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Effects of surfactants on the microstructure and some intrinsic properties of porous building ceramics fabricated by gelcasting

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Abstract

Porous building ceramics were fabricated by gelcasting and the effects of surfactants on their microstructure and some intrinsic properties such as sound absorption and thermal conductivity were investigated. Preliminary tests on solubility in water, foaming capacity and foam stability of different surfactants were carried out to evaluate their foaming ability. Porous ceramic fabricated using an anionic ammonium lauryl sulphate surfactant with large foaming ability showed lower density, higher open and total porosities, and broad pore size distribution. Total porosities of three porous ceramics fabricated using different surfactants were found to be similar to that of the corresponding air volume fractions of the three foamed slurries. Sound absorption and thermal conductivity of the porous ceramics as construction tile were further characterized. Porous ceramic with higher porosity presented a higher value of sound absorption coefficients and lower thermal conductivity.

Keywords: Gelcasting; Porous ceramics; Surfactant; Construction ceramic tile

1. Introduction

Porous ceramics, known as reticulate ceramics or ceramic foams preferred by several quotes [1–8], have found a wide variety of applications including filters, membranes, sensors, catalyst carriers, piezoelectric ceramics, and biomedical and construction materials [2]. In particular, the gelcasting technique is based on the combination of foaming an aqueous slurry and its in situ polymerization. Firstly, the incorporation of bubbles into the slurry is achieved conventionally by mechanical agitation in a special N_2-gas controlling system. A surfactant is necessary for stabilizing bubbles produced in the slurry by reducing the surface tension at the gas–liquid interfaces [3]. Surfactants are amphiphilic molecules with a hydrophobic portion, or a non-polar portion, and a hydrophilic head group. By this kind of configuration, surfactants tend to migrate to gas–liquid interfaces with the hydrophobic part being expelled from the solvent and a hydrophilic part remaining in contact with the liquid, leading to a low surface tension of the gas–liquid interfaces. Subsequently, in situ polymerization of organic monomers occurs for the stabilization of foams. Despite the fact that much work was done in the past on the development of new monomer systems for the purpose of eliminating surface spallation of green bodies and/or of substitute conventional, toxic monomer systems [6,9–12], little work was focused on the investigation of the effects of surfactant on the microstructure and intrinsic properties of the porous ceramics obtained by the gelcasting technique [3].

Glazed ceramic tiles as building material have the advantages of weather resistance, durability and beauty. However, they have the disadvantages of the heavy weight and machining difficulty. Many academic and industrial researchers tried to develop porous building ceramic tiles. Recently, we reported about fabrication of porous ceramic tile by the gelcasting technique using industrial wastes such as low-grade silica, glass and alumina grain [6,7]. The obtained porous ceramics exhibited high porosities of around 60% with flexural strength ranging from 15 to 45 MPa, i.e. a figure adequate to ceramic tile for building

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Table 1
Preliminary evaluation of water-solubility of different surfactants

Surfactants	Chemical name	Classification	Phenomenon
A	Ammonium lauryl sulphate	Anionic	Soluble
B	Fatty alcohol ethoxy sodium	Anionic	Soluble
C	Poly(oxyethylene)sorbitan monolaurate	Nonionic	Soluble
D	Poly(oxyethylene)nonylphenylether	Nonionic	Soluble (high viscosity)
E	Poly(oxyethylene)octylphenylether	Nonionic	Soluble (high viscosity)
F	Poly(oxyethylene)monooleate	Nonionic	Soluble (high viscosity)
G	Sorbitan monolaurate	Nonionic	Insoluble (suspension)
H	Poly(oxyethylene)oleate	Nonionic	Insoluble (suspension)
I	Poly(oxyethylene)laurate	Nonionic	Insoluble (suspension)
J	Poly(oxyethylene)laurylether	Nonionic	Insoluble (suspension)
K	Poly(oxyethylene)polyoxypropylene monobutylether	Nonionic	Insoluble (phase-separation)
L	Poly(oxyethylene)monobutylether	Nonionic	Insoluble (phase-separation)
M	Dialkylsulfosuccinate	Anionic	Insoluble (sol)

application. Here, we report the effects of surfactants on the microstructure, sound absorption and thermal conductivity of porous ceramics.

2. Experimental procedure

2.1. Evaluation of foaming ability of surfactants

In the first step, preliminary evaluation of water-solubility of 13 surfactants with anionic or nonionic characteristics was performed in a glass beaker with surfactant concentration of 20%. Approximately 100 ml of surfactant–water solution was stirred for 5 min using a double-bladed mixer operating at speed of 900 rpm. Results are listed in Table 1. Surfactants A, B and C were soluble in water and their viscosities were relatively low. Surfactants D, E and F were soluble in water but their viscosities were too high to make slurry and molding. Surfactants G to M were insoluble or partially soluble in water. From the results of preliminary evaluation, ammonium lauryl sulphate (anionic, named A), fatty alcohol ethoxy sodium (anionic, named B) and poly(oxyethylene)sorbitan monolaurate (nonionic, named C) showed water-solubility and relatively low viscosity and were selected for further tests in this paper.

Subsequently, estimate of foaming capacity of the three surfactants in water solution was carried out in a home-made experimental apparatus (Fig. 1). The apparatus consists of a glass tube with glass balls (diameter size 5 mm) stacked at the bottom. An air bottle is connected to a flow meter which is linked to the bottom of the glass tube. Approximately 10 ml of water solution with surfactant concentration of 20% are poured into the glass tube. The air is then injected from the top of the glass tube at a flow rate of 400 ml/min for 30 s by controlling the gas flow meter and the foam volume as a function of time is visually monitored and measured after injection of air.

2.2. Fabrication of porous ceramics by the gelcasting technique

Industrial and mining wastes such as low-grade silica, glass and alumina grain were used as raw materials after grinding down to about 15 μm. Monofunctional methacrylamide (MMA) and difunctional *N*,*N*′-methylenbisacrylamide (MBAM) were used as monomers. To initiate and accelerate gelation of the monomers, ammonium persulfate (APS) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were used as initiator and catalyst, respectively. Ammonium citrate was used as a dispersant for the solid particles. The composition of the slurry is summarized in Table 2.

The gelcasting process for the fabrication of porous ceramics is shown in Fig. 2. The initial slurry with a waste concentration of 68% was prepared by ball-milling. Then, foaming of slurry was conducted by mechanical stirring of the slurry using a double-bladed mixer operating at speed of

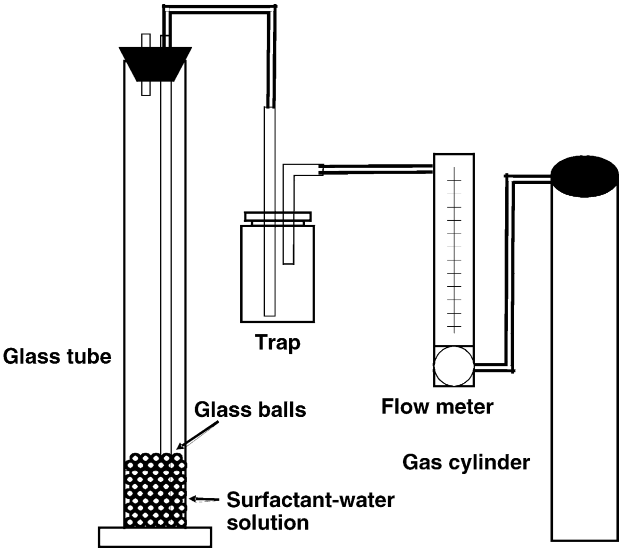

Fig. 1. Schematic diagram of the experimental apparatus for the foaming capacity test.

Table 2
Composition of the slurry for gelcasting

Substance	Amount (g)
Wastes	680.00
Distilled water	239.66
Monomer	63.91
Cross-linker	15.98
Initiator	0.22
Catalyst	0.22
Dispersant	0.61
Surfactant (ml)	1.65

900 rpm, with assistance of the surfactant. This procedure was performed in a sealed chamber under a controlled N_2 atmosphere. After addition of initiator and catalyst, the foamed slurry was poured into a plastic mold for in situ solidification. The wet gelled sample was then de-molded, dried at 298 K in a controlled-humidity drying chamber for 5 days. Sintering of the sample was carried out at 1273 K for 3 h.

2.3. Characterization

Density and open and total porosities of the sintered samples were determined by Archimedes' method. The theoretical density of the fully densified ceramic (2.68 g/cm^3) was used as a reference to calculate the relative porosity. The average pore and pore size distribution were obtained by using Image-Pro Plus 4.5 (Planetron, Inc.), following the microscopy observations performed under Eclipse E600 POL (Nikon).Sound absorption was measured by a vertical incidence sound absorption device (two-microphone impedance measurement tube, BK4206A, Brüel&Kjær). The sound absorption performance of the ceramics is defined by the sound absorption coefficient (α), which is the ratio of the unreflected sound intensity at the surface to the incident sound intensity [13]. The sound absorption coefficient α can be calculated using the following relationships:

$$\alpha = 1 - \left[\frac{(n-1)}{(n+1)}\right]^2$$

$$n = \frac{P_{\mathrm{MAX}}}{P_{\mathrm{MIN}}}$$

where n is the standing wave ratio, and P_{MAX} and P_{MIN} the maximum and minimum sound pressures in the impedance tube.

Thermal conductivity was obtained by a quick thermal conductivity meter (QTM-type-500, Kyoto Electronics Manufacturing).

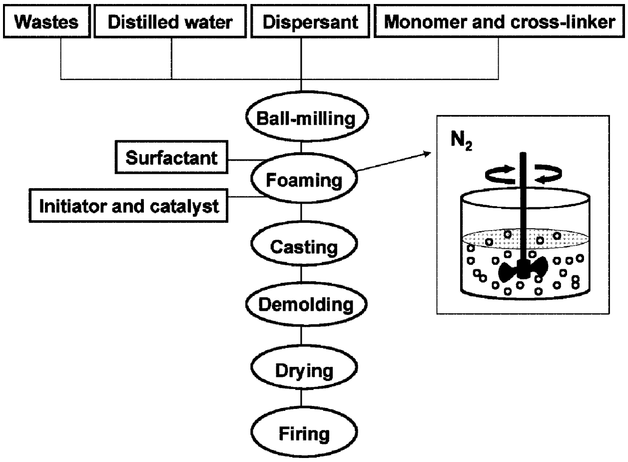

Fig. 2. Flow-chart of the gelcasting process for the fabrication of porous ceramics.

3. Results and discussion

3.1. Evaluation of foaming ability of surfactants

The gelcasting technique combines the foaming of an aqueous slurry of a ceramic powder and organic monomers and the in situ polymerization of the foamed slurry. In a conventional foaming procedure, bubbles are introduced into the slurry by vigorous stirring under N_2 atmosphere. Some bubbles may shrink and disappear whilst others coalesce to form large bubbles. So, the changes in the foam structure prior to solidification are important because they influence the final microstructure of the solid foams. A surfactant is generally used to stabilize bubbles formed in the liquid phase by decreasing the surface tension of the gas–liquid interfaces. So, the foaming character of surfactants is one important factor for the fabrication of porous ceramics by gelcasting. In the preliminary study, three surfactants A, B and C showed water-solubility and relatively low viscosity and were selected for further tests to estimate the foaming capacity (see Section 2.1). The foaming capacity of the selected surfactants as a function of time in water solution is shown in Fig. 3. Anionic surfactant B shows the highest foam volume after the injection of air. The foam volume decreases with time increase. Foams completely disappear

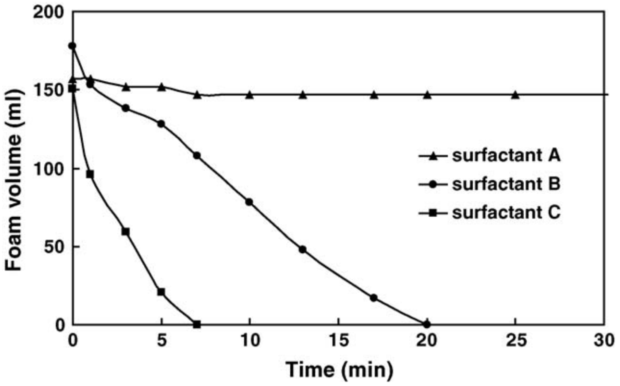

Fig. 3. The foaming capacity of three surfactants as a function of time in water solution.

after 20 min. Nonionic surfactant C appears to provide a quicker decreasing trend of foam volume than surfactant B. The disappearance of foam is caused by various macroscopic phenomena including Ostwald ripening which tends to make the small bubbles coalesce to form large ones, Van der Waals forces, electrostatic forces, steric forces, etc. Compared to surfactants B and C, surfactant A can keep a relatively high foam volume for a long measured time, indicating a better foaming stability.

Further experiments were performed in order to investigate the effect of surfactants on the foam stability of the slurry. Approximately 100 g ball-milled slurry was poured into a glass baker and was stirred for 3 min using a double-bladed mixer operating at speed of 900 rpm. The volume of foamed slurry was measured after 30 min. The air volume fraction (φ_a) is 69, 51 and 21% for surfactants A, B and C, respectively, which further confirms a higher foaming ability for anionic surfactant A.

3.2. Effect of surfactants on the microstructure of porous ceramics

Fig. 4 shows optical photographs of porous ceramics fabricated using different surfactants. For porous ceramics fabricated using surfactants A and B, a large number of pores are in contact each other causing opened pores. The structure of porous ceramics with interconnected and open pores is very important because it is related to intrinsic properties such as mechanical, permeability, and thermal conductivity properties [6,14,15]. On the contrary, most pores in the sample fabricated using surfactant C are separate. Fig. 4 also indicates that the pore sizes are different between the three different samples. Following the microscopy observations, the average pore and pore size distribution of porous ceramics were obtained by using image analysis. Fig. 5 shows the pore size distribution of the three porous ceramics. The relative height of the peak displays the extent of pores with similar size. The sample fabricated using surfactant A shows a double-peak around 100 μm. By contrary, only a sharp peak at 40 μm is observed in sample fabricated using surfactant C. When using surfactant B, a single peak around 80 μm appears. The mean pore sizes are listed in Table 3, which shows 116.4, 95.9 and 53.5 μm for the three samples, respectively.

The total porosities of the three porous ceramics, as presented in Table 3, are 64.7, 52.3 and 22.6%, which are similar to that of the corresponding air volume fractions of the three foamed slurries (see Section 3.1). The results indicate that the foams in slurry produced by mechanical agitation in N_2-gas controlling system could remain in the sintered body. The closed porosity of sample fabricated using surfactant C has the highest value of 18.0%, which agrees with the microscopy observation which shows most pores in this sample to be individually dispersed in the structure. The above results confirm that surfactants with different chemical structure and foaming ability can

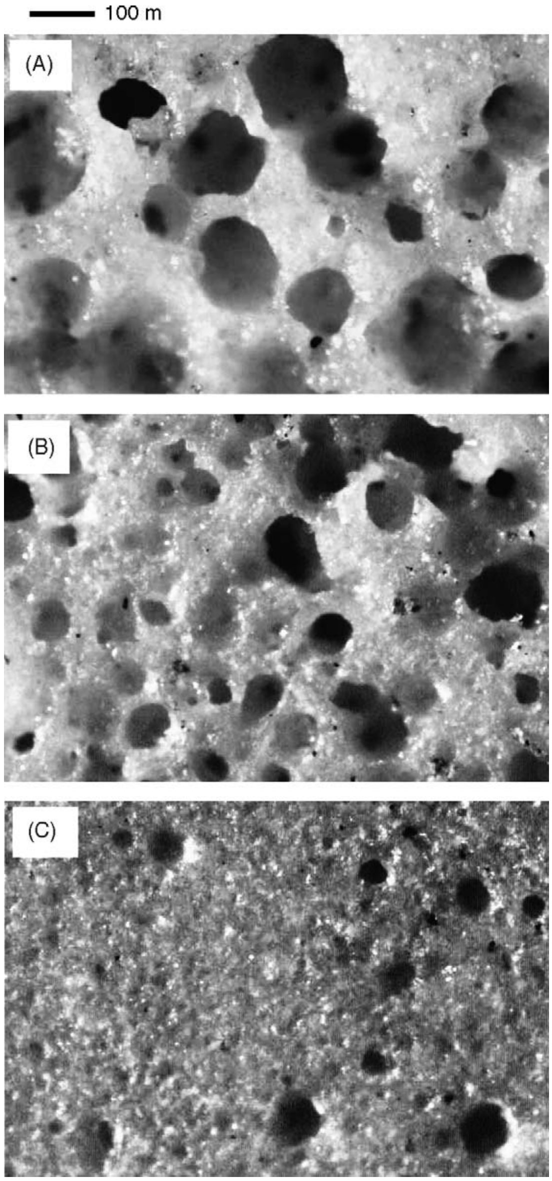

Fig. 4. Optical photographs of porous ceramics fabricated by gelcasting using different surfactants.

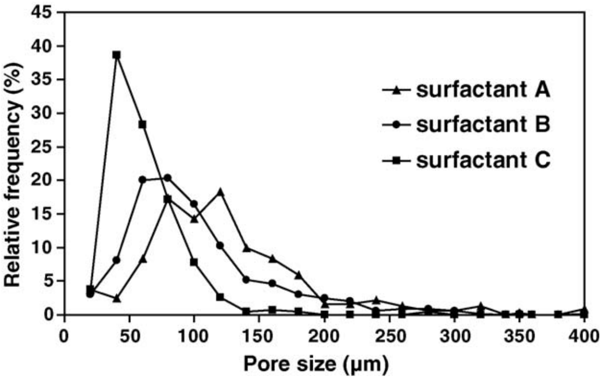

Fig. 5. Pore size distribution of porous ceramics fabricated by gelcasting using different surfactants.

Table 3
Microstructure parameters and thermal conductivities of porous ceramics fabricated by gelcasting using different surfactants

Surfactants[a]	Mean pore dimension (μm)	Total porosity (%)[b]	Closed porosity (%)	Open porosity (%)	Final density (g/cm^3)	Thermal conductivity (W/m K)
A	116.4	64.7	11.3	53.4	0.736	0.45
B	95.9	52.3	13.7	38.6	1.24	0.64
C	53.4	22.6	18.0	4.0	2.12	1.18

[a] A: ammonium lauryl sulphate; B: fatty alcohol ethoxy sodium; C: poly(oxyethylene)sorbitan monolaurate.

[b] The air volume fraction in the corresponding foamed slurry is 69, 51 and 21% for surfactants A, B and C, respectively.

significantly influence the microstructure of porous ceramics fabricated by gelcasting.

3.3. Sound absorption property

Recently, extensive research has been focused on the development of new sound absorbing materials and on noise reducing mechanisms [13,16,17]. Porosity had been reported to play an important role in the sound absorption performance of the porous materials [13,17]. The sound absorption characteristics of the three porous ceramics fabricated by gelcasting are shown in Fig. 6. The sound absorption coefficient (α) is below 0.2 for the sample fabricated using surfactant C in the studied frequency range, indicating a poor sound absorption performance. Porous ceramics fabricated using surfactants A and B display obvious high α value. We can see from Table 3 that these two samples show higher total and open porosities. It is concluded from above results that higher porosity coincides with a more pronounced performance of sound absorption.

3.4. Thermal conductivity

Thermal conductivity is one of important properties of porous ceramics [15,18]. Some microstructure parameters such as porosity and pore size distribution were reported to be related to the property of thermal conductivity. According to Sepulveda et al., the higher porosity could enhance the point-defect scattering, which may be a result of the increase in the solid-pore areas and the decrease in the minimum solid areas, and the scattering by Umklapp processes [15]. The three porous ceramics fabricated using surfactants A, B and C show thermal conductivity of 0.45, 0.64 and 1.18 W/m K, respectively. As noted previously, the porous ceramic fabricated using surfactant A displays the highest open and total porosities, which results in a large thermal insulation property.

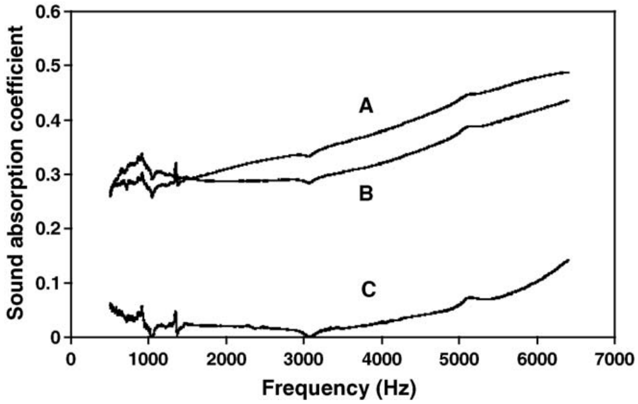

Fig. 6. Sound absorption as a function of frequency for porous ceramics fabricated by gelcasting using different surfactants: (A) ammonium lauryl sulphate, (B) fatty alcohol ethoxy sodium, and (C) poly(oxyethylene)sorbitan monolaurate.

4. Conclusion

Surfactants with different foaming ability can significantly influence the microstructure and some intrinsic properties such as sound absorption and thermal conductivity of porous ceramics fabricated by gelcasting. Porous ceramic fabricated using an anionic surfactant ammonium lauryl sulphate with large foaming ability showed lower density, higher open and total porosities, and broad pore size distribution. Further characterization demonstrated that this higher porosity sample presented a higher value of sound absorption coefficient and a lower thermal conductivity.

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