



Isopropanol as an air–liquid interface reformer in the processing of cellular silica

Sarika Mishra^{a,*}, R. Mitra^b

^a Non Ferrous Materials Technology Development Centre, P.O. Kanchanbagh, Hyderabad, India

^b Indian Institute of Technology, Kharagpur, India

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ABSTRACT

A novel method for the preparation of ceramic foams with uniform pore and pore size distribution through the addition of isopropanol (iPr-OH) has been discussed. Small amounts of isopropanol were added to silica based aqueous suspensions and the foams were prepared by foam casting method. The rheology of silica based suspensions and properties of the resulting foam are examined and compared with that of samples prepared without iPr-OH addition within similar experimental conditions. Silica foams produced using this novel method displays comparatively higher density, smaller and uniform pores with narrow pore size distribution and significantly improved mechanical strength. The porosity of 79 vol.% and the pore size distribution of 4–25 μm were obtained. The compressive strength of 1.4 MPa with a Young's modulus of 143 MPa was achieved as compared to the low values of compressive strength and elastic modulus of 0.332 and 60 MPa, respectively for the samples without iPr-OH addition.

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1. Introduction

Porous materials are of significant interest due to their wide applications in catalysis, separation, lightweight structural materials, thermal insulation and biomaterials etc. [1]. The incorporation of porosity within a tailored structure gives porous ceramics many intrinsic properties such as low mass, high permeability, high surface area, low specific heat and low thermal conductivity [2]. Various processing routes have been developed in the past decades to prepare porous ceramics, such as (i) polymeric sponge method [3], (ii) solid-state sintering [4], (iii) sol–gel process [5], (iv) replication of polymer foams by impregnation [6] and (v) gelcasting [7,8]. Several methods for the preparation of porous ceramics have been addressed in previous review articles [9,10]. In a recent study [11], a comprehensive overview of the methodologies has been provided. Unfortunately, most of the above mentioned processes only form structures with randomly arranged irregular pores with a wide variety of sizes and have limited flexibility to control pore volume fractions in the final structure. There had been efforts in the recent years, to fabricate porous ceramics with controlled pore and pore size distribution through hetero coagulation of PMMA template [1], additions of fugitive particles, like starch and latex binders [12], saw dust of groundnut shell [13], wheat grains [14] and green peas for ceramic hollow spheres [15], etc.

In a multi component slurry based processing route, foaming leads to the formation of a distribution of air bubbles, whose sizes

are a function of interplay between surface tension and viscosity. While the rise in viscosity impedes both bubble growth and collapse, increase in the surface tension creates a barrier for the nucleation of air bubbles and promotes bubble growth to reduce the surface area to volume ratio. It is possible to retard the bubble growth and collapse by increasing the viscosity of the medium, or decreasing the surface tension of the incorporated bubbles, so as to kinetically stabilize the foam. Addition of isopropanol (iPr-OH) has been known to reduce the surface tension of aqueous solutions [16]. Therefore, the reduction in surface tension in aqueous suspensions by modifying the air–liquid interface by the addition of iPr-OH may provide an opportunity to control the size of air bubbles formed in the suspension during foaming. Such reduction in the size of air bubbles can be used to reduce the pore size. In other words, iPr-OH additions to slurries can be used to tailor the pore size distribution of the cellular constructs. With this intend, this study was conducted and the cellular silica constructs were fabricated.

This paper presents a novel route for the preparation of silica foams through aqueous suspensions with the use of small amount of isopropanol (iPr-OH). The effect of iPr-OH addition (in small amount) on the viscosity as well as foaming behavior of the resultant silica based slurries and overall foam properties have been examined. The microstructure–mechanical property relationship of the resultant foams has also been discussed.

2. Experimental procedure

Fused silica powder (Industrial grade, $d_{50} = 10 \mu\text{m}$) along with 5 wt.% alumina and 0.05% CTAB (98% pure, CR grade, S.D. Fine Chemicals Ltd.) was ball milled for 100 h using alumina milling media and this pre-treated powder was used for making silica foams. The alumina particles were added in order to inhibit the devitrification

* Corresponding author. Tel.: +91 40 2434 1332; fax: +91 40 2434 2567.
E-mail address: uptecsarika@rediffmail.com (S. Mishra).

of fused silica glass in the final component which otherwise forms cristobalite, giving rise to internal stresses on sintering. This powder mixture was ball milled (in wet condition) in the presence of CTAB (~2 ppm) in order to impart partial hydrophobicity to the silica powder particles. The binder solution comprised of 4-vol.% PVA, 10-wt.% sucrose and colloidal silica (40% SiO₂ content) in 5 vol.%. The total binder content [PVA solution + sucrose + colloidal silica] consisted of ~16% in the overall suspension. Small amounts (0.5–1 vol.%) of isopropanol (iPr-OH, 99% pure, LR grade, S.D. Fine Chemicals Ltd.) were added at the end, to the suspension. Suspensions of pre-treated silica powder were made in aqueous medium by milling the constituents at 30 rpm for 2 h. Finally, the milled suspension was subjected to foaming for 3–4 h for entraining air into suspension. The foamed suspensions after aging for 10–15 min were casted into suitable moulds. The cast samples were then dried under controlled condition (Osworld humidity chamber, $T = 30^\circ\text{C}$, relative humidity = 40–80%) in graded fashion up to 100°C . Finally, fully dried samples were sintered at 1100°C for 1 h. Similarly, silica foam samples were also made without iPr-OH addition [17].

The rheological behavior of the as prepared silica suspensions was examined using a rotary viscometer in parallel plate configuration (40 mm diameter, 1 mm gap) with a solvent trap (Model AR1000, TA Instruments, New Castle, DE). The measurements were performed at room temperature (27°C) at shear rates varying from $0.5\text{--}50\text{ s}^{-1}$ prior to the foaming step. The measured flow curves for the as prepared slurries were fitted with a power law model [18–20], represented in Eq. (1):

$$\eta = k\gamma^{n-1} \quad (1)$$

In Eq. (1), η is the viscosity of the slurries and γ is the applied shear rate, while k and n are the consistency factor and non-Newtonian index, respectively.

The samples of both the types were characterized for density determination. The microstructures of sintered foam samples were studied through optical microscopy (Biovis MV500 Image Acquisition) and the pore size distribution was characterized through mercury porosimetry (Quantachrome Poremaster, Ver 4.01). For compression tests, cylindrical samples (9.25 mm diameter and 18 mm height) were compression tested (Instron 5500 R Universal Testing Machine) using a 1-kN load cell and at a crosshead speed of 0.05 mm/min. Following Brezny and Green [21], wooden spacers of 9 mm diameter and 6 mm height were fixed to both the flat ends of the cylindrical samples so that the load transfer to the samples is uniform throughout the cross section.

3. Results and discussion

3.1. Physical property

The rectangular sintered panels of silica foams without iPr-OH showed the densities of 0.236 g/cc. (10.5% of the theoretical, theoretical density 2.25 g/cc.) with a linear shrinkage of 11%. On the other hand, samples on iPr-OH addition (with similar solids loading of 32%) showed increased green as well as sintered densities, which was recorded as 0.570 g/cc. (25.33% of the theoretical) and 0.473 g/cc. (20% of the theoretical), respectively with a linear shrinkage of 10%.

3.2. Rheology

The hydrophobized silica powder particles subjected for preparing suspension were able to disperse uniformly and hence stabilized the suspension. The pH of the suspension was recorded as

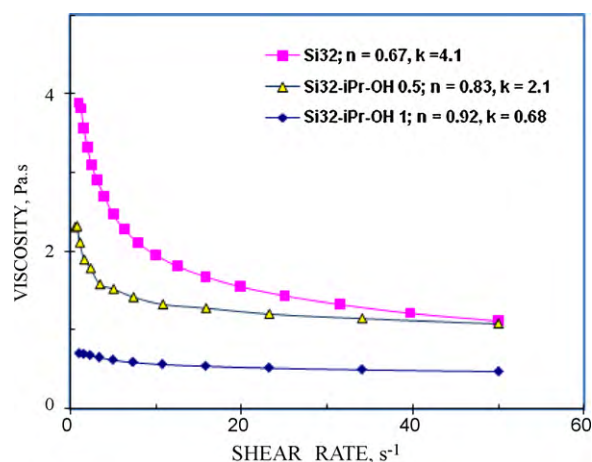


Fig. 1. Plots showing the variation of viscosity with shear rate for silica slurries with 0, 0.5 and 1 vol.% iPr-OH.

8.02 whereas the zeta potential of these particles in the suspension (with CTAB + additives) was measured as -25 mV . Results related to the rheological behavior for the silica slurries with and without iPr-OH addition are shown using plots of viscosity against the shear rate in Fig. 1. The term Si32 in Fig. 1 represents slurry with 32 vol.% solids loading without iPr-OH, whereas the terms Si32-iPr-OH0.5 and Si32-iPr-OH1 represent the slurry with 32 vol.% solids loading with 0.5 and 1 vol.% iPr-OH, respectively. On examination of the plots in Fig. 1, it is clear that: (i) the slurries with and without iPr-OH addition are shear thinning in nature; (ii) for shear rates $<50\text{ s}^{-1}$, the viscosities of slurries with iPr-OH are less than that without iPr-OH (the values of k_s for the slurry with 0.5 and 1 vol.% iPr-OH are about 1/2 and 1/7th of that in slurry without the iPr-OH); and (iv) at a given shear rate, the viscosity of slurry with the higher iPr-OH content is less, and the difference is more significant at lower shear rates. As addition of iPr-OH leads to the reduction of surface tension of water in aqueous suspensions, the overall flowability of the suspensions is improved.

Table 1 shows the results related to foaming behavior as well as the relative densities of wet foams, green bodies and sintered foams prepared from suspensions (after milling and foaming operations) with and without the iPr-OH additions. As the slurry with the higher iPr-OH content (1 vol.%) shows the lowest viscosity (Fig. 1), which remains almost constant even at high shear rates, its air entrainment results into pourable foams with very small size air bubbles, which in turn is responsible for high green density of 0.572 g/cc. (Table 1). The foams obtained from the slurry with 1 vol.% iPr-OH have shown uniform pore size distribution with good handling

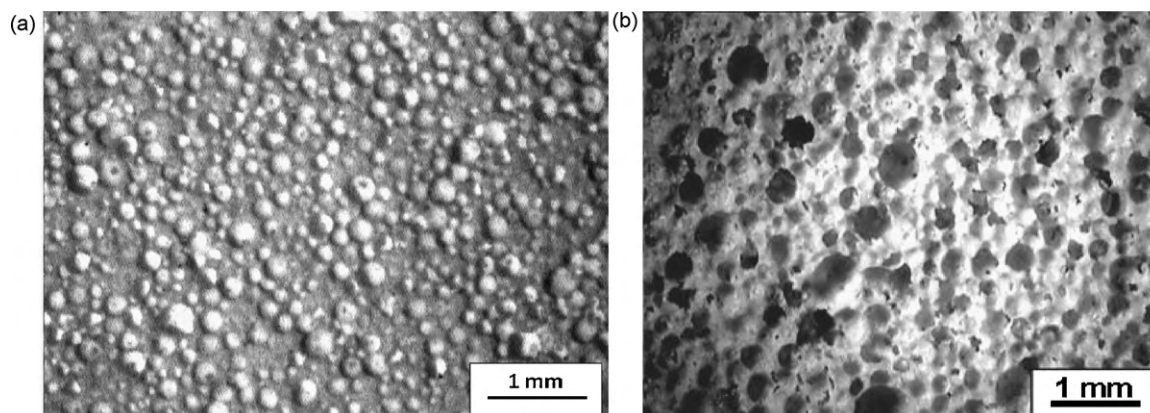


Fig. 2. Optical micrographs of silica foams (a) with iPr-OH and (b) without iPr-OH.

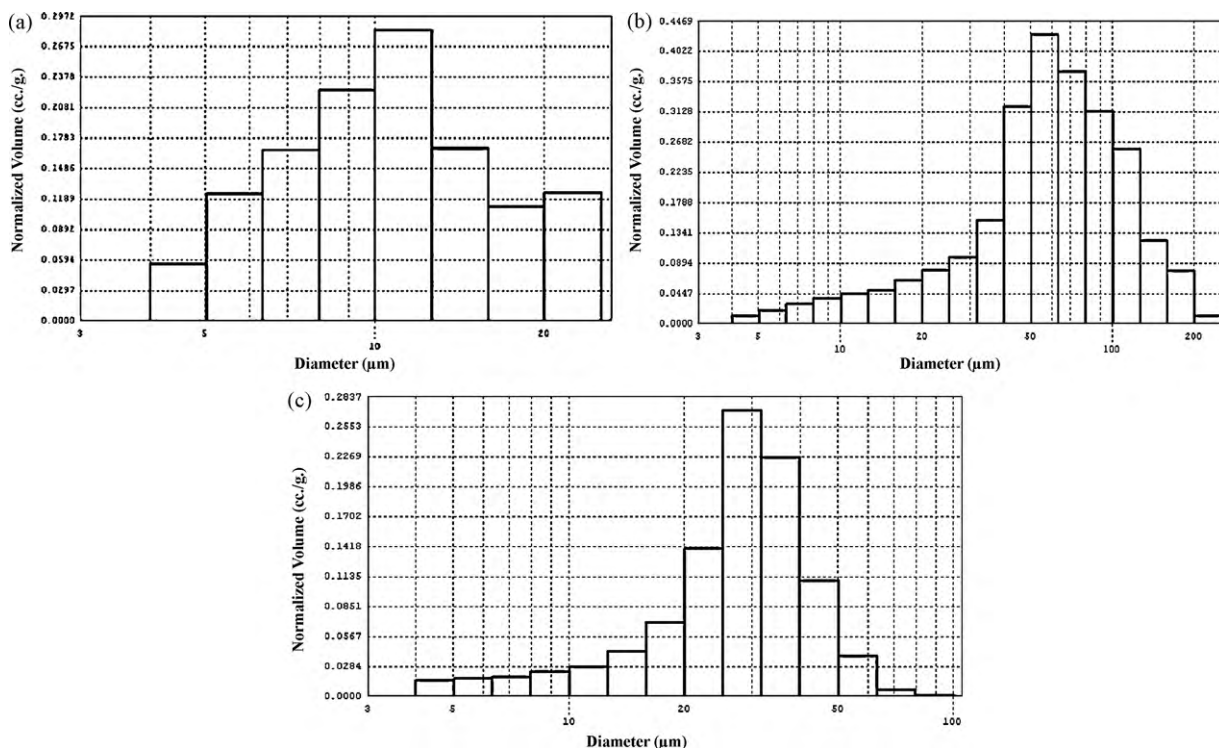


Fig. 3. Histograms of normalized volume (cc./g) as a function of pore size distribution for silica foams, (a) with iPr-OH, 21% dense, 32% solids loading, (b) without iPr-OH, 11% dense, 32% solids loading, and (c) without iPr-OH, 20% dense, 38% solids loading.

strength. A close look at Table 1 indicates that the slurries having $\leq 0.5\%$ iPr-OH content has foamed well. However, since the samples obtained from slurries with ~ 0.5 vol.% iPr-OH have shown very low handling strength, the slurries with 1 vol.% iPr-OH content are recommended for processing of the foams to be used as finished products.

Addition of iPr-OH (in small volume) provides dual advantage in the processing of foams; at one end it helps in reducing the surface tension at the gas–liquid interface in the aqueous suspension and on the other end, it partially dissolves (weakens) the long chain surfactant molecule of CTAB (16C chain adhered to the powder particle surface) as well as the polymeric bond of PVA (solvolysis). Hence by lowering the net steric hindrance effect, the overall flowability improves which is necessary for the pouring operation.

The improvement in the overall flowability of the suspensions symbolizes the overall reduction in suspension viscosity (Fig. 1). We can see this trend through the examination of Fig. 1 that with the increase in the addition of iPr-OH, the viscosity lowers gradually, i.e. the rate of dissolution of CTAB/PVA (C-chain) increases, which in turn affects the foaming capacity of the suspension (Table 1).

3.3. Microstructure and pore size distribution

The optical micrographs of both the samples with 1 vol.% iPr-OH and without iPr-OH (similar solids loading of 32%) are shown

Table 1
Effect of iPr-OH concentration on the foaming behavior of the suspensions and final foam densities (green and sintered).

S. no.	iPr-OH content, vol.%	Foaming behavior	Wet foam density, g/cc.	Green density (apparent/RD)	Sintered density (RD)
1	0	Well foamed	0.37	0.270 (0.120)	0.11
2	0.25	Well foamed	0.36	0.258 (0.115)	0.10
3	0.50	Well foamed	0.40	0.236 (0.105)	0.10
4	1.00	Less foamed	0.72	0.572 (0.254)	0.21

in Fig. 2 a and b, and the corresponding histograms of normalized volume (cc./g) as a function of pore size distribution are shown in Fig. 3 a and b. Analysis shows that the pores are small and uniform with narrow pore size distribution, in the range of 4–25 μm for the samples with iPr-OH addition in contrast to bigger pores and larger pore size distribution, in the range of 10–200 μm for the samples without iPr-OH addition. Indeed, both the samples exhibit open and interconnected porosity. On the other hand, for the sake of comparison, the microstructure of silica foams (20% dense, solids loading 38 vol.%, without iPr-OH) prepared through foam casting method, shows the pores sizes in the range of 10–50 μm (Fig. 3c).

The total porosity in the foam is proportional to the amount of air incorporated into the suspension during the foaming process. Wet foams are thermodynamically unstable systems, and can easily get destabilized through destabilization mechanisms such

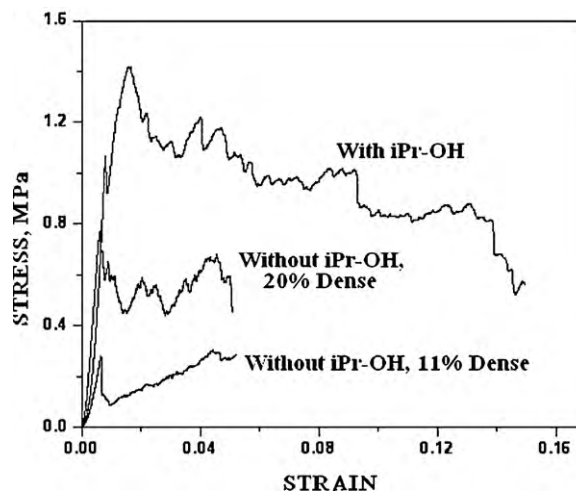


Fig. 4. Stress–strain curves for silica foams with and without iPr-OH addition.

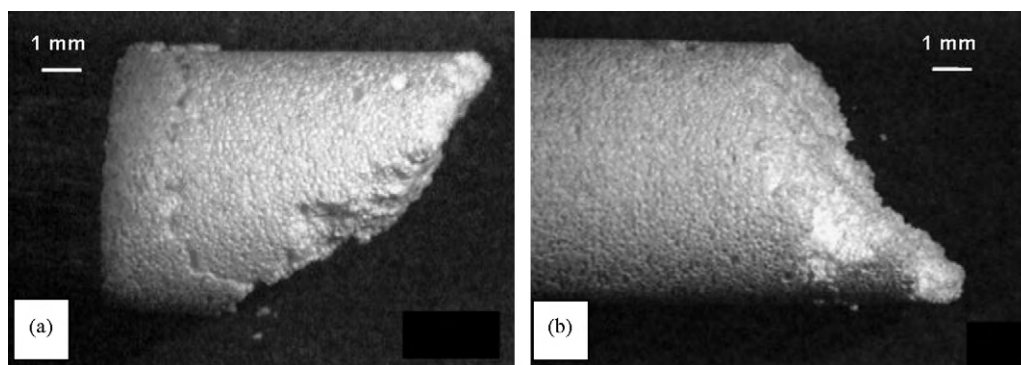


Fig. 5. Optical micrographs of the fractured foam surfaces for the sintered samples (a) with and (b) without iPr-OH addition.

as Ostwald ripening, and subsequent collapse. The increase in size of incorporated bubbles results in a wide distribution of pores in the final foam. Additionally, a surfactant is added in a suspension to improve the stability of wet foams, by lowering the surface tension of the gas–liquid interface and thus increase the lifetime of the foam. However, these surfactants are not able to completely avoid bubble growth due to their low energy of attachment, which is only a few kT 's for a single surfactant molecule. For this reason, iPr-OH is added to serve the purpose.

The overall surface tension of the gas–liquid interface in the suspension is further reduced gradually with the addition of iPr-OH, thereby reducing the final pore sizes (i.e. higher ppi) additionally. This forms an interfacial shield that hinders the gas diffusion outwardly thereby impedes bubble growth and subsequent collapse due to Ostwald ripening and consequently stabilizes the overall foamed suspension with narrow bubble size distribution.

The results suggest that addition of iPr-OH decreases the pore size and pore size distribution in the resultant foam significantly in a controlled manner. Since the size distribution of air bubbles in the foam is affected by surface tension, it is possible to control the pore sizes via addition of iPr-OH through a decrease in surface area to volume ratio, thus also stabilizing the foam kinetically without compromising the solids loading and therefore the slurry viscosity.

3.4. Mechanical behavior

Fig. 4 presents the plots of stress–strain curves for silica foams prepared with 1 vol.% iPr-OH and without iPr-OH addition. All the samples exhibit mechanical behavior typical of cellular materials. It is also evident from Table 2 that the average compressive strength and average elastic modulus increases significantly with iPr-OH addition.

The examination of fractured foam surfaces under optical microscope (Fig. 5) reveals that the failure has occurred at an angle to the applied stress axis, indicating the role of shear. Also, the buckling and folding phenomena of struts are considered as failure mechanism in foams with struts being the supporting member under compression and shear load [22]. The results suggest that iPr-OH addition increases the relative density (RD) of the samples increasing the volume fraction of solid within the struts, thus densifying

the struts, and exhibiting an overall higher load bearing capacity per unit volume of foam.

4. Conclusions

The foam casting method with combination of iPr-OH offers a novel route for fabrication of porous ceramics with controlled pore and pore size distribution. The ability of iPr-OH to control the 3D pore geometry in wet foams collectively with the wet foam stability makes it a potential process additive for the fabrication of cellular constructs with tailored wide range porosity and size distribution. The rheological studies on silica based suspensions have exhibited that the final properties of the foams depend on the slurry composition due to the change in the viscoelastic behavior and flow properties of the slurry with change in the slurry additives. The suspensions prepared in the study have been found to be non-Newtonian, and have shown shear thinning behavior at higher shear rates. The final pore size can be tailored by changing the viscosity, shear rate (applied during mixing and foaming) and the surface tension of the suspension.

The density, microstructure and mechanical properties of silica foams prepared using this method are compared with that of sample prepared using conventional foam casting method. The novel route resulted into higher density, small and uniform pores and narrow pore size distribution and with significantly improved mechanical strength as compared with foams of similar density and without iPr-OH. The interplay of viscosity and surface tension (at air–liquid interface) due to the addition of iPr-OH has shown a significant effect on the viscoelastic flow behavior, foaming characteristics and stability of the air bubbles in a suspension through air–liquid interface modification, which in turn affects the overall pore volume fraction and porous architecture of the finished foams.

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Table 2
Effect of iPr-OH addition on the mechanical properties of silica foams.

Solids loading, vol.%	Density, %	Processing	Max. average compressive strength, MPa	Average elastic modulus, MPa
32	21	With iPr-OH	1.43	143
38	20	No iPr-OH	0.87	117
32	11	No iPr-OH	0.33	60

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