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Gelcasting of ceramic suspension in acrylamide/polyethylene glycol systems

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Abstract

A new polyethylene glycol/acrylamide-based gelcasting system has been developed. The new system performs at least as well as, and in some cases better than, the original acrylamide-based system. The development of this system is for the sake of eliminating the surface-exfoliation phenomenon of green bodies gelcast in air. This study concentrates attention on dispersion, rheological and gelation behavior in the new system and flexural strength of green body.

Keywords: Alumina; Polyethylene glycol; Gelcasting; Surface-exfoliation

1. Introduction

Gelcasting, which has been developed by Janney and coworkers [1,2], utilizes the polymerization of a monomer in the suspension solution of ceramic powder via a free radical initiator and produces strong green bodies, which can be removed from the mould fairly quickly. Thus, it is a combination of polymer chemistry with slip processing. The problem about inhibition of oxygen in free radical polymerization in air is unavoidable [3,4], resulting in the surface-exfoliation phenomenon of green bodies [5].

To avoid the inhibition of oxygen and the resulting surface-exfoliation, gelling of the ceramic slurry normally is carried out in N_2 atmosphere[1,6]. In industrial production, however, a technical process under nitrogen gas not only is difficult, but also increases the cost of production. The present study is intended to resolve this problem via a chemical method. In an attempt to develop components of aqueous system, we had investigated the gelcasting with adding non-ionized water-soluble polymers and noticed that the surface-exfoliation phenomenon of green bodies gelcast in air was eliminated via adding a proper amount of polymers to the monomer solution [7]. A new introduced component is not toxic, which provides the possibility for further industrialization.

The polyethylene glycol is the simplest structure of the non-inoized water-soluble polymers. Its physical conformation with 10,000 molecular weight is a white wax-state solid. The polyethylene glycol possesses good stability, adhesional wetting, low toxicity and the characteristic that it burns out completely, resulting in wide application in the casting of ceramic.

The purpose of this paper is to investigate and discuss the effect of water-soluble polymer polyethylene glycol (PEG) with a molecular weight of 10,000 on gelcasting of alumina, in the precondition of that the surface-exfoliation phenomenon of green bodies cast in air is inhibited.

2. Experimental

2.1. Materials

The starting ceramic powder used in this study was a commercial high-purity α-Al_2O_3 powder with an average particle size 3.47 μm. For gelcasting, acrylamide [$C_2H_3CONH_2$ (AM)] was used as the monomer,

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N,N′-methylenebisacrylamide [$(C_2H_3CONH)_2CH_2$(MBAM)] as a coupling agent, *N,N,N*′*,N*′-tetramethylethylene- diamine [TEMED] as a catalyst, ammonium persulphate as an initiator. To improve the dispersion of the powder and fluidity of the suspension, an organic base, ammonium citrate is used as a dispersant. Polyethylene glycol with a molecular weight of 10,000 was purchased from Tianjin Chemical Company, China.

2.2. Preparation of suspensions

2.2.1. Determinatin of PEG amount

A proper amount of PEG may eliminate the surface-exfoliation phenomenon of green bodies cast in air, but decreases the fluidity of the suspension. To determine the optimum amount of PEG, which is enough to eliminate the surface-exfoliation phenomenon of green bodies cast in air, the following experiments were performed. The suspensions with various amounts of PEG were gelcast. The amount of PEG and the degree of surface-exfoliation are shown in Table 1. The suspension with 1.3 wt.% PEG (based on alumina) has a better fluidity and has no surface-exfoliation phenomenon. Thus 1.3 wt.% PEG was chosen as additive for the suspensions in following experiments.

2.2.2. Process of gelcasting with PEG

The PEG (1.3 wt.%, based on alumina) and dispersant (0.25 wt.%, based on alumina) were first completely dissolved using mechanical stirring for 5 min in a premix solution, which has been prepared by dissolving AM and MBAM in deionized water. The premix solution serves as a dispersing media for the ceramic powder, then the alumina powder was added. The suspensions, with solids loading of 50 vol.% were mixed manually and then milled for 24 h in a nylon resin jar using alumina balls as a milling media to break down the agglomerates and to achieve a good homogeneity. The prepared suspensions were used to evaluate their rheological properties and viscoelastic properties. The prepared suspension (25 ml) with 100 μl initiator and 50 μl catalyst was used to evaluate the gelling characteristics and to fabricate samples. The samples were inspected on their surface and their flexural strength was measured.

Table 1
Relationship between the amount of polyethylene glycol and the degree of surface-exfoliation of green body

Amount of PEG (wt.%)	Surface of sample	Viscosity (Pa s)	
		Shear rate 1.18 s^{-1}	Shear rate 21.1 s^{-1}
0	Exfoliation	0.447	0.105
0.5	Exfoliation	0.684	0.874
1.0	Exfoliation	0.709	0.981
1.3	No exfoliation	0.730	1.09
1.5	No exfoliation	0.882	1.55
2.0	No exfoliation	1.6	3.57

2.3. Methods and measurements

Rheological characterization was performed on Modular Compact Rheometer (MCR300, Physica Instrument Corporation, Germany) at 25 °C, with a concentric cylinder measurement geometry, CC27, having gap between the inner and outer cylinder walls of 1.33 mm. The sample volume was ~23 ml of fluid. Steady shear measurements were performed at 0.1–250 s^{-1} by stepping up in shear rate. Viscoelastic measurements were performed with the same measurement geometry, applying a strain amplitude range of 0.1–20% at constant frequency of 1.27 Hz and measuring the stress and the phase shift. The strain amplitude is expressed as percentage of the maximum applied strain, which was about 0.20 rad.

For the measurement of Zeta potential, a suspension was made at a loading of 5 vol.% solids. This suspension was allowed to age for 24 h with continuous stirring. The 0.4 ml of the above suspension was then diluted to 200 ml to give a final working solution with loading of 0.01 vol.% solids for analysis. Tests of the Zeta potential of alumina powder were performed, in two different solutions: 10^{-2} M potassium nitrate (KNO_3), and 2.8 wt.% PAM in 10^{-2} M potassium nitrate (KNO_3). The pH was adjusted with HCl and NaOH solutions of appropriate concentration. Zeta potential was calculated from the measured electrophoretic mobility in the pH interval from 3 to 12 for alumina using ELS (Electrophoretic Light Scattering) method (Brookhaven Instrument Corporation, USA). The measurement was carried out at 25±0.1 °C.

Bulk density of dried specimens was determined by the Hg immersion method based on Archimedes' principle. The flexural strength of green body was examined by a tri-axial shear instrument. Three-point bending was employed for the test, with a span of 30 mm. The bars of green bodies were normally 5×6×42 mm in size. The SEM images of fracture surfaces of the specimens of green bodies were examined with a S-450 scanning electron microscope (SEM).

3. Results and discussion

3.1. Dispersion of Al_2O_3 powder

Zeta potential is a very important physical parameter, which can affect the stability of aqueous ceramic slurry; the higher the zeta potential, the higher the repulsive energy and the more stable the slurries. Fig. 1 present

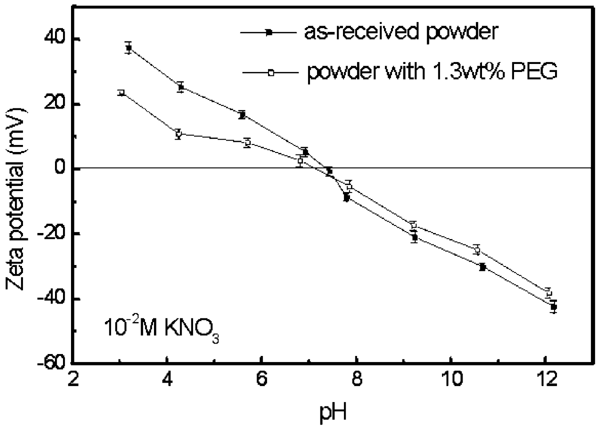


Fig. 1. Zeta potential of the Al_2O_3 powder in water without and with 1.3 wt.% PEG.

the measured results of zeta potential in the case of adding 1.3 wt.% PEG with respect to alumina powder in a 0.01 wt.% alumina suspension. The zeta potential for alumina powder only ranged 38 mV at pH 3 to −40 mV at pH 12 with an iep at pH 7.3, and that of the case containing 1.3 wt.% PEG ranged 24 mV at pH 3 to −38 mV at pH 12 with an iep at pH 7.1.

The effect of 1.3 wt.% PEG on the surface charge of alumina with a change in pH was investigated and it was found that PEG did not dissociate and hardly affected a change in alumina surface charges.

3.2. Steady shear properties of Al_2O_3 suspensions with PEG

3.2.1. Effect of solids loading on viscosity

The viscosity of a suspension is strongly dependent on the solids volume fraction, with the viscosity approaching infinity at a maximum volume fraction, Φ_m, where Φ_m relates to the particle concentration at which the average separation distance between the particles tends to zero and the particles pack together, making flow impossible.

Fig. 2 shows the relative viscosity of Al_2O_3 suspensions without and with 1.3 wt.% PEG versus the solids loading at a shear rate 110 s^{-1}. The relative viscosity is the ratio between the viscosity of the suspension and the viscosity of monomer solution (1.45 mPa s). The experimental points are fitted to a modified Krieger–Dougherty equation [10]:

$$\eta_r = (1 - \Phi/\Phi_m)^{-n} \quad (1)$$

where Φ_m and n are used as fitting parameters. The best fit of the experimental data to Eq. (1) shows that Φ_m is lower for the Al_2O_3 suspension with PEG ($\Phi_m = 0.52$) compared with the Al_2O_3 suspension ($\Phi_m = 0.58$). The difference of value of Φ_m illustrates that the addition of PEG has an influence on packing behavior of particles, but this influence is not strong.

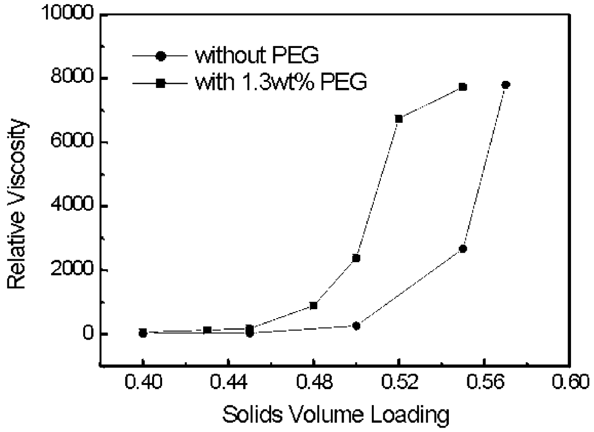


Fig. 2. Effect of solids loading on the relative viscosity of Al_2O_3 suspensions without and with 1.3 wt.% PEG at a shear rate 110 s^{-1}.

3.2.2. Fluid model of the suspension with PEG

The steady shear data of the suspensions without and with PEG are shown in Fig. 3. Both of these suspensions display the same type of rheological behavior. Shear thinning occurs at low shear rates and shear thickening at very high shear rates. However, these suspensions showed quite large differences in viscosities at the same volume fraction of solids as seen in Fig. 3. The suspension without PEG has the lower viscosity and the critical point from shear thinning to shear thickening occurs at higher shear rate ($\gamma = 32$ s^{-1}) while the suspension with PEG exhibited a higher viscosity and the critical point from shear thinning to shear thickening occurs at lower shear rate ($\gamma = 4$ s^{-1}).

Concentrated colloidally stable suspensions display shear thinning because of a perturbation of the suspension structure by shear [11]. At low shear rates, the suspension structure is close to equilibrium because thermal motion dominates over the viscous forces. At higher shear rates, viscous forces affect the suspension structure, and shear thinning occurs. At high shear rates, the viscosity increases as the shear rate increases. Hoffman [12] suggested that shear thickening is a consequence

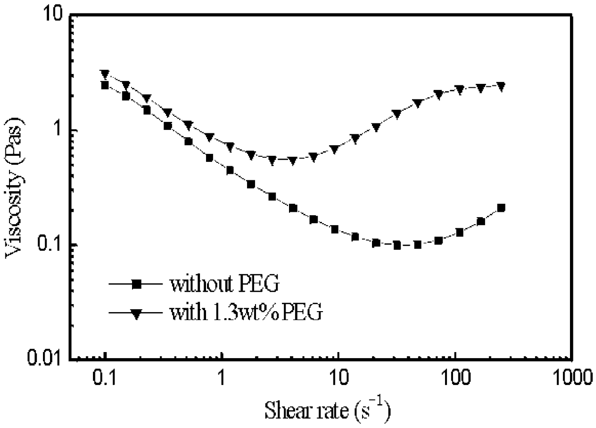


Fig. 3. Viscosity of the suspensions without and with 1.3 wt.% PEG.

of an order-to-disorder transition of the particle microstructure.

3.2.3. *Influence of ball milling period on viscosity*

With the addition of polymers such as PEG into monomer solution, the system becomes a mixture of organic monomer and polymer. It is important that the PEG absorb on the ceramic particle surface as homogeneously as possible. For this reason, ball milling of ceramics with PEG has been commonly used. Steady shear properties of Al_2O_3 suspensions with PEG at various ball milling periods are shown in Fig. 4. It can be seen from Fig. 4 that the optimum ball milling period is 24 h for the alumina suspension with PEG additions. All of the suspensions are characterized by a shear thinning behavior at low shear rates and tend to a thickening behavior at high shear rates except the suspension with 0 h ball milling period. These results imply that polyethylene glycol molecule would be absorbed on the alumina particles, and influence the interaction between particles during ball milling.

3.3. *Viscoelastic properties of Al_2O_3 suspensions with PEG*

Fig. 5 shows the log–log plot of the variation of G' and G'' with the solids loading of alumina suspension with 1.3 wt.% PEG. Where G' is the storage modulus and G'' is the loss modulus. G', which is proportional to the elastic modulus of the gel, characterizes the elastic response of the gel. G'', which is proportional to the viscous modulus of the gel, characterizes the viscous response of the gel. The modulus of the suspension shows a gradual change from more viscous ($G' < G''$) to more elastic ($G' > G''$) with increasing volume fraction. At relatively low solids loading, there is a weak interaction between the particles or/and PEG, which are only slightly compressed. Under these conditions, the suspension behaves as a viscous fluid with little elastic contribution. When the solids loading is increased, G'' becomes relatively large until a critical solids loading ($\Phi_m = 0.47$) is reached where $G' \approx G'''$, above which greater interparticle interaction occurs. Above the critical solids loading, G' continues to increase until it becomes close to G^* (complex modulus, $G^* = G' + iG''$, where $i = (-1)^{1/2}$) Under these conditions, the system becomes predominantly elastic, with significant interpenetration and compression of the chains occurring. This is also reflected in a rapid increase in dynamic viscosity η' and the whole suspension behaves like a gel.

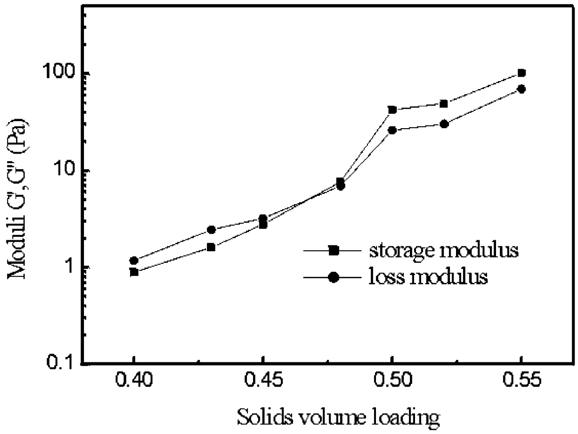


Fig. 5. Variation of G' and G'' with the solids loading of alumina suspension with 1.3 wt.% PEG at constant frequency1.27 Hz.

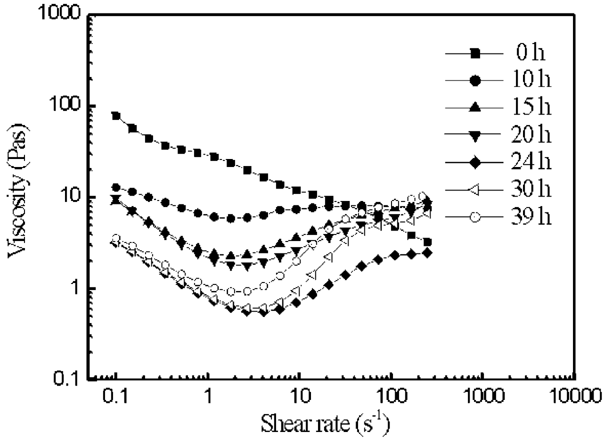


Fig. 4. Effect of ball-milling time on the viscosity of suspensions without and with adding 1.3 wt.% PEG.

3.4. *Gelling process*

For gelcasting the polymerization was induced by an initiator and the reaction can be accelerated by a catalyst and temperature. When using an initiator and at the same time the amount of catalyst and the temperature were fixed, we can observe the structural change of the suspension versus time [13].

Fig. 6 shows how the storage modulus of alumina/PEG slurry varies with time. In Fig. 6 it can be seen that

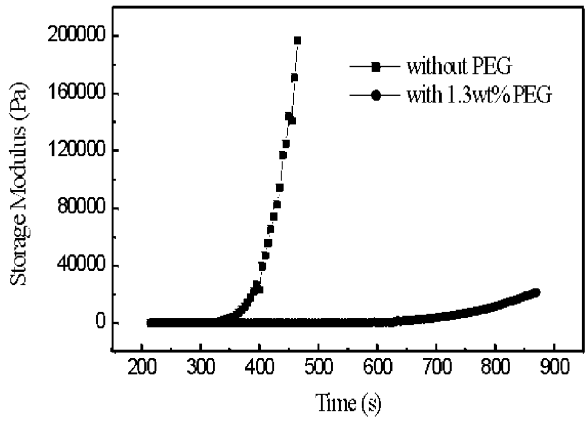


Fig. 6. Relationship of the storage modulus of alumina suspension versus solidified time.

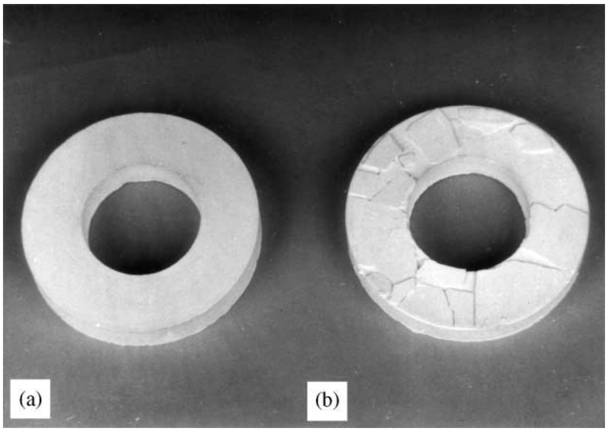


Fig. 7. Surface of alumina green body prepared from the suspensions with 1.3 wt.% PEG (a) and without PEG (b).

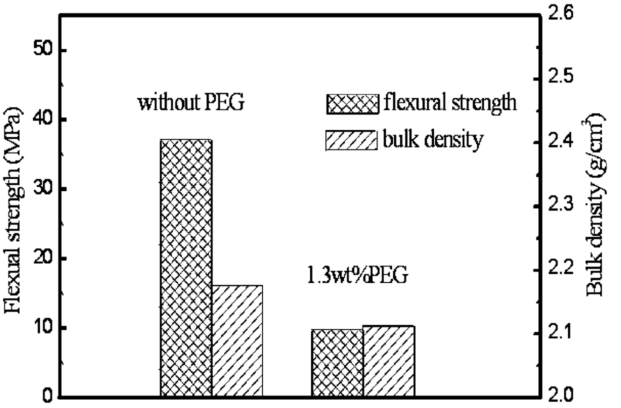


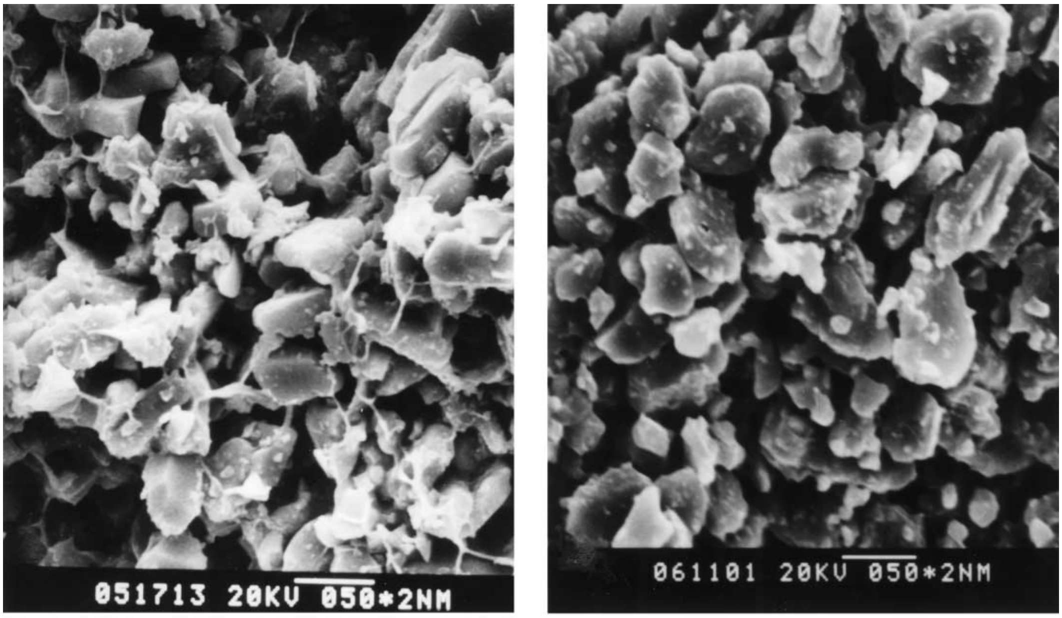
Fig. 8. Bulk density and flexural strength of dried green bodies without and with 1.3 wt.% PEG.

the increase of the storage modulus is more rapid and reaches a higher level at same temperature without PEG, compared to ones of slurry with PEG. The storage modulus of the slurry with PEG is lower than that of the slurry without PEG, which indicates the strength of green body with PEG is less than that of the green body without PEG.

The reason for the fact that the storage modulus of the suspension with PEG varies earlier and higher than that of the suspension without PEG is probably due to the fact that the contact among monomers AM might be interfered and hindered by PEG in the solution. Hence longer time would be required for AM to become a hydrogel in the presence of PEG. Above 350 s, the monomer starts to polymerize, resulting in an increased viscosity and an elastic viscoelastic response (Fig. 5).

3.5. Physical properties of gelled sample from the alumina suspension with PEG

Acrylamide/polyethylene glycol-based gelcasting system is a viable alternative to those based on in situ polymerization of monomeric systems. This study highlights the importance of suspension composition (i.e., polymer, monomer, cross-linking agent, and solid content) and rheological and gelation behavior. A minimum PEG concentration in solution is required to inhibit the surface-exfoliation phenomenon. By a series of experiments it is concluded that 1.3 wt.% PEG is the optimum concentration. Fig. 7 shows the surface of an annular cylinder of alumina obtained by using the present method. In Fig. 7(a) and (b) shows green bodies gelcast from a slurry with additions of 1.3 wt.% PEG



(a) (b)

Fig. 9. Microstructures of green bodies prepared from suspension without PEG (a) and with 1.3 wt.% PEG (b).

and a slurry without PEG. It can be seen that the surface of the green bodies without PEG has a surface-exfoliation phenomenon, but the surface-exfoliation phenomenon of green bodies gelcast in air was eliminated when adding 1.3 wt.% PEG to the monomer solution. The mechanism that inhibit surface-exfoliation phenomenon of green bodies gelcast in air via addition of polymer refers to our further study.

An advantage of gelcasting over slip casting is the high strength of the dried green body. In this study, after adding 1.3 wt.% PEG the density and strength measured were approximately 53.1% of theoretical density (TD) and 9.7 MPa as seen in Fig. 8. The addition of 1.3 wt.% PEG decreased the green density and the green strength of the dried bodies compared to the strength of green body without PEG (37 MPa). However, also the reduced strength is enough to be green-machined inexpensively into even more complex shapes. The decrease in strength can be explained by the microstructure of the green body.

Fig. 9(a) and (b) shows the microstructures obtained by the gel formed by polymerization of monomer without and with PEG mixed with alumina. There is a good microstructure with very few pores for both green bodies without and with PEG. But it can be also observed that there is obvious structure of network for green body without PEG compared to green bodies with PEG.

4. Conclusions

A new gelcasting system based on aqueous Al_2O_3–PEG–AM suspensions cross-linked with a coupling agent MBAM was developed. An advantage of this system over monomer-based system is that it eliminates the surface-exfoliation phenomenon of green bodies gelcast in air and makes gelcasting on easy process. Addition of 1.3 wt.% PEG has little influence on dispersion of alumina slurry and on its rheological properties. A marked decrease in both, gelation rates and flexural strength of ceramic parts, is observed for gelcasting suspensions with PEG. But, existing flexural strength of ceramic parts (9.7 MPa) is enough to machine inexpensively into more complex shapes.

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