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Alumina gelcasting by using HEMA system

Kai Cai*, Yong Huang, Jinlong Yang

Department of Materials Science & Engineering, Tsinghua University, Beijing 100084, PR China

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Abstract

A low-toxicity gel system based on the polymerization of low-toxicity 2-hydroxyethyl methacrylate (HEMA) was successfully developed. In order to obtain high solid loading ceramic slurry with low viscosities, a polyelectrolyte dispersant was selected. The results based on alumina suggested that the polyelectrolyte dispersant was more effective for the new HEMA system than tri-ammonium citrate (TAC), which was widely used for dispersing alumina powders. The green alumina bodies derived through the HEMA exhibited a mechanical strength as high as 18 MPa. SEM photos revealed that the green body also had a high homogeneity. Dense complex-shaped ceramic parts were produced through the new gelcasting system.

Keywords: Gelcasting; Mechanical properties; Al_2O_3

1. Introduction

Gelcasting is an attractive near-net-shape ceramic forming technique for making high-quality complex-shaped ceramic parts. In this process a high solid loading ceramic slurry obtained by dispersing the powders in a pre-mixed monomer solution is cast in a mould of the desired shape. After adding an initiator the entire system polymerizes in situ and green bodies of excellent mechanical property but with only a few percents of polymer can be obtained. Thus, the dried green body can be machined easily and the time-consuming binder burning out program can be excluded.[1,2] However, industry has been reluctant to use the technique because the most frequently used monomer in the system, acrylamide, is a neurotoxin. Alternative gelation chemicals, such as cellulose that can gelify on heating or polysaccharide and gelatine that can gelify on cooling have been tried, but the results were not encouraging.[3–6] It is difficult to obtain low viscosity slurry with high solid loading required by gelcasting in macromolecular solutions and low green strength seems also inevitable in these systems. Therefore, developing new gel systems that have similar or superior properties to the acrylamide-based systems and yet low in toxicity has become an area of intense interest in the field for more than 10 years.

An alternative monomer to acrylamide must be water-soluble and can gelify in aqueous solution. 2-Hydroxyethyl methacrylate ($CH_2{=}C(CH_3)COOCH_2CH_2OH$, HEMA) is an innoxious reagent, which is commonly used for soft lens material, for adhesive dentistry as a hydrophilic primer and as an ingredient in some adhesive resins. HEMA is prone to polymerize due to the vinyl bond in its molecule while the hydrophilic hydroxy group makes it possible to form water-compatible polymer. This article reports our results of a novel gelcasting system that uses HEMA as the monomer for forming alumina ceramics. In order to obtain high solid loading suspension for the new system, a polyelectrolyte dispersant JN281 (ammonium salt of poly(acrylic acid)) was selected. The rheological measurements indicated that the polyelectrolyte dispersant was more effective for the HEMA system than the frequently used tri-ammonium citrate (TAC). The pyrolysis property of the new system during sintering and the microstructure of the green body were also studied. The data proved that HEMA was a very promising monomer for gelcasting of ceramics.

2. Experimental procedure

The alumina powder is a commercial grade An-0.5 produced by China Xinyuan Aluminum, Inc., which has a mean particle size of ∼2.0 μm. The main composition of the powder is listed in Table 1. HEMA produced by

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* Corresponding author. +86 10 6277 1160.
E-mail address: caikai@tsinghua.org.cn (K. Cai).

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Table 1
Chemical composition of the alumina powder (wt.%)

Al_2O_3	α-Al_2O_3	SiO_2	Fe_2O_3	Na_2O	B_2O	Loss on ignition
>99.7	>95	0.05	0.03	0.05	0.04	0.1

Beijing Eastern Acrylic Chemical, Co., was used as the monomer. The crosslinker *N*,*N*-methylenebisacrylamide ($(C_2H_3CONH)_2CH_2$, MBAM), the catalyst *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) and the initiator $(NH_4)_2S_2O_8$ (analytically pure) are just the same as those used in the AM gelcasting system, which were produced by Beijing Hongxing Biological and Chemical Factory, Xingfu Fine Chemical Company and Beijing Third Reagent Company, respectively. The polyelectrolyte dispersant JN281 was provided by Beijing Pinbao Co. Before test the ceramic powder and the dispersants were added into the premix solution and thoroughly ball-milled for about 24 h to give a well-dispersed homogeneous suspension.

Zeta potentials were measured by a Zetaplus apparatus (Brookhaven Instruments Corp., USA). The alumina particles were suspended in a 0.01 M potassium chloride solution so that a constant electrical double-layer thickness can be maintained. A 0.05 wt.% alumina suspension was used for the measurement. Rheological properties of the ceramic slurries were measured by an advanced MCR300 rheometer (Physica, German). The details of how the gelcast polymers were pyrolyzed were determined via thermogravimetric analysis (TGA) in air by using a Dupont Thermal Analyst 2000 type instrument. The room-temperature mechanical strength of the green bodies was determined by three-point flexural tests. Microstructure of the sample was observed by a HITACHI S-450 scanning electron microscopy (SEM).

3. Results and discussion

3.1. Development of high solid loading Al_2O_3 suspension

The most critical factor for the successful production of ceramics by gelcasting technique is producing a flowable and stable slurry with a solid loading as high as possible. Dispersion of ceramic powder in the premix solution is determined by the attractive and repulsive forces in the system. For metal oxide particles these interactions are largely dictated by attractive van der Waals forces and electrostatic repulsive forces, etc.[7] The former forces are essentially constant for identical surfaces while the latter ones can be modified over a wide range by surfactants, which can change the surface charge density or electrical double-layers of the particles. This can be reflected by the zeta potential values (ζ) of the powder particles. ζ values of Al_2O_3 particles dispersed in KCl in the absence of dispersant and in the presence of 0.25 wt.% TAC and 1 wt.% JN281 are shown in Fig. 1. Where the dispersant content used are the optimum values with which the minimum viscosities can be obtained. In absence of dispersant the ζ value of Al_2O_3 particles changes from 8.37 mV at pH 3.2 to −14.89 mV at pH 11.6, with an isoelectric point (IEP) at about pH 5.7. Adding dispersants changes the IEP to pH 3.9 and 2.6 for TAC and JN281, respectively, and results in more negative ζ values. Of the two dispersants JN281 can provide a more negative ζ value. This suggests that JN281 should be more effective as far as the repulsive electrostatic force is concerned. It should be pointed out that the IEP value of pH 5.7 for alumina is relatively smaller than those from many literature, this may be due to the commercial alumina source used as well as the instrument error. Addition of monomer HEMA does not shift the IEP but it does decrease the relative ζ values, suggesting that the uncharged HEMA molecule either screen the charge developed at the solid/liquid interface or be preferentially absorbed onto the surface of the alumina particles.

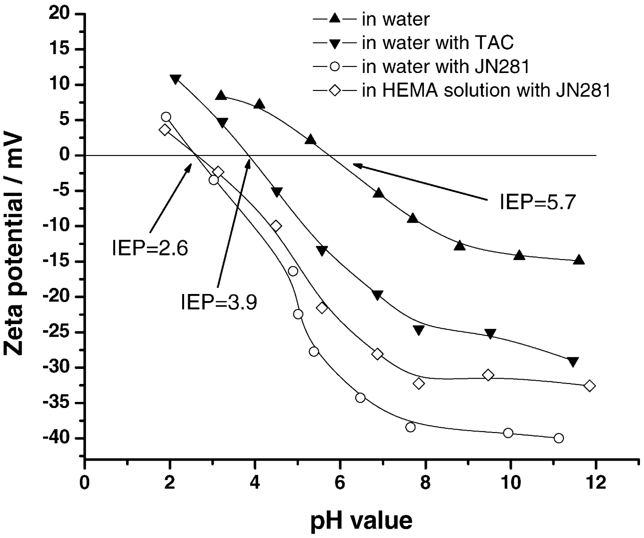

Fig. 1. Zeta potential versus pH values of different alumina suspensions.

Fig. 2 shows the viscosity as a function of the shear rate for different alumina slurries. The high viscosities at the beginning of the curves indicate a “Bingham” behaviour of all the suspensions. The alumina slurry without any dispersants show much higher viscosity even at a low solid loading of 40 vol%. Adjusting pH value to 10.3 shows little effect on the viscosity (acid pH value of 3.4 showed almost overlapped viscosity curve as that of pH 10.3). While addition of dispersant can greatly decrease the viscosity. Compared with the suspension in 20 wt.% AM solution, which has almost the same viscosity as the suspension in water,[8] addition of 20 wt.% HEMA slightly increases the viscosities. This agrees with the ζ value increase after adding HEMA. Maybe due to the relatively more complex molecule structure and bigger molecule weight of HEMA, it showed a more obvious electricity screening effect than AM. The 40 vol% slurries in water show a shear-thinning behavior while the slurries in HEMA and AM premix solutions show a shear-thinning behaviour at low shear rates and a shear-thickening behaviour at high shear rates. Shear-thinning behaviour indicates that

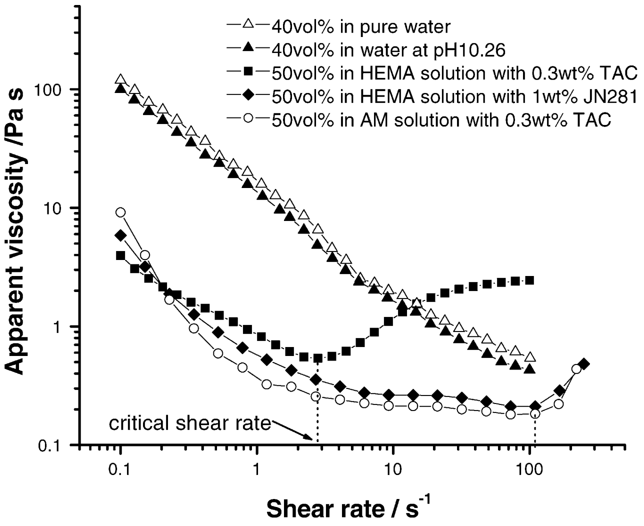

Fig. 2. Effects of dispersants and monomers on the viscosity of different alumina slurries.

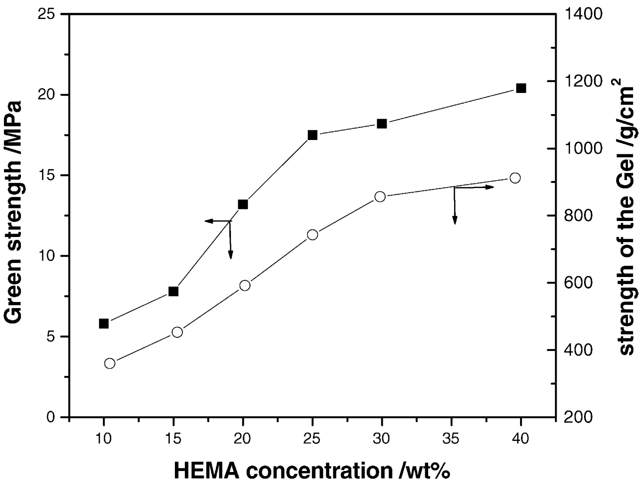

Fig. 3. Influence of HEMA content on the gel strength and green body strength.

the flow brings about a more favorable two-dimensional structure arrangement of the particles rather than a three-dimensional one, because flow induced two-dimensional arrangement is a layered structure so a low resistance of the particles movement between different layers and a low viscosity can be obtained.[9] Due to the damage of the unstable two-dimensional arrangement at very high shear rates, critical shear rate, the viscosity increases again and a shear-thickening behaviour appears. The suspension with JN281 shows a much lower viscosity and the critical shear rate is moved to a higher level compared with that of the TAC system in HEMA solution. This suggests that JN281 is more effective than TAC in stabilizing the suspension and in decreasing the so called "phase volume fraction" in HEMA solution,[9] although TAC is very effective in AM premix solution. It has been reported by Tari that increase of the zeta potential may not assure a good dispersion.[10] Because each particle may have an interaction size or effective diameter that is approximately its real diameter plus twice the range of total surface forces, the larger effective diameter of higher ζ value particles may cause a high viscosity in its suspension. However, we should be careful about the "interaction size" when we want to correlate it with the viscosity. First, it may be only effective for high solid loading suspension with small particle sizes. In addition, it is difficult to judge what a ζ value may cause the increase of "interaction size" that can counteract the prevention of particle aggregation by the electrical repulsion. The electrostatic repulsion is well accepted as one of the important stabilization mechanisms of dispersants. Here the results seem to be consistent with the zeta potentials. Even so, we can not draw the conclusion that JN281 has better electrostatic stabilization. However, no matter if the higher ζ value of JN281 means a better electrostatic stabilization or not, it seems reasonable that its better dispersion should also be attributed to its steric stabilization. Generally, steric stabilization requires adsorption of reasonably dense polymer layer on each particle, and in turn a sufficient supply of polymer in the solution.[11] This may account for the higher optimum content level of JN281 than TAC.

3.2. Green strength and microstructure

Influence of HEMA content in premix solution on the gel strength and on the green body strength derived from 50 vol% alumina slurries are shown in Fig. 3. Here the gel strength was examined by a simple device as that used by Chen et al.[6] As expected, both gel strength and green strength increase with HEMA content. It has been reported that HEMA only forms water-compatible gel at very high concentrations of at least 40 wt.%.[8] But our results in Fig. 3 shows that with a HEMA premix concentration of 20 wt.% a green strength of about 13 MPa can be obtained. The discrepancy might be ascribed to the difference of the HEMA source. Considering both mechanical property and production cost a HEMA concentration of 25 wt.% should be adopted. Higher amounts of HEMA have little effect on the green strength. Although the strength of the green body derived from HEMA is less than that derived from AM (28 MPa) with the same solid loading, it is much larger than that derived from the gelatine (8 MPa) etc.[6]

Fig. 4 shows the density and shrinkage values of the alumina samples prepared by the new system. There exists a linear shrinkage of about 1.74% and a relative density of 51.2% can be obtained at a solid loading of 50 vol%. Increasing solid loading leads to a smaller shrinkage value and a more dense structure. This is easy to be understood because these data are mainly determined by the solid loading used in the forming process. Fig. 5 shows the SEM photos of alumina samples obtained by HEMA system and those by AM system at the same solid loading of 50 vol%, which also show no obvious difference. There are no obvious cracks or pores in the bodies although the alumina powder has a

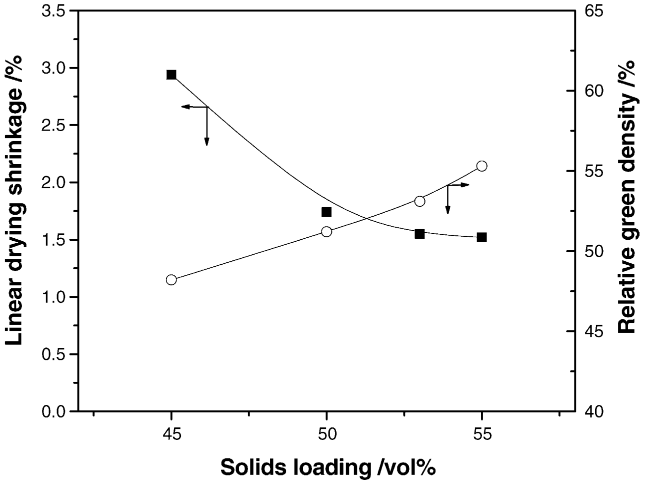

Fig. 4. Density and shrinkage values of the alumina samples prepared by using the new system.

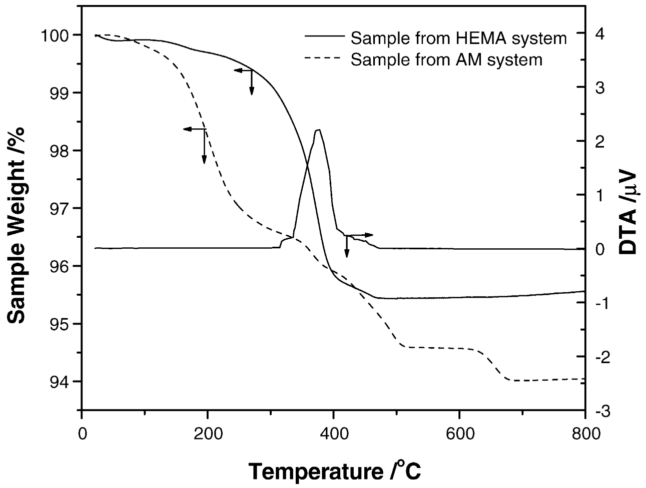

Fig. 6. Pyrolysis processes of the green bodies made from HEMA system and from AM system.

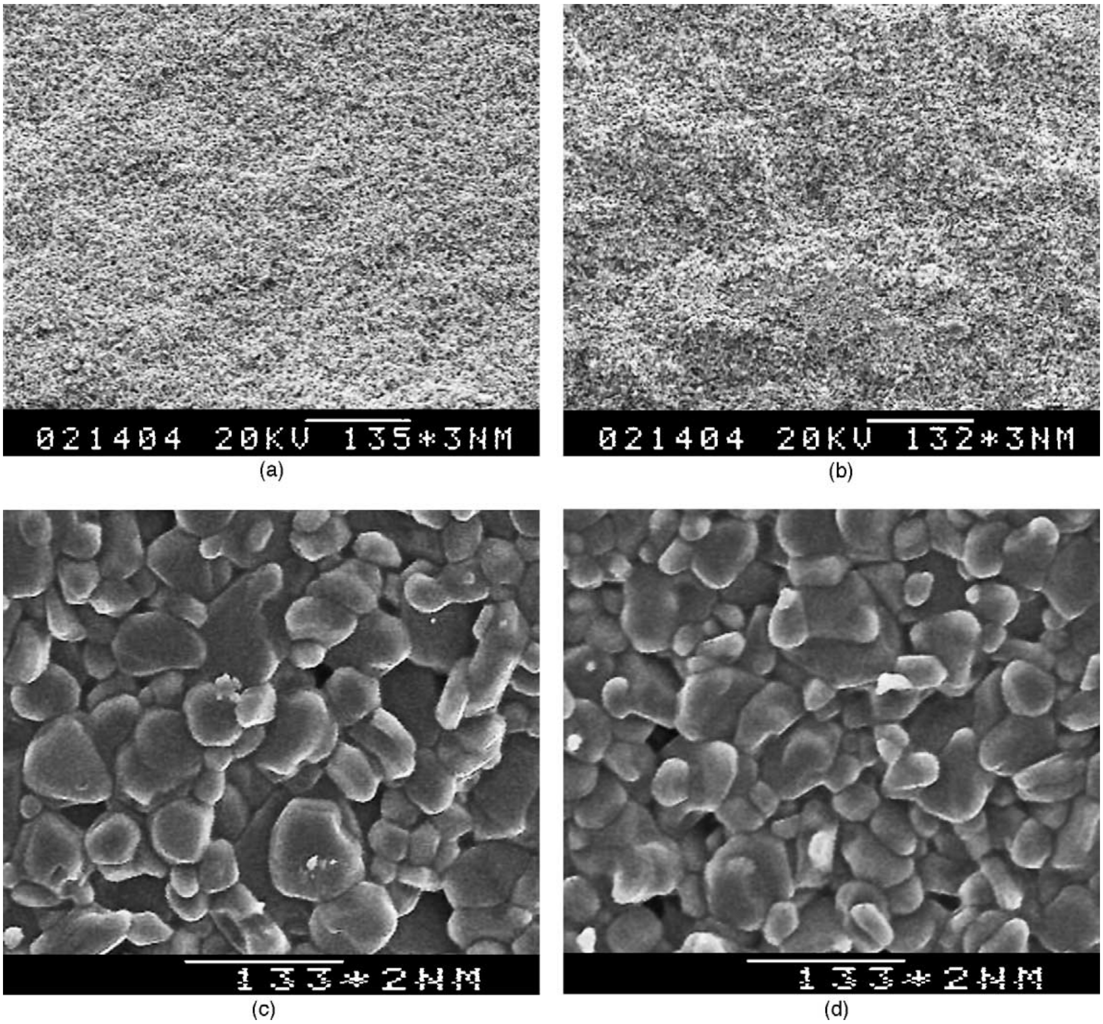

Fig. 5. Comparison of microstructures of alumina samples from different systems. (a) Green body from HEMA system, (b) green body from AM system, (c) sintered body from HEMA system and (d) sintered body from AM system.

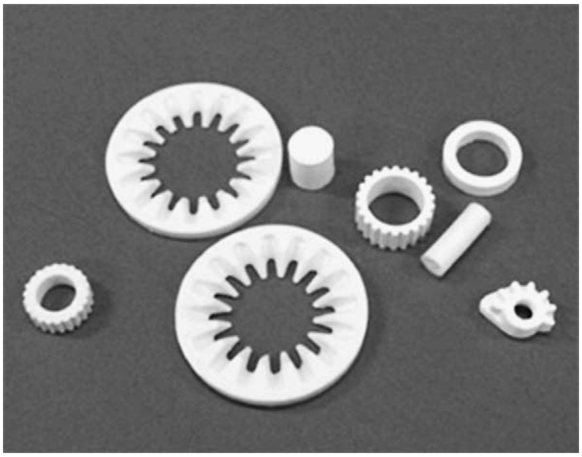

Fig. 7. Illustration of the ultimate alumina ceramic parts fabricated by using HEMA system.

relatively big particle size of 2.0 μm. Homogeneous structure could be obtained through both systems, suggesting that well-dispersed slurry, good deairing and casting could be achieved by the new gelcasting system.

3.3. Binder burnout investigation

The pyrolysis process of the polymerized HEMA in the dried green alumina sample during sintering in air is determined via thermal analysis. From the TGA and DTA curves shown in Fig. 6 (50 vol% alumina from 25 wt.% HEMA solution) we can see that the green body formed in the new system has mainly one mass loss process in the temperature range of 110–465 °C with a small endothermic DTA peak, which should be ascribed to the burnout of the cross-linked polymer network. Comparatively, TGA curve of the green body made from 25 wt.% AM premix solution at the same solid loading shows several mass loss processes. The mass loss before 200 °C may be mainly due to the removal of water while the mass loss in the range of 352–680 °C may be ascribed to the pyrolysis of PAM molecule. Because there is only one focused mass loss process at a relatively low temperature range, polymerized HEMA may be removed more easily than PAM. Based on the TGA results, adding for only 1 h at the constant temperature of 600 °C is enough for the removal of the remnants of the decomposed polymer during the sintering of the ceramics. The ultimate complex-shaped alumina parts successfully fabricated through a premix solution containing 25 wt.% HEMA and with JN281 as the dispersant are illustrated in Fig. 7.

4. Conclusion

A new in situ colloidal ceramic forming system based on the polymerization of innoxious HEMA was developed. HEMA was used as the monomer in the new gel system for gelcasting of alumina. High solid loading slurry in the new premix solution with low viscosity was achieved after selecting a polyelectrolyte dispersant. Its dispersion effect was contrasted with TAC and the dispersion mechanism was discussed. Microstructure and pyrolysis process of the green bodies made from the HEMA system during sintering are also investigated. Dense, strong and homogeneous near-net-shape alumina parts were successfully fabricated.

Acknowledgements

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