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Rheology and gelation behavior of gel-cast cordierite-based glass suspensions

H. Bartar Esfahani, B. Eftekhari Yekta *, V.K. Marghussian

School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Narmak, Tehran 16846-13114, Iran

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Abstract

A cordierite-based glass suspension was shaped by gel-casting method. Effects of various parameters like pH, volume fraction of glass particles, gelling agents and dispersant on the rheology of the prepared slurries were investigated. The results demonstrated that using sodium tripolyphosphate (STPP) dispersant brings about a suspension of minimum viscosity. The bending strength of the dried gels was increased with the gelling agents. In addition, the utilization of cross linkers at a fixed concentration of monomer led to the gradual enhancement of the bending strength of the dried bodies. A bending strength of ~11 MPa was obtained for the most promising dried gel cast bodies.

Keywords: Gel casting; Cordierite glass ceramics

1. Introduction

It is known that using colloids for making ceramic bodies have many benefits which are achievable by controlling the interaction forces between particles in suspension [1]. The interaction forces in colloid systems are considered as the Van der Waals and electrostatic forces and steric hindrance [2,3]. The latter mechanism involves the addition of chain-like molecules that are adsorbed onto the ceramic particles and provides a buffer zone around each particle.

In production of ceramic green bodies by casting methods, reducing the amount of liquid phase and simultaneously keeping the viscosity of the system within an acceptable range play important roles [2]. Otherwise, there will be a high probability of non-uniformity and distortion of the produced body, as a result of its low green density [1]. In order to avoid such problems, different methods based on gelation of the slurries has been established, including water-assisted injection molding, gel casting and direct coagulation casting.

Gel casting is a relatively simple process for producing a body with final dimensions close to its initial green size. In this method, ceramic slurry containing polymerizable additives is poured into a mold of the desired shape. Hence the particles without having the opportunity of settling down in the slurry adhere to each other due to the occurrence of gelation process and adopt the shape of the mold. Finally, the body after being removed from the mold is dried and sintered.

Both aqueous and organic solutions can be used in gel casting process; however, because of environmental reasons, aqueous solutions are more attractive [2–7].

One of the main advantages of the method is the relatively small amounts of organic matters (2–6 wt%) and catalysts used in this process [4]. Depending on the density of the ceramic powders, high amounts of solid particles, e.g. 72–85 wt%, can be used in the suspension. This high concentration of solid material causes lower drying and firing shrinkages of the body [1].

Green bodies prepared by this process have high bending strength values (3–4 MPa), so that they can be machined easily without the risk of cracking.

Various bodies with different densities, ranging from fully dense to highly porous, have been produced by the gel casting method [8–10]. Furthermore, this method has the capability of producing bodies weighing from <1 g up to >6 kg. Complex shapes with thin sections as small as 0.2 mm can also be produced by this method [11].

In the present work the role of commonly used deflocculates, monomers, initiators and catalyst substances on the rheology

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* Corresponding author. Tel.: +98 21 77240157; fax: +98 21 77240480.
E-mail address: beftekhari@iust.ac.ir (B. Eftekhari Yekta).

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and gelation behavior of cordierite-based glass slurries and the green bend strength of the resulting bodies have been studied.

The sintering and crystallization behavior of the green bodies, in order to convert them to cordierite glass ceramics, have also been investigated. The results of these studies would be published separately.

2. Experimental procedure

The chosen glass composition containing 49.02 SiO_2, 33.35 Al_2O_3, 13.19 MgO, 2.96 V_2O_5 and 1.5 BaO (wt%) previously has successfully been converted to cordierite glass ceramics [12].

The raw materials used to make the glass were acid washed silica sand ($SiO_2 > 99.8\%$) and reagent grade aluminum hydroxide (BDH 3059090), magnesium oxide (Applichem A2387.1000), vanadium oxide (Merck 8240250) and barium carbonate (Merck 1714). The thoroughly mixed materials were melted in an alumina crucible at 1630 °C in an electric kiln for 1 h. The molten glasses were then quenched in cold distilled water.

The obtained frits were ground in a planetary mill for various times until its particle size distribution lied exactly within the Andreasen range. The particle size distribution of glass powder was determined by a Laser particle size analyzer (Analysette 22, Fritch, Idar-Oberstein, Germany).

Acryl amide (AM) (Merck Prolabo 79-06-1), N′,N-ethylene bisacrylamide (MBAM) (Merck Prolabo 110-26-9), ammonium persulfate (APS) (Merck 1.01201.0500) and tetra methyl ethylene diamine (TEMED) (Merck 1.10732.0100) were used as monomer, cross linker, reaction initiator and catalyst, respectively.

The slurries were prepared by dispersing the glass powder in a water-based solution of the monomers and dispersant, and finally with the addition of the initiator and the catalyst.

The slurries after stirring for 5 min were cast into a polyethylene container and held for 24 h at room temperature to ensure a complete polymerization. The polymerized samples after removing from the mold, first dried naturally at room temperature for 48 h and then in an electric dryer at 80 °C for 24 h.

The rheological behaviors of suspensions were examined in increasing and decreasing rates of shear, using a rheometer (Physica MCR 300).

The flexural strength of dried samples was determined according to ASTM D720 procedure.

3. Results and discussion

It is known that if the particle size distribution of a solid material in a suspension is located within a certain range as determined by Andreasen, the viscosity of suspension could be minimized [13]. Fig. 1 shows the particle size distribution of the used glass powder and the two extremes estimated by the Andreasen equation. Obviously, the particle size distribution of the ground glass powder is located within the Andreasen extremes.

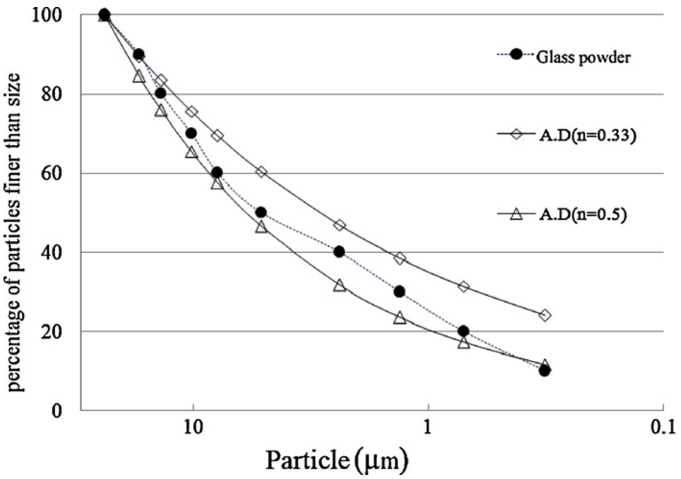

Fig. 1. Particle size distribution of the used glass powder and the two extremes estimated by the Andreasen equation.

Fig. 2 shows the viscosity of suspensions containing 70 wt% glass powders as a function of shear stress for various pH values of 3, 4, 8 and 12, in both increasing and decreasing shear rate modes. It should be noted that the maximum viscosity in each graph indicates the starting point of experiment, and the right and left hand branches of each curve belongs to the rising and falling runs of the shear rate, respectively. The rising and falling runs of shear rates have been illustrated by the right and left direction arrows in the figures.

It can be seen that each suspension shows a hysteresis in its viscosity–shear stress behavior and a higher viscosity is observed when the measurement was carried out by the gradual increase of shear rates rather than the decrease of the rates. The hystereses reveal that all of the suspensions have a shear thinning and/or thixotropy behavior which is less intense for suspensions with higher pH values. The latter suspensions also have the lowest viscosity values. As this behavior is influenced by dispersion or agglomeration of the particles in suspensions, it can be said that more disperse suspensions are those having higher pH values. Therefore, the pH value of 12 was considered to be suitable and kept constant for all subsequent experiments.

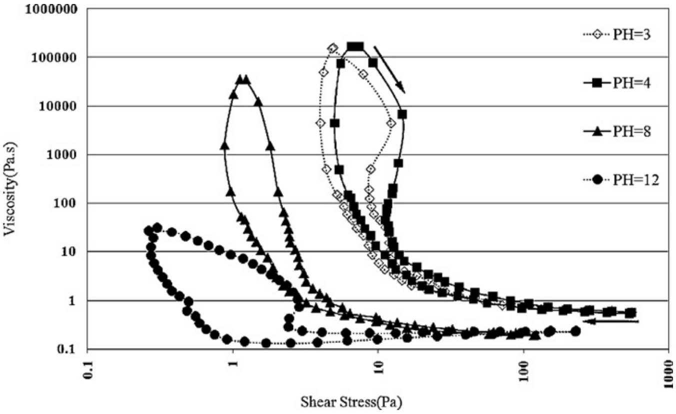

Fig. 2. The viscosity of suspensions containing 70 wt% glass powder as a function of shear stress for various pH values of 3, 4, 8 and 12.

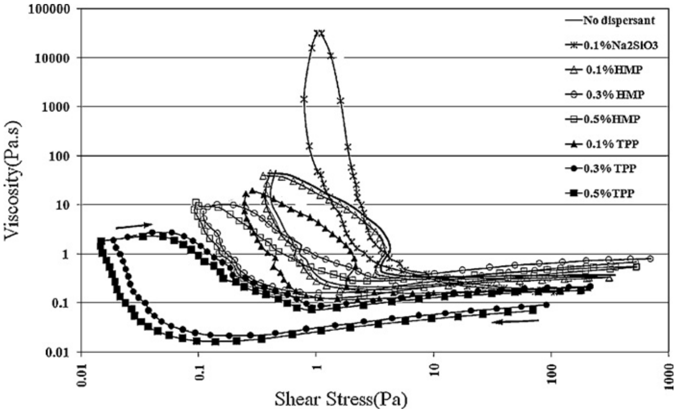

Fig. 3. The viscosity of suspensions containing 70 wt% glass powder, at pH = 12, and different amounts of sodium silicate, sodium hexametaphosphate and sodium tripolyphosphate, as a function of shear stress.

A dispersant can also affect the rheology of suspensions. Therefore, by fixing the pH value at the level of 12, the suspensions were studied at the presence of 0.1, 0.3 and 0.5 weight parts of sodium tripolyphosphate (TPP), sodium hexametaphosphate (HMP) and sodium silicate dispersants, respectively. Fig. 3 illustrates the results of these studies.

The figure shows that while sodium silicate increases the viscosity of suspension, sodium hexametaphosphate (HMP) and sodium tripolyphosphate (TPP), on the contrary, decrease the viscosity. Regarding the lower viscosity of sodium tripolyphosphate containing suspension, 0.3 wt% of it was considered as the most favorable dispersant in this work.

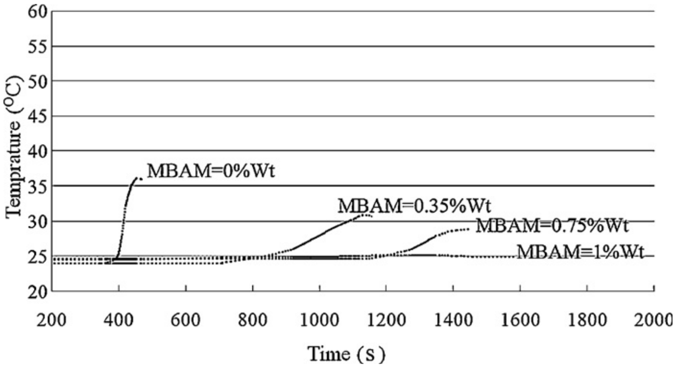

Fig. 4. The variation in temperatures with time during gelation of suspensions containing various amounts of the cross-linker, AM = 3% and APS = 0.4%.

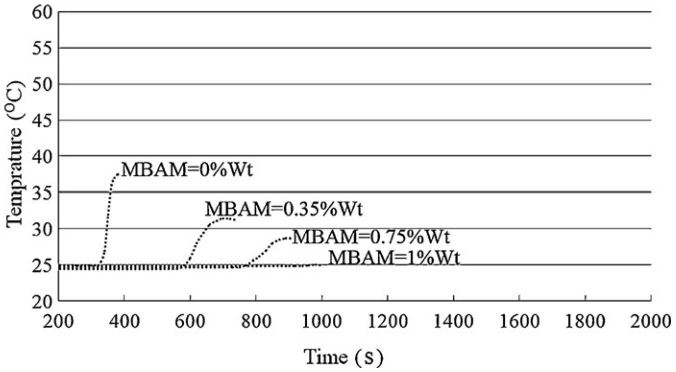

Fig. 5. The variation in temperatures with time during gelation of suspensions containing various amounts of the cross-linker, AM = 3% and APS = 0.8%.

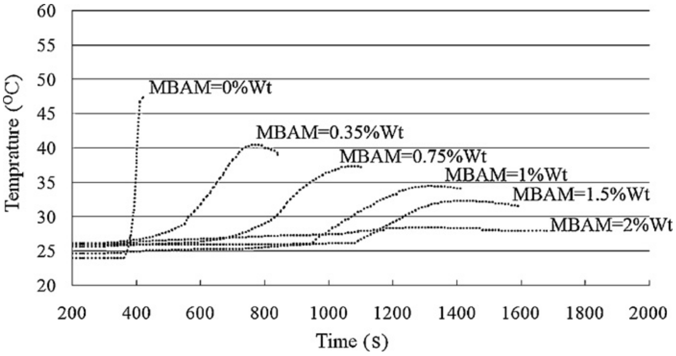

Fig. 6. The variation in temperatures with time during gelation of suspensions containing various amounts of the cross-linker, AM = 4% and APS = 0.4%.

To find the optimum amounts of polymers which could guarantee suitable idle and gelation times and good mechanical strength of gel-cast bodies, various weight parts of them were added to the above-mentioned suspension.

It is known that the gelation of a suspension is an exothermic reaction. Therefore, in the current work the measurement of temperature changes of the cast suspensions vs. time was considered as a criterion for determination of the onset time and the subsequent rate of the gelation process.

Figs. 4–9 demonstrate the variation in temperatures of suspensions containing various amounts of initiator, monomer and cross-linker. According to these figures, the generated heat which comes from the gelation process shows a strong dependence on the monomer and the cross-linker amounts as well as their ratio. The comparison of various compositions indicates that increasing the cross-linker at a constant amount of monomer leads to increasing of the onset gelation time and reduction of gelation temperature.

On the other hand, the comparison of suspensions containing equal amounts of cross-linker MBAM indicates an elevation of the suspension's temperature with increasing the monomer AM content as well as increasing the slope of T–t curves.

Furthermore, the gelation idle time shows a considerable less sensitivity to the variation of monomer content rather than to the cross-linker.

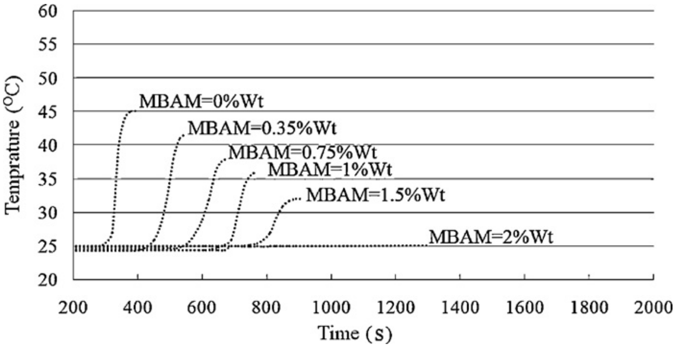

Fig. 7. The variation in temperatures with time during gelation of suspensions containing various amounts of the cross-linker, AM = 4% and. APS = 0.8%.

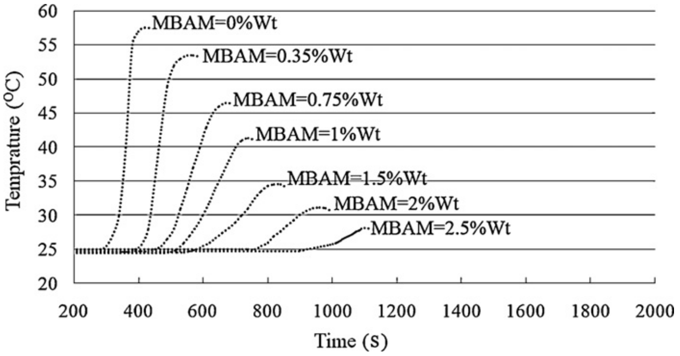

Fig. 8. The variation in temperatures with time during gelation of suspensions containing various amounts of the cross-linker, AM = 5% and APS = 0.4%.

Fig. 10 shows the effect of the AM, MBAM and initiator (APS) values on the bending strength of dried gel cast samples containing 70 wt% of glass powder, 0.3 wt% dispersant and 0.2 wt% of the catalyst TEMED.

It can be seen that regardless of AM values the bending strength of the gel cast bodies increases gradually with the amount of cross linker [14]. Furthermore, the cross linker-enriched compositions show an excellent dried flexural strength of ~11 MPa, which is only accessible by the gel casting method.

It seems that when the cross linker amounts approach ~2.5 wt% the links of the AM macromolecules reach the saturation level. The latter condition makes the polymerized matrix more resistant against crack initiation and/or crack growth mechanisms. It is also interesting to note that higher gelation rates resulting from higher amounts of APS, e.g. 0.8 wt%, is apparently ineffective in this regard. Apparently, a higher gelation rate leads to a lower degree of ordering and perfectness in the structure of polymerized materials.

Regarding the above results it can be suggested that the optimum composition, from the view point of gelation behavior and mechanical properties, should contain 5 wt% monomer, 2.5 wt% cross linker, 0.8 wt% initiator and 0.2 wt% catalyst.

Fig. 11 shows a homogeneous and compact microstructure of a dried gel cast specimen containing the aforementioned additives as a typical example of these gel cast bodies.

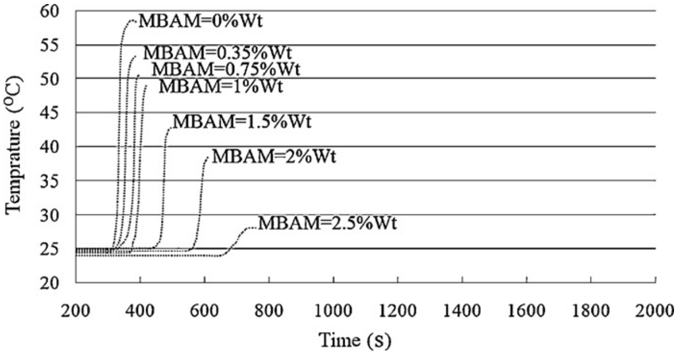

Fig. 9. The variation in temperatures with time during gelation of suspensions containing various amounts of the cross-linker, AM = 5% and APS = 0.8%.

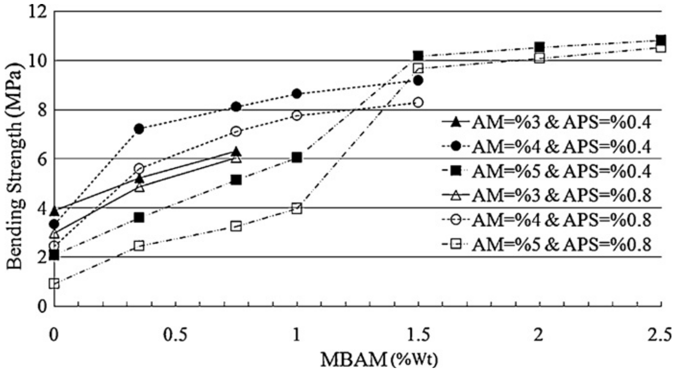

Fig. 10. The effect of the AM, MBAM and initiator values on the bending strength of dried gel cast samples containing 70 wt% of glass powder, 0.3 wt% dispersant and 0.2 wt% of the catalyst TEMED.

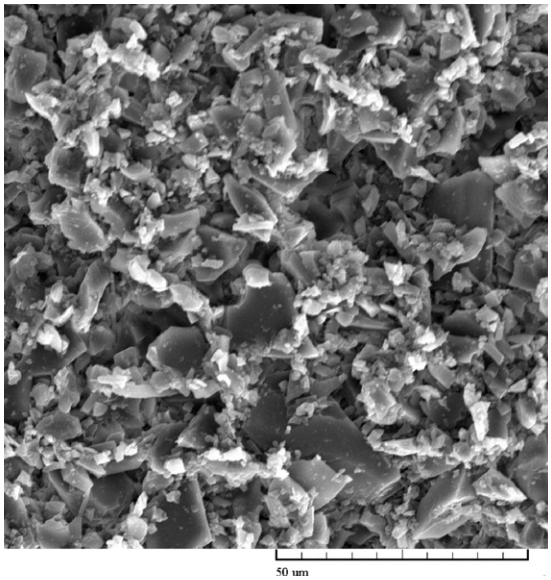

Fig. 11. The texture of the dried gel-cast sample containing 5 wt% monomer, 2.5 wt% cross linker, 0.8 wt% initiator and 0.2 wt% catalyst.

4. Conclusions

All of the polymer-free suspensions showed shear thinning behavior. This behavior was less intense for suspensions with higher pH values. The latter suspensions also exhibited the lowest viscosities. Sodium tripolyphosphate was the most effective dispersant regarding the above-mentioned properties.

The results showed that the measurement of temperature changes of the cast suspensions vs. time can be a suitable method to investigate the gelation process. Accordingly, increasing the cross linker/monomer ratio led to the extension of the gelation time, and to the reduction of gelation temperature. Bending strength values of the dried gel cast bodies was also affected by the above-mentioned ratio and was increased with it. This behavior was attributed to the increase in number of bonds formed between monomers and cross linkers.

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