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Gelation behavior and mechanical properties of gelcast lead zirconate titanate ceramics

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Abstract

Gelcasting is a novel forming method in fabricating complex ceramic parts. A low-toxicity gelling system with excellent properties based on Hydantion epoxy resin and 3,3′-Diaminodipropylamine (DPTA) was developed for gelcasting PZT ceramics. Effects of solid loading on the rheological properties, gelation behaviors and mechanical properties were investigated. The solid loading of PZT suspension which was suitable for the gelcasting reached as high as 55.0 vol%. The presence of PZT powder exhibited a catalytic effect of the polymerization reaction of the suspension calculated by the activation energy E_a. The mean flexural strength, the characteristic strength and Weibull modulus of the green bodies reached the maximum of 34.1 ± 3.3 MPa, 35.6 MPa and 11.1, respectively, when the solid loading was 55.0 vol%. After sintering at 1120 °C, excellent irregular shaped pillar accurately reproduced the form of the mold and the structural integrity maintained well over a large area.

Keywords: Gelcasting; Lead zirconate titanate; Epoxy resin; Rheology; Weibull analysis

1. Introduction

High frequency ultrasonic transducers with the working frequency above 30 MHz have received wide attention, for their potential high resolution imaging applications, such as ophthalmology, dermatology, and small animal studies.[1] 1-3 piezoelectric composites[2,3] have been intensively studied to meet the need for high frequency ultrasonic transducers due to the low acoustic impedance and higher electromechanical coupling coefficient compared with the bulk ceramics. To enhance the performance of the piezocomposite, the interference from the spurious mode should be avoided. Development of piezoelectric pillar arrays with irregular shapes was an effective solution so that the spurious modes within the composite could be spread over a broad enough frequency range to have negligible effect on the composite performance.[4,5] However, the current fabrication techniques, i.e. dice and filling,[6] injection molding,[7] laser micromachining,[8] and viscous polymer processing (VPP),[2] were incompatible with the dimensions and irregular-shaped designs.

Gelcasting was an attractive near-net-shaped forming method with high fidelity for ceramic materials. The merits including high homogeneity and excellent mechanical properties, offered great advantage for fabricating fine-scaled ceramic parts. A key part of gelcasting process was the preparation of the high solid loading ceramic suspension with proper fluidity, in order to minimize the shrinkage and obtain the product with high accuracy. Many efforts were made to develop the gelling systems for the Lead Zirconate Titanate (PZT) gelcasting process.[3,9–14] Among the gelling systems, ethylene glycol diglycidyl ether was the most promising one. The advantages were evident with the development of low viscosities of slurries and high strengths of green bodies, which ensured the microscaled PZT pillar arrays with lateral dimensions of <10 μm and height of 100 μm to be successfully achieved.[7] However, the unfavorable characteristics of EGDGE including irritative to the skin and eyes, in need of a careful storage and variable in the water solubility from source to source limited its application.

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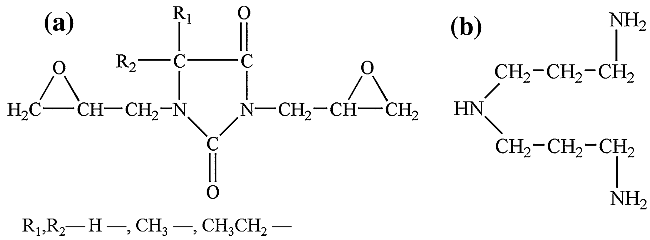

Fig. 1. Molecular structural formula of (a) epoxy resin and (b) DPTA.

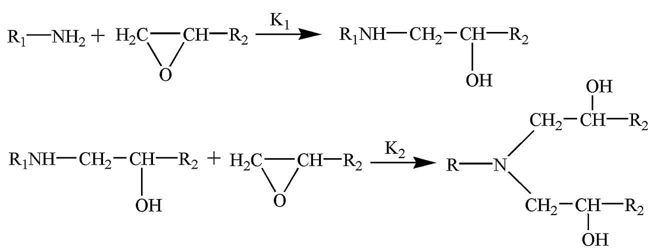
Fig. 2. Reaction equation of amino-epoxy cure[16].

Hydantion epoxy resin,[15] among the existing epoxy resin, exhibited the best performance, such as the low viscosity of 129.8 mPa s and the highest green strength of 43.4 MPa with the addition of 15.0 wt% resin, when the Al_2O_3 powder was used as model. Our previous study revealed the feasibility of the Hydantion epoxy resin system in PZT slurries and obtained PZT pillar array with high aspect ratio and square shape. In this paper, the effects of solid loading on the rheological properties, the gelation behavior of the PZT suspensions as well as the mechanical properties of the PZT green bodies were systemically investigated. Excellent irregular shaped pillar with the structural integrity over a larger area was successfully achieved.

2. Experimental

2.1. Materials and procedures

PZT powder (PZT5-A, Baoding Hengsheng Acoustics Electron Apparatus Co. Ltd., China) with a mean particle size of 0.25 μm was used as raw material. Hydantion epoxy resin (MHR154, Meihua Chemicals Co. Ltd., China) and 3,3′-Diaminodipropylamine (DPTA, Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) were used as the epoxy resin and hardener, respectively. The molecular structural formulas of Hydantion epoxy resin and hardener were shown in Fig. 1(a) and (b), respectively. The typical amino-epoxy cross-link reaction can be expressed in Fig. 2.[16] The premix solution was prepared by dissolving 15.0 wt% Hydantion epoxy resin into the distilled water. Various PZT suspensions were prepared by ball milling different amounts of PZT powder into the premix solution for 24 h. Ammonium polyacrylate (HydroDisper AG165, Shenzhen Highrun Chemical Industry Co. Ltd., China) was added as the dispersant. After adding 1–2 drops of 1-octanl as the antifoaming agent and 0.25 mol/eq DPTA, the suspensions were degassed in a vacuum desiccator for 5 min and then poured into a silicone mold (Suzhou Institute of Nano-Tech and Nano-Bionics, China). 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 8 h. Binder burnout was carried out at 600 °C for 1 h with a heating rate of 1 °C/min and sintering was carried out at 1120 °C for 0.5 h with a heating rate of 5 °C/min, followed by natural cooling.

2.2. Characterizations

The rheological properties of PZT suspensions were measured by a rotational rheometer (AR2000 EX, TA Instruments, USA) with a diameter of 40 mm parallel plate and a gap of 200 μm. The as-prepared suspensions were pre-sheared at a shear rate of 100 s^{-1} for 1 min and a pause for 30 s before the viscosities were measured within the shear rate range of 1–1000 s^{-1} at 20 °C. The gelation behavior of the suspensions were measured by monitoring the apparent viscosity η_{app} as a function of time at a constant shear rate of 0.1 s^{-1} for different temperatures and solid loading. A thin layer of silicone oil was applied to the exposed edge of the samples to minimize the water loss during the test. The flexural strengths of green bodies with the dimensions of 35 × 4 × 3 mm^3 were determined by three-point bending tests using an electronic universal testing machine (KD11–2, Shenzhen Kaiqiangli Technology Co. Ltd., China) with a crosshead speed of 0.5 mm/min and a span of 28.0 mm. The microstructures of the polydimethylsiloxane (PDMS) mold and the sintered PZT arrays were observed by scanning electron microscopy (NOVA NANOSEM 230).

2.3. Weibull analysis

The flexural strengths of the ceramic bodies were greatly determined by the variability of the flaw distributions. Therefore in order to determine the strength and reliability of the material, Weibull statistics[17] is applied via Eq. (1).

$$P_f = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right] \quad (1)$$

Where P_f is the fracture probability, defined by the relation $P_f = (i - 0.3)/(N + 0.4)$, in which i is the ranking number of the specimen in strength from least to greatest, N is the number of total samples. m is the shape parameter (Weibull modulus). σ_0 is the scale parameter or the characteristic strength ($\sigma_{63.21\%}$).

3. Results and discussion

3.1. Rheological behavior

Fig. 3 shows the effects of the dispersant concentrations on the viscosities of 45.0 vol% PZT suspension containing 15.0 wt% Hydantion epoxy resin. All suspensions exhibited a shear-shining behavior. At shear rate of 100 s^{-1}, low viscosity ensured the suspension fill the mold sufficiently, producing high-accurate smooth and uniform green bodies. After casting, high viscosity at low shear rate prevented the settling of particles. As the dispersant concentration increased, the viscosity of the suspension decreased dramatically firstly and then increased slightly. As the