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Effect of Monomers Content and their Ratio on Gelcasting of Fused Silica Ceramics

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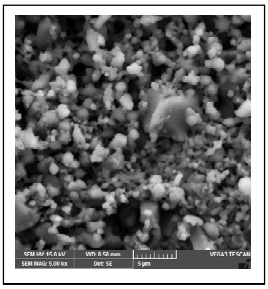
ABSTRACT

Fused silica ceramics with high flexural strength, and low warpage and shrinkage were casted using gelcasting, a near net shape fabrication technique. Methylacrylamide (MAM) and N,N′-methylenebisacrylamide (MBAM) were used as monomers. The effects of monomers content (MAM and MBAM) and their ratio (MAM/MBAM) on the flexural strength, warpage and shrinkage rates on fused silica ceramics were investigated. The warpage and shrinkage rates of fused silica bodies decreased with increasing monomers content, while by increasing the ratio of monomers, warpage and shrinkage rates got increased. Flexural strength of the green body also decreased with increasing mononers content. With the increasing ratio of monomers, the flexural strength first increased and then decreased, indicating that there is an optimum value for the ratio of monomers. The maximum flexural strength obtained in this study was as high as 43.2 MPa.



[Keywords: Gelcasting, Fused silica, Monomers, Flexural strength, Warpage, Shrinkage]

Introduction

Fused silica has good thermal shock resistance, very low thermal expansion, low dielectric constant and loss tangent, high chemical resistance and excellent optical qualities.[1–4] It is used for antenna windows, heat shields, insulators for electronic applications, aerospace applications and for semiconductor manufacturing.[5–8] Fused silica is a non-crystalline form of silicon-di-oxide.[9]

Nowadays ceramic composites are used widely in many applications by combining different ceramic materials. Advanced ceramics possess some superior properties such as higher strength, lower environmental impact and better reliability. Nevertheless, higher cost and shape limitation hinder further development and wider application of ceramics. Therefore, developing a new process for making complex-shaped ceramics with lower cost is required.

About a decade ago Oak Ridge National Laboratory (ORNL) developed a new ceramics forming process called gelcasting.[10] In gelcasting, concentrated ceramic slurry is created by mixing ceramic powder and monomer solution. After this, ceramic suspension is poured into a mould to get the desired shape, and during heating *in-situ* polymerization takes place to form a green body. The green body is then dried in controlled humidity conditions and further sintered for binder removal. Monomer and cross-linker will hold the ceramic particles together by forming macromolecular network and helps in the formation of pores in the ceramic body.[11] Warpage, shrinkage and flexural strength of the fused silica body can be affected by increasing the monomers content. The effect of various parameters, such as monomers content, drying conditions and its geometry on the warpage and shrinkage have been investigated by Erik Adolfsson;[12] it has been found that uniform drying under controlled conditions and symmetrical geometry reduce the warpage and shrinkage of the green body.

Shrinkage in green body during drying can be decreased by higher monomers content. The problems associated with cracking and warping will be reduced by lower shrinkage. Shrinkage of green body will lead to warpage during drying and the three dimensional network of the cross-linked polymers will collapse. Too higher solid loading will lead to increase in viscosity which makes the slurry difficult to cast into mould. An appropriate dispersant is added for attaining the flowability in the slurry.

So far not much work has been done on the preparation of fused silica ceramics using gelcasting by increasing the monomers content. In the present work, preparation of fused silica ceramics by merely increasing the monomers content is done. The monomers content and their ratio both affect the properties of the green component and finally the sintered fused silica component.

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Experimental Procedure

Materials

A commercial fused silica powder of 99.9% purity (M/s Ants Ceramics Pvt Ltd, Thane, India) with 1-5 μm average particle size and 2.2 g.cm^{-3} density, and commercially available dispersant Darvan 821A were used in this study. Methylacrylamide (MAM) was used as monomer, N,N′-methylenebisacrylamide (MBAM) as cross-linker, polyethelene glycol 400 (PEG-400) as surfactant and ammonium persulfate (APS) as initiator (all Alfa Aesar). Diluted HNO_3 and NaOH (both S. D. fine chemicals, India) were used for pH adjustment and distilled water as solvent.

Slurry Preparation

The flow chart of gelcasting is shown in Fig. 1. Gelcasting of fused silica was carried out using different monomers content and also at different monomers ratio. Firstly premix solution was prepared by mixing Darvan 821A dispersant (1 wt% monomer content), PEG (surfactant), monomers MAM and MBAM (10-30 wt% fused silica) in distilled water by magnetic stirring. After that solid loading of 65 vol% fused silica was added to the premix solution and stirred for about 6 h. The slurry was deaired for 15-20 min and then the initiator ammonium persulfate APS (1 wt% monomer content) was added for initiating polymerization. Finally, the slurry was cast into a glass mould and heated at 75°-80°C for 1 h for polymerization to take place. After the monomers had polymerized, the green bodies were demoulded. The samples were then dried in a controlled humidity oven for 24 h. Then binder burnout was carried out in a high temperature furnace at 600°C for 1 h with a heating rate of 2°C/min. The samples were then sintered at 1250°C with a heating rate of 4°C/min for 3 h in air atmosphere. These experiments were done for different monomers contents up to 30 wt% and different monomers ratios 3, 5, 10 and 15.

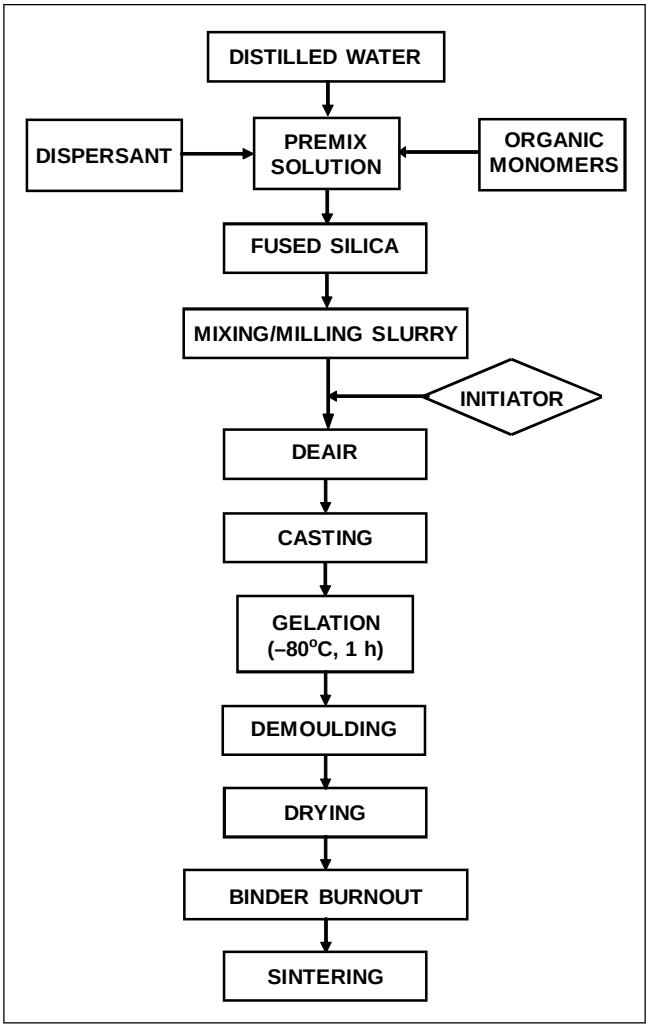

Fig. 1 – Flow chart showing gelcasting process

Characterization

X-ray diffractometer (PANalytical X'Pert Powder, Netherlands) was used to observe the patterns behaviour of as-received powder. The morphologies of as-received powder and gelcast green bodies were observed by scanning electron microscope (VEGA 3 LMU, TESCAN, Czech Republic). pH of the slurry was measured using a digital pH meter (Digisun Electronic, India), and a stress-controlled rotational rheometer (Anton Paar 1000, Anton Paar Instruments, Austria) was used to determine rheological properties of the slurries with different solid loadings. Viscosities of the slurries were measured at shear rates ranging from 0.1 to 100 s^{-1} with parallel plate geometry (25 mm in diameter) at room temperature. The samples were cut into rectangular bars of dimension 3 × 4 × 40 mm^3 from a square block of 5 × 50 × 50 mm^3 by removing the warped surface, using a high speed diamond cut-off saw (MTI corporation, USA) to measure flexural strength by 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). The % warpage (W) and % shrinkage (S) were calculated using the following equations:

$$W = \frac{h - h'}{D} \times 100\% \quad ..(1)$$

where h is the maximum height of the green body after drying and h' is the height of the green body before drying.

$$S = \frac{D' - D}{D} \times 100\% \quad ..(2)$$

where D' and D are the diameters of the green body before drying and after drying, respectively.

Results and Discussion

The morphology and XRD patterns of fused silica are shown in Figs. 2a and 2b, respectively. Solid loading was kept constant to investigate the influence on the shrinkage and warpage rate, and flexural strength. Figure 3 shows the microstructure of fused silica sintered body with non uniform distribution of fused silica particles at 30 wt% monomers content and monomers ratio 15. The rheology of slurries was investigated and is shown in Fig. 4. The

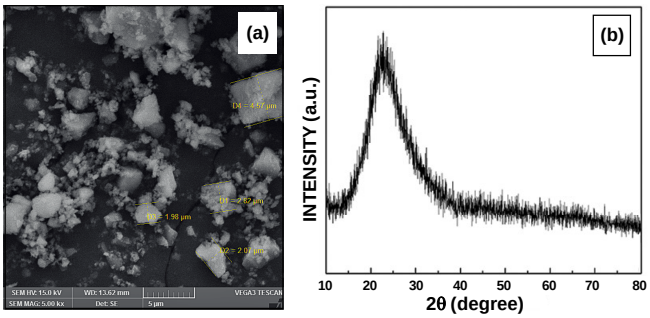

Fig. 2 – (a) Morphology, (b) XRD patterns of fused silica powder

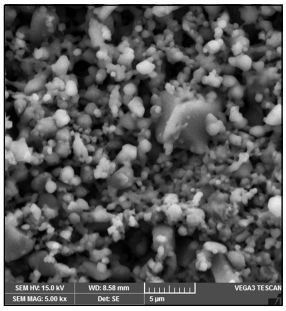

Fig. 3 – SEM picture of fused silica sintered body

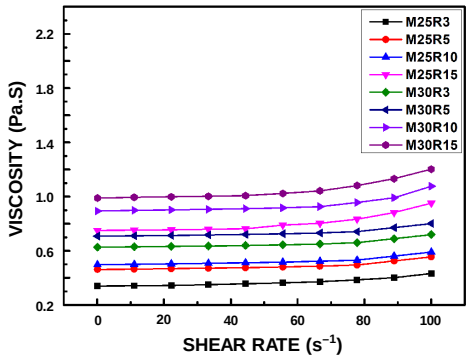

Fig. 4 – Variation of viscosity of the slurries at various monomers content and their ratio

pH of the slurries was adjusted to 4-4.5 based on the previous studies to avoid hydrolyzation[13] using diluted HNO_3 and NaOH. Slurries having viscosity below 1 Pa.s at shear rate around 20 s^{-1} are suitable for pouring into mould with better fluidity.[14] Figure 4 shows that on increasing the monomers content and monomers ratio, the viscosity increases marginally from 0.34 to 0.99 Pa.s and the slurries exhibit shear thickening behaviour due to the formation of three dimensional structural network.

Warpage and Shrinkage

The green bodies with smooth surface were obtained as the surface exfoliation was avoided by the addition of PEG-400. There were significant changes in the warpage of fused silica green bodies due to different monomers content and their ratio in the fused silica bodies.

The effect of monomers content and their ratio on % warpage and % shrinkage are shown in Figs. 5a and 5b,

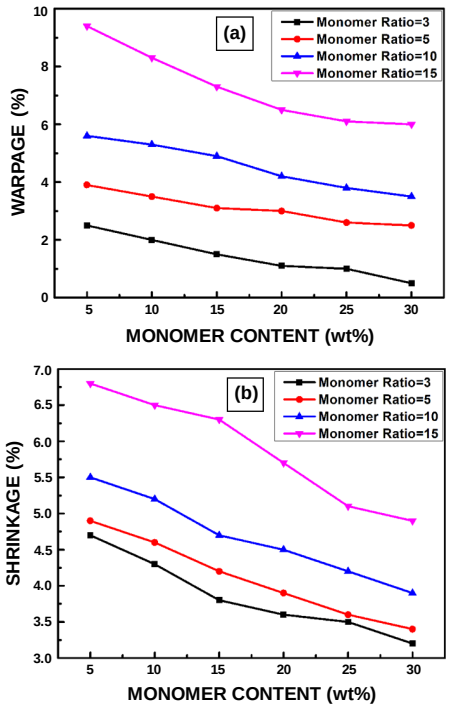

Fig. 5 – Effect of monomers content and their ratio on fused silica green body as a function of (a) warpage, (b) shrinkage

respectively. The % warpage and % shrinkage of fused silica bodies got reduced with increase in the monomers content; by increasing the ratio of monomers the % warpage and % shrinkage got increased. The result of differential shrinkage is warpage. The green body does not warp or deform but reduce dimensionally, if the shrinkage in body is uniform throughout. The most important factors that influence % warpage and % shrinkage during drying are density, homogeneity and strength of the three dimensional network. Internal stresses due to non symmetrical shrinkage during drying cause warpage. While drying the green body, the moisture by capillary action is transported to the surface of the body and evaporated at constant rate to the atmosphere; during this process compressive stresses are formed. The polymer network collapses due to these stresses, and the fused silica particles, attached to the network, move towards each other that causes shrinkage. The movement of particles ceases once they all touch each other. Figures 6a and 6b show warpage and shrinkage in green gelcast samples,

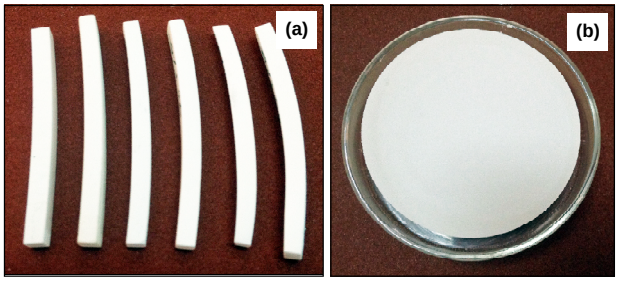

Fig. 6 – (a) Warped samples, (b) shrinked sample

respectively. The % warpage and % shrinkage in sintered samples were very less than those in green samples and the maxima were about 2.15% of the total volume.

Flexural Strength

The effects of monomers and their ratio on the flexural strength of green and sintered bodies are shown in Figs. 7a and 7b, respectively. Flexural strength was performed on samples after removal of warped surface. As the monomers content increases, the flexural strength of the green body increases. As the ratio of monomers increases the flexural strength increases, reaches maximum value and then decreases which shows that there is an optimum value in the ratio of monomers. In sintered bodies the flexural strength reaches maximum and gets reduced as the monomers content increases. During organic binder burnout the pores were formed which affects the flexural strength in sintered bodies. If the ratio of monomers is low, the flexural strength of green body remains low as the three dimensional network structure is too coarse, and if the ratio of monomers is high the three dimensional network structure is too loose that results in the non-uniform distribution of fused silica particles which causes decrease in the flexural strength.[15] The three dimensional network structures are compact at optimum ratio of monomers and the distribution of fused silica particles is uniform. The maximum flexural strength obtained in this study is as high as 43.2 MPa at monomers content 10 wt% and ratio of monomers 10.

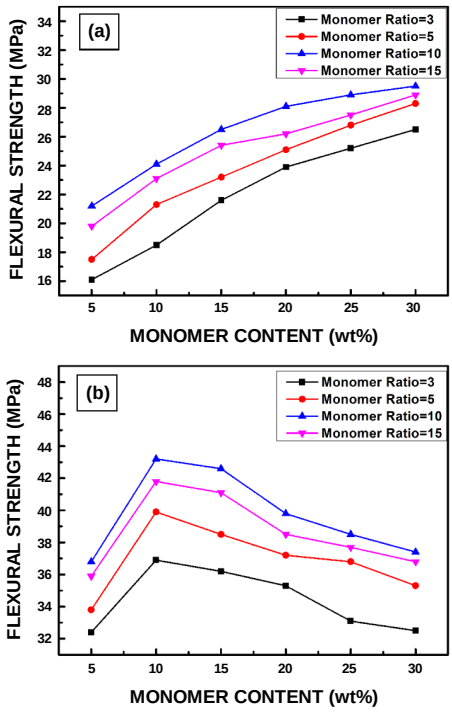

Fig. 7 – Effect of monomers content and their ratio on flexural strength of fused silica (a) green body, (b) sintered body

Conclusions

Gelcasting process was employed in this study to prepare fused silica ceramics. The effect of monomers content and their ratio on % warpage, % shrinkage and flexural strength of fused silica bodies were investigated. % warpage and % shrinkage were decreased by increase in the monomers content. However, by increasing the ratio of monomers the % warpage and % shrinkage were increased. As the monomers content increased the flexural strength of green bodies increased, while in sintered bodies, the flexural strength reached maximum and got reduced as the monomers content increased. Flexural strength increased with increase in ratio of monomers, reached maximum value and then decreased, which shows that there is an optimum value in the ratio of monomers. The flexural strength obtained was as high as 43.2 MPa at monomers content 10 wt% and ratio of monomers 10.

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