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A new aqueous PEGDMA/AM system for 3YSZ gelcasting

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Abstract

Poly(ethylene glycol)(400)dimethacrylate (PEG(400)DMA) was used as main binder and cross-linker to gelcast 3YSZ, while acrylamid (AM) as minor monomer. Influences of PEG(400)DMA and dispersant content on rheological property (including zeta potential and viscosity) of the slurry as well as on the flexural strength of green body were discussed. Effect of PEG(400)DMA on surface exfoliation of green body gelcast in air was also investigated. Zeta potential of the slurry was significantly affected by PEGDMA after substituting PEGDMA for AM. Improved rheological property and flexural strength of green body were obtained by adding 1.35 wt% dispersant to slurry. Flexural strength of green body prepared by 45 vol% solid loading slurry reached 18.7 MPa at 6.5 wt% monomer concentration. Surface exfoliation of green body was eliminated when slurry was solidified in air at 70 °C with 3.5 wt% PEG(400)DMA/AM in slurry.

Keywords: Low-toxic; Gelcasting; PEG(400)DMA; Surface exfoliation

1. Introduction

Gelcasting is a new powder forming process developed by Oak Ridge National Laboratory in 1990s to fabricate high-quality, complex-shaped ceramic materials. In such process, the monomers in slurry polymerize in situ to hold the particles together [1]. This adaptable forming process can meet various application requirements, such as fabricating YSZ microthruster for microelectromechanical system [2], cordierite based glass–ceramic body [3] and grain-oriented ferroelectric ceramics [4]. But conventional AM gel system is neurotoxic and surface exfoliation of green body due to oxygen inhibition in free radical polymerization brings about difficulty in dimensional control. The above two problems have confined the industrial application of gelcasting [5].

Some natural macromolecules (such as chitosan, methyl cellulose, sodium alginate and gelatine) can form gel network by forming intermolecular hydrogen bonds or chelating with multivalent ions. Those natural macromolecules have been used in ceramic gelcasting previously [6–10], indicating that polymerizable low-toxic polymers or oligomers can also be applied in ceramic gelcasting. Two methods can be used to resist surface exfoliation. One method is to operate in N_2 atmosphere to expel O_2 [11], but it is complicated and costly. Another one is to add a proper amount of water-soluble polymers, such as poly(vinylpyrrolidone) (PVP) [12] or polyethylene-glycol (PEG) [13], to the slurry to serve as substitute binders for polyacrylamid for ceramic particles on the surface layer. However, the strength of green body would also be decreased. If those additive polymers could copolymerize with the monomers (e.g. AM) in gel system, then the strength of green body would be improved for stronger gel network constructed. Also the toxicity of the system could be reduced if AM was substituted by none or low toxic polymers or oligomers which act as monomer or cross-linker.

Polyether-contained oligomer PEGDMA with methacrylate end-group on either side of the long chain can act as cross-linker and difunctional monomer in free radical polymerization to form branchy gel network structure. Oligomer PEGDMA ($M \approx 875$) was used as cross-linker in MAM/PEGDMA gel system and poly(ethylene glycol)dimethacrylate (MPEGMA, $M \approx 300$) was used as monomer in MPEGMA/MBAM gel system to gelcast Al_2O_3 ceramics respectively [14]. Flexural strengths of green body were 12.2 MPa in MAM/PEGDMA system and 3 MPa in MPEGMA/MBAM system respectively,

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but the relative PEGDMA content was low (MAM: PEGDMA = 3:1, mass ratio) and it did not benefit much to reduce the toxicity of the system. It might be deduced that higher oligomer PEGDMA content was conducive to reducing toxicity of the gel system and resisting surface exfoliation when polymerized in air. In present work, we tried to use PEG(400)DMA as main binder and cross-linker to substitute AM to develop a low-toxic system for ceramic gelcasting with no surface exfoliation of green body, while AM as minor monomer. Influences of PEG(400)DMA and dispersant content on rheological property (including zeta potential and viscosity) of the slurry as well as on the flexural strength of green body were discussed. Effect of PEG(400)DMA on surface exfoliation of green body gelcast in air was also investigated.

2. Material and methods

2.1. Raw materials

Commercial 3 mol% yttria-stabilized zirconia powder (3YSZ, $D_{50} = 0.8$ μm, Guangdong Huawang Zirconium Materials Co. Ltd. China) was used as raw material. Acrylamid (AM) was used as minor monomer, PEG(400)DMA (Guangzhou Deco Composite Technology Co. Ltd. China) as cross-linker and main binder, ammonium persulphate (APS) as initiator, *N*,*N*,*N*′,*N*′-tetramethylenediamine (TEMED) as catalyst and ammonium polyacrylate (PAA-NH_4, synthesized from polyacrylic acid and ammonia) as dispersant.

2.2. Preparation of slurry and green body

AM, PEG(400)DMA, PAA-NH_4 were dissolved in deionized water to prepare a premix solution. The mass ratio of PEG(400)DMA to AM was 4:1. 3YSZ powder was gradually added to the premix solution, and ball milled for 12 h in a nylon jar. The resulting slurries with various dispersant concentration (based on 3YSZ), monomer concentration (based on 3YSZ) and solid loading were subjected to viscosity measurement and further treatments. The ratio of total mass of PEGDMA and AM to the mass of ceramic powder was defined as monomer concentration.

0.7 vol% (based on volume of slurry) of 33 vol% TEMED water solution and 1 vol% (based on volume of slurry) of 20 wt% APS water solution were respectively added to above slurry, followed with mechanical mixing and vibration degassing. Then the slurry was cast into a vaseline-coated aluminum alloy mold, heated to 70 °C (or at 25 °C for comparing) and kept for 0.5–2 h to ensure that the polymerization was adequately carried out. Wet green body was demoulded from mold and placed in air for 24 h, and then dried at 100 °C until reaching constant weight. The resulting green body was subjected to flexural strength test or further treatments.

2.3. Characterization

Zeta potential of slurry was measured by Zeta Potential Analyzer (ZetaProbe, Colloidal Dynamic Inc., USA) at 25 ± 1 °C. The pH of slurry was adjusted with HCl and NaOH. Viscosity of the slurry was measured by NDJ-1 Rheometer at 25 ± 1 °C at 6 r/min shear rate.

Flexural strength of green body was measured by three-point bending test with a span of 30 mm using electronic universal testing machine. Green body was polished to the dimension of about 5 mm × 6 mm × 45 mm with a grinding machine. The green body density was calculated from the weight and dimensions, as in Ref. [14].

Fracture surface of tested green sample and surface of green body were observed by VHX-1000C ultra-depth three-dimensional microscope (KEYENCE Corporation).

3. Results and discussion

3.1. Effect of PEG(400)DMA on zeta potential of slurry

Fig. 1 shows the relationship between pH and zeta potential of 5 vol% solid loading slurries with 5 wt% AM or 1 wt% AM + 4 wt% PEG(400)DMA respectively. The isoelectric point (IEP) of slurry with 5 wt% AM was about 8.3, while that of slurry with 1 wt% AM + 4 wt% PEG(400)DMA was about 8.9, which was more alkaline than that of slurry without PEGDMA, indicating an increasing of net positive charge on the surface of ZrO_2 particles. Moreover, absolute value of zeta potential at different pH obviously increased after substituting PEGDMA for AM in slurry. According to electric double layer model, the potential difference between slipping plane of the electric double layer and the bulk fluid determines zeta potential [15], which increases with the decreasing of amount of counter-ions adsorbed on the particle surface. Part of the negative charged ions might be blocked by PEGDMA oligomer chains which had already adhered to the surface of the ZrO_2 particles, and hence made it difficult for those negative charged ions to be adsorbed on the particle surface, as shown in Fig. 2. Structures of adsorbed layer and diffusion

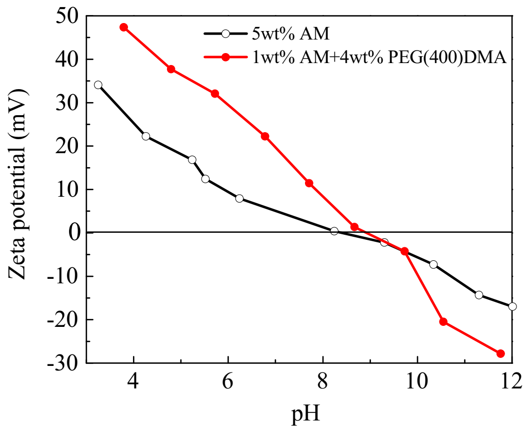

Fig. 1. Zeta potential of 5 vol% solid loading suspension with 5 wt% AM and 1 wt% AM + 4 wt% PEG(400)DMA.

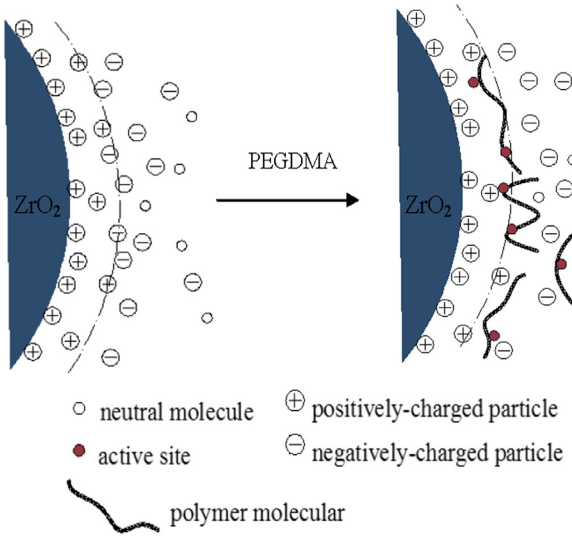

Fig. 2. Schematic illustration of adsorbed species on ZrO_2 particle surface before and after adding PEGDMA.

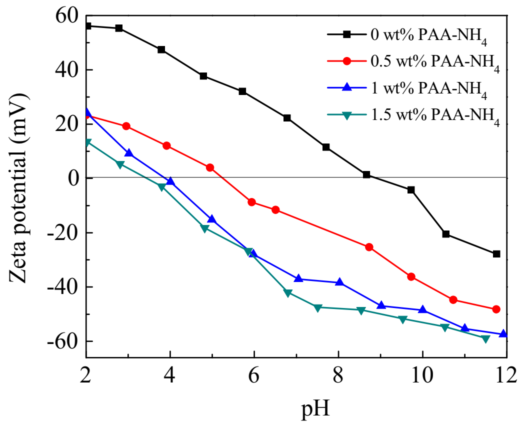

Fig. 3. Effect of PAA-NH$_4$ concentration on zeta potential of slurry with 5 vol% solid loading and 5 wt% monomer.

layer of electric double layer might be changed by adding PEGDMA to the slurry, which resulted in the changes of IEP and absolute value of zeta potential at different pH.

3.2. Effects of PAA-NH$_4$ on rheological property of slurry and green body strength

Fig. 3 shows the effect of PAA-NH$_4$ concentration on zeta potential of slurry with 5 vol% solid loading and 5 wt% monomer concentration. With PAA-NH$_4$ concentration increasing from 0 wt% to 1.5 wt%, IEP of the slurry decreased from 8.9 to 3.4. With more than 1.0 wt% PAA-NH$_4$ content in slurry, absolute values of zeta potential were higher than 40 mV in alkaline condition, which was likely to provide electrosteric stabilization for the slurry. At low acidic pH, zeta potential of slurry without PAA-NH$_4$ was higher than 40 mV, above which electrostatic stabilization of the slurry was supposed to be efficient, but yttria was prone to dissolve at low acidic pH [16]. Thus, alkaline condition was preferable to prepare stable 3YSZ slurry with fine rheological property. Proper amount of PAA-NH$_4$ was beneficial to improve the rheological property of slurry at alkaline pH value.

Effects of PAA-NH$_4$ concentration on viscosity of slurry with 45 vol% solid loading and 3.5 wt% monomer as well as on flexural strength of green body prepared by above slurry were studied, as shown in Fig. 4. With the PAA-NH$_4$ concentration increasing from 1.2 wt% to 1.35 wt%, viscosity of slurry decreased to about 47.5 Pa s. However, continuing to increase the PAA-NH$_4$ concentration would deteriorate the rheological property of slurry. Effect of PAA-NH$_4$ concentration on flexural strength of green body was in accordance with that on rheological property. Higher flexural strength of green body (about 12.5 MPa) was obtained with 1.35 wt% PAA-NH$_4$ than that with other concentration. Green body prepared by slurry with appropriate rheological property would be less interfered by pore or other inhomogeneous defects which might significantly deteriorate the mechanical property of green body.

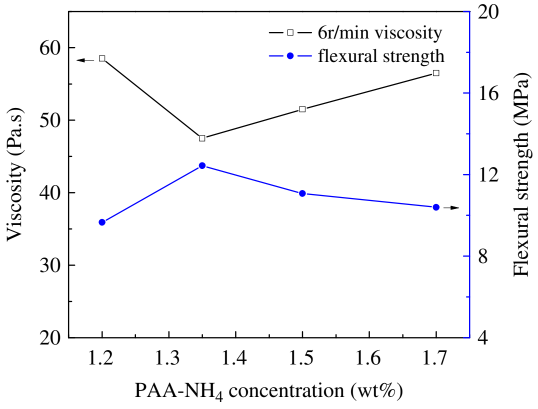

Fig. 4. Effects of PAA-NH$_4$ concentration on viscosity of slurry and flexural strength of green body.

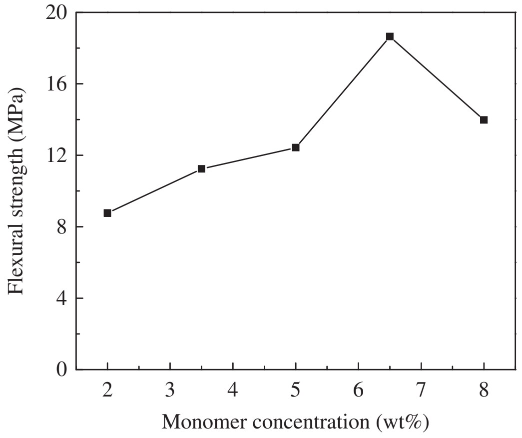

Fig. 5. Effect of monomer concentration on flexural strength of green body prepared by slurry with 45 vol% solid loading and 1.35 wt% PAA-NH$_4$.

3.3. Effect of monomer content on green body strength

Green bodies were prepared by slurry with 45 vol% solid loading and 1.35 wt% PAA-NH_4 to investigate the effect of monomer content on green body strength. The relative density of green body was 51.5%–54.5%. Fig. 5 shows the flexural strength of green bodies with various monomer concentrations. When monomer concentration increased from 2.0 wt% to 6.5 wt%, the flexural strength increased rapidly from less than 10 MPa to 18.7 MPa, then decreased to about 14 MPa at 8.0 wt%. Polyether-contained oligomer PEG(400)DMA with methacrylate end-group on either side of the long chain may adhere to the particle surface (as illustrated in 3.1) and form branchy gel network structure during polymerization. Increasing of monomer concentration in slurry resulted in constructing stronger gel network to hold the ceramic powders tighter, thus the strength of the green body increased.

Fig. 6 shows the fracture surface of green body prepared by slurry with (a) 6.5 wt% monomer and (b) 8.0 wt% monomer. Pores could be found in the sample with 8.0 wt% monomer, which caused by poor rheological property of the slurry. Pores-free sample showed high flexural strength of green body, indicating that PEG(400)DMA/AM gel network could provide bind force strong enough to ensure excellent mechanical property.

3.4. Surface morphology and microstructure

Fig. 7 shows the surface morphologies of green body prepared by slurries with 45 vol% solid loading that solidified at different temperatures in air. When monomer concentration was 2.0 wt% and solidified at 25 °C or 70 °C respectively, surface exfoliation existed, as shown in Fig. 7(a) and (b).

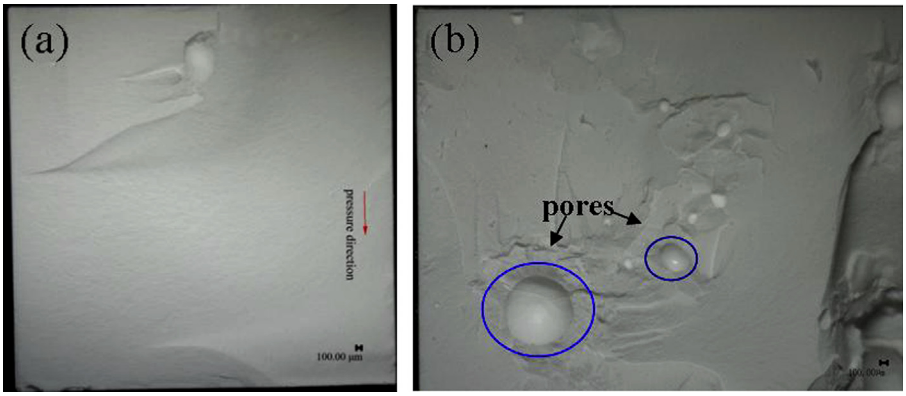

Fig. 6. Fracture surface of green body prepared by adding (a) 6.5 wt% and (b) 8.0 wt% monomer in slurry with 45 vol% solid loading and 1.35 wt% PAA-NH_4.

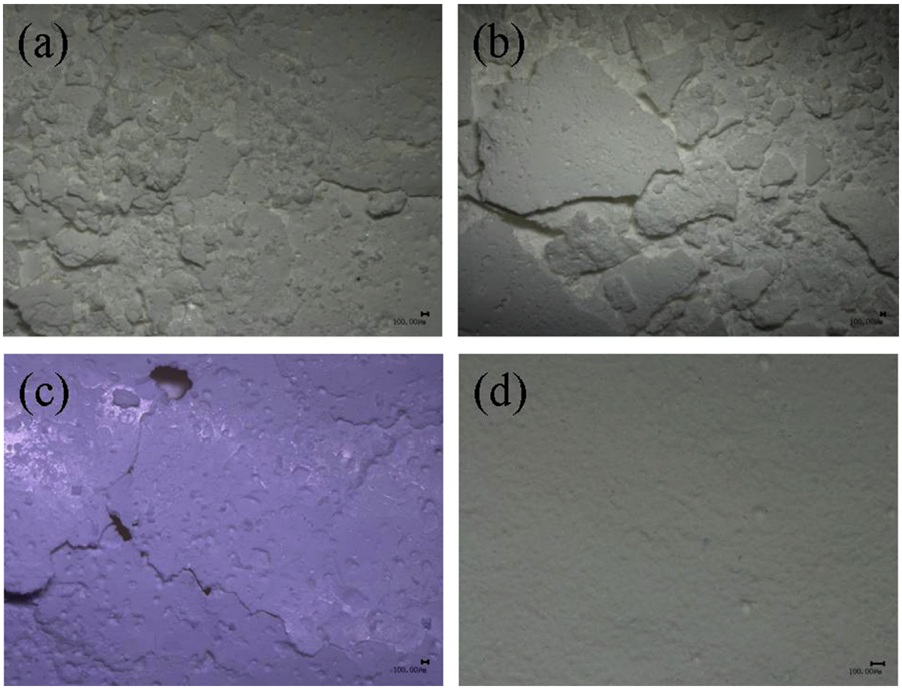

Fig. 7. Surface morphologies of green body prepared by slurries with different monomer concentrations and solidified at different temperatures in air. (a) 2.0 wt% monomer concentration, 25 °C, (b) 2.0 wt% monomer concentration, 70 °C, (c) 3.5 wt% monomer concentration, 25 °C and (d) 3.5 wt% monomer concentration, 70 °C.

While monomer concentration was 3.5 wt% and solidified at 25 °C, surface exfoliation still existed, but slightly suppressed for increasing of PEG(400)DMA in slurry, as shown in Fig. 7(c). When monomer concentration was 3.5 wt% and solidified at 70 °C, surface exfoliation was completely eliminated, as shown in Fig. 7(d). By comparing Fig. 7(c) and (d), it could be seen that higher temperature also had some contribution to suppressing surface exfoliation. When solidified at lower temperature, diffusion of oxygen from air into slurry may be partially hindered by PEG(400)DMA, but still cannot totally avoided. At elevated temperature like 70 °C, surface exfoliation of green body solidified in air can be eliminated for synergistic effect of hindering from PEG(400)DMA and faster polymerization.

4. Conclusions

In present study, a new mixed low-toxic aqueous PEG(400) DMA/AM gel system with PEG(400)DMA as cross-linker and main binder was successfully applied to gelcast 3YSZ. Flexural strength of green body prepared by slurry with 45 vol% solid loading reached 18.7 MPa. Surface exfoliation of green body were eliminated when solidified in air at 70 °C with PEG(400)DMA/AM gel system.

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