Effect of dispersant on the rheological properties of gelcast fused silica ceramics

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Abstract. Fused silica ceramics with high flexural strength, low porosity, low dielectric constant and loss tangent were fabricated by gelcasting, a near-net shape fabrication technique. Fused silica suspensions with solid loading as high as 73 vol.% with low viscosity has been prepared using various dispersants in acidic and alkaline regions/medium. Commercially available Darvan 821A, Darvan C-N, Dolapix A88 and Dolapix CE64 were used as dispersants. Investigations were carried out to determine the suitable dispersant and effects of dispersant percentage, pH value, zeta potential, and solid loading on the rheological properties of the suspension. Darvan 821A showed better results in the suspension of fused silica particles in aqueous gelcast system. At 1250°C the flexural strength of fused silica bodies is as high as 52.3 MPa, and the dielectric constant and loss tangent (1 MHz) were as low as 3.25 and $1.52 \times 10^{-3}$ for solid loading of 70 vol.% respectively. Such properties are highly desirable for ceramic radomes used in lower range missiles.

1. Introduction

Fused silica is a non-crystalline form of silicon dioxide (quartz, sand) commonly made by fusion of pure silica sand [1]. Nowadays fused silica is one of the essential materials for many engineering and aerospace applications such as radomes, heat shields, antenna window, and crucibles[2-5], because of its interesting and prominent properties such as low coefficient of thermal expansion, low thermal conductivity, low dielectric constant, low loss tangent, low density, high chemical stability, high corrosion resistance, high softening temperature, high thermal shock resistance and good mechanical properties at high temperatures [6-8].

Ceramic components can be fabricated by various conventional forming techniques such as hot pressing, slip casting, cold isostatic pressing, tape casting, injection molding, freeze casting, and recently gelcasting [9]. Gelcasting is the most suitable process for fabrication of ceramics components with complex shape and near net shape. Certain advantages of gelcasting such as high green strength, uniformly dense, defect free and green machinability are due to its considerations as an attractive manufacturing process for manufacturing complex shapes including radomes [10]. This process was developed by Janney and Omate [11] at Oak Ridge National Laboratory, which involves the dispersion of ceramic powders in aqueous/non-aqueous solvents mixed with monomer, binder, initiator, and/or catalyst forming slurry. The slurry is then poured in to the mold having complex shape cavity where in situ polymerization of slurry takes place to form a polymer-solvent gel. This can be initiated by either by adding catalyst or heat. In gelcasting the density of ceramic components depend
on the solid loading in the slurry, which depends on dispersant type and concentration, and pH of the medium [12].

The main objective of present work is to determine the suitable dispersant and effects of dispersant percentage, pH value, zeta potential, and solid loading on the rheological properties of fused silica ceramics.

2. Experimental Procedure

2.1. Materials

Commercial fused silica powder of 99.9% purity (M/s. Ants Ceramics Pvt. Ltd., Thane, India) with an average particle size of 1-5 μm having density of 2.2 g/cm³ was used in this study. The chemical composition of fused silica powder is given in table 1 and the morphology is shown in figure 1. Deionised water was used as solvent.

| Chemical name      | SiO₂ | Al₂O₃ | Fe₂O₃ | Na₂O | K₂O | CaO | MgO |
|--------------------|------|-------|-------|------|-----|-----|-----|
| Content (%)        | 99.9 | 0.04  | 0.05  | 0.005| 0.004| 0.003| 0.003|

![SEM micrograph of fused silica powder.](image)

Figure 1. SEM micrograph of fused silica powder.

In the process of gelcasting methacrylamide (CH₂=C(CH₃)CONH₂) (Alfa Aesar) and N,N'-methylenebisacrylamide ((CH₂=CHCONH)₂CH₂) (Alfa Aesar) were used as organic monomer and cross-linker respectively. Ammonium persulfate, (NH₄)₂S₂O₈ (Alfa Aesar) was used as an initiator. Dispersants such as Darvan 821A, Darvan C-N, Dolapix A88 and Dolapix CE64 were used for dispersing fused silica in slurries for high solid loading and low viscosity.

| Dispersant     | Manufacturer            | Chemical basis                              |
|----------------|-------------------------|---------------------------------------------|
| Darvan 821A    | R.T. Vanderbilt, Norwalk, CT | Poly(acrylic acid)- ammonium salt          |
| Darvan C-N     | R.T. Vanderbilt, Norwalk, CT | Ammonium polymethacrylate                  |
| Dolapix CE64   | Zschimmer & Schwarz, Lahnstein, Germany | Carboxylic acid preparation              |
| Dolapix A88    | Zschimmer & Schwarz, Lahnstein, Germany | Amino alcohol                              |
The description of dispersants was shown in table 2. Surface exfoliation phenomenon green bodies cast in air was eliminated by adding Polyethylene glycol 400 (Alfa Aesar). Diluted HNO₃ and NaOH (both S.D. fine chemicals, India) were used for pH adjustment.

2.2. Slurry preparation
The detailed flowchart of gelcasting process is shown in figure 2. Firstly, premix solution was prepared by completely dissolving known amounts of dispersant (0-0.75 wt%, based on fused silica concentration), PEG (3 wt%, based on fused silica concentration), MAM and MBAM (10 wt%, based on fused silica concentration in the ratio of 5:1) in deionised water by magnetic stirring (5MLH, Remi, India).

![Flowchart of gelcasting process](image)

**Figure 2.** Detailed flowchart of gelcasting process.

Secondly, fused silica powder was added in regular intervals for homogenous dispersion of ceramic particles into the premix solution by magnetic stirring for about 6 h in a glass beaker. Then the slurry was degassed for 20-25 min in a vacuum deaeration container after addition of APS (1 wt% of monomers). Gelation of the slurry can be accelerated using catalyst or heat driven process. Addition of the Catalyst, \( N,N,N,N'\text{-tetramethylethylenediamine (TEMED) caused immediate consolidation of the slurry, and acceleration of the reaction was too fast to be under control. Hence, heat driven process is applied for gelation of the slurry. The slurry was casted into a nonporous glass mold and soaked at 75-80 °C for 1 h for polymerization to take place. After gelation the green part was demolded, and dried under controlled temperature and humidity conditions to avoid cracking and deformations caused by rapid drying. The green bodies were sintered in a high temperature muffle furnace with molybdenum disilicide (MoSi₂) as heating elements, under air atmospheric conditions at 1º/min upto 600ºC and...
soaked for 1 h to pyrolyze organic compounds. Then these were heated at 2º/min to the sintering temperature of 1300ºC and were soaked for 3 h.

2.3. Characterization

X-ray diffractometer (PANalytical X’Pert Powder, Almelo, Netherlands) was used to observe the phase formation behavior of sintered bodies. The morphology and microstructure of as-received powder and gelcast bodies were observed by scanning electron microscope (VEGA 3 LMU, TESCAN, Czech Republic). Zeta Potential Analyzer (Zetasizer Nano ZS, Malvern Instruments Ltd, UK) was used to determine the Zeta potential. The pH of slurry was measured by a digital pH meter (Digisun Electronic, Hyderabad, India) and a stress-controlled rotational rheometer (Anton Paar 1000; Anton Paar Instruments, Graz, Austria) was used to determine rheological properties of the slurries with different solid loadings. The viscosities of the slurries were measured at a shear rate ranging from 0.1 to 100 s⁻¹ with a parallel plate geometry (25 mm in diameter) at room temperature. The samples were cut into rectangular bars of dimensions 3mm x 4mm x 40mm using high speed diamond cut-off saw (MTI corporation, USA) to measure flexural strength by the three-point flexural method with a span length of 30 mm and at a crosshead speed of 0.5 mm/min using an universal testing machine (H10K-S, Tinius Olsen Testing Machine Company, USA). Bulk density and apparent porosity of bodies were measured by Archimedes principle using kerosene as solvent. Dielectric constant and loss tangent were measured by impedance analyzer at 1 MHz (MTZ-35, Bio-Logic, France).

3. Results and Discussion

3.1. Zeta potential and pH value

The potential difference between the dispersion medium (solvent) and the stationary layer of fluid attached to the dispersed ceramic particle is the zeta potential. The factors influencing the fluidity and stability of the slurry are its pH value and dispersant. To improve the dispersion of ceramic particles in solvent, dispersants are added. The relation between stability and zeta potential is that the ceramic particles with higher absolute value of zeta potential exhibit higher stability due to the higher electrostatic repulsion between particles in slurries. The zeta potential of fused silica slurries with various dispersants varying in the range 0-0.75 wt% as a function of pH value are shown in figure 3.

![Figure 3. Zeta potential of fused silica with various dispersants and wt%](image-url)

Figure 3. Zeta potential of fused silica with various dispersants and wt%.
The zeta potential of fused silica particles without dispersant vary from 6.61 mV at pH 1 to -45.9 mV at pH 9. It can be seen that the isoelectric point (IEP) is at pH 2.4 and the absolute value of zeta potential increases as pH value increases, but in some cases zeta potential is decreased. It is observed that, of all the dispersants addition of 0.5 wt% Darvan 821A gives the maximum value of zeta potentials which is about -68.6 mV at pH 11, which is most suitable for obtaining well dispersed fused silica slurries. Other than 0.5 wt% Darvan 821A are 0.75 wt% Dolapix A88, 0.25 wt% Darvan 821A, 0.25 wt% Darvan CN, 0.75 wt% Dolapix CE64 and 0.5 wt% Dolapix A88 shows the zeta potential values of -52.9 mV, -51.9 mV, -51.8 mV, -48 mV and -47.5 mV at pH 11 respectively. The zeta potentials of the remaining slurries are lower than that of slurry without dispersant.

The pH value of slurry also plays an important role on the rheological properties of slurries. It is observed that high absolute zeta potential value is obtained by increasing the pH value which increases the dispersability of the slurry. But at higher pH values, the slurry becomes thick and the viscosity rises sharply due to the formation of hydroxide layer on the surface of fused silica particles and this process is known as hydolyzation. Diluted HNO$_3$ and NaOH were used for adjusting the pH value of the slurries about 4-4.5 based on the previous studies.

3.2. Dispersant

To control the dispersion of powder particles in slurry, dispersants are added. The effect of dispersant on the interaction of particles in slurry can be observed in figure 4.

![Image of ceramic particles](a) Dispersion
(b) Weak Flocculation
(c) Coagulation

**Figure 4.** Illustration of ceramic particles
(a) Dispersed system, (b) & (c) Non-Dispersed system.

The uniformity of powder dispersion in the gelcasting method allows for uniform sintering, and high relative density is easily reached when gels are produced with high solids loading. In gelcasting process the homogenous particle dispersion allows to obtain uniform sintering and high relative density when the castings are produced with high solids loading [13] It is therefore necessary to understand how an optimum suspension of ceramic particles can be created [14]. The zeta potential of fused silica slurry is higher at 0.5 wt% of Darvan 821A as shown in Figure.3. Each type of dispersant gives a different zeta potential value at particular amounts. Fused silica ceramics without addition of dispersant shows a maximum zeta potential value of -34.5 mV at pH 5 respectively, which shows that the slurry at pH 4-4.5 can be gelcasted without addition of dispersant.

3.3. Solid loading

Higher solid loading of fused silica slurries is required to improve the mechanical properties of gelcast bodies. But viscosity increases as the solid loading increases which makes the slurry difficult to cast in
the mold. This is due to flocculation and coagulation caused by the reduction of solvent (water) present in between the ceramic particles. Slurries with viscosity lower than 1 Pa.s at the shear rate of 20 s\(^{-1}\) are suitable for casting in to the mold with better fluidity [15, 16]. Hence slurry with 73 vol.% solid loading and 0.5 wt% Darvan 821A is suitable for casting in to the mold. The variation of viscosity as a function of the shear rate ranging from 0.1–100 s\(^{-1}\) for different solid loadings is shown in figure 5.

![Figure 5](image.jpg)

**Figure 5.** Variation of viscosities of the slurry at various solid loadings.

The amount of dispersant, Darvan 821A was 0.5 wt% based on the weight of fused silica powders. From the curve it can be seen that there is an increase in viscosity from 0.224 to 0.352 Pa.s for increase in solid loadings from 60 to 70 vol.% and for solid loading 73 vol.% viscosity is 0.465 Pa.s with shear thinning behaviour at the shear rate of 1–20 s\(^{-1}\) and over this shear rate exhibited shear-thickening behaviour. The increase in viscosity is due to the agglomeration at high solid loadings.

3.4. Mechanical Properties

The microstructure of sintered fused silica ceramics is shown in Figure 6. The variation of bulk density and apparent porosity of fused silica ceramics with 0.5 wt% Darvan 821A as a function of solid loading for sintered ceramics are shown in Figure 7.

![Figure 6](image.jpg)

**Figure 6.** SEM micrograph of sintered fused silica ceramics.

![Figure 7](image.jpg)

**Figure 7.** Bulk density and apparent porosity of sintered bodies.
As the solid loading increases from 60 vol.% to 73 vol.%, the bulk density increases from 1.52 to 1.88 g/cm³ and the apparent porosity decreases from 41.94 to 32.71% respectively. This variation is due to flocculation and coagulation.

The variation of flexural strength with sintering temperature is shown in figure 8. It can be seen that the flexural strength gradually increases with the increase in sintering temperature up to 1250 °C and on further increase of temperature flexural strength is decreased. This is because of the formation of cristobalite due to excessive crystallization of the silica. Cristobalite has a coefficient of thermal expansion (0.27 × 10⁻⁶/°C) much higher than that of amorphous silica (0.54 × 10⁻⁶/°C) and its strength is less than that of amorphous silica [17]. Also upon cooling, cristobalite will undergo a phase transformation from α to β that leads to volume variation and micro cracks are formed which are observed in silica ceramics sintered at 1300 °C that reduce the strength of sintered fused silica ceramics. XRD patterns of fused silica sintered at various temperatures can be seen in figure 9. The maximum flexural strength obtained for sintered fused silica ceramics is 52.3 MPa at 1250 °C.

![Figure 8. Effect of sintering temperature on flexural strength.](image1)

![Figure 9. XRD patterns of sintered fused silica ceramics.](image2)

The dielectric constant and loss tangent (1 MHz) of fused silica ceramics obtained at 1250 °C with 70 vol.% were 3.25 and 1.52×10⁻⁶ as shown in figure. 10. Dielectric constant normally relies on the porosity of materials. The dielectric constant increases gradually with increase in sintering temperature. However the loss tangent decreases and increases with sintering temperature. These are due to excessive crystallization and formation of cristobalite which deteriorates the dielectric properties.

![Figure 10. Effect of sintering temperature on dielectric constant and loss tangent.](image3)
4. Conclusions
Aqueous gelcasting is used to fabricate fused silica ceramics with superior properties. Darvan 821A is used as dispersant and a dosage of 0.5 wt% showed better results over other dispersants in the suspension of fused silica particles. Solid loading as high as 73 vol.% with low viscosity and good fluidity are obtained. The maximum flexural strength obtained is as high as 52.3 MPa for a solid loading of 70 vol.% respectively. The dielectric constant and loss tangent (1 MHz) of fused silica ceramics were as low as 3.25 and 1.52×10⁻³ respectively.

5. References
[1] Wan W, Huang C, Yang J, Zeng J and Qiu T 2014 Effect of sintering temperature on the properties of fused silica ceramics prepared by gelcasting Journal of Electronic Materials 43 2566-2572.
[2] Zhu Y, Pan Y, Xu H and Guo J 2009 Investigation of the devitrification and microwave penetrating properties of fused silica Journal of Non-Crystalline Solids 355 785–790.
[3] Qi G J, Zhang C R and Hu H F 2006 Continuous silica fiber reinforced silica composites densified by polymer-derived silicon nitride: Mechanical properties and microstructures Journal of Non-Crystalline Solids 352 3794-3798.
[4] Yan W W, Shi L Y, Yuan S, Zhao Y, Fang J H, and Zhao J 2010 Single-step synthesis of nanoporous silica colloids Mater. Lett. 64 1208-1210.
[5] Han J C, Hu L Y, Zhang Y M, Jiang Z H and Zhou Y F 2010 In situ synthesis of hierarchically porous silica ceramics with unidirectionally aligned channel structure Scr. Mater. 62 431–434.
[6] Wen G, Wu G L, Lei T Q, Zhou Y and Guo Z X 2000 Co-enhanced SiO₂-BN ceramics for high-temperature dielectric applications J. Eur. Ceram. Soc. 20 1923–1928.
[7] Haris J N and Welsh E A 1973 Fused Silica Design Manual, AD-766494.
[8] Smith D G and Chowdary M 1975 The fracture toughness of slip-cast fused silica Mater. Sci. Eng. 20 83-88.
[9] Kandi K K, Thallapalli N and Chilakalapalli S P R 2015 Development of silicon nitride-based ceramic radomes — a review Int. J. Appl. Ceram. Tec. 12 909–920.
[10] Wang S H, Cui W L, Yang X F, and Yuan X D 2007 Forming of large thin walled fused silica shapes by gelcasting Key Eng. Mater. 336 1005-1008.
[11] Janney M A and Omate O 1991 Method for molding ceramic powders using a water-based gel casting, U.S. Patent 5028362 A.
[12] Omate O, Janney M A, and Nunn S D 1997 Gelcasting: from laboratory development toward industrial production, J. Eur. Ceram. Soc., 17 409–413.
[13] Shanti N O, Hovis D B, Seitz M E, Montgomery J K, Baskin D M, and Faber K T 2009 Ceramic laminates by gelcasting, Int. J. Appl. Ceram. Tec. 6 593–606.
[14] Sigmund W M 2000 Novel powder-processing methods for advanced ceramics J. Am. Ceram. Soc. 83 1557–74.
[15] Li Y and Guo Z 2008Gelcasting of WC–8wt%Co tungsten cemented carbide International Journal of Refractory Metals & Hard Materials 26 472–477.
[16] Kong D, Yang H, Wei S, Li D and Wang J 2007 Gel-casting without de-airing process using silica sol as a binder Ceram. Int. 33 133–139.
[17] Wan W, Yang J, Zeng J and Qiu T 2013 Gelcasting of fused silica glass using a low-toxicity monomer DMAA Journal of Non-Crystalline Solids 379 229–234.