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Gelcasting of SiC using epoxy resin as gel former

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Abstract

Epoxy resin was used as gel former in SiC gelcasting. A hardener as cross-linker causes a nucleophilic addition reaction of epoxy resin instead of free radical reaction of the acrylamide-based gel former system to avoid oxygen and mould materials (plastic and rubber) inhibition. The gelling behavior of premix solution and slurry was investigated by the change of elastic modulus (G′) changing during gelling. Data show 3.4 wt% hardener in 15 wt% epoxy resin solution to be the optimized content to obtain gel with high-G′. Both the polymerization process and the gelation process depend greatly on temperature, which is beneficial for mixing and casting. Green bodies fabricated with epoxy resin show that rubber do not inhibit in the process.
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Keywords: SiC; Gelcasting; Gel former system; Gelation process; Rheological properties

1. Introduction

Gelcasting is a novel forming method in fabricating complex shaped ceramic parts, which was first developed by Janney and Omatete at the Oak Ridge National Laboratory (ORNL), Oak Ridge, USA [1–3]. The original study on gelcasting involved an in situ polymerization of acrylamide (AM) initiated by initiators, as the setting mechanism for forming the green body. Some low in toxicity gel formers were developed, such as methacrylamide (MAM) and methacrylic acid (MAA), to meet the requirements of industry. However, it was found that those monomers polymerization based on free radical reaction have some disadvantages: the oxygen inhibition [4], and the mould materials inhibition. The plastic mould produced easily, as well as rubber mould which is flexible and easy to de-mould, cause an inhibition. Most seriously, some organic components, which were added to decorate the ceramic particle surface, also inhibit the polymerization [5]. That is some ceramic powders cannot be formed well by gelcasting method, such as SiC. The other disadvantage is the uncontrolled gelation during slurry degassing, which causes a failed casing.

Recently, a water-soluble epoxy resin and hardener system was used in gelcasting of alumina by Mao et al. [6]. The polymerization involved the epoxide group of epoxy resin and the active hydrogen of amine is a nucleophilic addition reaction instead of free radical reaction. As results of the steady polymerization mechanism, epoxy resin as gel former can avoid not only oxygen inhibition but also the mould materials inhibition in gelcasting process.

The aim of the present work was extending this gelcasting system to SiC forming. The effects of temperature, hardener content and solid loading on the gelation were investigated by measuring the elastic modulus during gelation process.

2. Experimental

2.1. Materials and procedures

A commercial SiC powder (FCP10, Norton, Norway) was used as raw material, with a mean diameter of 0.97 μm (zeta plus, Brookhaven Instruments, USA)and a BET surface area of 8.99 m^2/g (ASAP2010,Micromeritics Instruments, USA). 15 wt% premixed solution was prepared with sorbitol polyglycidyl ether (SPGE) (EX614-B, Nagase Chemtex, Japan) as premix solution. Tetramethylammonium hydroxide (TMAH, 25 wt%) used to dispersing SiC slurry was supplied by Shanghai Chemical Reagent Co., Ltd., China. De-ionized water

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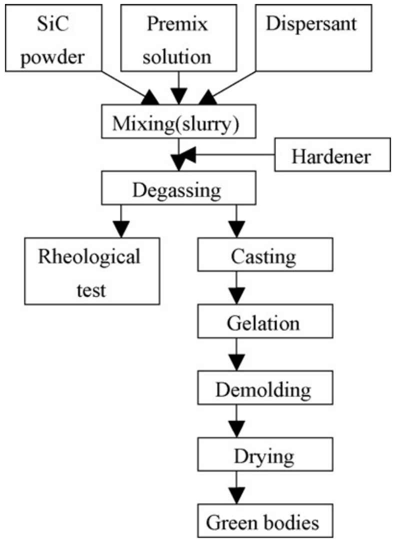

Fig. 1. Flowchart of gelcasting process.

was used for all solutions preparing. The gelcasting process flow chart is shown in Fig. 1.

2.2. Rheological measurement

The elastic modulus G′ during polymerization and gelation was measured by stress-controlled rheometer SR5 (Rheometric Scientific Inc., USA) equipped with a four-blade vane geometry, called vane method [7–11]. The vane geometry was calibrated with various content solutions of polyacrylamide by dynamic stress sweep test in the previous work [12]. The container was soaked in a water-bath, of which the temperature was carefully controlled. All of the measurements were carried out in the same conditions: frequency = 1 Hz; strain = 0.1%. The viscosity of SiC slurry was measured with 25 mm parallel plate fixture in steady-rate sweep mode (gap 1.0 mm).

3. Results and discussion

3.1. Polymerization of premix solution

Fig. 2 shows the elastic modulus G′ of premix solutions during polymerization process with various contents of hardener as function of time at 40 °C. To obtain high-G′ gels, the optimized content of hardener was 3.4 wt%. Less amount of hardener cause a viscous gel and more hardener leads to a fragile one. Idle time determined by the abrupt change of G′ shows the dependence on the hardener content. The effect of temperature on the polymerization process of premix solution is shown in Fig. 3, in which idle time shows great dependence on the temperature, the lower the temperature the longer time for gelling, which meets the mechanism of polymerization. The dependences of idle time on the hardener content and temperature are beneficial for gelling controlling.

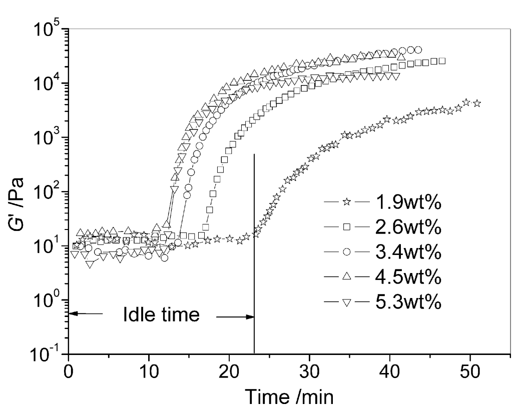

Fig. 2. Influence of hardener content on the G′ of formed gels at 40 °C.

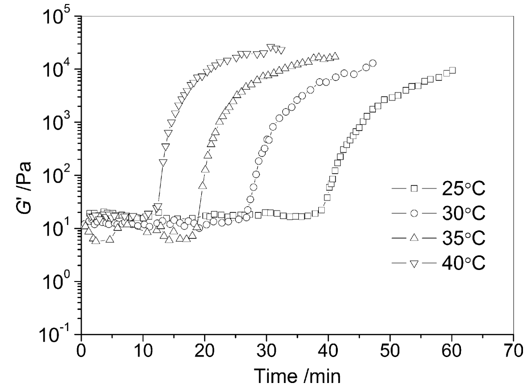

Fig. 3. Effect of temperature on the polymerization process of premix solution with 3.4 wt% hardener.

3.2. Viscosity of SiC slurry

The influence of epoxy resin on the viscosity of SiC slurry is shown in Fig. 4. 0.15 wt% TMAH based on SiC powder is added as a dispersant [13]. Viscosity is increased in the presence of viscous epoxy resin and hardener. 51.3 vol% SiC with viscosity 0.36 Pa s at 100 s^{-1} can be prepared as shown in Fig. 5, which is suitable for both casting and high green body density.

3.3. Gelation process of SiC slurry

The G′ changes during gelation process of slurry are shown in Fig. 6 and Table 1 demonstrated the influence of solid loading

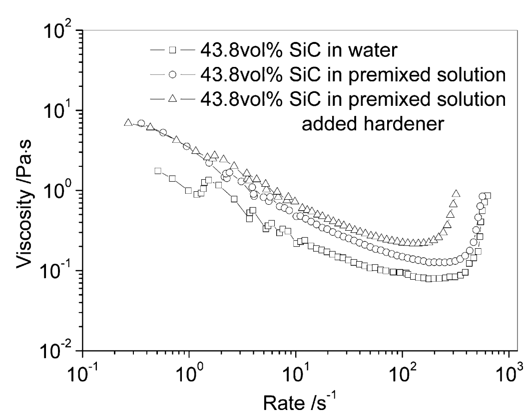

Fig. 4. Effect of epoxy resin and hardener on the viscosity of 43.8 vol% SiC slurry.

Table 1
Effect of temperature and solid loading on the G′ and idle time

Solid loading (vol%)	Temperature (°C)	Elastic modulus ($\times 10^6$ Pa)	Idle time (min)
	30	2.00	10.5
43.8	35	1.72	7.4
	40	1.54	5.5
	30	2.04	8.4
47.8	35	1.62	6.0
	40	1.37	4.3
	30	2.17	4.8
51.3	35	1.81	2.1
	40	1.54	0.8

and temperature on the gelation process. Compared to the polymerization of premix solution, idle time of gelation is reduced, which can be observed not only with epoxy resin system but also with acrylamide system [2]. The idle reduction was attributed to the ‘‘container’’ effect of slurry in the presence of ceramic powder [14]. For slurry gelation, shorter polymer chain line is needed to connect the particles and fill the interstice of particles in the slurry, while for premix solution gelling the polymer needs to grow up to fill the gap (the gap between cup and vane blades, 1.0 mm). The interstice of particles which is a few nanometers, as well as the gap is equal to a container which holds the gel. The smaller the container the shorter polymer chain line needed to connect the particles, which causes the great reduction of idle time. With increasing solid loading, density of particles is increased and the ‘‘container’’ is reduced, which results in idle time decreasing. According to Table 1, idle time is reduced from 10.5 min to 4.8 min as solid loading increased from 43.7 vol% to 51.3 vol% at 30 °C.

According to Table 1, high-G′ wet green bodies are obtained at 30 °C, and slurry is completely solidified within 1 h. Some complex shape green bodies with solid loading 51.3 vol% are made at 30 °C using rubber mould as shown in Fig. 7, which shows the capability of epoxy resin as gel former in gelcasting of SiC and rubber do not cause inhibition on the process.

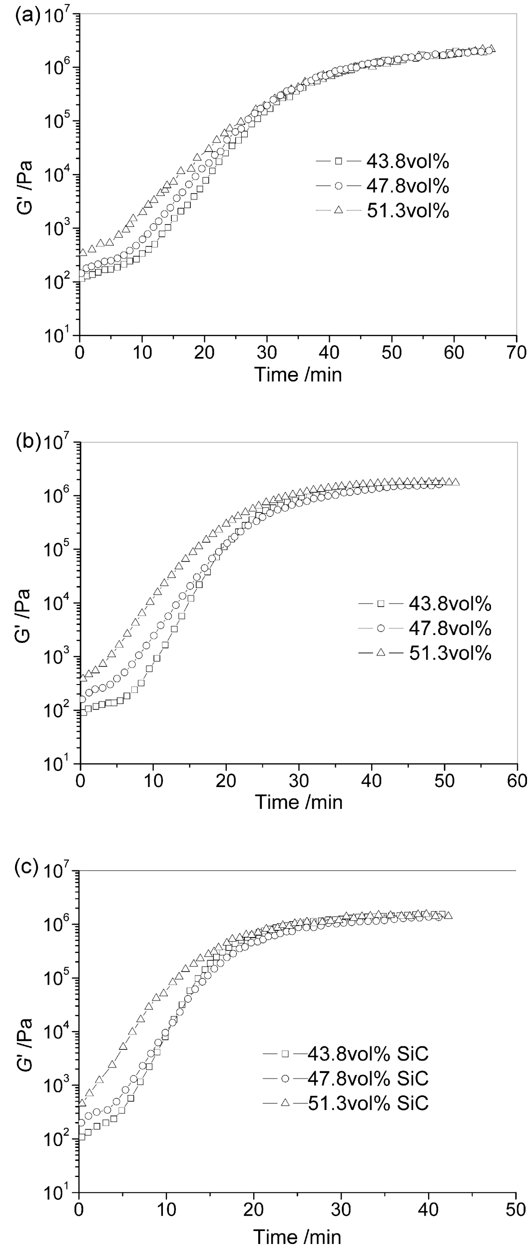

Fig. 6. Effect of solid loading on the gelation process of SiC slurry at different temperatures: (a) 30 °C, (b) 35 °C, (c) 40 °C.

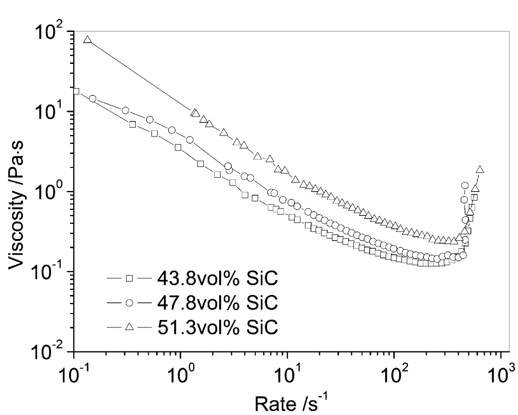

Fig. 5. Viscosity of SiC slurry with varied solid loading SiC slurry in premixed solution.

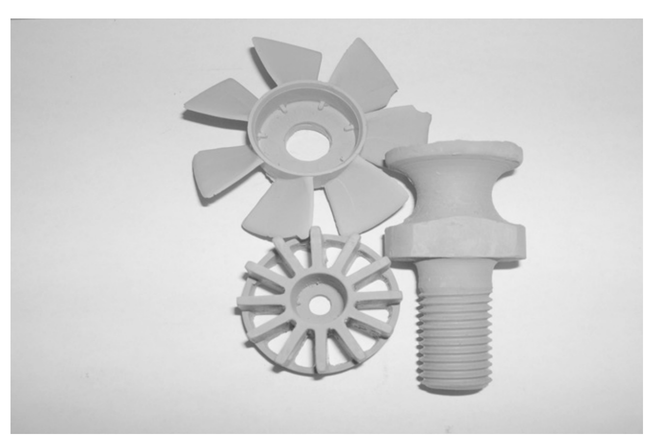

Fig. 7. Green bodies made by gelcasting process using rubber moulds.

4. Conclusion

A water-soluble epoxy resin has been used as gel former in gelcasting of SiC to avoid the inhibition of oxygen and mould materials. The G′ in the polymerization process and gelation of SiC slurry was tested by a vane rheometer, which showed that the gel former system is suitable for gelcasting of SiC.

For slurry, 51.3 vol% slurry is prepared with viscosity 0.36 Pa s at 100 s^{-1}. For gelling, 3.4 wt% hardener based on 15 wt% premix solution was used to obtain high-G′ gel at 30 °C. Some green bodies with solid loading 51.3 vol% were made using rubber mould, which showed that the gel former system can have an application to fabricate complex shape ceramic parts.

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References

[1] O.O. Omatete, M.A. Janney, Gelcasting—a new ceramic forming process, J. Am. Ceram. Soc. 70 (10) (1991) 1641–1649.

[2] A.C. Young, O.O. Omatete, M.A. Janney, P.A. Menchhofer, Gelcasting of alumina, J. Am. Ceram. Soc. 74 (3) (1991) 612–618.

[3] O.O. Omatete, M.A. Janney, S.D. Nunn, Gelcasting: from laboratory development toward industrial production, J. Eur. Ceram. Soc. 17 (2–3) (1997) 407–413.

[4] D. Benda, J. Snuparek, V. Cermak, Oxygen inhibition and influence of pH on the inverse emulsion polymerization of acrylic monomers, J. Eur. Ceram. Soc. 37 (6) (2001) 1247–1253.

[5] M.J. Dong, X.J. Mao, Z.Q. Zhang, Q. Liu, Gelcasting of SiC: gelation process with three initiator systems, Mater. Rev. 22 (X) (2008) 385–387.

[6] X.J. Mao, S. Shimai, M.J. Dong, S.W. Wang, Gelcasting of alumina using epoxy resin as gelling agent, J. Am. Ceram. Soc. 90 (3) (2007) 986–988.

[7] H.A. Barnes, N.Q. Dzuy, Rotating vane rhemetry—a review, J. Non-Newtonian Fluid Mech. 98 (1) (2001) 1–14.

[8] A.W. Saak, H.M. Jennings, S.P. Shah, The influence of wall slip on yield stress and viscoelastic measurements of cement paste, Cement Concrete Res. 31 (2) (2001) 205–212.

[9] X.D. Zhang, D.W. Giles, V.H. Barocas, K. Yasunaga, C.W. Macosko, Measurement of foam modulus via a vane rheometer, J. Rheol. 42 (4) (1998) 871–889.

[10] N.Q. Dzuy, D.V. Boger, Direct yield stress measurement with the vane method, J. Rheol. 29 (3) (1985) 335–347.

[11] M. Keentok, J.F. Milthorpe, E. O'Donovan, On the shearing zone around rotating vanes in plastic liquids: theory and experiment, J. Non-Newtonian Fluid Mech. 17 (1) (1985) 23–35.

[12] M.J. Dong, Z.Q. Zhang, Q. Liu, D.L. Jiang, Measurement of modulus in ceramic gelcasting process by vane geometry, J. Inorg. Mater. 19 (6) (2004) 1277–1281.

[13] W. Li, P. Chen, M.Y. Gu, Y.P. Jin, Effect of TMAH on rheological behavior of SiC aqueous suspension, J. Eur. Ceram. Soc. 24 (14) (2004) 3679–3684.

[14] M.J. Dong, X.J. Mao, Z.Q. Zhang, Q. Liu, Gelcasting of zirconia using water soluble epoxy resin as gel former, J. Chin. Ceram. Soc. 36 (7) (2008) 999–1002.