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Ceramics International 38 (2012) 6923–6926
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Gelcasting of alumina ceramics with improved green strength

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Received 13 April 2012; received in revised form 9 May 2012; accepted 9 May 2012
Available online 23 May 2012

Abstract

Hydantion epoxy resin with excellent water solubility and low toxicity which are important factors in aqueous gelcasting of ceramics in air condition was firstly developed. The effect of Hydantion epoxy resin on the rheological property, gelation behavior and mechanical property was presented using Al_2O_3 as the model system. The results showed that the idle time of Al_2O_3 suspensions with the addition of Hydantion epoxy resin is sufficient for casting at room temperature. With the addition of 15 wt% Hydantion epoxy resin, the flexural strength of Al_2O_3 green body reached 43.4 MPa, which is the highest so far among the existing gelling systems and is 2.6 times higher than the result in reported water-soluble epoxy resin systems.

Keywords: A. Suspensions; C. Strength; D. Al_2O_3; Gelcasting

1. Introduction

Gelcasting is an attractive near-net-shaped colloidal processing for making components [1–3], and has been widely used for a range of ceramics and metals by means of in situ polymerization of organic monomers and cross-linkers in a high solid loading suspension. Homogeneity and high mechanical strength of the green body offer great advantages for machining in the green state and for fabricating parts with fine structures. The addition of small quantities of organic monomers avoids a long and complicated binder burnout schedule [4].

Although the frequently employed acrylamide (AM) monomer can offer the alumina gelcasting bodies a high green strength of 37.11 ± 1.67 MPa [5], the disadvantages like neurotoxicity and sensitivity to oxygen [2] limit its application. Much attention has recently been paid on the development of alternative gelling systems [6], including polyvinyl alcohol [7], gelatine [8], agarose [9], and sodium alginate [10,11]. Among these alternatives, the water soluble epoxy resin [12,13] is a promising gelling system, such as ethylene glycol diglycidyl ether (EGDGE) [13]. The advantages of this gelling system are evident as low viscosities of slurries and high strengths of green bodies. However, there still exist some unfavorable characteristics of EGDGE, including that it is irritative to the skin and eyes, in need of a careful storage and variable in the water solubility from source to source. Hence, developing a new epoxy gelling system is necessary to further improve the gelcasting processing. In this context, Hydantion epoxy resin is an interesting candidate since it is not toxic and has extremely high water solubility due to the strong hydrophilic amide groups. Hydantion epoxy resin is crystallized at room temperature, which is convenient for the transportation and storage. The aim of this work is to investigate the gelcasting system involving Hydantion epoxy resin in Al_2O_3 suspension. The effects of the content and the gelling temperature of Hydantion epoxy resin on the rheological behavior of Al_2O_3 suspensions, the properties of green and sintered bodies have been evaluated.

2. Experimental procedure

Commercial Al_2O_3 powder (AES-11, 99.8%, Sumitomo Chemical Co. Ltd., Tokyo, Japan) with a mean particle size of 0.5 μm was used as raw material. 50 vol% slurries were prepared by ball milling alumina powders with

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.05.027

10–15 wt% aqueous premix solution of Hydantion epoxy resin (MHR-070, Meihua Chemicals Co. ., China). 0.65 g ammonium polyacrylate (HydroDisper A168, Highrun Chemical Industry Co. Ltd., China) per 100 g alumina was added as the dispersant. 0.25 mol/eq 3,3′-Diaminodipropylamine (DPTA, > 98%, Tokyo Chemical Industry Co. Ltd., Japan) based on the epoxy resin was added as the hardener. Before pouring into polydimethylsiloxane (PDMS) molds, the slurries were degassed in a vacuum desiccator. Drying was carried out in three steps, including at ambient environment for 24 h, at 40 °C for 4 h and at 80 °C for 20 h. Sintering was carried out at 1550 °C for 2 h.

The viscosities of Al_2O_3 slurries were characterized using a rotational rheometer (AR2000 EX,TA Instruments, USA) with a diameter of 40 mm parallel plate. Slurries were all pre-sheared at a shear rate of 100 s^{-1} for 10 s. The measurements were performed within the shear rate range of 1–1000 s^{-1} at 25 °C. Additional measurements were made at a constant shear rate of 0.1 s^{-1} to probe the time-dependent evolution of η_{app} during gelation at varying temperatures and epoxy resin concentrations [14]. The flexural strengths of the green body were determined by three-point bending tests using an electronic universal testing machine (KD11-2, KEJALI Technology Co., Ltd., China) with a crosshead speed of 0.5 mm/min. The relative green and sintered densities were measured by the Archimedes' method. The microstructures of the fractural surfaces of green and sintered bodies were observed by scanning electron microscopy (NOVA NANOSEM 230).

3. Results and discussion

Fig. 1 shows the effects of Hydantion epoxy resin concentrations on the viscosities of 50 vol% Al_2O_3 slurries with 0.65 wt% HydroDisper A168 as a function of the shear rate. All the four suspensions displayed a shear-thinning behavior which is beneficial for casting the slurry. As expected, the viscosity of the suspension was largely influenced by the epoxy resin concentrations. The viscosity of the suspension with 15 wt% Hydantion epoxy resin at 100 s^{-1} were about 2.6 times higher than that of the suspension without Hydantion epoxy resin, from 49.5 mPa s to 129.8 mPa s. However, the suspension with even 15 wt% Hydantion epoxy resin displayed a rather low viscosity, which was still suitable for the gelcasting process.

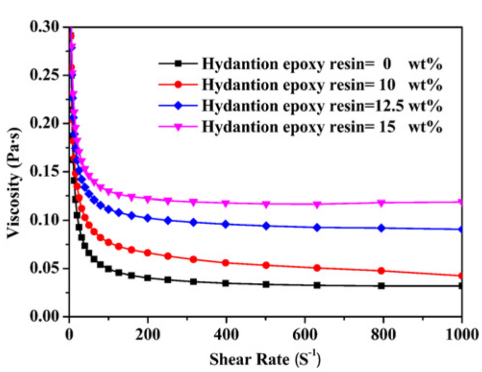

Fig. 1. Viscosity of 50 vol% Al_2O_3 slurries with different Hydantion concentrations as a function of the shear rate.

Fig. 2(a) shows the gelation behavior of 50 vol% Al_2O_3 suspensions containing 10 wt% Hydantion epoxy resin after adding 0.25 mol/eq DPTA, in accordance with the temperature and the gelation time. The apparent viscosity η_{app} increased with the increase of the gelation time, indicating the formation of the macromolecular network based on epoxy-amine reaction. The gelation behavior became retarded at decreased temperatures and no gelation was observed at 15 °C during the test period. After the addition of the hardener, η_{app} firstly exhibited a flat curve of relatively low viscosity, followed by a rapid increase as the viscosity diverged to infinity. This period of constant low viscosity is called idle time. The idle time of Al_2O_3 suspensions increased from less than 350 s to more than 3000 s while the temperature decreased from 65 °C to 15 °C. At 15 °C, the viscosity of the suspension at shear rate 100 s^{-1} increased from 77.1 mPa s before adding the hardener to 313.3 mPa s after adding the harder and going through the gelation behavior test for 1 h. The suspension still had the fluidity ($\eta < 1.0$ Pa s at 100 s^{-1}) necessary to ensure good mold filling behavior [13]. Therefore, by lowering the temperature prior to casting, the handling time can be dramatically increased. Fig. 2(b) shows the effects of Hydantion concentrations on gelation behavior of 50 vol% Al_2O_3 suspensions at 65 °C. The trends were similar to the results in Fig. 2(a), however, the gelation kinetics of Al_2O_3 suspensions displayed a tendency to increase with the increase of Hydantion epoxy resin concentrations.

Fig. 3 shows the mechanical properties and relative densities of the dried green bodies with different Hydantion epoxy resin concentrations. As Hydantion epoxy resin concentrations increased from 10 wt% to 15 wt%, the flexural strength increased from 10.7 MPa to 43.4 MPa. With the addition of the same concentration of the gelling agent, Hydantion epoxy resin system showed significantly higher green strength than EGDGE system, i.e. 43.4 MPa vs. 16.9 MPa [13]. This may be attributed to higher water solubility of Hydantion epoxy resin which led to the gels distribution more uniformly and higher flexural strength. With the increase of Hydantion epoxy resin concentrations from 10 wt% to 15 wt%, the relative density increased from 54.7% to 62.2%. Fig. 4(a) shows the SEM micrographs of the fracture surface of alumina green body obtained from 50 vol% alumina suspension with 15 wt% Hydantion epoxy resin. Al_2O_3 particles were packed uniformly without any large defect and slender polymer chains can be observed connecting the particles, which were responsible for the high strength of the green body. After sintering at 1550 °C for 2 h in air, the average flexural strength and relative density were 300.2 ± 34.1 MPa and 97.0% ± 0.6% respectively, which were comparable to those derived from another epoxy resin gelling agent, SPGE, i.e. 335 ± 47 MPa and 98% with

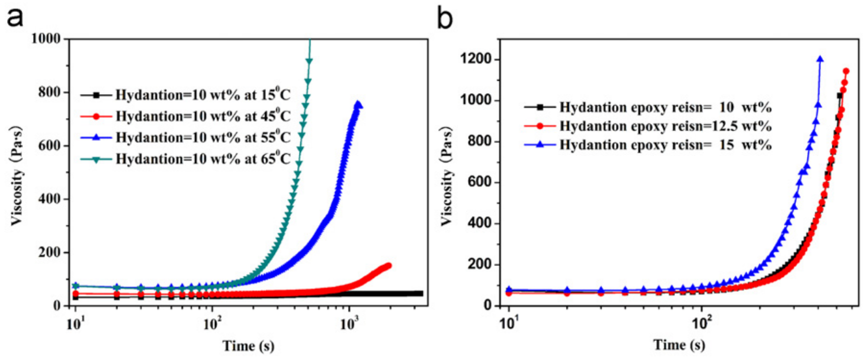

Fig. 2. Semilog plots of η_{app} as a function of gelation time for 50 vol% Al_2O_3: (a) with 10 wt% Hydantion epoxy resin at different temperatures and (b) with different Hydantion epoxy resin concentrations at 65 °C.

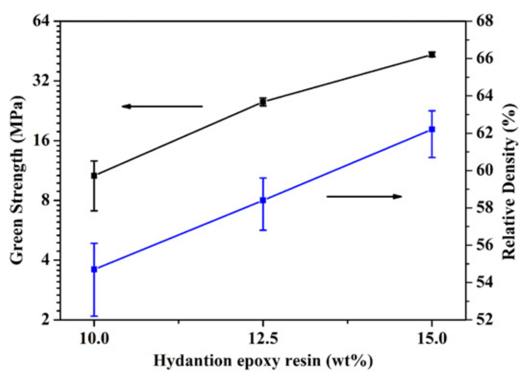

Fig. 3. Effects of Hydantion epoxy resin concentrations on the flexure strength and the green density of dried alumina green bodies. The error bars represent the distribution range of the measured results, while the points represent the average values.

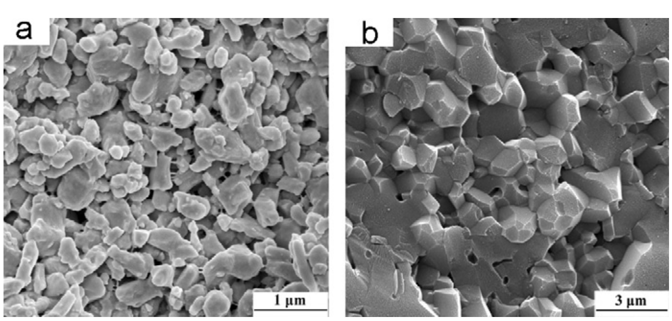

Fig. 4. Typical SEM micrographs of fracture surfaces of alumina green body (a) and sintered body (b) obtained from 50 vol% alumina suspension with 15 wt% Hydantion epoxy resin crosslinked by 0.25 mol/eq DPTA.

a sintering temperature of 1650 °C [12]. The fracture surface of the sintered ceramics exhibited a homogenous and dense microstructure, as shown in Fig. 4(b).

4. Conclusions

Hydantion epoxy resin and polyamine hardener system were developed for gelcasting alumina ceramic. The rheological and gelation behavior of Al_2O_3 suspensions, as well as green body properties were strongly influenced by Hydantion epoxy resin concentrations. The idle time decreased with the increase of gelling temperature and no significant gelation was observed at 15 °C. With the addition of 15 wt% Hydantion epoxy resin, the flexural strength and relative density reached 43.4 MPa and 62.2% for green Al_2O_3 ceramic, respectively, and were 300.2 MPa and 97.0% for sintered Al_2O_3 ceramic, respectively.

Acknowledgments

This work was financially supported by the Natural Science Foundation of China (Grant no. 51072235), the Ph.D. Programs Foundation of Ministry of Education of China (Grant no. 20110162110044) and the New Century Excellent Talents program (Grant no. NCET-10-0802).

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