Application of gelcasting to the fabrication of piezoelectric ceramic parts

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Abstract

Gelcasting is a novel method for the molding of ceramic powder based on a synthesis of concepts derived from traditional ceramics and polymer chemistry. Although a wealth of literature has been published describing the application of the technology to the fabrication of structural ceramics, little has been reported about its application to the fabrication of functional ceramics. In order to extend the technology to the fabrication of piezoelectric ceramics in this article the colloidal chemistry of PZT powders in aqueous solution, the rheological behavior of the PZT suspension and the influence of dispersants on the rheology of the suspension and on the electrical properties of the gelcast PZT samples are investigated. Because the electrical properties of PZT are very sensitive to the chemical composition of the sample, unsuitable selected dispersants can result in the deterioration of the electric properties of the material although concentrated PZT slurry with low viscosity can be obtained by different dispersants.
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1. Introduction

Piezoelectric materials are widely used in ignitors, actuators, micromotors and in transducers. The high hardness and fragility of the material render it unsuitable for mechanical processing and fabrication. In some methods used for the fabrication of piezoelectric materials, such as tape casting or injection molding, the ceramic phase is dispersed in a nonaqueous solvent; an organic binder is required in order to support the structure of the prepared ceramic. This leads to a series of problems such as debinding in the later processing and geometry distortion of the ceramics after sintering. Gelcasting is an attractive near-net-shape forming method for making high-quality complex-shaped ceramic parts, which has received much attention in recent years due to its simplicity and to the high homogeneity, high strength and good mechanical property of the green product.[1,2] In this process a high solids loading slurry obtained by dispersing the ceramic powders in the pre-mixed monomer and cross-linker solution is cast in a mould of the desired shape without additional pressure. When heated, the monomer and cross-linker polymerize to form a three-dimensional network structure, thus the slurry is solidified in situ and green bodies of the desired shape with low polymer content are obtained. The dried green bodies made in this way can be machined easily and the time-consuming binder burnout program can be excluded. Gelcasting is a suitable way for manufacturing materials having complex and intricate features. It can also be useful in the manufacture of large components that have simple shapes. As an example, consider a ring that is 60 cm in diameter with a cross-sectional thickness of 2.5 cm. Making such objects by die pressing, loads of hundreds of tons may be required. In contrast, such a ring can be made very easily by gelcasting through plastic or metal molds at very little expense. Since its invention in 1991 gelcasting has been carefully studied for the fabrication of structural ceramics. However, little of this method has been known for the formation of piezoelectric ceramics. A key factor for the successful application of gelcasting technology lies in the development of a ceramic slurry with high solids loading and low viscosity. In this article the colloidal chemistry of PZT powders, the rheological

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property of the PZT suspension and the influence of dispersants on the suspension are investigated. In addition, the electrical properties of PZT type material are very sensitive to the chemical composition and can be affected to a large degree by trace amount of other elements and impurities. Therefore in order to investigate the effect of the entire forming process on the electrical properties of the final products, the electrical properties of gelcast PZT samples are also carefully studied and compared with those of die pressed ones.

2. Experimental

PZT powders near the MPB composition $(Pb(Zr_{0.52}Ti_{0.48})O_3)$ was prepared by the conventional mixed-oxide processing technique. Stoichiometric amounts of Pb_3O_4, ZrO_2 and TiO_2 oxides were thoroughly ball-milled for 24 h, then calcined at 850 °C for 2 h. The synthesized powder has a mean particle size of about 1.5 μm, which was characterized by XRD before use. The diffraction peaks at the 2θ angles of 22.0, 31.4, 38.4, 44.9, 50.4 and 55.5 shown in Fig. 1 correspond to the perovskite PZT (100), (110), (111), (200), (210) and (211) peaks, respectively. This demonstrates that perovskite PZT phase was obtained.

Acrylamide (C_2H_3CONH, AM) was used as the monomer and *N,N*-methyl-enebisacrylamide $[(C_2H_3 CONH)_2CH_2, MBAM]$ was used as the cross-linker. AM and MBAM were dissolved in deionized water to give the premix solution. *N,N,N′,N′*- etramethylethyl-enediamine (TEMED) and $(NH_4)_2S_2O_8$ were used as catalyst and initiator for the polymerization respectively. After several trials Triammonium citrate (TAC) and two commercial polyelectrolyte dispersant JN281 [ammonium salt of poly(acrylic acid)] and SGA [sodium salt of poly(acrylic acid)] were selected to improve the flowability of the ceramic slurry. The morphology of the ultimate ceramic parts was observed by a HITACHI S-450 scanning electron microscopy (SEM). Zeta potentials were measured by a Zetapuls analyzer (Brookhaven Instrument Corp., USA). The rheological properties of the ceramic slurries were measured by advanced rheological equipment MCR300 (Physica, German). Binder burnout profiles of the gelcast sample in air were obtained by standard thermogravimetric analysis (TGA) using a Dupont Thermal Analyst 2000 analyzer. The density of the sintered samples was measured by the Archimedes method. Piezoelectric coefficient d_{33} were determined by using a ZJ-3A piezometer. Electrical properties of the samples were measured by a HP4194A impedance analyzer. The remnant polarization of the samples was measured by using a RT6000HVS ferroelectric test system (Radiant Technology Incorporation, USA).

3. Results and discussion

3.1. Colloidal chemistry and rheological property of the PZT suspension

Low solids loading and hard agglomerates in suspensions can result in deleterious surface and bulk defects in the finished ceramics. Key factors for the successful production of ceramics by gelcasting technique are the homogenization and dispersion of the powder in the premix solution and the stability of the suspension, which are determined by attractive and repulsive forces, whose behavior is directly dependent on the zeta potential of the powders.[3] The higher this potential with the same polarity, the more important is the electrostatic repulsion between particles. On the other hand, when close to the isoelectric point (IEP) the particles tend to flocculate. Zeta potentials of PZT aqueous suspensions without dispersant and of those with 0.5% TAC and 1.5% JN281 by weight of PZT at different pH values are shown in Fig. 2. PZT suspensions at a loading of
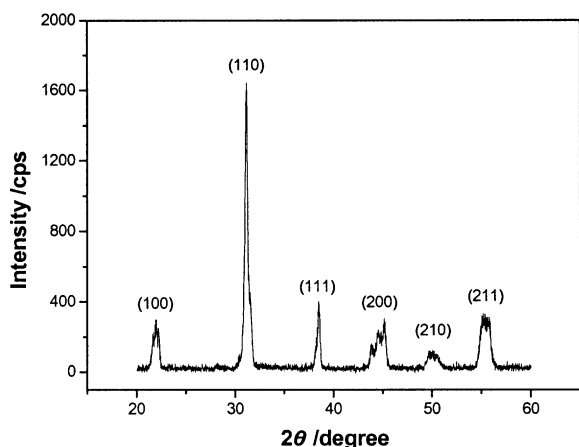

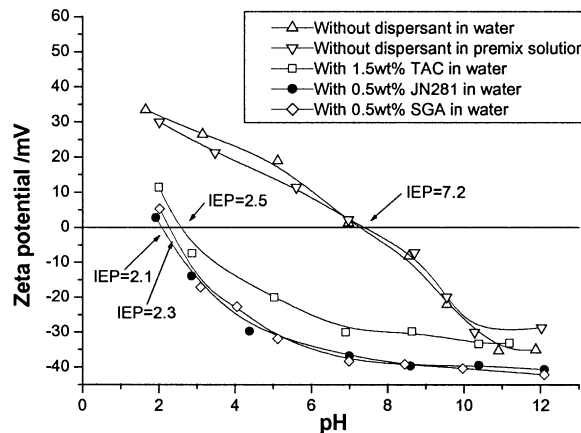Fig. 1. XRD patterns of the synthesised PZT powder.

Fig. 2. Effect of dispersants on the zeta potentials of the PZT suspensions at different pH values.

0.06 vol.% solids were used for the analysis. The effect of monomer on zeta potential is also illustrated. The zeta potential of pure PZT suspension changes from 33 mV at pH = 1.7 to −35.1 mV at pH = 11.9 with an IEP at about pH = 7.2, suggesting that neutral environment is disadvantageous in order to acquire good dispersion. Addition of monomer has little effect on the zeta potential values and IEP position, but it seems to slightly decrease the relative value of the potential. This indicates that the uncharged AM molecule either screen the charge developed by the PZT powders in solution or preferentially absorb onto the surface of the PZT particles. With the addition of TAC, JN281 and SGA the IEP of the PZT powders is moved to pH = 2.5, 2.1 and 2.3, respectively. In the range of neutral environment to pH = 12, the zeta potential is almost constant. Addition of dispersants results in more negative potential values and the absolute potential values of these systems suggest that JN281 and SGA should be more effective than TAC for good dispersion of the powders.

Fig. 3 shows the viscosity as a function of the shear rate for different PZT slurries. Because the PZT powders will "jam up" at about 35 vol.% solids loading in the suspensions without dispersant, a 30 vol.% solids loading is used to test these systems. Adjustment of pH values to either acid or basic conditions has little effect on the viscosity while addition of dispersants can greatly decrease the viscosity. This indicates that the electrostatic stabilization mechanism alone is not sufficient for good dispersion of the PZT powders. Effect of the dispersants can be attributed to both electrostatic and steric stabilization mechanisms. The high viscosities at the beginning of the curves indicate a "Bingham" behavior of the suspensions and all systems show shear-thinning behavior at low shear rates. Because shear flow will cause relative movement of the particles in the suspension, shear-thinning behavior can be attributed to a
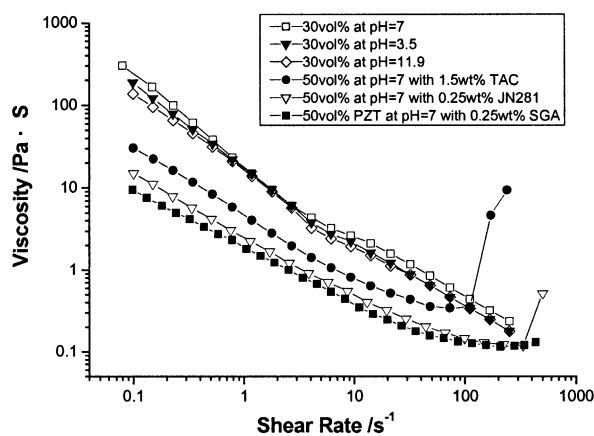
certain kind of rearrangement of the relative spatial disposition of the particles,[4] i.e. a certain kind of shear flow-induced structure. For concentrated suspensions of hard solid particles in Newtonian liquids it was generally accepted and has been verified by optical diffraction, small angle neutron scattering (SANS) and birefringence studies in many suspension systems that the flow-induced structure is an layered structure,[4–7] because it can provide a low resistance of the particle movement between different layers under the shear flow. For the systems containing dispersants, especially for those containing TAC and JN281, when the shear rates increase to a critical value (γ_c) a shear-thickening behavior appears. Shear-thickening might indicate that the flow-induced structure is destroyed. It is evident from the viscosity values and shear-thickening behaviors that for the three dispersants SGA is the most effective one and TAC is the most ineffective one, while JN281 shows a similar effect to that of SGA. In addition, PZT slurries in the premix solution have almost the same viscosity values as those in the pure water, suggesting that addition of AM (at a concentration of 15%) has little effect on the viscosity. These phenomena are consistent with the zeta potential results, indicating that the dispersants work by increasing the stability and resisting aggregate of the ceramic particles by both electrostatic and steric stabilization mechanism.

For a dispersant there exists an optimum concentration at which just enough dispersant is present in solution to provide maximized coverage of the PZT powder and any excess dispersant may be harmful in decreasing viscosity. Change of viscosity with dispersant concentration at a steady shear rate is shown in Fig. 4. Here a PZT solids loading of 48 vol.% is used in case of "jamming up" of the suspensions at low dispersant concentrations. From Fig. 4 we can see that the optimum concentration of TAC, JN281 and SGA are about 1.8, 0.3 and 0.6 wt.% of the PZT powder respectively.
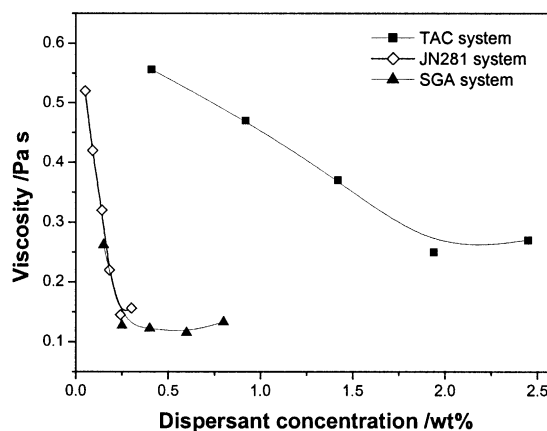

Fig. 3. Influence of dispersants and pH value on the viscosity of the PZT suspensions.

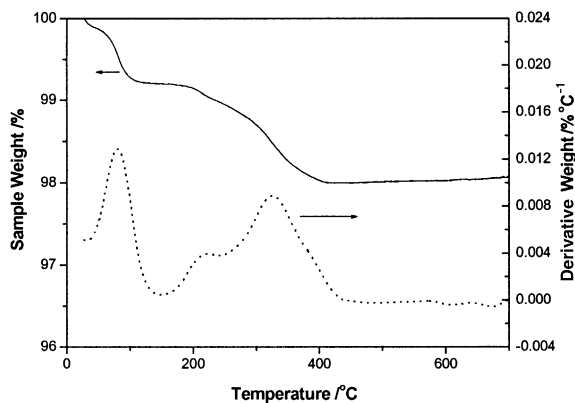Fig. 4. Effect of dispersant concentration on the viscosity of PZT suspensions under a steady shear rate of 110 s⁻¹.

Fig. 5. TGA and DTG curves of gelcast PZT sample in air at a heating rate of 5 °C min^{-1}.

3.2. Binder burnout and microstructure

The details of how the gelcast PZT sample is pyrolyzed are determined via thermogravimetric analysis (TGA) in air at a heating rate of 5 °C min^{-1}. The TGA together with the DTG curve of the green body (50 vol.% solids loading) obtained from PZT slurry with TAC as the dispersant are shown in Fig. 5. Green body derived from PZT slurry using JN281 or SGA as the dispersants has the same weight loss characteristic. From the DTG curve we can see three detached peaks at about 82, 220 °C and 330 °C respectively. Mass loss ends at about 450 °C, where a total mass loss of only about 2% is achieved and following that is a plateau stage. Mass loss may be attributed to the trapped water and the burnout of the cross-linked polymer network. This pyrolysis procedure is similar to that of a gelcast Al_2O_3 sample,[8] except for a lower mass loss value of 2% before 800 °C than that (about 4%) for and Al_2O_3 sample having the same solids loading. This is caused by the density difference of the two materials. Because of the small content of the organic substance, time-consuming

debinding program can be excluded during the sintering of the ceramics.

SEM micrographs showing the fracture surfaces of gelcast PZT sample at a solids loading of 50 vol.% by using JN281 as the dispersant is shown in Fig. 6. The sample prepared by the conventional die pressing way while sintered under the same sintering procedure is also shown in the figure for comparison. Both samples exhibit dense and homogeneous microstructure and there is no obvious difference between them. No macropores (100 μm level) can be found in Fig. 6b, suggesting that no or little gas-discharging reactions occurred during the gel-forming process. Those gelcast samples by using TAC and SGA as the dispersant have the similar homogeneous microstructure as those shown in Fig. 6. However, further magnified SEM photos of the samples shown in Fig. 7 indicate some difference of the samples. Fig. 7a–c show similar microstructure, where most of the grains are in the range of 3–8 μm and are fractured in an inter-granular manner. While Fig. 7d shows a partly trans-granular fracture manner and the grains are in the range of 4–7 μm.

Some parameters of gelcast PZT samples prepared at the optimum dispersant concentration and those of die pressed sample are listed in Table 1. Density and shrinkage of these samples show little difference, indicating that high-quality PZT ceramic parts can be successfully fabricated by gelcasting. However, by comparing the standard deviation of the density values of ten samples we can find that gelcast can provide more homogeneous samples. Fig. 8 illustrates some complex-shaped PZT ceramic parts fabricated by the gelcasting approach.

3.3. Electrical properties

For piezoelectric ceramics, we require that the forming process must not affect the electrical properties of the material. It is well known that the properties of the
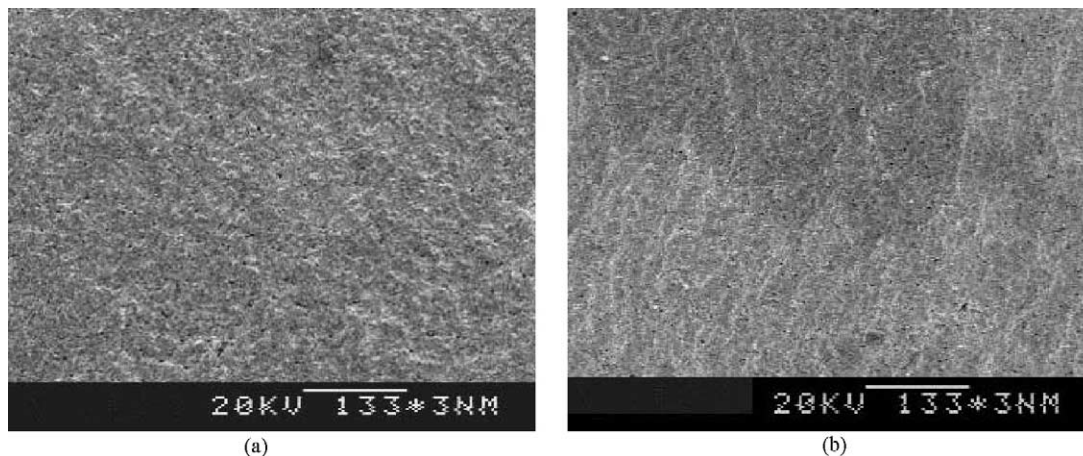

Fig. 6. SEM photos showing the fracture surfaces of PZT green bodies prepared by different methods: (a) gelcast by using JN281 as the dispersant; (b) die pressed at 80 MPa.
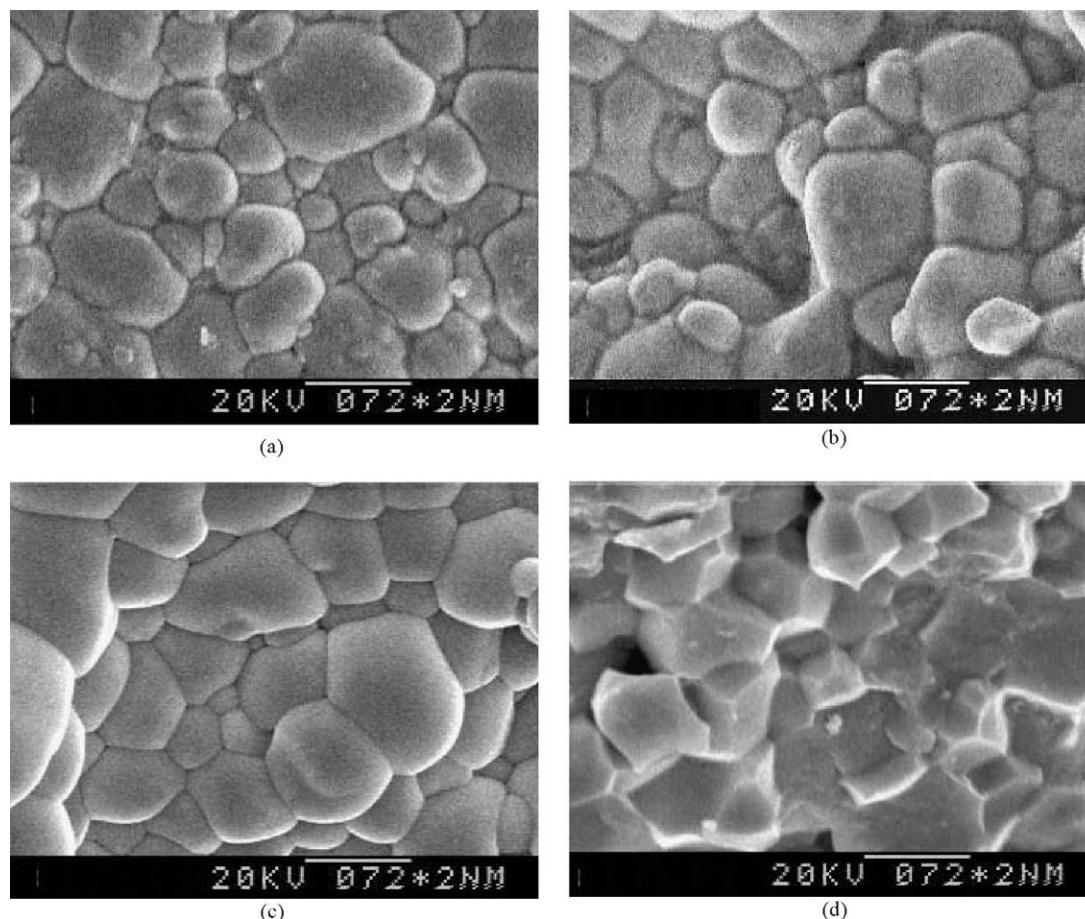
Fig. 7. Comparison of microstructure of different PZT samples: (a) die pressed sample, (b) gelcast by using TAC as the dispersant, (c) gelcast by using JN281 as the dispersant, (d) gelcast by using SGA as the dispersant.

Table 1
Comparison of some parameters of PZT sample prepared by gelcasting at a 50 vol.% solids loading with different dispersants and that by dry pressing with a pressure of 75 MPa

Sample	Mean density (g/cm^3)	Standard deviation of density (g/cm^3)	Linear shrinkage (%)
Die pressed at 80 MPa	7.62	0.082	14.8
Gelcast with 1.8 wt.% TAC	7.66	0.071	15.9
Gelcast with 0.3 wt.% JN281	7.72	0.056	16.8
Gelcast with 0.6 wt.% SGA	7.71	0.068	16.9

PZT-type ceramics can be substantially changed by the substitution of some elements for the Pb or Zr/Ti sublattices. There are mainly two types of dopants, i.e. the donor type (soft type), and the acceptor type (hard type). As a result, the electrical properties of PZT are very sensitive to the chemical composition of the sample and can be affected to a large degree by trace amount other elements and impurities.[9–11] In order to testify if

the sample forming process leads to the deterioration of the properties of the material, the electrical properties of gelcast were investigated and compared with those of the die pressed samples.

From Table 2 we can see that the gelcast samples prepared by using TAC or JN281 as the dispersant show similar electrical properties with those of the die pressed samples. While gelcast samples prepared by using SGA as the dispersant show much difference. Because the only difference of the three gelcast samples lies in the different dispersants, these results indicate that SGA might be the cause of the deterioration of the properties. Considering the composition of the dispersants, TAC and JN281 may be seemed as organic substance and which can be excluded during the sintering procedure. On the contrary, the Na^+ ion in SGA may be inevitably reserved in the ultimate PZT samples. The acceptor type doping ions include Mg^{2+}, Fe^{3+}, K^+, Na^+, Mn^{2+} etc. From the valence and ion radius (1.02 Å) of Na^+, it may be seemed as a substitution ion for the B site Pb^{2+} (ion radius 1.18 Å) in the lattice. Consistently, The parameters of the PZT sample using

Table 2
Comparison of some electrical parameters of PZT samples prepared by gelcasting with 50% solids loading and by die pressing at a pressure of 80 MPa

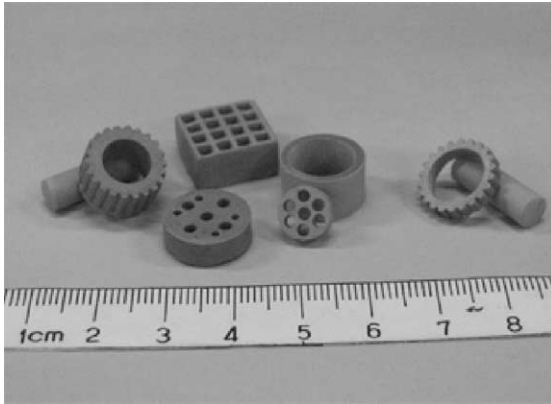| Sample	Mean d_{33} (pC/N)	Standard deviation of d_{33} (pC/N)	ϵ	K_p	Q_m	tgδ	P_r/μC/cm^2
Die pressed at 80 MPa	200	8.51	859	0.52	460	0.0038	25.9
Gelcast with 1.8 wt.% TAC	213	3.93	878	0.54	478	0.0039	25.6
Gelcast with 0.3 wt.% JN281	215	3.52	866	0.51	446	0.0041	26.5
Gelcast with 0.6 wt.% SGA	175	3.65	762	0.43	512	0.0026	22.4

Fig. 8. Illustration of the ultimate PZT ceramic parts fabricated by gelcasting approach.

SGA as the dispersant in Table 2 disclose an obvious hardening dopant modified characteristic compared with the die pressed sample, i.e. a higher mechanical quality factor Q_m, a higher loss tangent tgδ, a lower dielectric constant ϵ, a lower coupling factor K_p, a lower d_{33} and a lower remnant polarization. Therefore, it might be deduced that the Na element in SGA has entered into the bulk phase of the PZT sample and consequently an obvious hardening effect was caused. Because sodium salts are widely used as dispersants for ceramic material and commercial dispersants might contain a variety of impurity ions, the results here also indicate that a critical step for the successful application of gelcasting to the forming of piezoelectric materials is to select a suitable dispersant. Pure organic dispersants may be a suitable choice in case of the deterioration of the electrical properties of the gelcast sample. In addition, more uniform d_{33} value of gelcast samples were obtained by contrasting the standard deviation of the data. This is consistent with the density data. 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 and high homogeneity can be obtained by gelcasting way. Another interesting result is that gelcast samples using TAC and JN281 as the dispersants show slightly higher mean d_{33} values than that of the die pressed samples. This might be ascribed to the higher density and higher homogeneity of the samples, while it might also be ascribed to some uncertain impurities introduced by the dispersants.

4. Summary

After developing concentrated PZT slurry with low viscosity, high-quality complex PZT parts are successfully fabricated by gelcasting technology. Because only a small amount of organic substance is added in the system by using this technology, the time-consuming binder burnout program can be excluded. The ultimate near-net-shape formed PZT samples also show dense and homogeneous microstructure and homogeneous electrical properties. While because the electrical properties of PZT type material are very sensitive to the chemical composition of the sample, unsuitable selected dispersants can result in the deterioration of the electric properties of the material although concentrated PZT slurry with low viscosity can be obtained by different dispersants. The results indicate that a critical step for the successful application of gelcasting to the forming of piezoelectric materials is to select a suitable dispersant. Pure organic dispersants may be a suitable choice in case of the deterioration of the electrical properties of the gelcast sample.

References

1. Young, A. C., Omatete, O. O., Janney, M. A. and Menchhofer, P. A., Gelcasting of alumina. *J. Am. Ceram. Soc.*, 1991, **74**, 612–618.
2. Gilissen, R., Erauw, J. P. and Smolders, A. et al., Gelcasting—a near net shape technique. *Mater Design*, 2000, **21**, 251–257.
3. Israelachvili, J., *Intermolecular & Surface Forces*, 2nd edn. Academic Press, London, UK, 1992.
4. Barnes, H. A., Shear-thickening (dilatancy) in suspensions of nonaggregating solid particles dispersed in Newtonian liquids. *J. Rheol.*, 1989, **33**, 329–366.
5. Barnes, H. A., Hutton, J. F. and Walers, K., *An Introduction to Rheology*. Elsevier Press, Oxford, 1989.
6. Ackerson, B. J., Shear induced order and shear processing of model hard sphere suspensions. *J. Rheol.*, 1990, **34**, 553–590.

7. So, J. H., Yang, S. M. and Hyun, J. C., Microstructure evolution and theological responses of hard sphere suspensions. *Chem. Eng. Sci.*, 2001, **56**, 2967–2977.

8. Janney, M. A., Omatete, O. O. and Walls, C. A. et al., Development of Low-toxicity gelcasting system. *J. Am. Ceram. Soc.*, 1998, **81**, 612–618.

9. Jaffe, B. and Cook, W., *Piezoelectric Ceramics*. Academic Press, London/New York, 1971.

10. Dong, D., Murakami, K., Kaneko, S. and Xiong, M., Piezoelectric properties of PZT ceramics sintered at low temperatures with complex-oxide additives. *J. Ceram. Soc. Jap. Int. Ed*, 1993, **101**, 1061–1065.

11. Lebrun, L., Guiffard, B. and Audigier, D. et al., Dielectric and piezoelectric properties of (La, Mg, F) and (Mg, Mn, F) doped PZT ceramics under low and high solicitations. *J Eur. Ceram. Soc.*, 2001, **21**, 1357–1360.