



Freeze gelcasting of hydrogenated vegetable oil-in-aqueous alumina slurry emulsions for the preparation of macroporous ceramics

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Abstract

Freeze gelcasting of hydrogenated vegetable oil-in-aqueous alumina slurry (HVO-in-AAS) emulsions has been studied for the preparation of macroporous ceramics. The emulsions with HVO to AAS volume ratios in the range of 1.34–2.69 prepared from a 30 vol.% AAS containing carrageenan using sodium dodecyl sulphate emulsifying agent at 85 °C undergo gelation on cooling to room temperature due to the solidification of HVO and physical cross-linking of carrageenan. Macroporous ceramics obtained by drying, HVO removal followed by sintering at 1500 °C of the gelled emulsion bodies had porosity in the range of 70.7–84% and contain cells of spherical to polygonal shape. The average cell size (13.24–3.6 μm) decreased and the cell interconnectivity increased with an increase in HVO to AAS volume ratio and mixing speed. The macroporous alumina bodies had high compressive strength (6.5–39.6 MPa) and Young's modulus (350–2352 MPa).

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1. Introduction

Macroporous ceramics are increasingly used in thermal insulation, lightweight structural parts, scaffold for tissue engineering, bio-implants, catalyst support and pre-form for polymer–ceramic and metal–ceramic composites.^{1–10} Polymer foam replication, direct foaming of ceramic powder suspensions and use of fugitive particles as pore templates are the common methods for the preparation of macroporous ceramics.¹¹ In polymer foam replication method, ceramic replica of a polymer foam is prepared by coating the polymer foam with a ceramic powder suspension followed by burning out the polymer foam and sintering.^{12–14} The reticulated ceramic foams prepared by this method have relatively low strength due to the porous strut. In the direct foaming method, gas bubbles incorporated in a ceramic powder suspension is stabilized using either surfactants or particles with suitable wetting characteristics.^{15–18} The foamed suspension cast in a mould is set by the in situ

polymerization of organic monomers or by coagulation of the powder suspension.^{19–24} The macropores created by this method have relatively large size and broad size distribution. In pore template based method, fugitive particles mixed with the ceramic powder is consolidated to produce a green body and the fugitive particles are subsequently removed by evaporation or dissolution in a solvent to produce the macropores. This method offers tunable pore size and narrow pore size distribution. Particles ranging from small colloidal crystals (PMMA nano beads) to large expanded polystyrene beads were used for the creation of macropores.^{25–33} Recently, macroporous ceramics are prepared by freeze casting of ceramic powder suspensions. In this, ceramic powder suspension cast in a mould is set by freezing the suspension medium. The subsequent removal of the frozen suspension medium by sublimation creates the macropores.^{34–38} Ceramics with unidirectionally aligned pores could be prepared by this method by the unidirectional cooling of the cast suspensions.

An alternative method for the preparation of macroporous ceramics is by using emulsion droplets as pore template. The high internal phase emulsion based method is successfully studied for the preparation of various macroporous polymer materials.^{39,40} The emulsion templating method is also reported

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for the preparation of macroporous ceramics with ordered pores through sol–gel route.^{41–44} In this, non-aqueous emulsion (oil-in-formamide) fractionated into a narrow droplet size was mixed with sols prepared by the hydrolysis and condensation of the metal alkoxides in formamide medium. Further condensation of the pre-polymer sol resulted in the deposition of ceramic layer over the emulsion droplet and gelation of the sol. The void spaces created by the removal of the emulsion droplet from the gel remain as macropores. However, the gels undergo large shrinkage during drying and sintering. Moreover, the preparation starting from ceramic powders is more economically viable than the sol–gel route. Recently, a method based on a high alkane phase emulsion using decane as the oil phase has been studied for the preparation of macroporous ceramics.^{45–47} In the present work, hydrogenated vegetable oil (HVO), a solid at room temperature, is used as the oil phase to facilitate the setting of the emulsion by cooling in a mould.⁴⁸ This method is very simple, low cost and environmental friendly.

2. Experimental

α -Alumina powder (A16SG grade) of average particle size 0.34 μm and specific surface area 10.4 m^2/g used was procured from ACC Alcoa, Kolkata, India. The food grade HVO (Dalda, Bunge India Pvt. Ltd., India) procured from a local market has a melting range of 40–41 $^\circ\text{C}$. Analytical reagent grade sodium dodecyl sulphate (Merck India Ltd., Mumbai) and carrageenan (Sigma–Aldrich, USA) were used as emulsifying agent and gelling agent, respectively. A 35 wt.% aqueous ammonium poly(acrylate) solution (Darvan 821A, Vanderbilt company Inc., Norwalk, CA) was used as a dispersant. Distilled water was used for the preparation of the alumina powder suspensions. Analytical reagent grade toluene used was procured from Merck India Ltd., Mumbai.

A 50 vol.% slurry was prepared by dispersing 100 g alumina powder in 25 ml water using the ammonium poly(acrylate) dispersant. The amount of dispersant used was 1 wt.% of the alumina powder. The slurry was ball milled in a polyethylene container using zirconia balls of 10 mm diameter for 12 h. The alumina powder to the zirconia ball weight ratio used was 1:4. The slurry was diluted to 30 vol.% with water and transferred to a 500 ml round bottom flask. The slurry in the round bottom flask was heated in a water bath at 90 $^\circ\text{C}$ for 30 min under constant mechanical stirring after adding accurately weighed amount of carrageenan. A mechanical stirrer with a speed control was used along with a Teflon paddle. The amount of carrageenan added was 1.5 wt.% of water present in the alumina slurry. The temperature of the water bath was reduced to 85 $^\circ\text{C}$ after completely dissolving the carrageenan. The HVO and sodium dodecyl sulphate emulsifying agent taken in a 250 ml beaker was heated in a water bath at 85 $^\circ\text{C}$ to melt the oil and to dissolve the emulsifying agent. The amount of emulsifying agent used was 0.4 wt.% of the HVO. The molten HVO containing the emulsifying agent was added to the alumina suspension present in the round bottom flask kept in the water bath at 85 $^\circ\text{C}$. The mechanical stirring was continued to form a stable emulsion. The emulsions were cast in cylindrical glass moulds of 22 mm diameter and 50 mm length

and then cooled by keeping in a refrigerator at 5 $^\circ\text{C}$ for 30 min. The gelled emulsion bodies removed from the moulds were dried at room temperature (~ 30 $^\circ\text{C}$) in an open air atmosphere. The HVO present in the dried emulsion bodies was removed by soxhlet extraction using toluene. The HVO removed bodies were sintered in an electrically heated furnace at 1500 $^\circ\text{C}$ for 2 h. The heating rate used was 2 $^\circ\text{C}/\text{min}$ up to 600 $^\circ\text{C}$ and then at 5 $^\circ\text{C}/\text{min}$. Shrinkage of the bodies during drying and sintering was obtained from the initial and final dimensions. The porosity of the sintered ceramics was calculated from the density obtained from their weights and dimensions.

The viscosity of the emulsions was measured at 85 $^\circ\text{C}$ using a RVT model Brookfield viscometer [Brookfield Engineering Inc., USA] with small sample adapter and a cylindrical spindle. A thermosel accessory along with the viscometer was used for heating the emulsions during the viscosity measurements. The microstructure of the sintered ceramics was observed on fractured surfaces using a scanning electron microscope (SEM, Hitachi S-2400, Hitachi High Technologies Corporation, Japan). The average pore size of the ceramics was measured from the respective microstructures with the help of ImageJ software.

The compressive strength of the macroporous sintered alumina bodies was measured using a universal testing machine (Instron 4469, Instron USA) at a loading rate of 1 mm/min. The cylindrical samples of 17 mm diameter and 35 mm length were used for the compressive strength measurement.

3. Results and discussion

The carrageenan dissolves in water present in the alumina slurry when heated at 90 $^\circ\text{C}$ for 30 min.⁴⁹ The 30 vol.% aqueous alumina slurry (AAS) containing the carrageenan showed the viscosity in the range of 1.05–0.125 Pa s at shear rates in the range of 4.65–93 s^{-1} at 85 $^\circ\text{C}$. On the other hand, the molten HVO containing sodium dodecyl sulphate showed the viscosity in the range of 0.15–0.025 Pa s. The HVO containing the surfactant slowly disperse in the aqueous alumina slurry when the two are mixed by mechanical stirring to form HVO-in-AAS emulsion. The stable emulsions with HVO to AAS volume ratio in the range of 1.34–2.69 could be prepared. This corresponds to an HVO concentration in the range of 65.8–79.4 vol.% when calculated by excluding the volume of the alumina powder, carrageenan and sodium dodecyl sulphate. The density of HVO is taken as 0.897 g/cm^3 for all the volume ratio calculations. It is well known that the oil-in-water emulsions with 30–74 vol.% of oil phase are medium internal phase emulsions and those with higher than 74 vol.% oil phases are high internal phase emulsions.⁵⁰ Herein, the emulsions at the HVO to AAS volume ratios in the range of 1.34–1.88 are medium internal phase emulsions as they contain 65.8–72.9 vol.% HVO. On the other hand, the emulsions at the HVO to AAS volume ratios in the range of 2.15–2.69 are high internal phase emulsions as they contain 75.5–79.4 vol.% HVO. Nearly 30 min are required for the complete dispersion of the oil in the aqueous slurry up to an HVO to AAS volume ratio of 2.41. Higher mixing time of nearly 2 h is required for the complete dispersion of HVO in AAS at HVO to AAS volume ratio of 2.69. In all the cases, an additional

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