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Effect of emulsion composition on the porosity characteristics of macroporous ceramics prepared by freeze gelcasting of naphthalene-in-aqueous alumina slurry emulsions

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Freeze gelcasting of naphthalene-in-aqueous alumina slurry emulsions prepared from slurries of various alumina concentrations were studied to prepare macroporous alumina ceramics of high porosity. The compressive strength and Young's modulus of the gelled emulsion bodies increased with an increase in naphthalene to alumina slurry volume ratio and a decrease in the alumina slurry concentration. Macroporous alumina ceramics obtained were characterized for their microstructure, porosity, pore size and compressive strength as a function of naphthalene to alumina slurry volume ratio and alumina concentration in the aqueous slurry. Porosity (65 to 90 vol.%) increased with an increase in naphthalene to alumina slurry volume ratio and a decrease in alumina slurry concentration. The compressive strength and Young's modulus of the macroporous alumina ceramics were fitted with the model equations proposed by Gibson and Ashby. The gelled emulsions showed paste-like consistency which enabled easy fabrication of macroporous alumina tiles by compression moulding.

Key words: Emulsion, Shaping, Freeze gelcasting, Porosity, Al_2O_3, Strength.

Introduction

Macroporous ceramics are increasingly used in applications such as high temperature thermal insulation, catalyst support, electrodes in solid oxide fuel cells, membrane substrate, molten metal filtration, bio-implants and pre-form for polymer ceramic and metal-ceramic composites [1-10]. Polymer foam replication, direct foaming of ceramic powder suspensions, use of fugitive particles as pore templates and freeze casting are the common methods for the preparation of macroporous ceramics [11, 12]. The properties such as compressive strength, thermal conductivity and permeability of macroporous ceramics can be tailored by controlling the volume fraction of pores, pore size, pore size distribution and pore interconnectivity [13]. This can be achieved by choosing suitable pore templates, which uniformly disperse within the ceramic powder suspension and on subsequent consolidation and pyrolysis give a suitable pore structure.

Oil droplets are ideal pore templates for the preparation of macroporous ceramics as they can be uniformly distributed in the aqueous ceramic powder suspensions by mechanical mixing in the presence of a suitable surfactant to form emulsions. The droplet size can be varied by controlling the mixing speed, surfactant concentration and the amount of the oil phase. The uses of emulsions as pore templates for the preparation of macroporous ceramics using sol-gel route has been widely studied [13-16]. Recently, a high alkane phase emulsion technique for the preparation of macroporous ceramics from aqueous powder suspensions using decane as the oil phase has been reported [16-19]. The drawback of this method is that it uses an oil phase which is a liquid at room temperature. Therefore, the emulsion cast in a mould need to be partially dried before the mould removal which limits the production rate. This could be easily remedied by using an oil phase which is a solid at room temperature. Abrantes, et al reported an emulsion template based method using liquid paraffin as pore template and collagen as the consolidating agent [20]. Recently, we have reported a freeze gelcasting process using oil phases such as hydrogenated vegetable oil and naphthalene which are solids at room temperature. In these, the emulsions prepared by dispersing the molten oil phase in aqueous alumina powder suspensions were set by cooling in a mould. The gelation of the emulsion is due to the solidification of the oil droplets and physical cross-linking of carrageenan, a gelling agent, dissolved in the aqueous suspension. Subsequent mould removal, drying, oil removal and sintering of the gelled emulsions resulted in macroporous alumina ceramics. The process is represented schematically in Fig. 1.

The advantage of naphthalene over wax and hydrogenated vegetable oil is that it could be easily removed by sublimation by keeping the dried bodies in an air oven at 70 °C [20-23]. Moreover, the removed naphthalene could be recovered by condensing on cold

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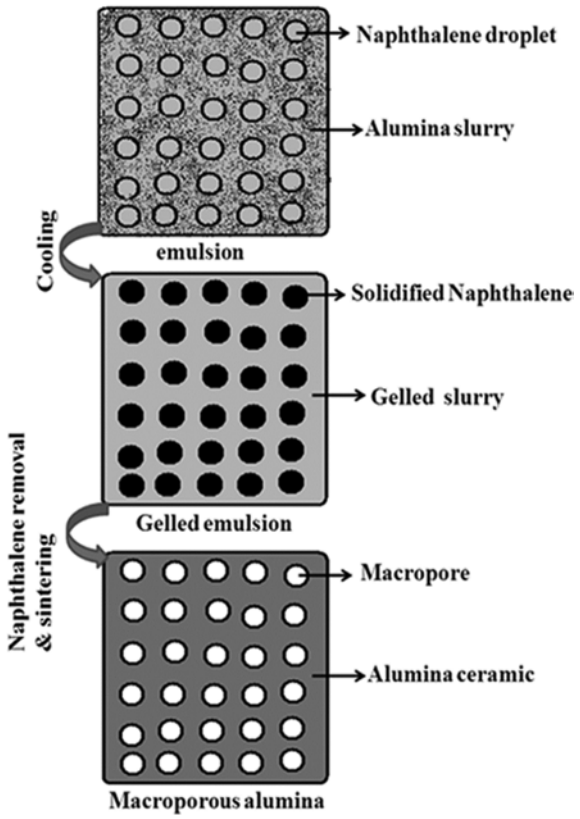

Fig. 1. Schematic of freeze gelcasting process.

surfaces and reused. Maximum porosity of only 78% was achieved by the freeze gelcasting process using an aqueous slurry of 30 vol.% alumina loading [23]. However, macroporous ceramics of higher porosity are highly desirable in applications such as high temperature thermal insulation as the thermal conductivity decreases with an increase of porosity. The present work reports the preparation of macroporous ceramics of high porosity from aqueous suspensions of low alumina concentrations. The effect of alumina concentration on the rheological behavior of emulsions, the strength of the gelled emulsion bodies and porosity, pore size, pore morphology and compressive strength of the macroporous alumina ceramics is reported. In addition, the possibility of shaping the gelled emulsions by compression moulding is also demonstrated.

Experimental

α-Alumina powder of average particle size 0.34 μm and specific surface area 10.4 m^2/g was procured from ACC Alcoa, Kolkata, India. Analytical reagent grade naphthalene and sodium dodecyl sulphate (emulsifying agent) were procured from Merck India Ltd., Mumbai. A 35 wt.% aqueous ammonium poly(acrylate) solution (Darvan 821A**)** used as dispersant was received from Vanderbilt Company Inc., USA. The carrageenan used as gelling agent was procured from Aldrich Chemical, USA. Distilled water was used for the preparation of alumina powder suspensions.

The procedure for the preparation macroporous alumina ceramics by freeze gelcasting of naphthalene-in-aqueous alumina slurry emulsions is reported in our previous publication [22]. Slurries of 10, 20 and 30 vol.% alumina loadings were prepared by dispersing the alumina powder in water using the ammonium poly (acrylate) dispersant. The slurries were ball milled in polyethylene bottles using zirconia grinding media on a roller ball mill for 12 hours. The slurries were transferred to 500 ml round bottom flasks. The carrageenan was dissolved in the alumina slurry by heating at 90 ºC under stirring using a mechanical stirrer with a Teflon paddle. The amount of carrageenan used was 1.5 wt.% of the water present in the aqueous alumina slurry. A solution prepared by heating the emulsifying agent and naphthalene in a beaker at 85 ºC was added to the aqueous alumina slurry containing the gelling agent. The amount of emulsifying agent used was 0.3 wt.% of the naphthalene. The contents in the round bottom flask were stirred for another one hour to form stable naphthalene-in-aqueous alumina slurry emulsions. The emulsions were prepared at naphthalene to alumina slurry volume ratios in the range of 1.0 to 1.86. The emulsions were cast into glass moulds and cooled to 5 ºC in a refrigerator to get the gelled emulsion bodies. The gelled bodies removed from the mould were dried in ambient conditions for 140 hours. The naphthalene in the dried bodies was removed by heating at 70 ºC in an air circulated oven. The naphthalene removed bodies were sintered at 1550 ºC in an electrically heated furnace for two hours. The heating rate used was 2 ºC/minute up to 600 ºC and then at 5 ºC/minute. The sintered bodies were unloaded after natural cooling of the furnace to room temperature. The porosity of the sintered ceramics was calculated based on the density obtained from their weights and dimensions.

The viscosity of the emulsions was measured at 85 ºC using a RVT model Brookfield viscometer [Brookfield Engineering Inc., USA] 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.

Stress-strain measurements of the gelled emulsion bodies and sintered alumina ceramics were carried out using a universal testing machine (Instron 4469, Instron USA). The loading rate used was 5 mm/minute and 1 mm/minute, respectively, for gelled alumina bodies and sintered alumina ceramics. Cylindrical samples of 22 mm

diameter and 45 mm length were used for the stress-strain measurement of the gelled emulsion bodies. On the other hand, sintered ceramic samples used were having 17 mm diameter and 35 mm length. The compressive strength and Young's modulus were obtained from the stress-strain graph.

The rheological characterization of the gelled emulsions was carried out by strain sweep, time sweep and frequency sweep measurements using a rheometer (Modular Compact Rheometer MCR-102, Anton Paar GmBH, Austria) at room temperature (~ 30 °C). Strain sweep measurements were done at a frequency of 1 rps using a 25 mm stainless steel disk in a parallel plate configuration. Time sweep measurements were done at 0.02% strain at a frequency of 1 rps. The frequency sweep measurements were done at frequencies in the range of 0.1 to 100 s^{-1} at 0.02% strain. The gelled emulsions were moulded into rectangular bodies of 10 cm × 10 cm × 2 cm size using a stainless steel mould. The emulsions prepared at naphthalene to alumina slurry volume ratio up to 1.25 from slurries of 10, 20 and 30 vol.% alumina loadings could be easily moulded by hand. On the other hand, gently pressing with a hand operated hydraulic press is used in the moulding of gelled emulsions at higher naphthalene to alumina slurry volume ratios. The pressure applied was ~ 3 MPa.

Results and Discussion

The freeze gelcasting process requires the naphthalene-in aqueous alumina slurry emulsions of low viscosity and yield stress. Fig. 2 shows the effect of composition on the viscosity of emulsions measured at a shear rate of 9.3 s^{-1} and at 85 °C. In the case of aqueous slurry of a specified alumina concentration, the viscosity of the emulsions increased with an increase in naphthalene to alumina slurry volume ratio. On the other hand, at fixed naphthalene to aqueous alumina slurry volume ratio, the viscosity of the emulsions increased with an increase in alumina slurry concentration. The emulsions with naphthalene to alumina slurry volume ratios in the range of 1 to 1.86 prepared from aqueous alumina slurries of concentrations in the range of 10 to 30 vol.% showed a viscosity in the range of 0.175 to 1.025 Pa.s at a constant shear rate of 9.3 s^{-1}.

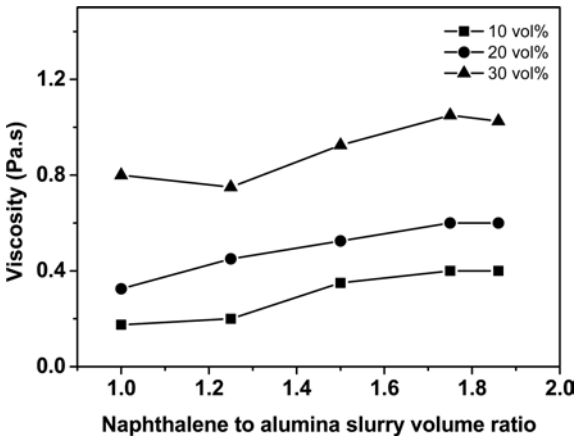

Fig. 2. Effect of naphthalene to alumina slurry volume ratio and alumina slurry concentrations on the viscosity of naphthalene-in-aqueous alumina slurry emulsions (shear rate- 9.3 s^{-1}).

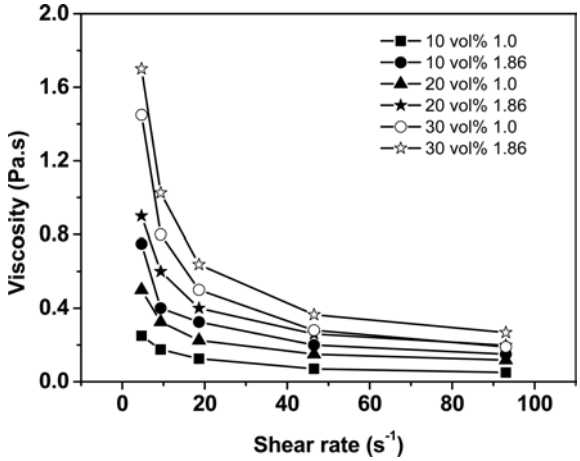

Fig. 3. Viscosity versus shear rate plot of the emulsions prepared at naphthalene to alumina slurry volume ratios of 1.0 and 1.86 at different alumina slurry concentrations.

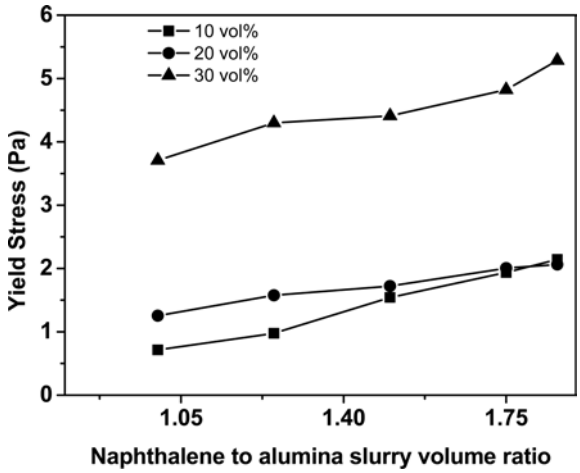

Fig. 4. Yield stress of emulsions at various naphthalene to aqueous alumina slurry volume ratios prepared from aqueous slurries of different alumina concentrations.

The naphthalene-in-aqueous alumina slurry emulsions in general showed shear thinning flow behavior. The shear thinning behavior of the emulsions increases with an increase in alumina concentration in the slurry and an increase in naphthalene to aqueous alumina slurry volume ratio. Fig. 3 shows viscosity versus shear rate plots of emulsions with naphthalene to alumina slurry volume ratios of 1 and 1.86 prepared from aqueous slurries of 10, 20 and 30 vol.% alumina concentrations. The emulsions obey Casson model [25]. That is, a plot of square root of shear stress versus square root of the shear rate gave a straight line graph. The yield stress obtained by extrapolating the straight lines to the Y-

axis plotted as a function of naphthalene to alumina slurry volume ratio and alumina concentration in the aqueous slurry is shown in Fig. 4. As in the case of viscosity, the yield stress of the emulsions also increased with an increase in naphthalene to alumina slurry volume ratio and alumina concentration in the aqueous slurry. The yield stress observed was in the range of 0.7 to 5.3 Pa for the emulsions with naphthalene to alumina slurry volume ratios in the range of 1 to 1.86 prepared from aqueous slurries of alumina concentration in the range of 10 to 30 vol.%. Viscosity and yield stress of the emulsions are sufficiently low to flow into any mould during casting.

The flow behavior of powder suspensions and emulsions depends on the interparticle and inter droplet Van der Waals interactions. In the case of naphthalene-in-aqueous alumina slurry emulsions, there are three types of possible Van der Waals interactions. They are between the alumina particles in the aqueous phase, between the naphthalene droplets and between alumina particles in the aqueous phase and naphthalene droplets. It is well known that these interparticle interactions increase with an increase in particle concentration and decrease in particle size. The increase in viscosity, shear thinning character and yield stress with an increase in naphthalene to alumina slurry volume ratio and alumina slurry concentration is due to this increase in the interparticle interactions.

The emulsions prepared from slurries of alumina concentrations in the range of 10 to 30 vol.%, gel on cooling to room temperature in a mould. Cooling in a refrigerator is used for faster cooling to reduce the gelation time. Unlike the high alkane phase emulsion based method, the freeze gelcasting of emulsion enables the mould removal immediately after gelation [17]. This resulted in higher production rate. For the successful mould removal, the gelled emulsion bodies should have sufficient strength and Young's modulus. Fig. 5 shows the representative stress-strain graphs of

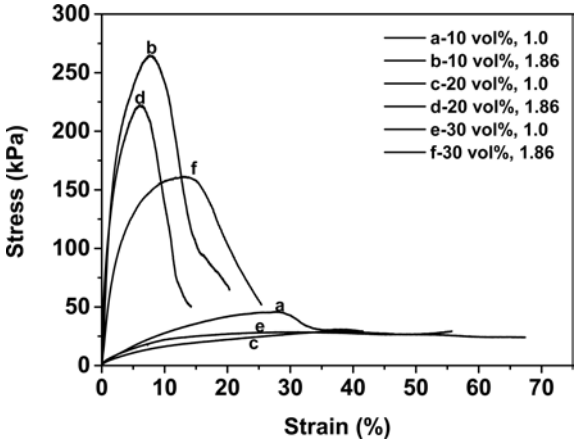

Fig. 5. Representative stress-strain graphs of gelled emulsions showing the effect of naphthalene to alumina slurry volume ratio and alumina slurry concentration.

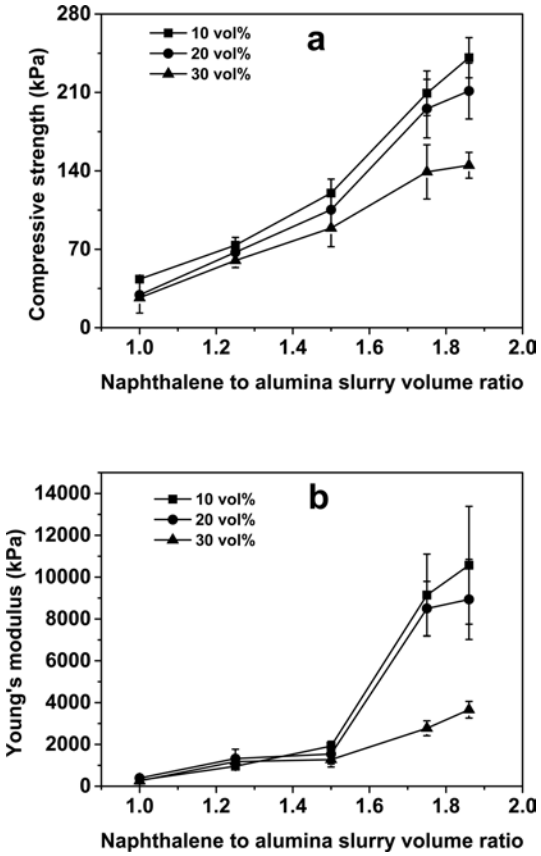

Fig. 6. The effect of composition on (a) compressive strength and (b) Young's modulus of the gelled emulsion bodies.

the gelled emulsion bodies. The stress-strain graphs show an initial linear region followed by a yield point and a stress maximum. After reaching the maximum, either the stress declines with increase of strain or remains plateau depending on the composition of the gelled emulsion. The slope of the linear region is taken as the Young's modulus and the stress maximum is taken as the compressive strength. The gelled emulsion bodies prepared from aqueous slurry of 10 vol.% alumina concentration fail after reaching the stress maximum due to the development of cracks irrespective of naphthalene to alumina slurry volume ratio. On the other hand, the gelled emulsion bodies prepared from 30 vol.% alumina slurry undergo sagging at the bottom after reaching the stress maximum at all naphthalene to alumina slurry volume ratios. The gelled emulsion bodies prepared from 20 vol.% alumina slurry at naphthalene to alumina slurry volume ratios higher than 1.5 fails by development of crack and the same prepared at lower naphthalene to alumina slurry volume ratios fail by sagging at the bottom.

Fig. 6 shows the compressive strength and Young's modulus of gelled emulsion bodies obtained at various naphthalene to alumina slurry volume ratios prepared from aqueous slurries of different alumina concentrations. At 30 vol.% alumina slurry concentration, the compressive strength of the gelled emulsion bodies increases linearly

with an increase in the naphthalene to aqueous alumina slurry volume ratio. However, at 10 and 20 vol.% alumina slurry concentrations, the gel strength increases slowly with naphthalene to alumina slurry volume ratio up to 1.5 and then rapidly. On the other hand, the Young's modulus increases slowly with naphthalene to aqueous alumina slurry volume ratio up to 1.5 and then rapidly. At particular naphthalene to alumina slurry volume ratio, the compressive strength and Young's modulus of gelled emulsion bodies decreases with an increase in concentration of alumina slurry. The average compressive strength and Young's modulus of gelled emulsion bodies obtained are in the ranges of 26.7 to 241 kPa and 256 to 10569 kPa, respectively. The obtained compressive strength and Young's modulus values are sufficient to resist deformation of the gelled emulsion bodies during mould removal and further handling.

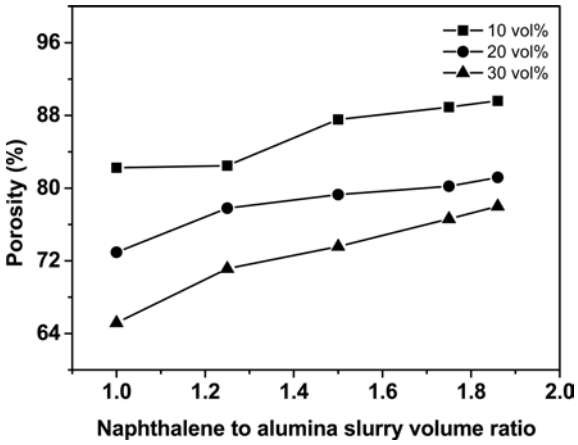

Fig. 7. Effect of naphthalene to alumina slurry volume ratio and alumina slurry concentration on porosity of the macroporous alumina ceramics.

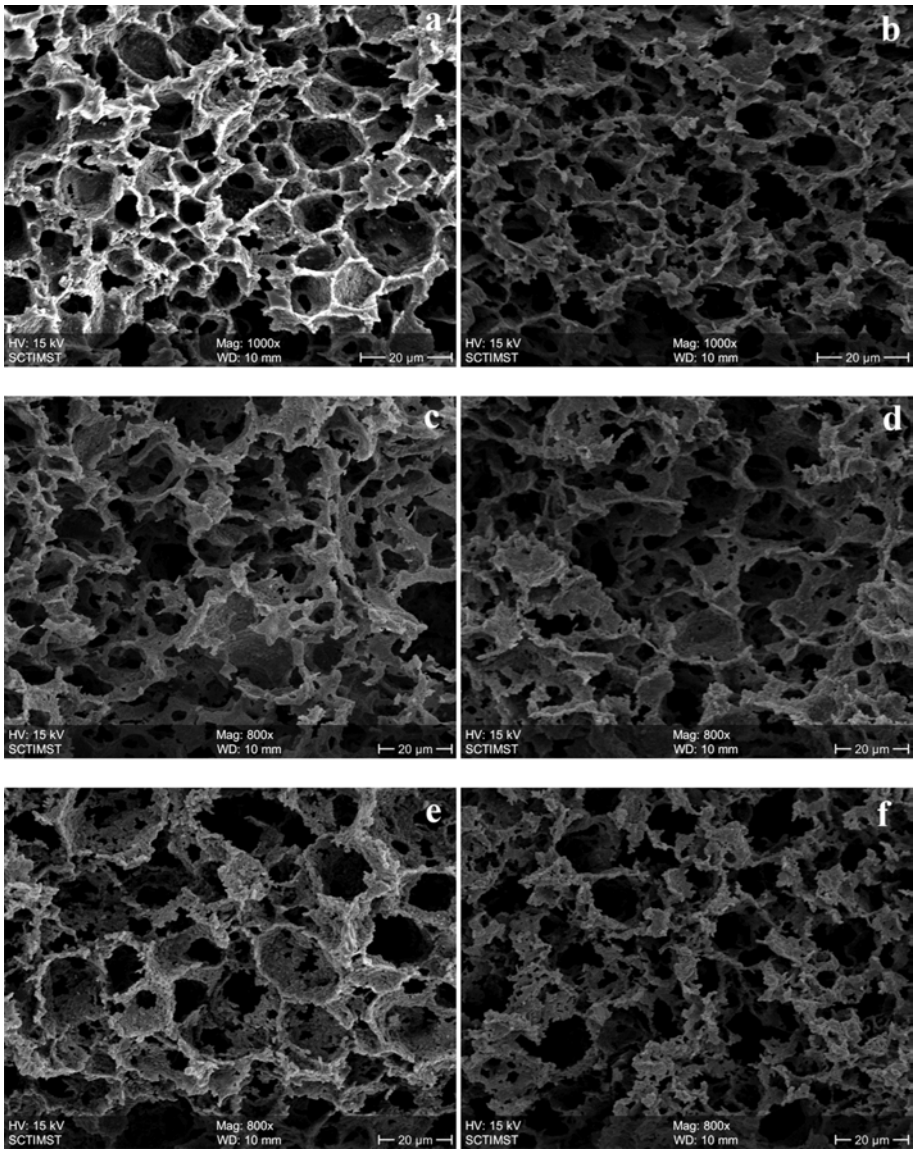

Fig. 8. Photographs (SEM) of macroporous alumina ceramics obtained from slurries prepared at different alumina loading. (a) 1.0; 30 vol.%, (b) 1.86; 30 vol.%, (c) 1.0; 20 vol.%,(d) 1.86; 20 vol.%, (e) 1.0; 10 vol.%, (f) 1.86; 10 vol.%.

The gelled emulsion body is a composite of solidified naphthalene droplets dispersed in a continuous matrix of gelled alumina slurry. The strength and modulus of a composite depend on the corresponding values of the matrix and reinforcement and the extent of stress transfer from the matrix to the reinforcement [26]. The stress transfer depends on the nature of the matrix-reinforcement interface. The gel obtained by cooling 1.5 wt.% aqueous solution of carrageenan in a refrigerator at 5 °C showed a compressive strength of 19 kPa and Young's modulus of 95 kPa. On the other hand, gelled bodies prepared from 10, 20 and 30 vol.% alumina slurries (without naphthalene) showed the compressive strength values of 14, 12.7 and 10.8 kPa, respectively. The corresponding Young's modulus values obtained are 90, 84 and 72 kPa, respectively. The decrease in strength and Young's modulus with an increase in alumina concentration indicates that the alumina particles disrupt the secondary interactions between carrageenan molecules, which are responsible for the gel formation. The compressive strength and Young's modulus of solid naphthalene measured using cylindrical bodies of length 45 mm and diameter 22 mm are 1632 kPa and 84338 kPa, respectively. The compressive strength and Young's modulus calculated using simple rule of mixtures for the gelled emulsion bodies from the corresponding values of gelled alumina slurries and solid naphthalene are in the ranges of 817.9 to 1067.6 kPa and 41996.2 to 54876.2 kPa, respectively. These values are much higher than the experimentally measured compressive strength and Young's modulus. This large difference is due to the poor stress transfer from the gelled alumina slurry to solid naphthalene as a result of weak gelled alumina slurry-naphthalene interface.

The gelled emulsion bodies did not show any visible crack during drying in an open air atmosphere at room temperature, naphthalene removal by sublimation at 70 °C and sintering at 1550 °C. Fig. 7 shows the porosity of the alumina ceramics plotted as a function of naphthalene to alumina slurry volume ratio and alumina concentration in the aqueous slurry. Porosity of the alumina ceramics obtained from the emulsions prepared from aqueous slurry of a specific alumina concentration increased with an increase in naphthalene to alumina slurry volume ratio. On the other hand, at particular naphthalene to aqueous alumina slurry volume ratio, the porosity of the macroporous alumina ceramics increased with a decrease in alumina concentration in the aqueous slurry. Macroporous alumina ceramics obtained from emulsions of naphthalene to alumina slurry volume ratios in the range of 1 to 1.86 prepared from alumina slurries of concentration in the range of 30 to 10 vol.% showed porosity in the range of 65 to 90%. The maximum porosity achieved, at naphthalene to alumina slurry volume ratio of 1.86, increased from 78 to 90% when the alumina slurry concentration decreased from 30 to 10 vol.%.

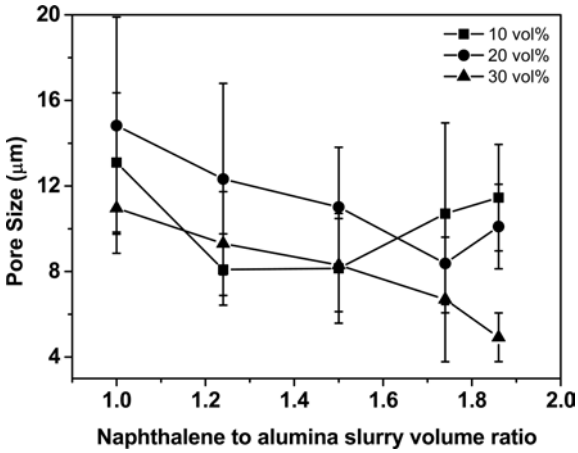

Fig. 9. Effect of naphthalene to aqueous alumina slurry volume ratio and alumina slurry concentration on the average pore size of the macroporous alumina ceramics.

Fig. 8 shows the microstructure of the macroporous alumina ceramics obtained from naphthalene-in-aqueous alumina slurry emulsions of naphthalene to alumina slurry volume ratios 1.0 and 1.86 prepared from slurries of 10, 20 and 30 vol.% alumina loading. Majority of the macropores show distorted spherical shape. The interconnectivity of the cells increased with a decrease in alumina concentration in the slurry and an increase in naphthalene to alumina slurry volume ratio. The thickness of struts and cell walls showed a decreasing trend with a decrease in alumina slurry concentration and an increase in naphthalene to alumina slurry volume ratio.

The average pore size measured from the SEM micrographs using ImageJ software plotted as a function of alumina concentration in the slurry and naphthalene to alumina slurry volume ratio is shown in Fig. 9. In the case of alumina ceramics obtained from the emulsions prepared at 30 vol.% alumina slurry, the average pore size decreases linearly from 15.2 to 9.5 μm when the naphthalene to alumina slurry volume ratio increases from 1 to 1.86. On the other hand, at the alumina slurry concentrations of 20 and 10 vol.%, the average pore size first decreases with an increase in naphthalene to alumina slurry volume ratio, reaches a minimum and then increases. The naphthalene to alumina slurry volume ratio at which the pore size minimum obtained was 1.75 and 1.5 for alumina slurry concentrations 20 and 10 vol.%, respectively. This is attributed to the decrease in the effectiveness of stirring due to the large volume of emulsions at higher naphthalene to alumina volume ratios prepared from slurries of lower alumina concentrations (same weight of alumina powder is used in all emulsion preparation).

The compressive strength and Young's modulus of macroporous brittle solids depend on porosity, pore size, pore interconnectivity and nature of struts and cell walls [27-30]. The effect of alumina slurry concentration and

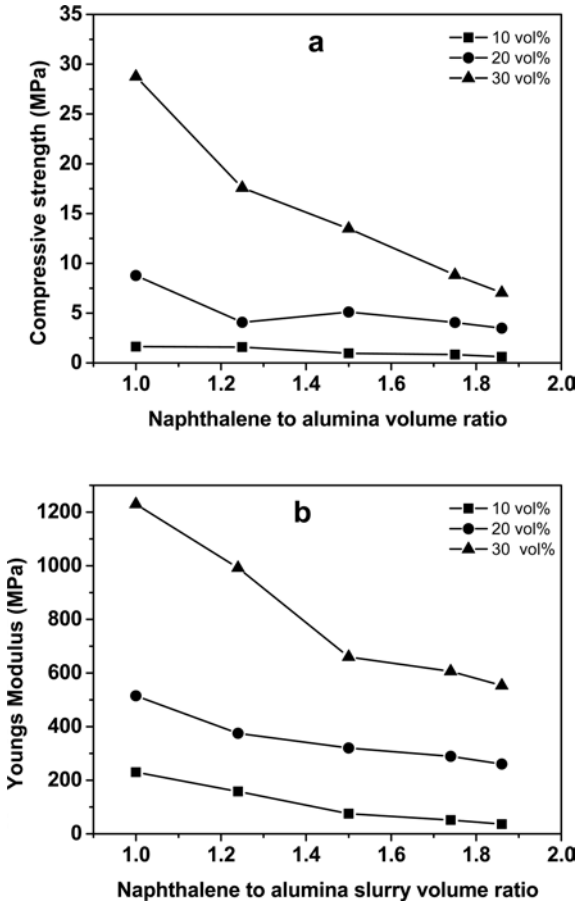

Fig. 10. Effect of naphthalene to alumina slurry volume ratio and alumina slurry concentration on the (a) compressive strength and (b)Young's modulus of the macroporous alumina ceramics.

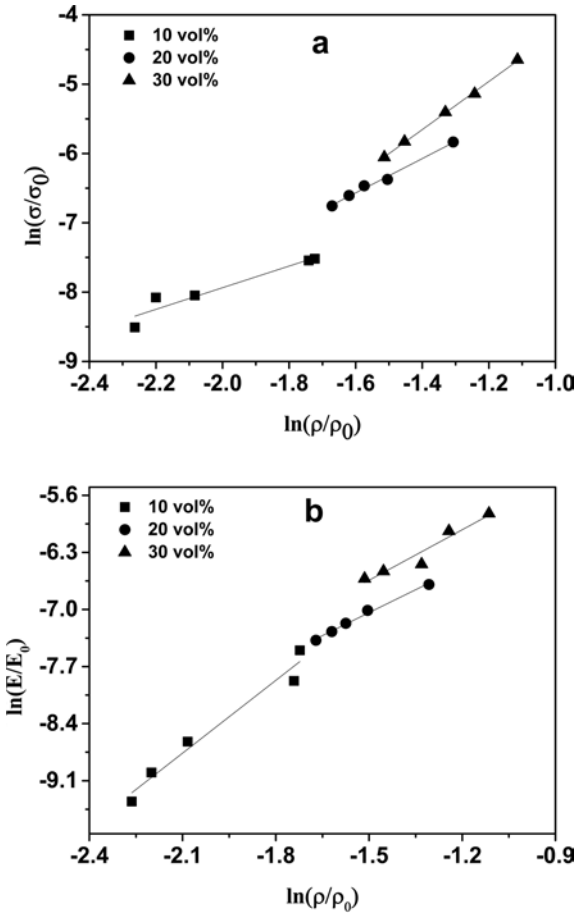

Fig. 11. Log-log plots of (a) σ/σ_0 against ρ/ρ_0 and (b) E/E_0 against ρ/ρ_0.

naphthalene to alumina slurry volume ratio on the compressive strength and Young's modulus of the macroporous alumina ceramics is shown in Fig. 10. The compressive strength and Young's modulus decreases with an increase in naphthalene to alumina slurry volume ratio and decrease in alumina concentrations in the alumina slurry. This is due to the increase in porosity in the alumina ceramic. The average compressive strength and Young's modulus values obtained were in the ranges of 0.60 to 28.75 MPa and 36 to 1230 MPa, respectively, for the alumina ceramics of porosity in the range of 65 to 90 vol.%.

The compressive strength and Young's modulus of brittle open cellular solids are best modeled using the following equations proposed by Gibson and Ashby [31].

$$\sigma/\sigma_0 = C\ (\rho/\rho_0)^n \quad (1)$$

$$E/E_0 = C\ (\rho/\rho_0)^n \quad (2)$$

Where σ, E, are the compressive strength and Young's modulus of the open cellular solid and σ_0, E_0 are the compressive strength and Young's modulus of the fully densified solid, respectively. ρ and ρ_0 are the density of open cellular and fully dense solid, respectively. The C and n are constants depending on the pore geometry and microstructure. Fig. 11 shows the plots of $\ln(\sigma/\sigma_0)$ versus $\ln(\rho/\rho_0)$ and $\ln(E/E_0)$ versus $\ln(\rho/\rho_0)$ of the macroporous alumina ceramics. The model plots are generated by considering the strength (σ_0) and Young's modulus (E_0) of fully dense alumina as 3 GPa and 416 GPa, respectively [32]. The values of model

Table 1. Values of model constants C, n and correlation coefficient R^2.

Alumina Slurry concentration	Compressive strength			Young's modulus		
	n	C	R^2	n	C	R^2
10 vol%	1.5602	0.0081	0.89189	2.9748	0.08092	0.9576
20 vol%	2.4752	0.0841	0.98996	1.8761	0.01463	0.9902
30 vol%	3.470	0.45088	0.99851	2.06771	0.02899	0.9107

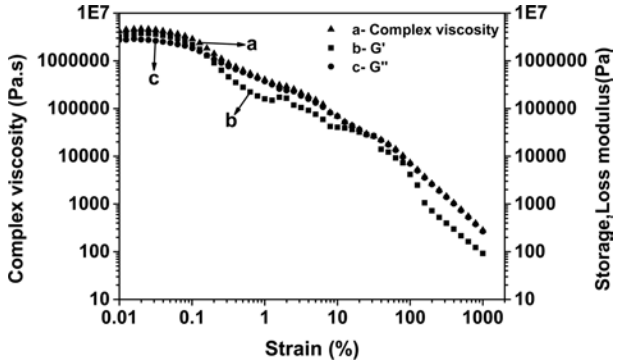

Fig. 12. Strain sweep graph of a typical gelled emulsion (Naphthalene to aqueous alumina slurry volume ratio of 1 and alumina slurry concentration of 10 vol.%).

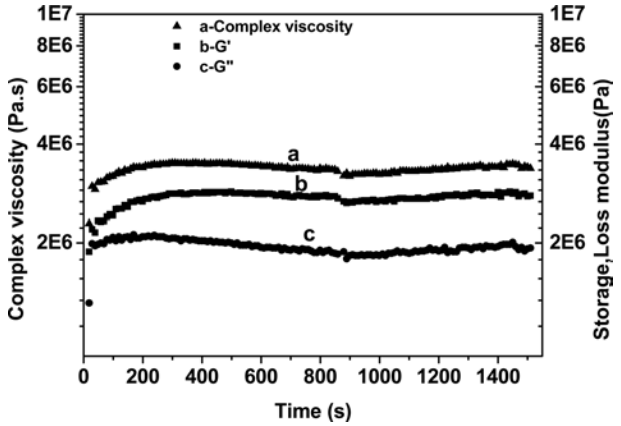

Fig. 13. Time sweep graph of a typical gelled emulsion (Naphthalene to aqueous alumina slurry volume ratio of 1 and alumina slurry concentration of 10 vol.%).

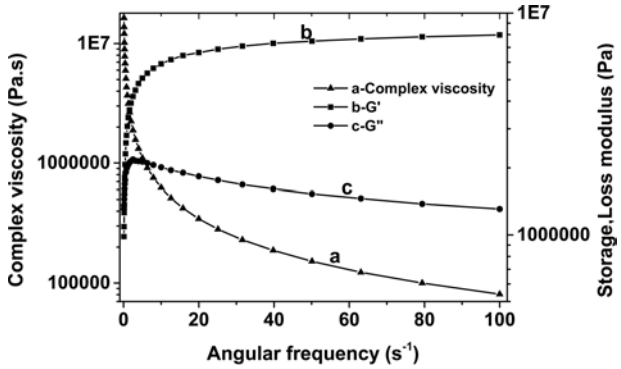

Fig. 14. Frequency sweep graph of a typical gelled emulsion (Naphthalene to aqueous alumina slurry volume ratio of 1 and alumina slurry concentration of 10 vol.%).

constants C and n as well as the correlation coefficient R^2 are given in Table 1. The model fitting with the compressive strength and Young's modulus data showed fairly high correlation co-efficient at all studied alumina slurry concentrations. The values of C and n for the relation between E/E_0 and ρ/ρ_0 are expected to be ~1 and ~2, respectively, for brittle open cellular foams with a cubic array of cells. On the other hand, the corresponding values expected for the relation between

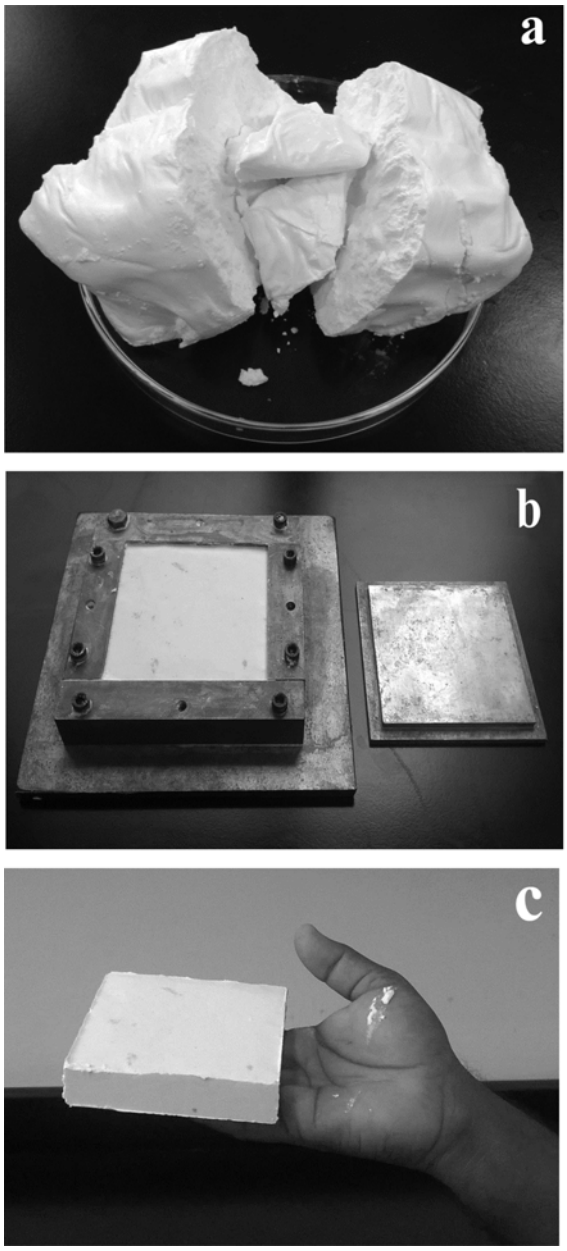

Fig. 15. Photographs of (a) gelled emulsion, (b) gelled emulsion moulded in a stainless steel mould and (c) the body after mould removal showing its stability during handling.

σ/σ_0 and ρ/ρ_0 are ~0.65 and ~1.5, respectively [31, 33, 34]. The values of C and n obtained in the present case differ from those values proposed by Gibson and Ashby. This difference is attributed to the deviation from the spherical shape of the cells and presence of micropores in the struts and cell walls.

Most of the practical applications require macroporous bodies in the form of rectangular tiles. Our attempt to fabricate rectangular bodies by casting the emulsions in stainless steel mould resulted in the formation of cavities in the casting due to the shrinkage during solidification [35]. Moulding of the gelled emulsion can be a solution for this problem. Gelled masses obtained by cooling

the naphthalene-in-aqueous alumina slurry emulsions have a paste-like consistency as evidenced from the rheological studies. Fig. 12 shows the results of strain sweep measurement carried out using a typical gelled emulsion. The gelled emulsions showed linear viscoelastic behavior up to a strain value of 0.1%. At larger values of strain, storage modulus (G'), loss modulus (G'') and complex viscosity of the gelled emulsions decreases with an increase in strain. This is typical behavior of a paste [36]. The observed storage modulus in the linear viscoelastic region for all the studied formulations is sufficiently high to form dimensionally stable bodies by moulding. The storage modulus in the viscoelastic region for the gelled emulsions falls within the ranges of 1×10^6 to 3×10^6 Pa. The time sweep measurement at a constant strain of 0.02% for a period of 25 minutes showed more or less constant value of storage modulus, loss modulus and complex viscosity indicating the stability of the gelled emulsions. Fig. 13 shows the results of time sweep measurement of a typical gelled emulsion. The frequency sweep measurement showed the graph corresponding to the variation of storage modulus and loss modulus with frequency is more or less parallel. The storage modulus value is much higher than the loss modulus. This behavior is characteristic of a gel [36]. Fig. 14 shows the results of frequency sweep measurement of a typical gelled emulsion.

The paste-like consistency of gelled emulsions enabled their shaping into rectangular bodies by compression moulding. Fig. 16 shows the photographs of a gelled emulsion and the same moulded in a rectangular steel mould. The emulsion bodies could be easily removed from the mould without any deformation. The bodies removed from the mould are stable for further handling during drying. The moulding of gelled emulsion is more productive as large volume of gelled emulsion could be easily prepared. Large bodies prepared by moulding the gelled emulsions did not show any crack during drying, naphthalene removal and sintering. Photographs of large sintered macroporous alumina bodies are shown in Fig. 15. The cylindrical body was prepared by casting naphthalene-in-aqueous alumina slurry emulsion in a glass mould and the rectangular body was prepared by moulding the gelled emulsion. The macroporous alumina ceramics obtained by moulding of gelled emulsions have similar porosity and microstructure as that obtained by casting of emulsion. The moulded body showed good surface finish compared to the cast one.

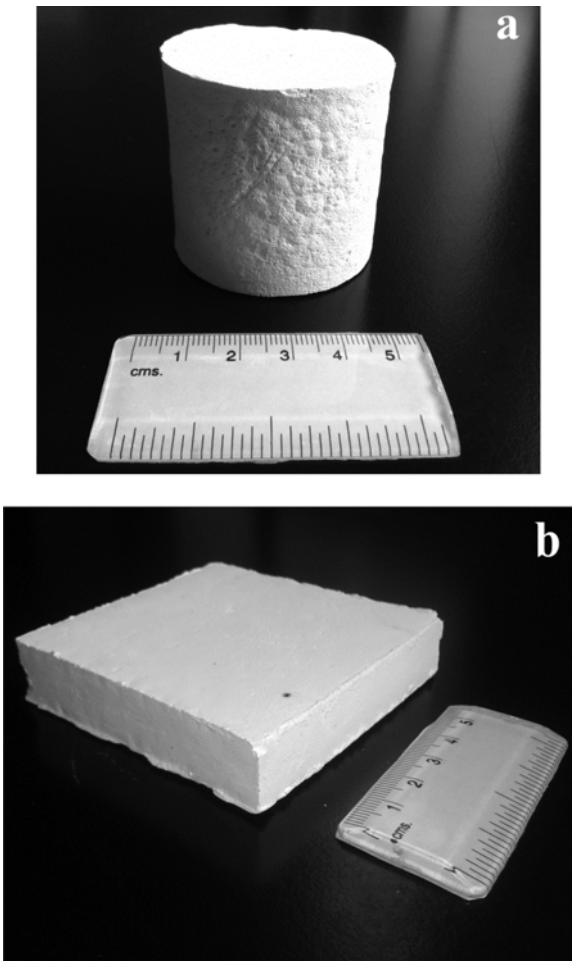

Fig. 16. Photographs of sintered alumina bodies fabricated by (a) casting naphthalene-in aqueous alumina slurry emulsion and (b) moulding the gelled emulsion.

Summary

Freeze-gelcasting of naphthalene-in-aqueous alumina slurry emulsions prepared from slurries of 10, 20 and 30 vol.% alumina concentration was studied to prepare macroporous ceramics of high porosity. The viscosity, shear thinning character and yield stress of the naphthalene-in-aqueous alumina slurry emulsions increased with an increase in naphthalene to alumina slurry volume ratio and alumina slurry concentration. The compressive strength and Young's modulus of the gelled emulsion bodies increased with an increase in naphthalene to alumina slurry volume ratio and decreases in alumina slurry concentration. Maximum porosity of the macroporous ceramics obtained at a naphthalene to alumina slurry volume ratio of 1.86 increased from 78 to 90% when the alumina concentration in the slurry decreased from 30 to 10 vol.%. The compressive strength and Young's modulus of the macroporous alumina ceramics obey the model proposed by Gibson and Ashby. The gelled emulsion showed paste-like consistency which enabled the preparation of macroporous alumina tiles by compression moulding.

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