.2. Foam preparation and stability observation

The as-received gibbsite particles were mixed with D.I. water, SDS, and 1-dodecanol in a fixed solids concentration of 10 vol.%. The concentration of SDS and 1-dodecanol was held at 8 and 16 mM, respectively [27]. The suspension pH was kept at 2.5 ± 0.1 by addition of HCl solution (1 M). For the gibbsite suspensions with the corn starch as the water-uptake binder, the starch concentration varied from 3.1 to 18.1 vol.% in terms of the total volume of the suspensions. The powdered suspensions were ball-milled in polyethylene bottles by using high-purity alumina balls as the milling medium for 20 h. The wet foams produced from the mechanical mixing of the milling operation were packed in non-porous molds followed then by drying in an oven (75 °C for 24 h) to form porous compacts with a dimension of 3 mm × 4 mm × 40 mm ready for the measurement of three-point rupture strength.

For the preparation of agar-added gibbsite foams, wet foams were first prepared by the ball-mixing of powdered suspensions consisting of the gibbsite particles with D.I. water, SDS, and 1-dodecanol in the proportion mentioned above. Prior the mixing operation, silica beads of 5 vol.% (in terms of the total suspension volume) were added to the suspensions for the sake of improved mechanical strength of the prepared gibbsite foams. Agar solution of various concentrations (0.2–1.0 wt.%, which are equivalent to concentrations of 0.03–0.16 vol.% of the total suspension volume) was then added to the prepared foams with vigorous agitations of 10 min. Viscosities of the wet foam solutions were found to increase after the agar addition, and the foams were eventually set by placing them into a freezer kept at −5 °C for 2 h.

2.3. Characterization

Field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan) was used for microstructural examinations of the cellular foams. A sessile drop-shape analyzer (FTA 2000, First Ten Angstroms Inc., U.S.A.) was used for the *apparent* contact-angle measurement which dispenses water drops from a syringe pointed vertically down onto the surface-smooth powder-compacted samples at 25 °C and captures the water profile on the samples by an optical system [27]. An average of at least five measurements was carried out for each batch of the gibbsite particles with various degrees of surface modifications. Mercury porosimetry (Autopore 9520, Micromeritics, U.S.A.) was used to measure the pore size and pore volume of the air- and freeze-dried gibbsite foams. A maximum pressure of 414 MPa was used for the measurement. The three-point flexural strength of the dried gibbsite samples was determined by an Instron (U.S.A.) with a spanning distance of 30 mm and a cross-head speed of 0.5 mm min^{-1}.

3. Results and discussion

3.1. Gibbsite foams prepared with corn starch

Fig. 1 shows stability of the gibbsite foams when the corn-starch concentration varied. In Fig. 1(a), contact angle (θ) decreases pronouncedly from 65° to below 50° as the corn starch was first added, revealing that the gibbsite surface became essentially more hydrophilic with presence of the corn-starch molecules. In accompany with the θ decrease, coalescence between the neighboring bubbles and the creaming of bubble aggregates began to prevail. This became particularly apparent after a short period of standing time (<3 h) for the wet foams with the starch concentration of 3.1 and 5.1 vol.%; to which, a marked reduction on the bubble volume is shown in Fig. 1(b) after 24 h. The corn starch is a form of glucose biopolymer, consisting of polysaccharide mixtures that include linear amylose and highly branched amylopectin as the major building blocks for the polymeric structure [2,5]. The condensed glucose units that build up the structure include plenty of hydroxyl groups in aqueous suspensions [2], facilitating then the more hydrophilic character found in Fig. 1(a). The starch particles are nonetheless generally insoluble in water at temperatures below 50 °C. In addition, the branched fraction in starch, i.e., the amylopectin, would hydrolyze preferentially in acid solutions and form a resistant complex on the surface to render ‘‘protection’’ toward further hydrolysis of the linear amylose [28]. At the working pH of 2.5 used in the study, an increased solubility by the hydrolysis of the acid-thinned starch is expected to occur when the ball-milling operation was simultaneously applied that sheared apart the starch aggregates and exposed new freshly un-hydrolyzed polysaccharide to the solution, resulted in a reduction in suspension viscosity so that the gibbsite surface became more hydrophilic.

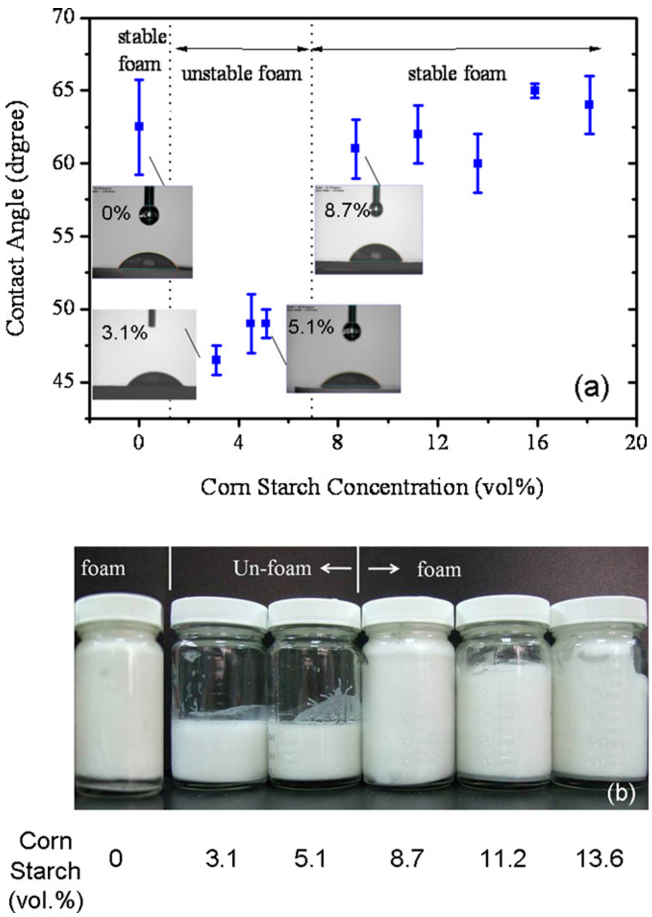

Fig. 1. (a) Contact angle vs. corn-starch concentration of the gibbsite-filled aqueous suspensions. The gibbsite loading was held at 10 vol.%. (b) Vials of the gibbsite foams with various corn-starch concentrations after being placed without disturbance for 24 h.

It may be interesting to note that the surface of gibbsite particles resumed back to a more hydrophobic one with contact angles above 60° when the corn-starch concentration increased above 8.7 vol.% (Fig. 1(a)). This enabled formation of stable foams without apparent creaming and disproportionation up to 24 h (Fig. 1(b)). Structural re-organization with the increased starch concentration is suspected the main cause for the observed change in the contact angle, arising partly from assembly of the amylopectin lamellae in the starch granules into blocks of various conformations as the starch concentration increases [29].

Upon subjected to oven drying at temperature (75 °C) above the gelatization temperature of the corn starch (ca. 40–60 °C, depending on biological source, plant genotype, chemical purity, and crystallinity of the starch origin), the starch polymers in the wet foam would swell in volume in addition to consume of water in the suspensions. This water-uptake capability stiffened the wet foam by increasing the van der Waals force acting among the gibbsite particles since the inter-particle separation was accordingly reduced. Fig. 2 shows typical microstructure of the dried gibbsite foams with the corn starch acting as the water-uptake binder. The foams consist essentially of packing aggregates of spherical void cells with an apparent cell size ranging from 100 to 300 μm. The closed cell morphology is in a significant contrast to that found in our earlier report [27] where open cells were observed when the

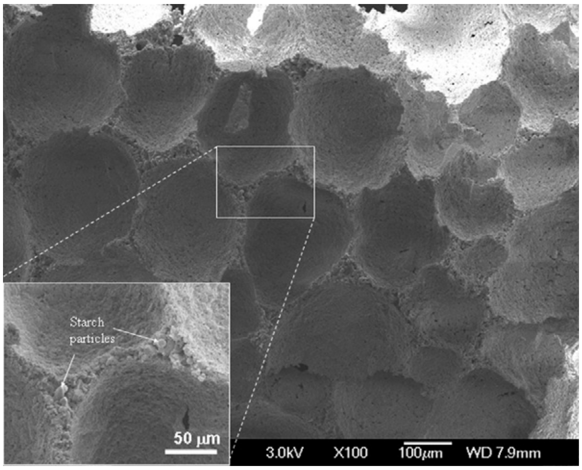

Fig. 2. Microstructure of the dried gibbsite foams with a corn-starch concentration of 11.2 vol.%. The inset shows an enlarged view at the strut area in which starch particles are apparent.

starch polymer was not added. This indicates that the gibbsite platelets were able to fully adsorb onto the air–water interface as the starch molecules are present in the suspension so that the *a/w* bubbles were all ‘‘armored’’ sufficiently to prohibit the occurrence of coalescence and drainage between bubbles. A closer examination of the inset in Fig. 2 further reveals that the packing particles at struts appear to be composed mostly from the starch particles with an equiaxed geometry while the layer directly in contact with the air appears to be mostly composed of the fine gibbsite particles with the platelet form. This finding reveals that the starch particles (which are more hydrophilic) tend to stay away from the air–water interface and reside more easily at the strut sites between bubbles to support the entire foam structure, leaving behind the gibbsite platelets to accumulate more effectively at the air–water interface so that the bubbles appeared to be fully ‘‘armored’’.

In Fig. 3, a bimodal pore-size distribution was typical for the dried gibbsite foams with the starch. A broad size distribution ranging from ca. 40 to 400 μm results, stemming primarily from the large void cells in Fig. 2. Small pores peaked at about 5 μm are also present, originating from those at the particle interstices and within the struts that hold up the cellular structure. Porosity of the dried gibbsite foams ranges from 77 to 86%; whilst, the three-point rupture strength is inversely dependent on the porosity and shows a flexural strength in a range of 240–82 kPa.

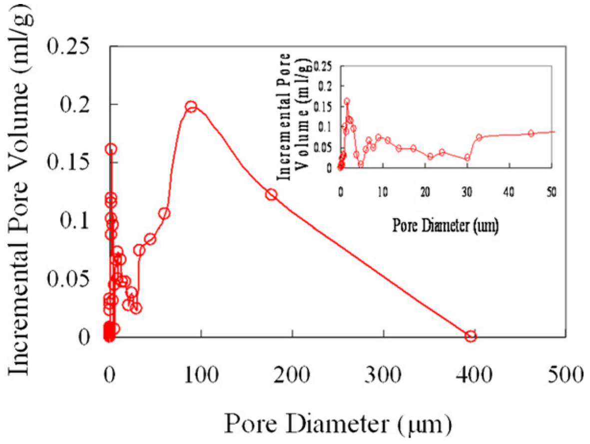

Fig. 3. Pore-size distribution of the dried gibbsite foams with a corn-starch concentration of 11.2 vol.% by mercury porosimetry. The inset shows an enlarged view at pore diameter less than 50 μm.

3.2. Gibbsite foams prepared with agar

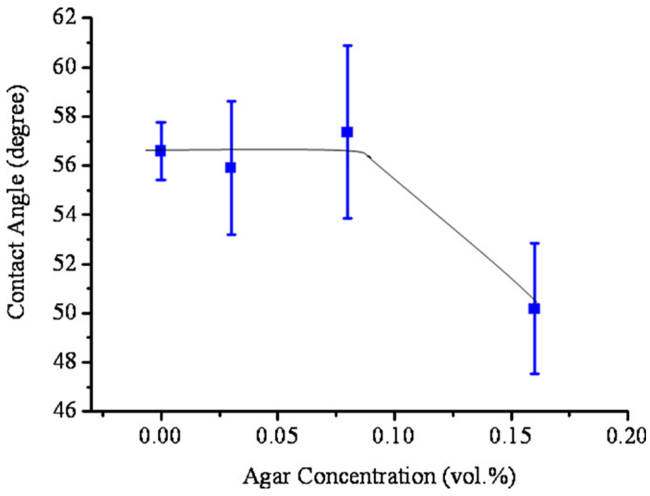

Fig. 4. Contact angle vs. agar concentration of the gibbsite-filled aqueous suspensions. The gibbsite loading was held at 10 vol.%.

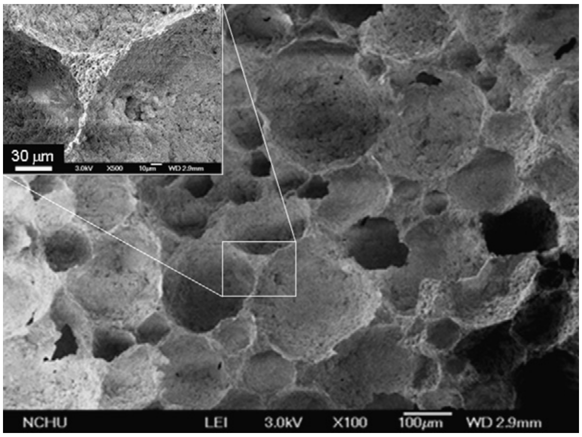

Fig. 5. Microstructure of the dried gibbsite foams with an agar concentration of 0.08 vol.%. The inset shows an enlarged view at the bubble contact in which a sharp cell wall is apparent.

Fig. 4 shows contact angles of the gibbsite foams when agar concentration was varied. In comparison, the contact angles remain at a constant value of 57° up to the concentration of 0.08 vol.%, but decreases pronouncedly with further increase in the agar concentration. This reduced θ gave rise to a pronounced bubble coalescence and drainage, leading to quick bubble disappearance so that the shaped gibbsite foams could no longer self-sustain. Fig. 5 shows the freeze-dried gibbsite foams with an agar concentration of 0.08 vol.%. In comparison to Fig. 2, aggregates of packing voids in Fig. 5 are characterized by presence of sharp cell walls with a typical wall thickness of ca. 2 μm in the inset. This is attributable to the increased tendency for the gibbsite bubbles to coalescence one another in accordance with the reduced contact angle, resulted in a broad

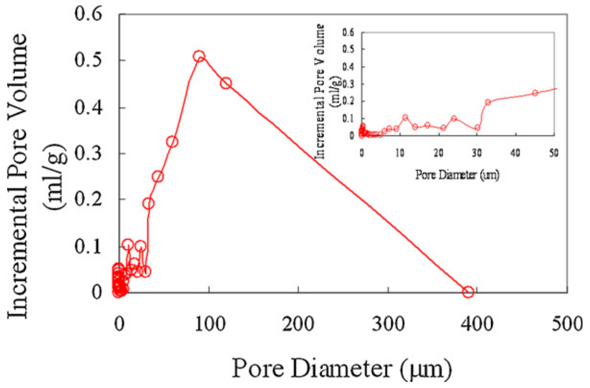

Fig. 6. Pore-size distribution of the dried gibbsite foams with an agar concentration of 0.08 vol.% by mercury porosimetry. The inset shows an enlarged view at pore diameter less than 50 μm.

cell-size distribution and a sharpened inter-bubble contact. A marked disappearance of the pores with a size smaller than 50 μm is found in Fig. 6 while the large cells remain. Porosity of the freeze-dried gibbsite foams falls in a range of about 85% while the three-point (green) rupture strength is at only 60 kPa, resulted primarily from the sharp cell walls that reduce the load-bearing area.

4. Conclusion

Corn starch and agar were used as a binder independently to the wet foams prepared by the adsorption of gibbsite platelets at the air–water interface with an aim that the consolidated strength of the porous green compacts can be improved by the water-uptake capability of the natural biopolymers. From the contact-angle measurement, the starch polymers appear to provide a suitable hydrophobicity so that the gibbsite platelets can reside at the air–water interface to render the foam stability as the starch concentration exceeds a critical concentration of 8 vol.%. Microstructure examination reveals that the starch particles prefer to stay at struts of the packing bubbles, facilitating then a sufficient coverage of the gibbsite platelets on the bubble surface so that the close-cell morphology results. On the other hand, the presence of agar molecules severely de-stabilizes the foam by allowing creaming and coalescence to occur between bubbles. This produces a sharp cell wall in the freeze-dried gibbsite foam when the agar concentration was kept under 0.08 vol.%. A reduced load-bearing area results, which gave rise to a weak rupture strength.

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