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Effect of emulsion composition on gel strength and porosity in the preparation of macroporous alumina ceramics by freeze gelcasting

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ABSTRACT

The freeze gelcasting of hydrogenated vegetable oil-in-aqueous alumina slurry (HVO-in-AAS) emulsions of HVO to AAS volume ratios in the range of 1.34–2.69 prepared from slurries of various alumina concentrations were studied to prepare macroporous ceramics of high porosity. The compressive strength (20–150 kPa) and Young's modulus (120–1550 kPa) of the gelled emulsion bodies increased with an increase in alumina slurry concentration and HVO to AAS volume ratio. Easy HVO removal from gelled emulsion bodies by extraction at room temperature with petroleum ether, a less toxic solvent, was achieved. The highest porosity achieved at a HVO to AAS volume ratio of 2.69 increased from 84 to 92.5% when the alumina concentrations in the slurry decreased from 30 to 10 vol.%. The cell size and cell interconnectivity of the ceramics depended on the alumina slurry concentration and HVO to AAS volume ratio. The Young's modulus of the macroporous ceramics modelled using the equation proposed by Gibson and Ashby showed large deviation in the model parameters, *n* and *C*, from the proposed values.

1. Introduction

Processing of macroporous ceramics from colloidal suspension of powders using suitable pore templates is well known [1–5]. Polymeric foams, fugitive solid particles and liquid droplets are used as pore templates for the preparation of macroporous ceramics. In the polymeric foam template method, a ceramic powder suspension coated on the surfaces of the webs of polymer foam is dried, heat treated to remove the polymer foam template and then sintered to produce the ceramic replica of the polymer foam [5–7]. This method produces highly porous reticulated ceramics. In the solid fugitive template based method, fugitive particles such as carbon particles, wheat particles, polymer beads, rice particles, polymer short fibres, crystals of organic molecules, etc. incorporated in a ceramic powder suspension are consolidated to produce the green body [8–16]. The fugitive particles in the green body assembly are subsequently removed by slow heating before sintering. The void space created by the removal of the fugitive particle remains as pore in the sintered ceramic. Though this method is quite simple and has very good control over the pore size, it produces macroporous ceramics having relatively low porosity. In the third method, immiscible liquid (oil) droplets are dispersed in a ceramic precursor sol or ceramic powder suspension using a suitable emulsifying agent to form an emulsion [17–23]. The emulsion is then set by gelation of the sol or ceramic powder suspension. The gelled emulsion body is dried, oil removed and sintered to produce the macroporous ceramics. Use of liquid droplet as pore template instead of fugitive solid particles provides many advantages. Primarily, the uniform dispersion of the immiscible liquid droplets in an aqueous slurry medium using an emulsifying agent could be obtained by simple stirring. The pore size could be manipulated by controlling the droplet size, which can be obtained by adjusting the emulsifying agent concentration and mixing speed. In addition, loading of liquid template even higher than 74 vol.% of the emulsion could be possible. Such emulsions are known as high internal phase emulsions [21]. This leads to macroporous ceramics with very high porosity and highly interconnected pore structure compared to that obtained by fugitive solid particle template method.

High alkane phase emulsions based on decane in aqueous alumina powder suspension have been studied for the preparation of macroporous ceramics [20–22]. In this, the emulsions cast in an open mould could be removed from the mould only after partial or complete drying. This limits the production rate. Recently, we have demonstrated an emulsion template method for the preparation of

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macroporous alumina ceramics using hydrogenated vegetable oil (HVO) as the pore template [24]. In this method, emulsions are prepared by stirring aqueous alumina powder suspension containing carrageenan with HVO at 85 °C using sodium dodecyl sulphate as an emulsifying agent. The emulsions cast in a mould undergo gelation due to the solidification of HVO and physical cross-linking of carrageenan. The gelled emulsions could be immediately removed from the mould, which enhances the production rate. In addition, gelled emulsion bodies could be dried in open air atmosphere without any humidity control and the HVO in the dried bodies could be removed by soxhlet extraction with toluene. Moreover, unlike the hydrocarbons, HVO is a nontoxic and natural renewable material. However, the use of toluene as solvent for HVO extraction creates concern as toluene is a toxic solvent. In this paper, we have systematically studied the effect of alumina slurry concentration and HVO to AAS volume ratio on the emulsion viscosity, strength of gelled emulsion bodies and porosity, pore size and compressive strength of the macroporous ceramics in addition to the fabrication of large ceramic bodies. Petroleum ether, a low toxic solvent, is used for HVO removal by extraction at room temperature. We could achieve a maximum porosity of 92.5% by this emulsion template method.

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 °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. Analytical reagent grade petroleum ether having a boiling range of 60–80 °C used for HVO extraction was procured from Merck India Ltd., Mumbai. Distilled water was used for the preparation of the alumina powder suspensions. Analytical reagent grade toluene used was procured from Merck India Ltd., Mumbai.

The procedure for the preparation of macroporous ceramics by freeze gelcasting of HVO-in-AAS emulsions is shown as a flowchart in Fig. 1. Emulsions of various HVO to AAS volume ratios were prepared by mixing slurries of 10, 20 and 30 vol.% alumina concentration containing carrageenan with the HVO using sodium dodecyl sulphate emulsifying agent in a round bottom flask at 85 °C for 1 h. The concentration of carrageenan and sodium dodecyl sulphate used was 1.5 wt.% of water in the alumina slurry and 0.4 wt.% of HVO, respectively. The amount of ammonium poly(acrylate) dispersant used was 1 wt.% of the alumina powder. The mixing was done by mechanical stirring at a constant speed of 350 rpm. 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 °C for 30 min. The gelled emulsion bodies removed from the moulds were dried at room temperature (~30 °C) in an open air atmosphere for 96 h. The dried emulsion bodies were immersed in petroleum ether in a closed vessel at room temperature for the removal of HVO. 100 ml petroleum ether was used for each gelled emulsion body of 45 mm length and 22 mm diameter. The solvent was renewed with a fresh one after every 4 h until the removal of more than 98% of the HVO. The HVO removed bodies were sintered in an electrically heated furnace at 1550 °C for 2 h. The heating rate used was 2 °C/min up to 600 °C and then at 5 °C/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 based on the density obtained from their weights and dimensions.

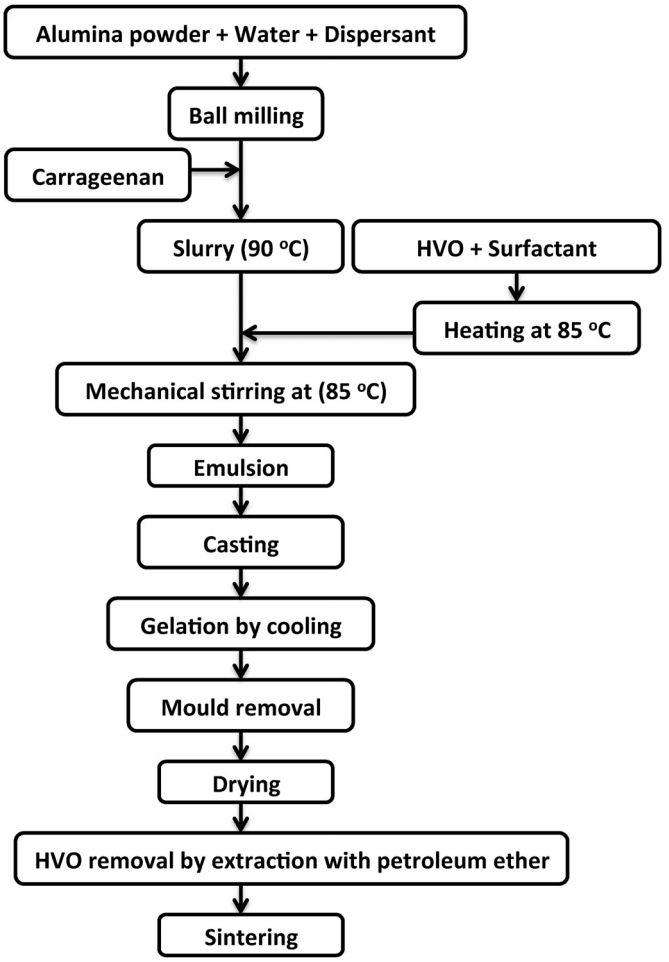

Fig. 1. Flowchart of the emulsion gelcasting process.

The viscosity of the emulsions was measured at 85 °C using a RVT model Brookfield viscometer (Brookfield Engineering Inc., Middleboro, MA) with a 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 stress–strain measurement of the gelled emulsion bodies was carried out using a universal testing machine (Instron 5500, Instron USA) at a loading rate of 5 mm/min. Emulsion bodies removed from the mould were immediately used for the stress–strain measurements. The diameter and length of the cylindrical gelled emulsion bodies used for the stress–strain measurement are 22 mm and 45 mm, respectively. The compressive strength and Young's modulus are obtained from the stress–strain graph. The compressive strength of the macroporous alumina ceramics was measured on cylindrical bodies of 18 mm diameter and 36 mm length using the same universal testing machine. The loading rate used was 1 mm/min.

3. Results and discussion

3.1. Rheological characterization of emulsions

The emulsions with low viscosity and yield stress are desirable for casting in a mould for the preparation of macroporous ceramic