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A modified gelcasting approach to fabricate microscale randomized 1–3 piezoelectric arrays

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ABSTRACT

A modified gelcasting approach was used to fabricate the microscale randomized 1–3 piezoelectric array, which involves the in situ polymerization of hydantion epoxy resin and 3,3′-Diaminodipropylamine (DPTA) in the lead zirconate titanate (PZT) suspensions with low viscosity and high solid loading. Rheological results demonstrated that the hydantion epoxy resin concentration had little effect on the viscosity of the premix solution, and therefore the optimized solid loading of the suspensions with 15.0 wt% resin could reach as high as 55.0 vol%. Weibull analysis also revealed that a more homogenous microstructure was obtained derived from the 55.0 vol% PZT suspension, where the Weibull modulus and the characteristic flexural strength reached the maximum value of 12.57 and 80.94 MPa. The excellent randomized piezoelectric pillar array with superior structural integrity and high fidelity was successfully fabricated.

1. Introduction

Ultrasonic transducers operating at frequencies above 30 MHz have been under considerable investigation, since they could offer real-time images of anatomical details of ophthalmology, dermatology, intravascular and small animal studies with the improved micro-scale resolution [1,2]. The preferred active material in ultrasonic transducer is the 1–3 piezoelectric composite [3], because of the advantageous properties including the low acoustic impedance and the high electromechanical coupling coefficient. However, the development of the high frequency piezoelectric composits has been limited by the difficulty of fabricating the miniature piezoelectric pillar arrays, since the commercial dicing technique [4] is incompatible with both the dimensions and designs necessary for high frequencies [5].

Gelcasting [6,7], is a promising near-net-shaped forming technique for making the complex-shaped ceramic components with high fidelity. The process is based on the in situ polymerization of monomers to consolidate the ceramic suspensions with high solid loadings into dense and strong bodies. Although the frequently used acrylamide (AM) monomer can offer the gelcast PZT bodies a high green strength of 20 MPa [8], the disadvantage of neurotoxicity limits its potential abroad application. To mitigate this problem, much efforts have been made to develop the low or non-toxic gelling systems [9,10]. Among these alternatives, ethylene glycol diglycidyl ether (EGDGE) [11] as one of the water soluble epoxy resins was a promising candidate. Due to the advantageous properties including the low viscosity of the suspension and the high strength of the green bodies, the periodic arrangement of the lead zirconate titanate (PZT) pillar arrays with different shapes and lateral dimensions of $< 10\,\mu m$ was successfully achieved [12]. However, there still existed some unfavorable characteristics such as irritative to the skin and eye, in need of a careful storage and variable in the water solubility from source to source.

Hydantion epoxy resin has extremely high water solubility due to the hydrophilic amide groups, as well as crystallized at room temperature in favor of the storage and transportation. In our previous study, compared with the reported gelling system, the green strength of the alumina body was significantly enhanced using hydantion epoxy resin system, while maintaining the great fluidity of the suspension [13]. Herein, we are pursued to investigate the effects of hydantion epoxy resin on the rheological properties and the gelation behavior of the premix solution. The PZT suspensions with different solid loadings were prepared using hydantion epoxy resin as gelling agent. The rheological properties of the obtained PZT suspensions and the properties of both green and sintered bodies were systemically

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investigated. Microscale randomized 1–3 PZT array with the structural integrity over a larger area was successfully fabricated and characterized.

2. Experimental

2.1. Materials and procedures

Commercial lead zirconate titanate powder (PZT5-A, Baoding Hengsheng Acoustics Electron Apparatus Co. Ltd., China) with an average particle size of 0.25 µm was used. The premix solutions with different concentrations were prepared with hydantion epoxy resin (MHR154, Meihua Chemicals Co. Ltd, China). Suspensions with different solid loadings were prepared by ball milling the PZT powder into the premix aqueous solution containing 15.0 wt% hydantion epoxy resin. 0.6 g ammonium polyacrylate (HydroDisper AG165, Shenzhen Highrun Chemical Industry Co. Ltd., China) per 100 g PZT powder was added as the dispersant. 0.25 mol/eq 3,3′-Diaminodipropylamine (DPTA, Tokyo Chemical Industry Co. Ltd., Japan) based on hydantion epoxy resin was added into the suspension as the hardener. The suspensions were vacuum cast into the PDMS mold. After 24 h consolidation at room temperature, the PDMS mold was carefully peeled off. The green bodies were gradually dried at 40 ℃ for 4 hrs and 80 ℃ for 8 hrs. Sintering was carried out at 1200 ℃ for PZT bulk samples and at 1120 ℃ for PZT arrays with a heating rate of 5 ℃/min respectively.

2.2. Characterizations

The rheological properties of PZT suspensions were measured by a rotational rheometer (AR2000 EX, TA Instruments, USA) fitted with a diameter of 40 mm parallel plate. All the measurements of viscometric properties were conducted at 20 ℃ within the shear rate range of 1–1000 s^{-1}. The gelation behavior of the premix solution and 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}. In order to reduce the impact of the flow history on the measurements, all the suspensions were pre-sheared at a shear rate of 100 s^{-1} for 1 min and a pause for 30 s before the measurements were performed. A thin layer of silicone oil was placed on the exposed edge of the samples to minimize the water loss during the test. The flexural strengths of green and sintered bodies 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. The microstructures of the sintered PZT arrays were observed by scanning electron microscopy (NOVA NANOSEM 230, FEI Co., Czech).

2.3. Weibull analysis

To evaluate the effect of the solid loading on the flexural strengths of the sintered bodies, the reliability of the strengths was assessed using a two – parameter Weibull analysis via Eq. (1) [14],

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

Where P_f is the fracture probability, defined as $P_f=(i-0.3)/(N+0.4)$, in which i is the ranking number of the specimen in strength from least to greatest, N is the number of total samples. σ_0 is the scale parameter or the characteristic strength ($\sigma_{63.21\%}$). m is the shape parameter (Weibull modulus). A high value of m indicates a low scattering of the strength data and more homogenous microstructure in samples, because the strength distribution strongly depends on the shape of the flaw distributions.

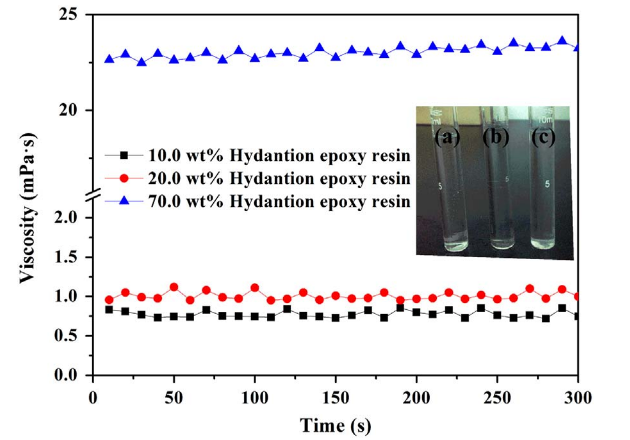

Fig. 1. Viscosities of the premix solutions with different epoxy resin concentrations as a function of the time at the shear rate of 100 s^{-1}. The insert map was the photograph of the premix solutions (a) 10.0 wt%, (b) 20.0 wt%, (c) 70.0 wt%.

3. Results and discussion

3.1. Rheological behavior

Fig. 1 shows the effects of the hydantion epoxy resin concentrations on the viscosities of the premix solutions. All the solutions were transparent and homogenous shown in the insert map, indicating the good water solubility of hydantion epoxy resin. Although the viscosity of the pure hydantion epoxy resin reached as high as 65 Pa·s (data not shown), that of the premix solution even with 70.0 wt% resin remained at an extremely low value of 22.68 m Pa·s, which might be attributed to the good water solubility and the small molecular weight of 182–192. The resin concentration had little effect on the viscosity of the aqueous solution, which was benefit for the preparation of the low viscosity suspension with high resin concentration. And this would provide the PZT green body a high strength, offering the great advantage for fabricating parts with fine structures.

Fig. 2(a) and (b) shows the effects of the solid loadings on the viscosities and the shear stresses of PZT suspensions containing 15.0 wt% hydantion epoxy resin. It can be observed that an increase in the solid loadings was concordant with an increase in the viscosities of the suspensions. And the suspensions exhibited a shear-thinning behavior when the solid loading was lower than 55.0 vol%. However, the rheological properties transformed to a shear-thickening behavior with increasing the solid loading up to 57.5 vol%. This phenomenon had been documented in other concentrated suspensions [15], which can be explained by the damage of the original layered structure above a critical shear rate. Although the viscosity of 57.5 vol% PZT suspension was only 0.45 Pa·s, the rheological behavior precluded the suspension for gelcasting. Since the procedures of mixing and casting were generally operated at high shear rate, the difficulty in uniformly mixing and sufficiently filling the mold increased with the increased viscosity.

A quantitative description of the shear stress – shear rate dependence of the PZT suspensions except 57.5 vol% was given using a Sisko model, which was expressed by the following equation [16],

$$\tau = \eta_{\infty}\gamma + m\gamma^n \quad (2)$$

where η_{∞} is the lower Newtonian plateau values of the viscosity, m is the consistency index, n is the power-law or flow index. The model parameters were presented in Table 1. As expected, higher solid loadings led to an increase in the consistency index m and an decrease in the flow index n. With the increase in the solid loading of the PZT suspension, the particle distance reduced and the interparticle interactions increased, which increased the degree of aggregation. Flow indexes are less than 1, reflecting the shear thinning nature of these