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Rheological characterization of a gelcasting system based on epoxy resin

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Abstract

The *in situ* polymerization of an aqueous system comprising epoxy resin and polyamine has been developed to consolidate ceramic suspensions in our previous study. In the present work, the polymerization of the aqueous solution was investigated by an oscillatory method in terms of storage modulus G'. The influences of the epoxy resin on alumina suspensions were evaluated by means of zeta potential and viscosity. The consolidation behaviors of suspensions with different solids were also studied.

Keywords: A. Suspension; D. Al_2O_3; Rheology; Gelcasting

1. Introduction

In the past decade, several consolidation techniques have been investigated with the aim of forming ceramic bodies directly from colloidal suspensions [1,2]. These techniques combine advantages such as the microstructural homogeneity and the ability to form complex-shaped ceramic parts [3]. Among which, gelcasting is a novel near-net shaping method, which was first developed at Oak Ridge National Laboratory by Janney and Omatete [4–6]. It has been applied to prepare various ceramics [7–9] and ceramic foams as well [10,11]. In this method, polymerization is a free radical reaction process which is inhibited by atmospheric oxygen, resulting in the surface-exfoliation phenomenon of green bodies [12]. Aggravatingly, for the consolidation of ceramic foams, 0.2% oxygen in atmosphere was sufficient to inhibit the reaction completely due to large numbers of bubbles in suspensions [13]. Hence, the polymerization procedure is usually carried out in a N_2 filled chamber. However, a technical process under nitrogen is complicated, hence increasing the cost of production, especially in the case of industrial production. To avoid the surface-exfoliation phenomenon, some polymers were added to the gelcasting systems [14–16]. But, these means are based on the sticky assistance of polymer molecules, and do not prevent the oxygen inhibition effect essentially [17]. The difference between surface and inside still exists, which will lead to defects and cracks during drying and sintering.

On the other hand, some natural polymers, such as polysaccharides, [18,19] alginates, [20,21] and proteins, [22] which may gel in atmosphere, have been reported as gelling agents. However, difficulties regarding fluidity of slurries and insufficient strength for handling green bodies discourage their further applications.

Recently, we developed a gelcasting system based on a water-soluble epoxy resin [23]. The advantage of this system is that it can be carried out in air atmosphere, for the polymerization is a nucleophilic addition reaction and not affected by oxygen. The polymerization of the system and the consolidation of ceramic suspensions are unacquainted, though the gelcasting procedure and the properties of obtained alumina ceramics have been studied. The aim of the present work is to study the rheological behaviors of the gelcasting system.

2. Epoxy resin and polyamine system

In the present study, an epoxide of sorbitol polyglycidyl ether (SPGE) was used and dipropylenetriamine (DPTA) was selected as its hardener. The chemical formulas of SPGE and DPTA are shown in Fig. 1. SPGE possesses a large amount of hydrophilic hydroxyl and ether groups, which make it soluble in water [24]. The curing condition of epoxy resin (e.g. pressure and temperature) depends on the added hardeners. Although

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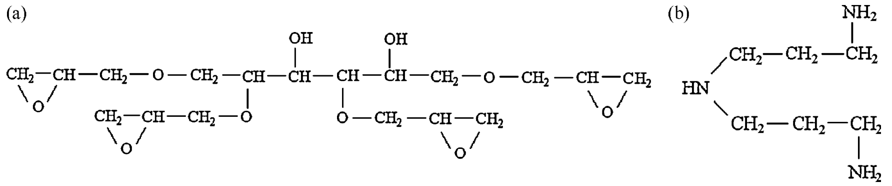

Fig. 1. Chemical formulas of (a) SPGE and (b) DPTA.

many kinds of hardeners are available for curing epoxy resin, DPTA is an excellent one because it can react with SPGE in aqueous solution under atmospheric pressure and room temperature.

The polymerization between SPGE and DPTA is a nucleophilic ring-opening reaction instead of free radical reaction, which is not inhibited by oxygen in air. Hence, the processing in the present work can be carried out in air atmosphere. The generally accepted scheme of an amino-epoxy cure involves three main reactions as shown in Fig. 2 [25]. Firstly, primary amine reacts with and links to the epoxide group, resulting in secondary amine. Then, secondary amine further reacts with the epoxide group. Finally, the formed hydroxyl continuously reacts with epoxide group until a three-dimensional network forms. Correspondingly, the liquid system is transformed to an elastic monolithic gel.

3. Experimental procedure

3.1. Synthesis of monolithic gels

SPGE (Nagase Chemtex, Osaka, Japan), whose epoxy equivalent (eq) weight is 173 g/eq, was first diluted in deionized water to a concentration of 15 wt.%. For cross-linking, 0.25–1.0 ml DPTA was added into 10 g resultant premix under agitation. To study the influence of temperature on polymerization, the processing was carried out at the temperature of 20–45 °C using a water bath.

3.2. Gelcasting of alumina

The gelcasting procedure in the present study was similar to that in our previous publication [23]. The suspensions containing 72, 76, 80 and 83 wt.% (40, 45, 51, and 56 vol.%) solids were prepared by ball-milling alumina powder (AES-11, Sumitomo, Japan) with 15 wt.% aqueous premix solution of SPGE. Polyacrylic acid ammonium salt (A-30SL, Toa Gosei Co., Tokyo, Japan) was added as dispersant with the amount of 0.75 ml for per 100 g alumina powder. DPTA was then added into the resultant suspensions as hardener for consolidation.

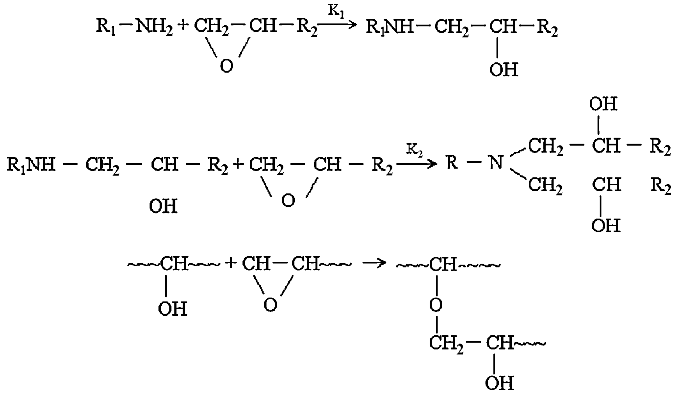

Fig. 2. The scheme for amino-epoxy cure.

3.3. Characterization methods

The zeta potentials of the diluted suspensions (about 0.01 wt.% solids) were measured by electrophoretic mobility using Zeta Potential Analyzer (ZetaPlus, Brookhaven, USA). Hydrochloric acid and sodium hydroxide solutions were used to adjust pH value. The zeta potential was determined as a function of pH value. Steady shear measurement of the viscosity at various shear rates was conducted with the stress-controlled rheometer (SR5, Rheometric Scientific Inc., Piscataway, NJ). The measurement was performed within the shear rate range of 1–1000 s^{-1} at a constant temperature of 25 °C. The polymerization of the aqueous solutions and the consolidation of the ceramic suspensions were monitored by means of oscillatory shear deformation using SR5, under a continuous frequency of 1.0 Hz and a constant strain of 0.4%.

4. Results and discussion

4.1. Polymerization kinetics

Controlling the gelation rate has been regarded as one of the most important factors in gelcasting of ceramics. The hardener concentration and gelation temperature determine the induction time and propagation rate. The polymerization of the aqueous system was monitored by an oscillatory shear deformation method, which effectively preserves the gelled sample integrity during measurement. At the beginning of gelation, the system was predominantly viscous and the value of storage modulus (G') was very low. When consolidation occurred, the system was transformed to a rigid gel, accompanying with a sharp increase of G'. The time from the beginning with a low G' to a sharp increase of G' was denoted as induction time. Induction time generally ranges from 5 to 120 min, which is appropriate for mixing and casting.

4.1.1. Influence of hardener concentration

There are totally five active hydrogen atoms of amine in DPTA molecule, which may link with epoxide groups. Thus, 0.2 mol DPTA is theoretically enough for per equivalent SPGE. However, the hardener is required a little more for a high gelation rate in practice. Fig. 3 shows the storage moduli of

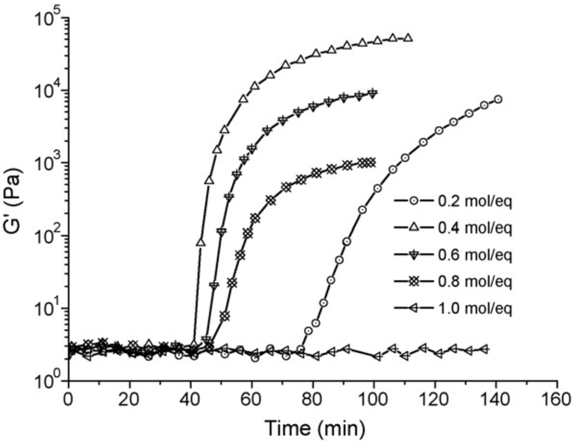

Fig. 3. Storage moduli of SPGE premix cross-linked with 0.2–1.0 mol/eq DPTA as a function of time.

15 wt.% SPGE premix cross-linked with 0.2–1.0 mol/eq DPTA as a function of time. For the addition of 0.2 mol/eq DPTA, the induction time was about 82 min and the storage modulus increased gradually with increasing time. While the amount of DPTA increased to 0.4–0.8 mol/eq, the induction time was shortened to 41–47 min. However, the storage modulus, which related to the strength of polymerized gel, decreased orderly. When DPTA increased to 1.0 mol/eq, the gelation did not occur with G' kept steadily low. Hence, an addition of 0.4 mol/eq DPTA was considered optimal.

Fig. 4 shows the correlative photographs of monolithic gels cross-linked with different amounts of DPTA. It was observed that the gel with 0.2 mol/eq DPTA added was opaque. With the increase of DPTA, the gel was transformed to translucent (0.4 mol/eq) and fully transparent (0.6 and 0.8 mol/eq). It was considered that phase separation (e.g. water-rich domains and water-poor domains) occurred in gels with a small amount of DPTA. Besides, the gel with 0.8 mol/eq DPTA was somewhat plastic. This was consistent with the low storage modulus in Fig. 3. Such behavior might be of benefit to counteracting stress concentration during drying procedure through plastic strain.

4.1.2. Influence of temperature

Generally, temperature is an important and controllable parameter in gelcasting of ceramics. It is a common method to mix and cast suspensions under a lower temperature and to consolidate them at a higher temperature. Fig. 5 shows the induction time with different DPTA additions as a function of temperature. The induction time (t_i) decreased with increasing temperature (T) for both concentrations of DPTA. The relationship may be expressed by an Arrhenius-type equation:

$$t_{\mathrm{i}} \propto \frac{1}{r} = A e^{E_{\mathrm{a}}/RT} \tag{1}$$

where r is the reaction rate, R is the gas constant, and E_a is the activation energy of polymerization reaction. Fig. 6 is the Arrhenius plot of the data for DPTA additions of 0.4 and 0.8 mol/eq calculated from Fig. 5. As expected, the logarithm of induction time was inversely proportional to the reaction

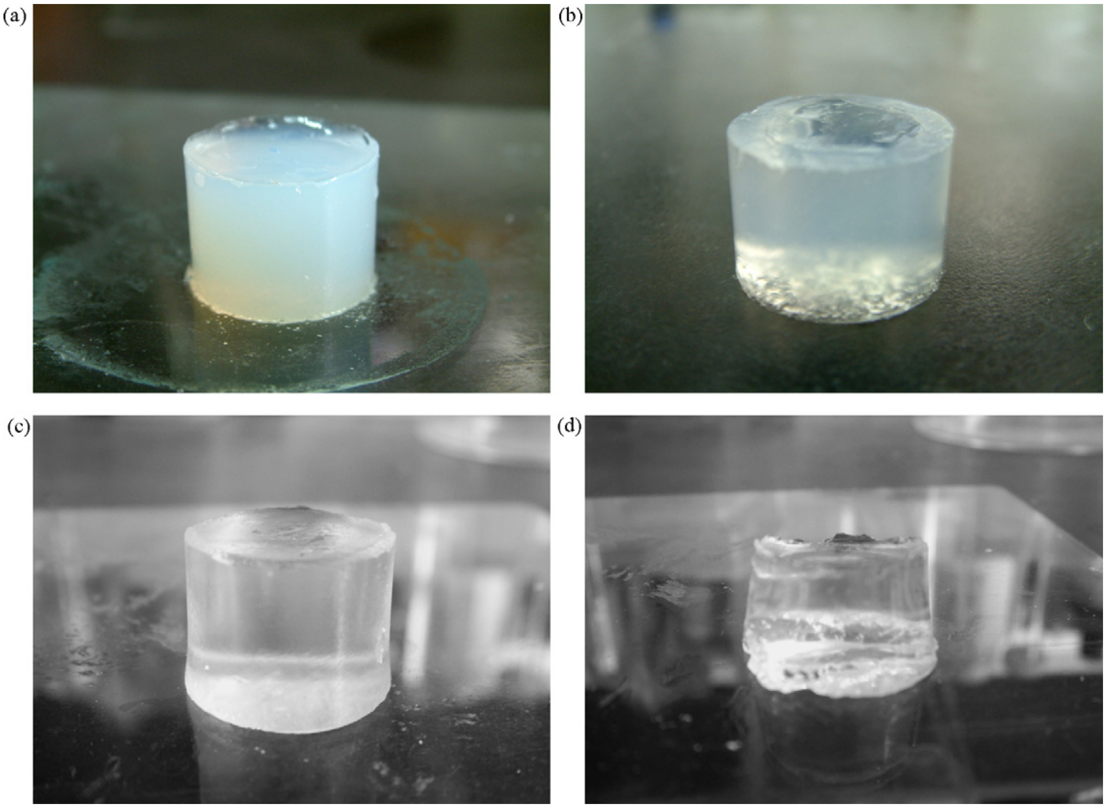

Fig. 4. Photographs of monolithic gels cross-linked with the DPTA amount of (a) 0.2, (b) 0.4, (c) 0.6, (d) 0.8 mol/eq.

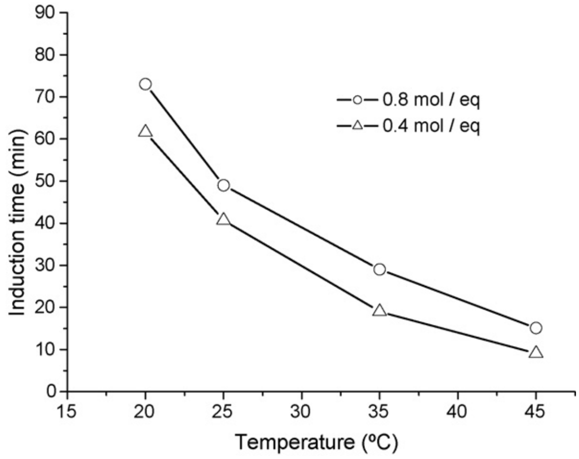

Fig. 5. Induction times as a function of temperature.

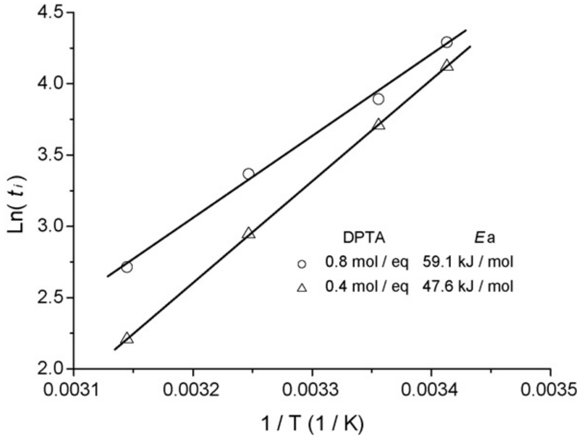

Fig. 6. Arrhenius plot of the data calculated from Fig. 5.

temperature. The calculated values of E_a for 0.4 and 0.8 mol/eq DPTA were 47.6 and 59.1 kJ/mol, respectively.

4.2. Zeta potential

The quantity of surface charge is an important characteristic of suspended particles, as it determines the dispersion and stability of suspension. Fig. 7 shows the effects of pH value on the zeta potentials of alumina suspensions. The isoelectric point (iep) of alumina in aqueous suspension was found to be at pH 8.7, which was in good agreement with reported values [1]. When the dispersant A-30SL added, negative surface charge was enhanced in the measuring range of pH value, which resulted in the shift of iep to 2.9. The change of the zeta potential could be a result of adsorption of COO^- groups on the surface of alumina particle. While the dispersant and SPGE were co-added, the curve of the zeta potential was similar to that of suspension with only dispersant. It was evidenced that SPGE scarcely affected the zeta potential of alumina with dispersant, i.e., SPGE is a promising agent for gelcasting of alumina. In a wide range of pH > 7, the zeta potential with dispersant and SPEG presented an intense negative charge, which makes it possible to prepare well dispersed alumina suspension [26].

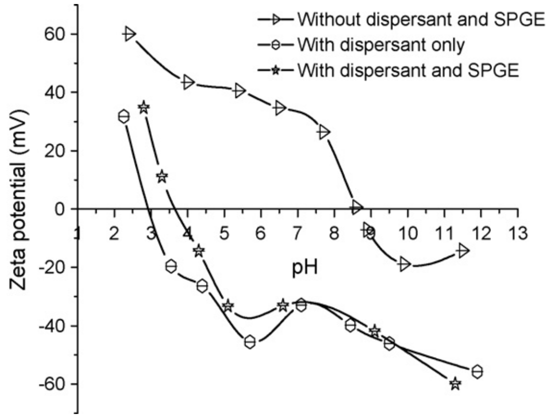

Fig. 7. Zeta potentials of alumina as functions of pH value.

4.3. Viscosity of suspensions

Good fluidity of suspension is beneficial for both mixing and casting in colloidal processing [27]. For a novel gelcasting system, the influence of epoxy resin on the viscosity of ceramic suspensions is one of the most important factors which should be considered. Fig. 8 shows the viscosity curves of suspensions with different solids dispersed in 15 wt.% SPEG premix. For comparison, the fluidity of suspension with 80 wt.% solids dispersed in water is also presented. It can be seen that the viscosity of suspension with 80 wt.% solids containing SPEG was higher than that without SPEG. However, the rheologic behavior of suspension with 80 wt.% solids containing SPGE was similar to that without SPGE.

The linear relationship in the measuring range between viscosity and shear rate for suspensions with 72, 76 and 80 wt.% solids in double log plot of Fig. 8 indicated that their rheologic behaviors could be described with the empirical Ostwald de Waele power-law model: [28]

$$\eta = K\dot{\gamma}^{n-1} \tag{2}$$

where η is the viscosity, $\dot{\gamma}$ is the shear rate, n is the power-law index and K is called the 'consistency' (with the unit of Pa s). The Ostwald de Waele line fitting parameters were summarized

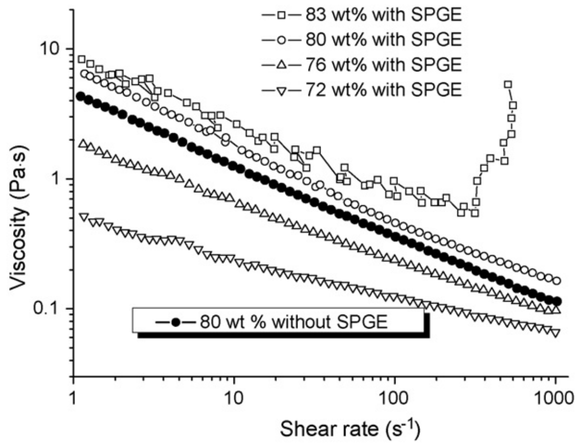

Fig. 8. Viscosity curves of suspensions with different solids.

Table 1
Ostwald de Waele line fitting parameters for suspensions with different solids

	72 wt.%	76 wt.%	80 wt.%	80 wt.%[a]
ln K	−0.726	0.611	1.892	1.482
$n - 1$	−0.294	−0.441	−0.559	−0.540
K (Pa s)	0.48	1.84	6.63	4.40
n	0.71	0.56	0.44	0.46

[a] For suspension without SPGE.

in Table 1. It can be seen that the index n was substantially below 1, describing a shear-thinning behavior exhibited. Furthermore, this index was similar in every case, confirming that the suspensions displayed a similar behavior of shear-thinning.

For suspension with 83 wt.% solids, shear-thinning behavior appeared at low shear rates and a sharp shear-thickening region did at high shear rates. Similar phenomena had been reported in many concentrated aqueous suspensions, and were considered as the result of the interaction between particles [28,29]. The conversion to shear-thickening for the suspension with 83 wt.% solids was unfavorable for high speed stirring during mixing and degassing.

4.4. Consolidation of suspensions

Fig. 9 shows the evolution of storage moduli of suspensions with different solids after adding 0.4 mol/eq DPTA at 25 °C. To evaluate the effects of solids on consolidation process, the storage modulus of aqueous system without solids is also displayed in Fig. 9. It can be seen that the induction time decreased with increasing solids. Especially, for the suspension with 83 wt.% solids, the increase of G' occurred at the beginning of the measurement. This might be attributed to the interaction between particles, as well as between particles and the polymer molecules. However, for all solids, the earlier values of G' were too low (<1000 Pa) for the suspensions to keep a fixed shape. At about 60 min, the storage moduli of all suspensions exceed 10^5 Pa, which was high enough for gelcasting bodies. At the latter stage, G' increased as the solids increased from 72 to 80 wt.% due to closer interact between alumina particles. However, for the suspension with solids up to 83 wt.%, G' was lower than that with 80 wt.%. This might be because the monolithic gel was disturbed by too much amount of alumina particles.

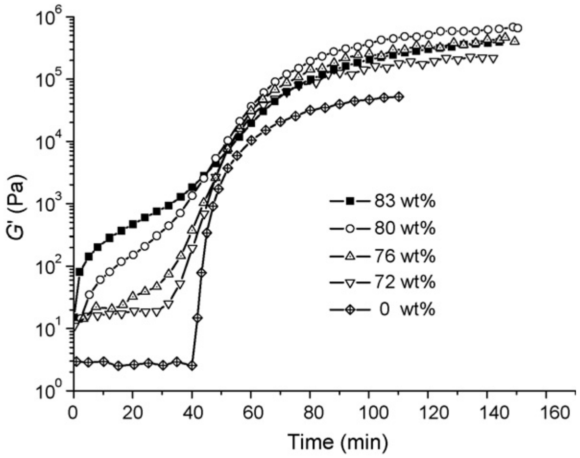

Fig. 9. Storage moduli of suspensions with different solids as a function of time.

5. Conclusions

The rheological behaviors of a gelcasting system based on SPGE/DPTA have been investigated. While the concentration of SPGE was fixed as 15 wt.% in water, the polymerization of the aqueous premix was influenced by DPTA addition and the temperature. Considering the induction time and the storage modulus, the addition of 0.4 mol/eq DPTA was considered optimal. The induction time decreased from about 60 to 10 min with temperature increased, fitting Arrhenius-type equation. While SPGE and the dispersant were co-added, the curve of the zeta potential was similar to that of suspension with only dispersant. The suspensions with 72–80 wt.% solids have good fluidity for gelcasting, though the viscosity of suspension containing SPGE was higher than that without SPGE. The induction time of consolidation of suspensions decreased with increasing solids. At the latter stage, the storage moduli of all suspensions exceed 10^5 Pa, which was high enough for gelcasting bodies.

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