Ceramics International 29 (2003) 403–406

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Gelcasting of PZT

Dong Guo*, Kai Cai, Longtu Li, Cewen Nan, Zhilun Gui

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science & Engineering, Tsinghua University, Beijing 100084, PR China

Received 6 February 2002; received in revised form 20 May 2002; accepted 1 July 2002

Abstract

Aqueous gelcasting of PZT is discussed in this paper. Concentrated PZT suspension (50 vol.%) with low viscosity is developed by using triammonium citrate as the dispersant. Zeta potential results suggest that the effect of TAC in decreasing the viscosity of the PZT suspension may be ascribed to its electrostatic stabilization mechanism. A premix solution containing 20 wt.% of AM monomer can provide a mechanical strength of 18 MPa for the green body obtained from 50 vol.% PZT suspension. SEM photos indicate that PZT ceramics with homogeneous microstructure can be fabricated. Comparison of piezoelectric coefficients of gelcast PZT samples with those of the die pressed PZT samples indicates that the additives, including the monomer, the crosslinker and the dispersant etc., show no influence on the piezoelectric property of the PZT samples.

Keywords: B. Electron microscopy; C. Piezoelectric property; D. PZT; Gelcasting

1. Introduction

Piezoelectric materials are widely used as actuators, sensors and transducers. But fabrication of the material is often a time-consuming task when special shapes are required because of the high hardness and fragility of the material. In some methods used for the fabrication of the material, such as tape casting or injection molding, the ceramic powders are dispersed in a non-aqueous solvent that containing a significant fraction of organic binders. This brings about a series of problems to the material such as debinding issues during sintering and heterogeneity of the sintered parts etc., so aqueous solvent with a low organic content is highly more desirable. Gelcasting is an attractive ceramic forming process for making high-quality ceramic parts [1]. In the process a high solids loading slurry obtained by dispersing the ceramic powders in the pre-mixed monomer and crosslinker solution is cast in a mould of the desired shape. When heated, monomer and crosslinker polymerize to form a three-dimensional network structure, thus the slurry is solidified *in situ* and green bodies of the desired shapes with low polymer content are obtained. Gelcast green bodies have high homogeneity and mechanical strength, which is of great advantage for handling of the parts before firing and for being able to produce large castings. Although there are plenty of literature describing the application of gelcasting technology to the forming of structural ceramics [1–4], no paper about its application to the forming of piezoelectric ceramics has been published. In this paper development of high solids loading PZT suspension with low viscosity is reported. The piezoelectric property and microstructure of gelcast PZT sample are also investigated.

2. Experimental

PZT powders of the MPB composition [$Pb(Zr_{0.52}Ti_{0.48})O_3$] and 2 μm in size were used. Acrylamide ($C_2H_3CONH_2$, AM) and *N*,*N*′-methylenebisacrylamide [$(C_2H_3CONH)_2CH_2$, MBAM] were used as monomer and crosslinker for polymerization, respectively. A AM to MBAM mass ratio of 24/1 is used in the premix solution. $(NH_4)_2S_2O_8$ was used as the initiator of the reaction, which was also accelerated by a catalyst *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED). Rheological properties of the PZT slurries were measured by an advanced rheological MCR300 (Physica,

* Corresponding author. Fax: +86-10-6277-1160.
E-mail address: guodong99@mails.tsinghua.edu.cn (D. Guo).

0272-8842/02/$22.00
PII: S0272-8842(02)00151-7

German). Zeta potentials of the powders were measured by a Zetaplus (Brookhaven Instrument Corp., USA). Microstructures of the samples were observed by a HITACHI S-450 scanning electron microscopy (SEM). Piezoelectric coefficient d_{33} of the samples were determined by using a ZJ-3A piezometer produced by Institute of Acoastics, Academia Sinica. Permittivity and dielectric loss data were determined by HP4194A impedance analyzer.

3. Results and discussion

3.1. Development of high solids loading PZT suspension

A key factor for the successful production of ceramics by gelcasting technique is producing a flowable and stable slurry with as high a solids loading as possible (at least 50 vol.%). Therefore in order to achieve a high solids loading PZT slurry with low viscosity, triammonium citrate (TAC) was selected as the dispersant for the PZT suspension. Its effect on the viscosity of the slurry after 24 h ball milling is shown in Fig. 1. From Fig. 1 we can see that all systems show a non-Newtonian "Bingham" fluid character, i.e. a shear thinning behavior. Before adding the dispersant the PZT slurry shows a very high viscosity at the beginning of the test even at a very low solids loading (30 vol.%). Adding only 0.4 wt.% (by weight of PZT) of TAC can greatly decrease the viscosity, indicating that TAC is a very effective dispersant for PZT. Then with the increase of TAC content the viscosity decreases slightly. When TAC content achieves 2.4 wt.% the viscosity increases again. Consistent with the viscosity results are the zeta potential values shown in Fig. 2. The system without TAC has an IEP (isoelectric point, $\zeta=0$) at about pH = 7.2 and a very small ζ of 1.3 mV before adding acid or alkali. Adding only 0.4 wt.% TAC can results in a ζ of −21.8mV in neutral environment. At a TAC content

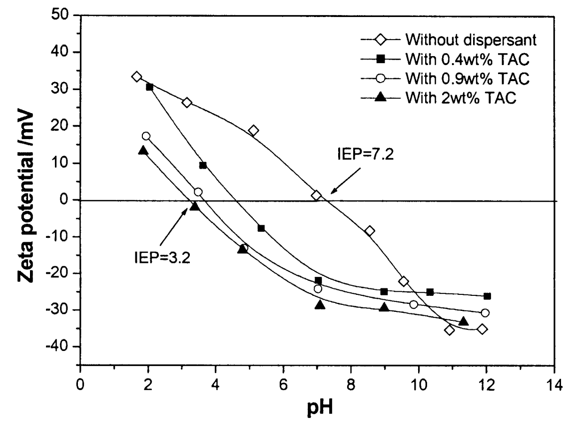


Fig. 2. Influence of dispersant content on the zeta potential of the PZT suspension.

of 2 wt.% a ζ of −28.8mV can be obtained and the IEP decreases to about pH = 3.2. For the systems containing TAC the ζ shows little change over a wide pH range of about pH = 7 to pH = 12, suggesting that adjustment of pH value is not necessary in these system. In fact, adjusting pH value to either basic or acid conditions has little effect on the viscosity.

In order to determine a suitable ball milling time, the milling time dependence of viscosities were also investigated and the results at a steady shear rate of 0.1 s^{-1} for 50 vol.% solids loading are shown in Fig. 3. At beginning the viscosity of the system decreases quickly as milling proceeds, then after a certain time of milling viscosity keeps almost constant. This may be partly attributed to the variation of effective TAC amount adsorbed by the PZT particles at different milling stage (see Fig. 3). Here TAC adsorption was measured by a thermogravimetric method [5]. PZT slurries were centrifuged at 3000 rpm for 60 min to extract the supernatant. Then the remaining TAC concentration in the supernatant is determined by TGA analysis. The amount of TAC adsorbed on PZT was then calculated

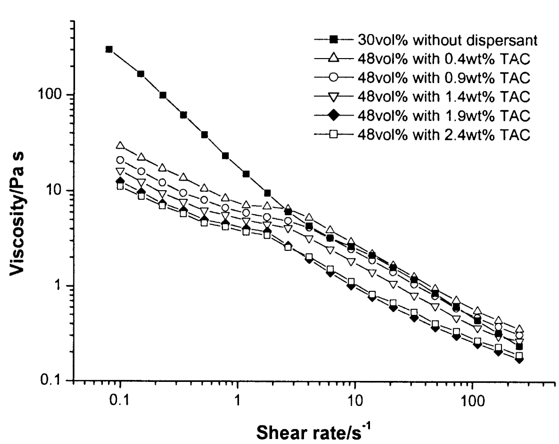


Fig. 1. Influence of dispersant content on the viscosity of the PZT suspension.

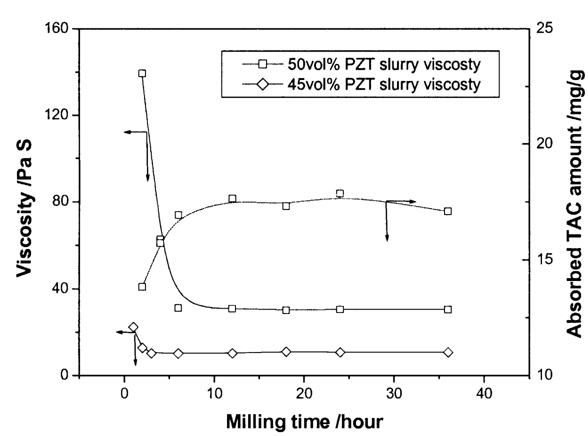


Fig. 3. Viscosity of PZT suspension and TAC amount absorbed by the PZT particles versus milling time.

by subtracting the left in supernatant from the total added amount. From the results we can see that the actual TAC amount adsorbed by the PZT particles is dependent on the milling time. Therefore a decreasing viscosity trend with milling time was observed. After about 5 h milling the adsorption seems to achieve equilibrium with a value of about 17.8 mg/g PZT and more milling produces no obvious change in the adsorption amount, as a result a stable viscosity appears. There also seems to exist a critical milling time of about 3 h at a lower solids loading of 45 vol.%. This critical milling time may be different at different milling conditions, but it reveals that a certain amount of milling is necessary for good dispersion of the suspensions.

3.2. Green strength

Influence of AM content in the premix solution on the green body strength is shown in Fig. 4. As expected, the green strength increases with AM content. However, the hardness of the green body is also increased with the AM content. This will result in processing problems during green machining of the body. Therefore a suitable AM content should make the green body strong enough to endure machining but not too strong to be machined easily. Based on our experience a moderate strength of about 18 MPa is sufficient and the suitable AM content is thus determined to be about 20 wt.%.

3.3. Binder burnout, microstructure and property examination

The pyrolysis process of the polymers in the gelcast PZT sample during sintering in air was determined by thermal analysis. From the TGA and DTA curves shown in Fig. 5 we can see that the gelcast green body has two main mass loss

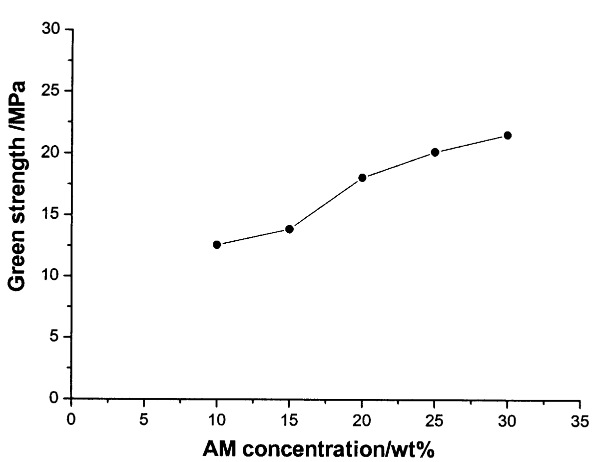


Fig. 4. Green strength of the PZT samples versus AM content at a solids loading of 50 vol.%.

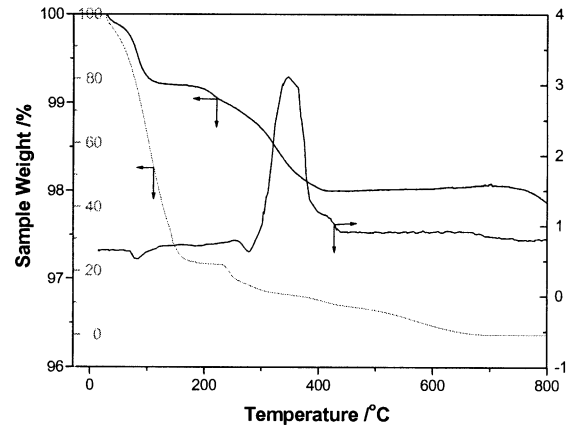
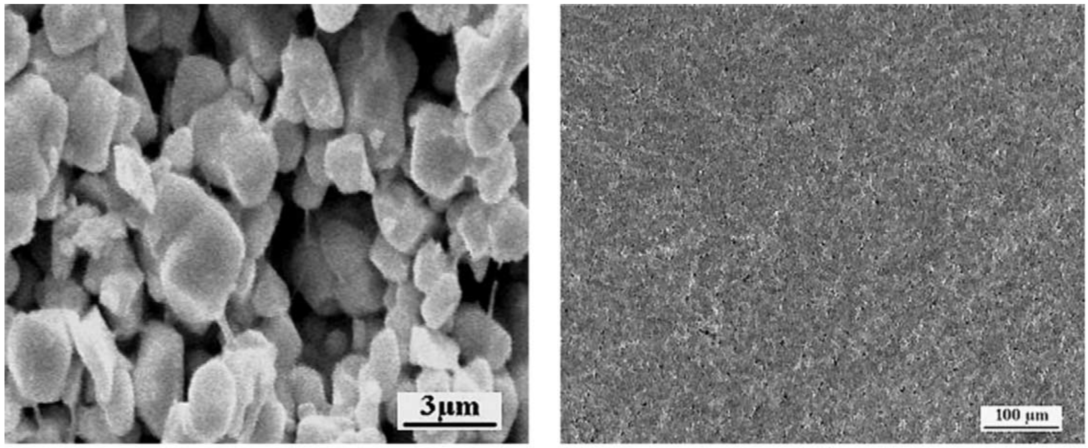


Fig. 5. TGA and DTA data of gelcast PZT green body. The light line and label are for neat gel.

processes. There is a small endothermic DTA peak with about 0.8 wt.% mass loss in the temperature range of 60 °C to 120 °C, which may be due to the removal of occluded water. The exothermal DTA peak together with another 1.2 wt.% mass loss in the temperature range of 210–415 °C may be ascribed to the burnout of the cross-linked polymer network. Similarly, neat gel also shows two main mass loss processes in the temperature of 45–170 °C and 230–650 °C. The difference is that pyrolysis of the green part is completed by about 415 °C while the neat gel is not fully pyrolyzed until it attains a temperature of about 650 °C. The mass loss at about 710 °C is due to the evaporation of Pb_3O_4. Because of the small content of polymers, there is only a small total mass loss value of about 2 wt.% before 800 °C for the green part, thus the time-consuming debinding program can be excluded during the sintering of the ceramics.

Fig. 6 shows the SEM photos of the fracture surface of gelcast PZT samples (50 vol.% solids loading). From Fig. 6a we can see that there does exist a little linear shape organic substance in the gelcast green body. From Fig. 6b we can see that a homogeneous microstructure can be obtained in gelcast sample. Consistent with the SEM examination are the density and electrical properties of the PZT samples shown in Table 1, where the parameters of conventional die pressed samples are also listed for comparison. In the table the mean values of five samples sintered under the same procedure by both approaches are compared. Gelcast samples show slightly higher mean d_{33} and density values than those of die pressed ones. And more uniform d_{33} and density values of gelcast samples were observed by contrasting the standard deviation of the two series of data. This reveals that high homogeneity can be obtained by gelcasting way. It seems that the high homogeneity of the PZT suspension obtained by adding dispersant and thoroughly milling has been effectively conserved in the green body after in situ polymerization of the system.



(a) (b)

Fig. 6. SEM photos showing the microstructures of gelcast PZT samples. (a) Gelcast green body, (b) sintered ceramic.

Table 1
Comparison of some parameters of PZT samples prepared by gelcasting with 50% solids loading and by die pressing at a pressure of 80 MPa

Sample	Total shrinkage	Mean density	Standard deviation of density	Mean d_{33}	Standard deviation of d_{33}	Permittivity	Dielectric loss
Gelcasting	15.9%	7.76 g/cm^3	0.071 g/cm^3	213 pC/N	3.93 pC/N	878	0.0039
Die pressing	14.8%	7.66 g/cm^3	0.082 g/cm^3	200 pC/N	8.51 pC/N	859	0.0038

Two samples also exhibit almost the same dielectric loss values. Because the electrical properties of PZT are very sensitive to the chemical composition of the sample, unsuitable dispersant might result in the deterioration of the electrical properties. The results indicate that TAC is a suitable dispersant and it does not affect the performance of the material.

4. Summary

After development of high solids loading PZT slurry with low viscosity by using suitable TAC as the dispersant. high-quality PZT ceramics were successfully fabricated by gelcasting technology. The dried green bodies have a mechanical strength of 18 MPa. The gelcast PZT samples also have dense and homogeneous microstructure and exhibit stronger piezoelectric effect than die pressed ones at the same sintering procedure.

Acknowledgements

The author would like to thank the National Natural Science Foundation of PR China (Grant No. 59995523) for its financial supports.

References

[1] O.O. Omatete, M.A. Janney, R.A. Strelow, Gelcasting—a new ceramic forming process, Ceram. Bull. 70 (1991) 1641–1649.

[2] M.A. Janney, W.J. Ren, G.H. Kirby, et al., Gelcast tooling: net shape casting and green machining, Mater. Manuf. Process. 13 (1998) 340–389.

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

[4] P.C. Hidber, T.J. Graule, L.J. Gauckler, Citric acid-a dispersant for aqueous alumina suspensions, J. Am. Ceram. Soc. 79 (1996) 1857–1867.

[5] S. Baklouti, C. Pagnoux, T. Chartier, et al., Processing of aqueous alpha-Al_2O_3, alpha-SiO_2 and alpha-SiC suspensions with polyelectrolytes, J. Eur. Ceram. Soc. 17 (1997) 1387–1392.