



Effect of amphiphile chain length on wet foam stability of porous ceramics

Naboneeta Sarkar^a, Jung Gyu Park^a, Sangram Mazumder^a, Ashish Pokhrel^b, Christos G. Aneziris^b,
Ik Jin Kim^{a,*}

^aInstitute of Processing and Application of Inorganic Materials, (PAIM), Hanseo University # 360, Seosan-si, Chungnam, 356–706, Korea

^bInstitute of Ceramics, Glass and Construction Materials, Freiberg University, Agricolastrasse 17, 09599 Freiberg, Germany

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Abstract

Inorganic oxide particles such as Al_2O_3 are partially hydrophobized using carboxylic acids of different chain length to produce wet foams exhibiting high air contents and remarkable stability. Stabilization of wet foam is achieved by in-situ hydrophobization which is very important to avoid the instability that occurs due to large interfacial area of the gas liquid interface. The concentration of amphiphilic molecules in the initial suspension and the chain length of their hydrophobic tail are modified to tailor the degree of surface hydrophobicity of the Al_2O_3 particles. Hydrophobization of Al_2O_3 surface is achieved through the adsorption of carboxylic acid exhibiting a functional hydroxyl group that efficiently anchors on the particle surface and a short hydrophobic tail remains in contact with the aqueous phase. The wet foam features adsorption free energy of 2.05×10^{-13} J to 8.22×10^{-13} J and Laplace pressure of 0.60 to 1.64 mPa which indicate good wet foam stability of about 80–90%. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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1. Introduction

Tailoring the surface chemistry of inorganic particles is an important aspect of ceramic processing which enables the fabrication of ceramic products used in number of applications such as filtration of molten metals and hot corrosive gases, high-temperature thermal insulation, support for catalytic reactions, filtration of diesel engine exhaust gases, etcetera [1]. These applications take advantage of unique characteristics of porous ceramics such as low thermal mass, low thermal conductivity, controlled permeability, high surface area, low density, high specific strength. These properties and functions of ceramics are very much dependent on their chemical composition and microstructure [2]. To control these features and allow formation of either open or closed cell ceramics with remarkable stability, direct foaming technique is used. This technique is based on the incorporation of gaseous phase into a ceramic suspension to produce wet foams which is later dried

and sintered to produce macroporous ceramics. However, the wet foams are thermodynamically unstable due to their large air-water interfacial area resulting in coalescence, Ostwald ripening and phase separation process [3,4]. Stabilization of wet foams is achieved by in-situ hydrophobization in which amphiphilic molecules are bound to the particle surface electrostatically [5]. These molecules exhibit a hydrophilic head group which adsorbs to the particle surface, whereas hydrophobic tail imparts the required hydrophobicity in the suspension [6].

The novel and versatile process of in-situ hydrophobization of an initially hydrophilic particle is explored to tailor the surface chemistry and stabilize the wet foam. This process enables preparation of high volume of wet foams by stabilizing the particles with different chain amphiphilic molecules containing less than eight carbon atoms in the hydrophobic tail [7,8] as shown in Fig. 1. The anchoring group of the molecules attaches to the particle surface and promote surface hydrophobization of colloidal particles [9,10]. The amphiphiles used here (Propionic acid, Butyric acid and Valeric acid) adsorb onto the Al_2O_3 surface through electrostatic interactions between the positively

*Corresponding author.

E-mail address: ijkim@hanseo.ac.kr (I.J. Kim).

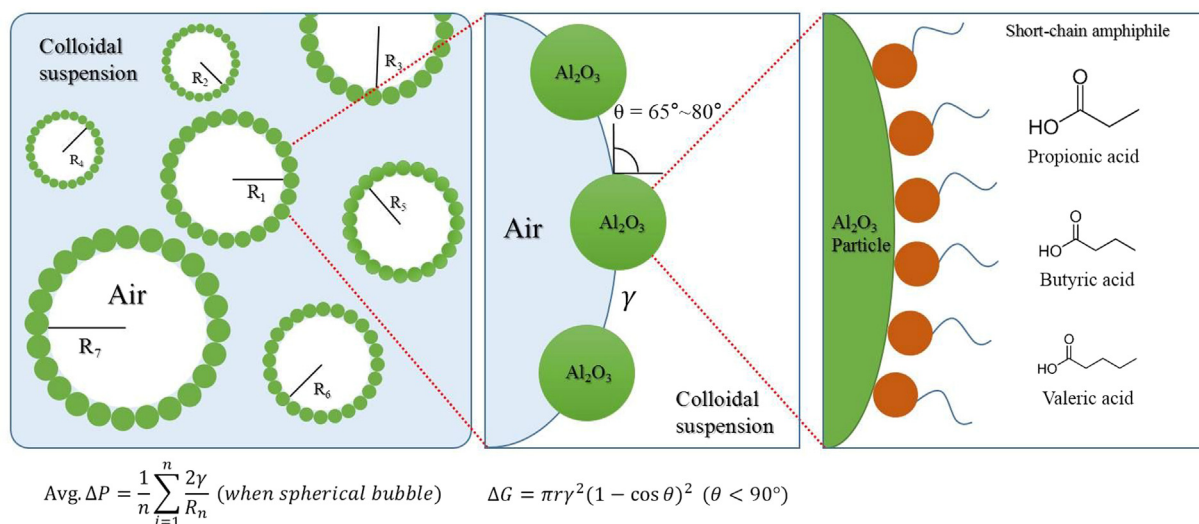


Fig. 1. Laplace pressure and particle free energy of partially hydrophobized Al_2O_3 suspension.

charged surfaces and negatively ionized amphiphilic molecules. Surface modification of particles using these amphiphiles was carried out at a pH close to the molecule's pK_a values. At this condition, approximately half of amphiphilic molecules is present as ionized form and thus easily adsorbed on the oppositely charged particle surface [11,12].

The aim of this work is to investigate the contact angle and surface tension of the colloidal suspension in order to indicate that in-situ hydrophobization has taken place which is important to prepare high-volume stable foams. We have used three amphiphile of different chain length to modify the colloidal alumina particles with various surface chemistries. The partially hydrophobized particles then adsorb to the air-water interface during the process of mechanical frothing which results in high volume stable wet foams [13]. Ueno and his associates studied the effect of Silica additive on porous alumina and they discovered that the porosity increased with the increase of silica content [14]. Wang et al. gave some interesting insights on using silica as a sintering additive on the sintering behaviour and dielectric properties of strontium barium niobate ceramics. The results indicated that the amorphous SiO_2 additive could accelerate the pore elimination, shorten the sintering time and enhance the density for $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ ceramics [15]. Later, Pokhrel et al. explained the effect of silica content on alumina porous ceramics to tailor the microstructure. Increase in porosity occurs linearly until the mole ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ reaches 1:0.5; beyond which it decreases drastically [16]. Therefore in this study, $\text{Al}_2\text{O}_3\text{-SiO}_2$ mole ratio was maintained at 1:0.25 for all the samples.

We have measured the bubble size of the resultant foams and from these data, the adsorption free energy and Laplace pressure were also calculated which show good wet foam stability of about 80–90% at an amphiphile concentration of 0.15–0.20 mol/L. The processing of wet foams (which includes drying and sintering) is developed and a relationship between the microstructures obtained using three different amphiphiles is drawn.

2. Experimental procedure

2.1. Materials

(i) α - Al_2O_3 powder (KC, South Korea) with average particle diameter (d_{50}) of 4 μm and density of 3.95 g/cm^3 ; (ii) SiO_2 powder (Junsei Chemicals Co. Ltd, Japan) with average particle diameter (d_{50}) of 3.5 μm and density of 2.65 g/cm^3 are used to prepare the suspension. The short chain carboxylic acid used for surface modification is Propionic acid, Butyric acid and Valeric acid (Fluka Analytical, Germany). Further chemicals used for this study are 10 (N) HCl (Yakuri Pure Chemicals, Osaka, Japan), 4 (M) NaOH solutions (Yakuri Pure Chemicals, Kyoto, Japan) for pH adjustments and double deionized water for suspension preparation and volume adjustment.

2.2. Preparation of suspensions

α - Al_2O_3 powder was added to de-ionized water and an aqueous suspension was prepared. Homogenization and De-agglomeration of suspension was carried out on a ball mill for at least 48 h at a rotation speed of 60 rpm using polyethylene bottles and zirconia balls (10 mm in diameter) with ball/powder ratio 2:1. After ball milling, short chain amphiphile of different concentrations (0.05, 0.10, 0.15 and 0.2 mol/L) were added drop wise to the suspension under mechanical stirring to hydrophobize the surface of Al_2O_3 particles as shown in Fig. 1. The mixing speed was kept constant at 500 rpm at different concentrations and different kind of amphiphiles as it can influence the foam characteristics. The amphiphiles were added as concentrate, no prior dissolution had been carried out. The pH of the suspension was adjusted to 4.75 by adding 4 (M) NaOH and/or 10 (N) HCl drop wise. By adding required amount of water, the solid content of the final aqueous suspension was set to 30 vol%. Finally, aqueous suspension of unmodified SiO_2 powder which was also ball milled separately in same condition; was added to the surface modified Al_2O_3 suspension in a mole ratio of 1:0.25 $\text{Al}_2\text{O}_3/\text{SiO}_2$ as shown in Fig. 2.

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