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Gelcasting of alumina with a mixed PVP–MAM system

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Abstract

A common and fatal problem of the low-toxicity gelcasting is the low flexural strength of green bodies. The objective of this study was to solve the problem by introducing water-soluble polyvinylpyrrolidone (PVP) polymer to the monomer system. The low-toxicity monomer and ceramic powder were selected as methacrylamide (MAM) and alumina, respectively. Flexural strength of green bodies was improved nearly by 30%, with no significant change in the property of sintered bodies when the addition amount of PVP is 2.8 wt.%. Influence of PVP content on rheological properties of alumina suspensions, their gelation time, and the microstructure of green and sintered bodies were investigated.

Keywords: D. Alumina; Polyvinylpyrrolidone; Methacrylamide; Gelcasting

1. Introduction

Gelcasting has been receiving an increasing attention as a new in situ colloidal forming of ceramics for a dozen of years. Monomer systems for the technology varied from crylic acid system in the non-aqueous category to acrylamide systems with a neurotoxin in the aqueous category and further to methacrylamide (MAM) with low toxicity [1–3].

Polyacrylamide itself is non-toxic and has been used for decades in biology for gel electrophoresis in DNA as well as for other technologies. Acrylamide monomer, however, is neurotoxic, which has been the major hindrance to the industrial development of gelcasting [4]. Some investigations were carried out to find less toxic monomers to replace acrylamide monomer. However, there are few reports on gelcasting with low-toxicity monomer system, mainly with methacrylamide monomer system [5–8]. So far, the low-toxicity gelcasting is still confronted with a common problem—low flexural strength of green bodies.

In this study, polyvinylpyrrolidone (PVP) was introduced into the methacrylamide monomer system to improve flexural strength of Al_2O_3 green bodies. The amount of PVP was optimized. Meanwhile, influence of PVP on rheological properties and gelling characteristics of Al_2O_3 suspensions was investigated. Microstructure of green and sintered bodies prepared from the monomer system with and without PVP was analyzed.

2. Experimental procedure

2.1. Raw materials

Physical and chemical characteristics of the starting high-purity α-Al_2O_3 powder (AKP-20, Japan Sumitomo Chemical Company) used in this study are shown in Table 1. The average particle size of the powder is 0.57 μm. Raw materials for the mixed PVP–MAM system are listed in Table 2.

2.2. Preparation of suspensions

The preparation of suspensions was similar to that of [9]. A 0.25 wt.% dispersant and 0, 1.0 or 2.8 wt.% PVP (based

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Table 1
Physical and chemical characteristics of alumina powder

Phase	α-Al_2O_3
Purity (%)	>99.9
Surface area (m^2/g)	4.2
D_{50} (μm)	0.57
Si (ppm)	<40
Na (ppm)	<10
Mg (ppm)	<10
Ca (ppm)	<10
Fe (ppm)	<20

on the weight of alumina powder) were firstly completely dissolved in a premix solution, which was prepared by dissolving proper amounts of MAM and MBAM in deionized water, to produce a complex solution. Alumina powder was then added into the solution by mechanical stirring till solids loading up to 50 vol.%. Afterwards, the mixtures were milled for 24 h in a nylon resin jar using alumina ball-milling media to break down agglomerates and to achieve good homogeneity. Rheological properties of the suspension were measured.

Binder burnout and subsequent sintering were carried out in stationary air and conducted separately. Binder burnout was carried out at 600 °C for 2 h, with a heating rate of 2 °C/min and natural cooling. Sintering was carried out at 1550 °C for 2 h with a heating rate of 1 °C/min from room temperature to 1250 °C and 0.5 °C/min from 1250 to 1550 °C, and a cooling rate of 1 °C/min to 1000 °C, followed by natural cooling.

2.3. Measurements

Shear viscosity is measured by a Modular Compact Rheometer (MCR300, Paar Physica, Germany) with a concentric-cylinder, CC27, with 1.33 mm gap between the inner and outer cylinder walls. Shear curves were performed at 0.1–250 s^{-1}. Measurement of the storage modulus of slurries was conducted at 25 °C, with frequency of 1 Hz and strain amplitude of 1%.

Flexural strength was examined by three-point flexure test with a span of 30 mm at a loading rate of 0.5 mm/min. The bars of green and sintered bodies were 5 mm × 6 mm × 42 mm and 3 mm × 4 mm × 36 mm, respectively. Six samples were used to calculate the average values and errors. Fracture surfaces of the green and sintered specimens were observed with a scanning electron microscope (JSM-6460LV, JEOL, Japan).

3. Results and discussion

3.1. Effect of crosslinker concentration on gelation time of the suspensions

The gelation process is one of the key steps of gelcasting. The gelation rate depends on polymerization rate of the organic monomer in the suspension. Generally, polymerization rate is related to the amount of initiator, concentration of monomer and polymerization temperature, and can be expressed as follows [10]:

$$R_p = [\mathrm{I}]^n [\mathrm{M}]^m \quad (1)$$

where [I] is initiator concentration, [M] monomer concentration, K a temperature dependent constant, and R_p the polymerization rate. Exponent n is 0.5–1 and m is 1–1.5 (one or two may reach 2). It should be pointed out in particular that the crosslinker is a kind of difunctional monomer in this system.

It is found that the gelation time (the period from adding initiator/catalyst to the start of gelation of the Al_2O_3 suspensions) varied with the content of crosslinker. Thus, the influence of crosslinker content on polymerization rate was studied, with constant MAM monomer content and various ratios of crosslinker to the monomer.

Table 3 shows the effect of crosslinker concentration (where it was expressed by the ratio of crosslinker to monomer) on gelation time of 50 vol.% Al_2O_3 suspensions with 2.8 wt.% PVP at 70 °C. It is noted in Table 3 that gelation time decreases rapidly with the increase in the amount of the crosslinker. When the crosslinker content is higher than 1:10, gelation time is in scores of minutes.

Table 2
Raw materials for the mixed PVP–MAM system

Function	Raw material	Manufacturer	Note
Monomer	Methacrylamide (MAM)	Aldrich, USA	Chemically pure
Crosslinker	*N*,*N*′-Methylenebisacrylamide (MBAM)	Hongxing Biological and Chemical Factory of Beijing, China	Chemically pure
Initiator	Ammonium persulphate (APS)	Beijing Third Reagent Works, China	Chemically pure
Catalyst	*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TEMED)	Xingfu Fine Chemical Institute, China	Chemically pure
Dispersant	Ammonium citrate	Beijing Chemical Reagent Company, China	Chemically pure
Solvent	Deionized water		Conductivity: 1.02 μS/cm
Polymer	Polyvinylpyrrolidone (PVP)	Aldrich, USA	K-30, chemically pure; average molecular weight: 10,000

Table 3
Effect of crosslinker on gelation time of alumina suspension (50 vol.% solids loading/2.8 wt.% PVP)

Concentration of crosslinker (20 wt.% MAM)	Gelation time (min)	Gelation status after 2 h
1:6	25	Complete
1:10	35	Complete
1:25	110	Incomplete
1:50	–	Not started

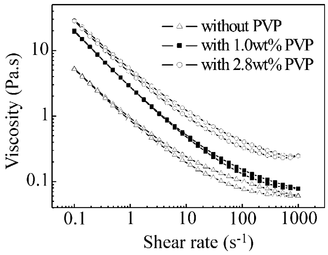

Fig. 1. Rheological behavior of alumina suspensions with and without PVP.

3.2. *Effect of the amount of initiator and catalyst on gelation time of the suspensions*

According to the principle of radical-free polymerization, initiator amount shows a remarkable influence on polymerization. Firstly, initiator forms free radicals of initiator, and then it reacts with monomer and forms free radicals of monomer as well as initiates polymerization. A catalyst may enhance polymerization rate. In this study, the amount of catalyst was fixed as a half of that of initiator.

Table 4 shows gelation time as a function of initiator amount in 50 vol.% Al_2O_3 suspensions with 2.8 wt.% PVP at 70 °C. Gelation time is reduced rapidly with the increase in the amount of the initiator. When a larger amount of initiators was used, the suspension gelled and solidified quickly, which made it difficult to control the gelation rate by modifying the temperature for gelation. The gelation of suspensions was relatively slow and a few days were required when a small amount of initiator was added to the suspension. The table shows that when 200 μl of 8 wt.% water solutions of the initiator (100 μl catalysts) were added, it is easy to control the gelation rate by modifying the gelation temperature.

3.3. *Effect of PVP content on rheological properties of the suspensions*

The rheological behavior of 50 vol.% suspensions containing various amounts of PVP is shown in Fig. 1. The suspensions containing 0 and 1.0 wt.% PVP show thinning behavior at whole measured range of shear rates, while the suspension containing 2.8 wt.% PVP exhibits first shear thinning at lower shear rates and then shear thickening at higher shear rates with a critical shear rate ($\gamma = 750\ s^{-1}$). At the same shear rates, the viscosity of those suspensions shows significant increase with the increase in the amount of PVP.

Concentrated stable suspensions usually exhibit shear thinning behavior because of a perturbation of the suspension structure by shearing [11]. At low shear rates, the suspension structure is close to equilibrium because thermal motion dominates over the viscous forces. At high shear rates, viscous forces affect the suspension structure, and, thus, shear thinning occurs. Shear thickening of the suspension with 2.8 wt.% PVP is assumed a consequence of an order-to-disorder transition of the particle microstructure, as suggested by Hoffmann in a previous study [12].

The rheological behavior depicted in Fig. 1 has been analyzed using the Herschel–Buckley model [13]:

$$\tau = \tau_y + k\gamma^n \qquad (2)$$

where τ_y is yield stress, τ shear stress, γ shear rate, n shear rate exponent and k a constant. The yield stress values presented in Table 5 were calculated according to the above model. The suspension containing PVP obviously exhibits a higher yield stress compared with the suspension without PVP. The yield stress of suspensions increases with polymer amount, which results in change in the interaction among particles and inner structure of the suspensions.

3.4. *Influence of PVP content on gelation time of the suspensions*

It is well known that storage modulus, which is proportional to elastic modulus of a gel, can be used to characterize elastic response of the gel. When the structure

Table 4
Effect of initiator on gelation time of alumina suspensions (50 vol.% solids loading/2.8 wt.% PVP)

Amount of suspensions (ml)	Ratio of monomer and crosslinker (20 wt.% MAM)	Initiator (8 wt.% APS, μl)	Catalyst (μl)	Gelation time (min)
25	10:1	50	25	100
25	10:1	100	50	35
25	10:1	200	100	18
25	10:1	400	200	11
25	10:1	600	300	6

Table 5
Herschel–Buckley parameters τ_0 and n of alumina suspensions without and with PVP (50 vol.% solids loading, 0.25 wt.% dispersant, 25 °C)

PVP content (wt.%)	Yield stress (τ_0, Pa)	Constant (k)	Exponent of shear rate (n)	Correlation ratio (R_{xy})
0	0.5462	0.2720	0.75592	0.99695
1.0	2.0894	0.5419	0.69092	0.99755
2.8	2.9347	1.5238	0.69385	0.99581

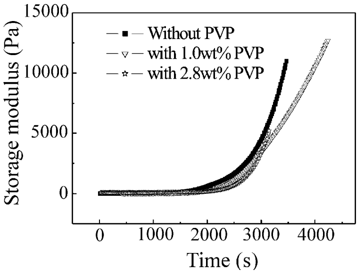

Fig. 2. Storage modulus of the suspensions with time.

of slurry is modified, the modulus of the slurry shows gradual change with time. Thus, gelling characteristics of alumina slurries were characterized by the time dependence of the storage modulus of PVP–MAM/Al_2O_3 slurries in Fig. 2 (the amounts of initiator and catalyst are 100 and 50 μl, respectively). It can be seen that the storage modulus reaches a higher level after a shorter time in the MAM only system than in the PVP–MAM mixed system. The reason why the storage modulus of the slurry in the MAM only system increases earlier than in suspensions containing 1.0 or 2.8 wt.% PVP is probably that the mutual contact of MAM monomers is hindered by the increase in viscosity of suspensions containing PVP. Hence, longer time would be required for MAM to become hydrogel in the presence of PVP. Above 1900 s, the monomer MAM starts to polymerize, resulting in an increasing viscosity and a viscoelastic response.

3.5. Effect of PVP on the properties of alumina green and sintered bodies

Flexural strength of the dried green bodies with and without PVP is listed in Table 6. Green strength of the samples with the addition of 2.8 wt.% PVP is 28 MPa, 30% higher than that of the green bodies without PVP. In previous studies, flexural strength of gelcast green bodies was found to be determined mainly by the strength of polymer gel [14,15]. During the polymerizing of MAM monomers, a complicated polymer network is likely to be formed in the monomer solution with 2.8 wt.% PVP through hydrogen bonds between PVP and PMAM, resulting in an intimate mix of polymer chains [16]. The monomer–polymer system with such a type of complicated polymer network shows relatively higher gel strength in contrast to a pure monomer system. Thus, the green bodies prepared from the suspension with the addition of 2.8 wt.% PVP show higher flexural strength as compared with those samples without PVP.

Table 6
Flexural strength of alumina green and sintered bodies

PVP content (wt.%)	Flexural strength (MPa)	
	Green bodies	Sintered bodies
0	22.13 ± 2.63	373.23 ± 11.36
1.0	22.76 ± 1.89	368.63 ± 4.30
2.8	28.45 ± 2.32	362.15 ± 7.22

Fig. 3 shows SEM micrographs of the alumina green bodies with and without PVP. All samples show a homogenous microstructure with rare pores. Polymer networks are visible in the micrographs. The microstructure of the green bodies prepared from the systems with or without PVP show no significant difference, which is also

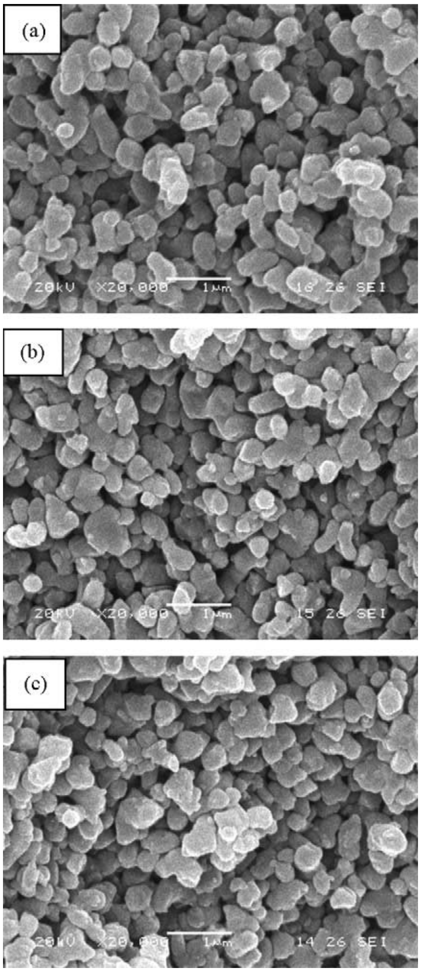

Fig. 3. SEM micrographs of the alumina green bodies prepared form the MAM monomer system: (a) without PVP; (b) with 1.0 wt.% PVP; (c) with 2.8 wt.% PVP.

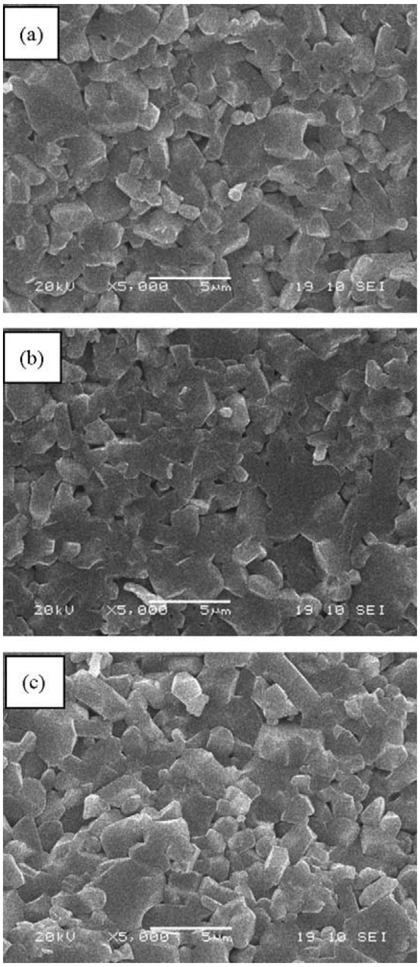

Fig. 4. SEM micrographs of the alumina sintered bodies prepared form the MAM monomer system: (a) without PVP; (b) with 1.0 wt.% PVP; (c) with 2.8 wt.% PVP.

the case for the microstructure of sintered bodies, as illustrated in Fig. 4. The ceramics exhibit uniform microstructures without exceeded grain growth. The data in Table 6 show that the flexural strengths of the ceramics are about 350–400 MPa irrespective to the amount of PVP in the MAM system.

4. Conclusions

Gelcasting with low-toxicity MAM monomer system was successfully applied to prepare alumina ceramics with the gelation time of the suspensions within tens of minutes. The process is still feasible and successful with the addition of PVP into the monomer system in case the amount of initiator and catalyst for gelation are optimized.

The concentrated stable Al_2O_3 suspensions exhibit a shear thinning behavior except the one with 2.8 wt.% of PVP, which is shear thickening at high shear rate. Viscosity of the suspensions increases with increase in the amount of PVP added into the MAM monomer system. According to the Herschel–Buckley model, the suspension with 2.8 wt.% PVP shows much higher yield stress (2.9347 Pa) in contrast to that (0.5462 Pa) of the slurries without PVP.

The addition of a proper amount (2.8 wt.%) of PVP improves flexural strength of the green bodies (by 30%), with only a slight decrease in the property of sintered bodies. The addition of PVP shows no significant influence on the homogeneous and dense microstructure of the green and sintered bodies prepared from the MAM system.

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