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The mechanical and electric properties of infiltrated PZT/polymer composites

Heng Chen *, Xianlin Dong, Tao Zeng, Zhiyong Zhou, Hong Yang

Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, PR China

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Abstract

Lead zirconate titanate (PZT) ceramics/polymer composites were fabricated by infiltrating polymer into porous PZT ceramics. The electrical and mechanical properties as a function of ceramic volume fraction were studied in this paper. With a decrease in the ceramic volume fraction, the dielectric constant of composite decreased while the hydrostatic figure of merit increased. For the same ceramic volume fraction, the fracture strength of the PZT/polymer composite was much higher than that of porous PZT, meanwhile the piezoelectric characteristics of composite were close to that of porous PZT. The hydrostatic figure of merit of the composite with a ceramic volume fraction of 68% was over 5000×10^{-15} m^2/N. This value is much higher than reported value of the composite with the same ceramic volume fraction. This kind of composite could be a promising candidate for sensors and actuators.

Keywords: C. Mechanical property; D. PZT/polymer composite; Hydrostatic figure of merit; Infiltration

1. Introduction

Lead zirconate titanate, $Pb(Zr_xTi_{1-x})O_3$ (PZT), and its related materials exhibit excellent piezoelectric properties. Hence PZT related ceramics have been widely used for a host of sensor and actuator applications [1–7]. However, poor acoustic impedance matching between the ceramics and the media limits the use of dense PZT ceramics as medical sensors, sonar and hydrostatic sensors. Acoustic impedance matching could be enhanced by reducing the density of piezoelectric material. Porous PZT is considered as a good substitute for dense PZT because its density is much lower than that of dense PZT. Moreover, porous PZT has lower permittivity and transverse piezoelectric coefficient [7–10], which can lead to better hydrostatic piezoelectric characteristics. However, it suffers from a poor mechanic strength which seriously restricts its application. In addition, the dampness can greatly deteriorate the electrical properties of porous PZT. To increase the mechanic strength of porous PZT, researchers have already focused on the PZT/polymer composite. Newnham et al. developed the concept of phase connectivity and found that PZT/polymer composites with 3–3 connectivity had promising characteristics for transducer applications [11]. There are numerous techniques to fabricate this kind of composites, in which infiltrating polymer into porous ceramic is one of the most promising methods due to convenient preparation and high performance [12–15]. By choosing different polymer, the hydrostatic piezoelectric coefficient can be adjusted to a large degree [16]. The polymer commonly used is polyurethane or epoxy resin. Another kind of polymer, hydrocarbon resin, can be a promising candidate for composition of PZT/polymer composite. However, few work of investigating on PZT/hydrocarbon resin composite has been reported. Most of the work focused on the electrical properties of composite, while the mechanical properties are seldom reported so far. In this work, a series of PZT-hydrocarbon resin composites were prepared ranging from 68 to 87% ceramic fraction using polymer infiltration technique. The mechanical and electrical properties of the porous ceramics and composites were investigated. And the effects of polymer and processing on the hydrostatic figure of merit were evaluated. It was found that the composite was a promising candidate for the underwater acoustic application.

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* Corresponding author. Tel.: +86 21 52412018; fax: +85 21 52413903.
E-mail address: chheng@mail.sic.ac.cn (H. Chen).

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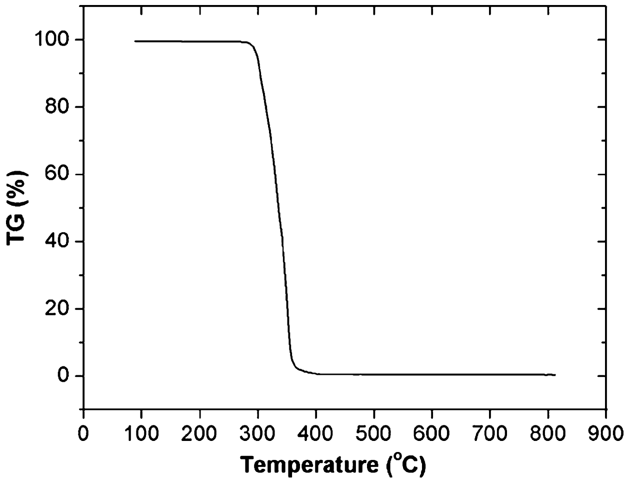


Fig. 1. TG curve of PMMA at a heating rate of 10 °C per minute.

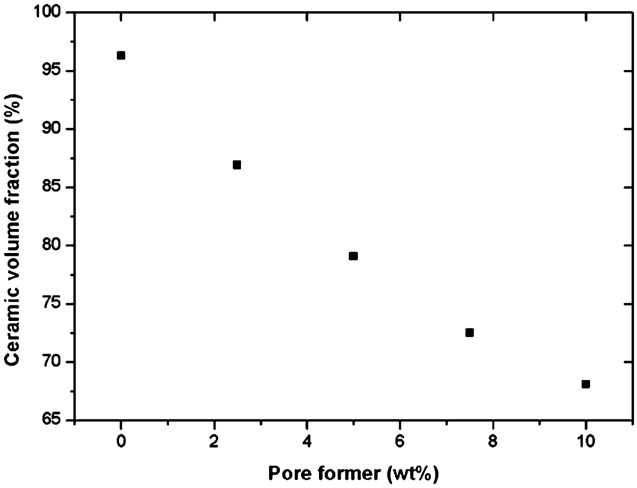


Fig. 3. The ceramic volume fraction as a function of pore former addition.

2. Experiment

The PZT powders with a selected composition of $Pb(Zr_{0.53}Ti_{0.47})O_3 + 0.5$ wt% Nb_2O_5 were synthesized using solid-state reaction. Porous PZT ceramics were prepared by mixing PZT powder with pore former polymethyl methacrylate (PMMA) powder. The size of PMMA was controlled between 425 and 600 μm. The compositions were PZT + α PMMA, where $\alpha = 0$, 2.5, 5, 7.5 and 10 wt%. The mixed powders were ball milled for 6 h with zirconia balls as the grinding media and alcohol as the solvent, and then dried at 40 °C. The powder with 5 wt% PVA addition was pressed at about 150 MPa to disk-shaped specimens (Ø18 mm × 1.5 mm) and rectangle-shaped specimens (6 mm × 8 mm × 46 mm). From the thermogravimetric analysis of PMMA shown in Fig. 1, PMMA burned out at 400 °C. Hence the optimum heating procedure was designed to begin with an initial heating rate of 120 °C/h to 240 °C followed by 30 °C/h to 420 °C and then 120 °C/h to 850 °C to completely burn out the PMMA and produce a green body with porous structure. The green bodies were then placed in a covered alumina crucible pitted with $Pb(Zr_{0.53}Ti_{0.47})O_3$ powders to reduce the volatilization of PbO and sintered at 1260 °C for 2 h in soaking furnace. The disk-shaped specimens were poled by applying a DC field of 3 kV/mm for 15 min in a silicone oil bath at 120 °C before infiltration.

The PZT/polymer composite was obtained by infiltrating liquid polymers into the pores of the porous specimens in a vacuum chamber at 170 °C for 3 h. The polymer was hydrogenated C5 aliphatic hydrocarbon tackifying resin (Yangzi-Eastman Ltd., China), and the density was 1.0×10^3 kg/m^3. The porous PZT and composite specimens were pasted with electric conductive adhesive (DAD40, Shanghai Research Institute of Synthetic Resins, China) as electrodes for electrical measurement. The standard bars (3 mm × 4 mm × 36 mm) were ground from the porous ceramics and composite bodies for mechanical measurements.

X-ray diffraction patterns (Rigaku RAX-10, Japan) of the sintered samples were performed with Cu Kα1 radiation at a step scan of 0.02° from 20° to 70° 2θ. The microstructures of PZT ceramics were observed by scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan). After infiltration, the microstructures of composites were observed by secondary

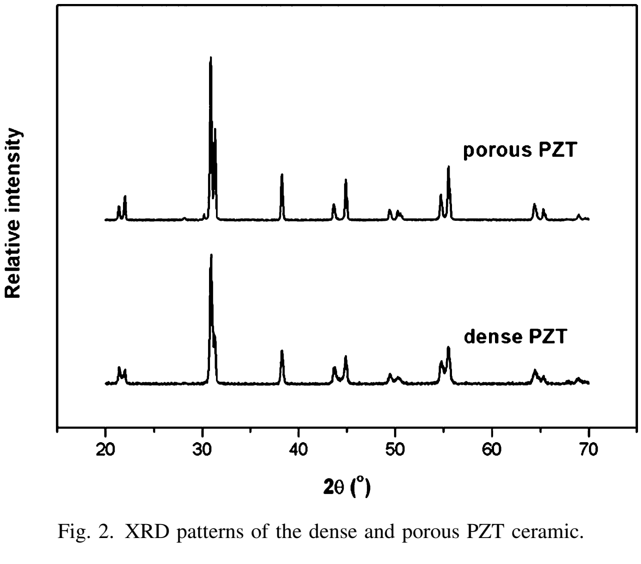


Fig. 2. XRD patterns of the dense and porous PZT ceramic.

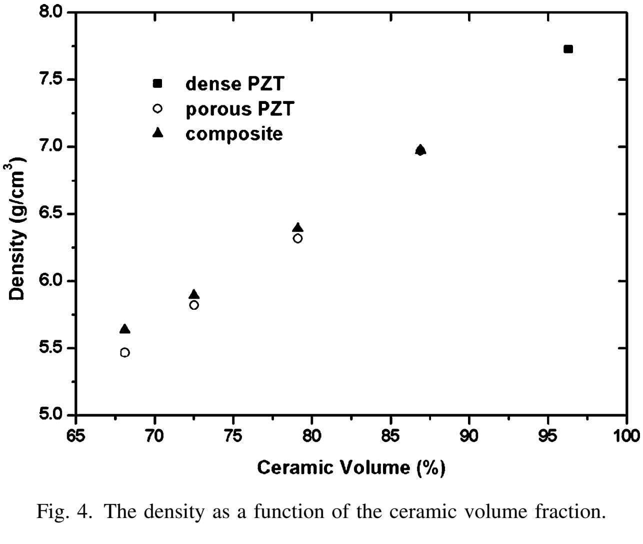


Fig. 4. The density as a function of the ceramic volume fraction.

electron image (SEI), backscattered electron image (BEI) and the composition was analyzed by energy dispersive spectrum (EDS). The densities and the ceramic volume fraction of porous and composite specimens were determined by the Archimedes method. Fracture strength was measured on the standard bars by three-point bending method (Instron 5566, USA). The piezoelectric charge coefficient (d_{33}) was measured by a direct method based on a Quasti-static d_{33}-meter. The capacitance (at 1 kHz) and the electrical impedance as a function of frequency were measured using the HP-4294A impedance analyzer. The electromechanical coupling factors and transverse piezoelectric coefficient were determined from the values of resonance and antiresonance frequencies, density, dimensions and dielectric constant.

3. Results and discussion

3.1. Microstructure and mechanical properties

Fig. 2 showed XRD patterns of the dense PZT, PZT–PMMA (10 wt%) ceramics sintered at 1260 °C for 2 h. Note that single perovskite structures were observed for both ceramics and no secondary phase was detected in the porous ceramic, which demonstrated that the PMMA did not influence the phase of PZT. The ceramic volume fraction as a function of the content of pore formers was shown in Fig. 3. With the increase in pore former addition, the ceramic volume fraction decreased. Compared with the porous PZT, the PZT/polymer composite had higher density due to the polymer infiltration (Fig. 4).

Typical SEM micrographs of polished surface of dense PZT, porous PZT ceramics and PZT/polymer composite were illustrated in Fig. 5. It was seen that a continuous porous network was formed in the porous PZT. The less ceramic volume, the more pores connected. As for the composite, the pores were impregnated with polymer. From cross section micrograph of the composite (Fig. 6), the polymer infiltrated all the open pores of porous PZT, even small ones. It was seen from the EDS results that the bright area was the PZT ceramic phase, and the dark area was polymer phase. It should be noted that the peak of gold was caused by vaporizing gold electrode during the pretreatment of the specimens.

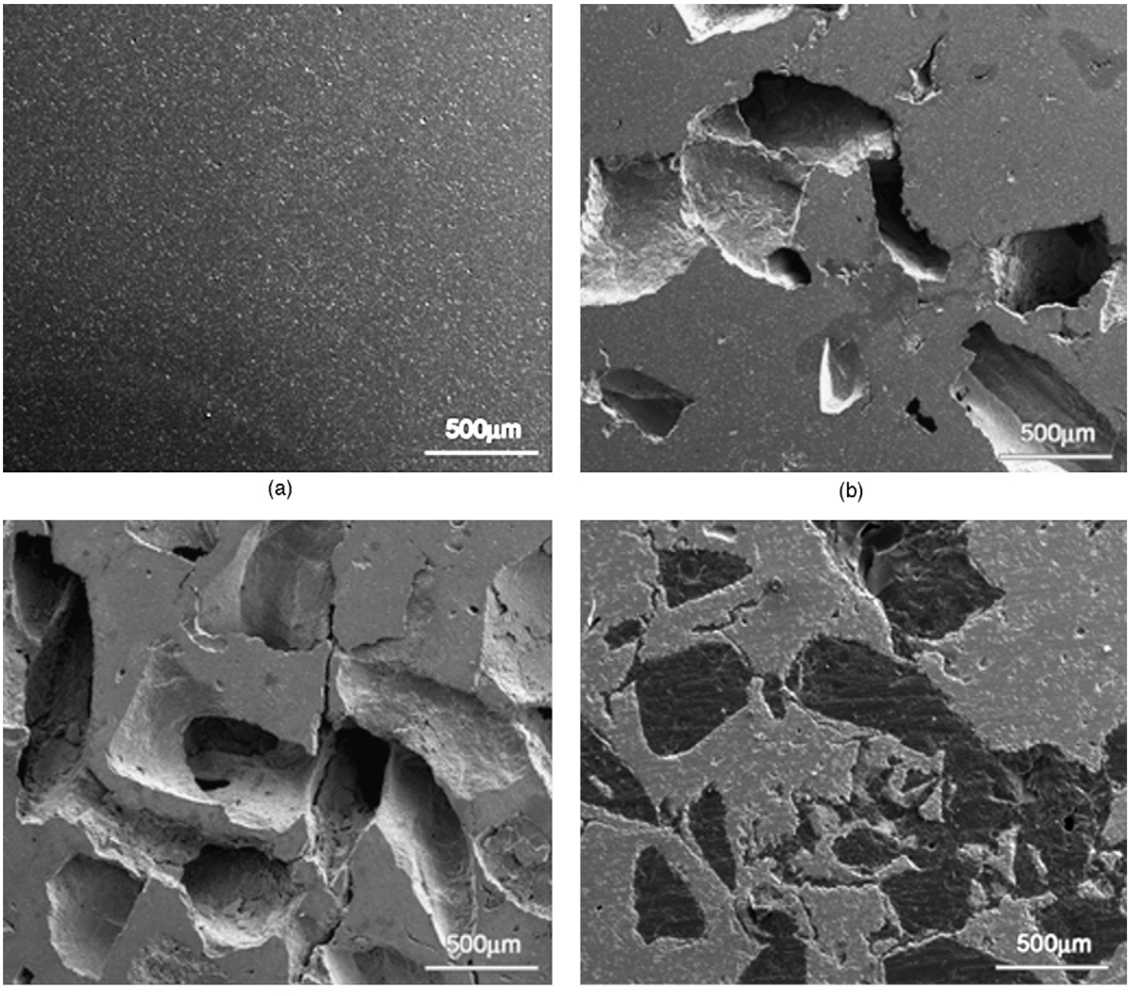
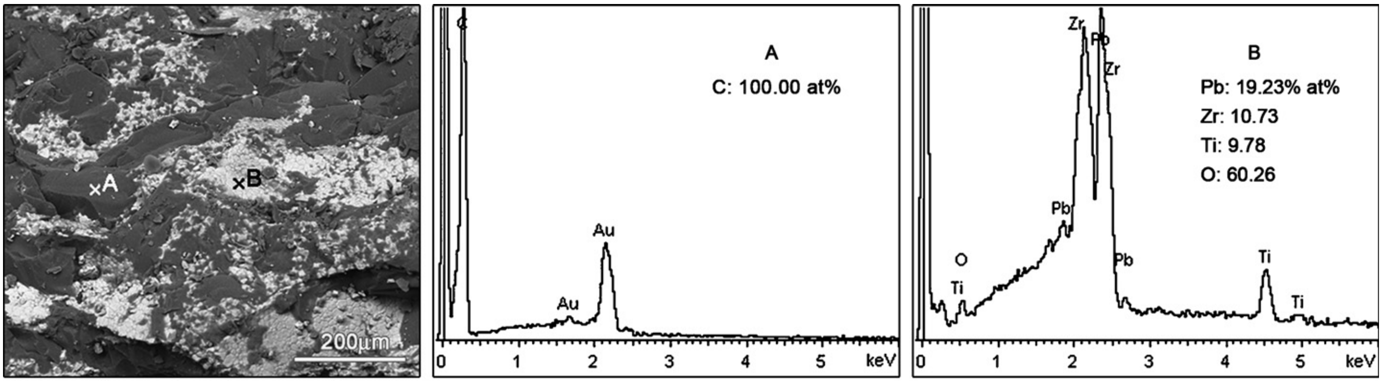


Fig. 5. SEI micrographs of polished surface (×40): (a) dense PZT, (b) porous PZT, 79% ceramic volume fraction, (c) porous PZT, 68% ceramic volume fraction and (d) PZT/polymer composite, 68% ceramic volume fraction.



(a) (b) (c)

Fig. 6. Morphology and composition analysis of cross section of PZT/polymer composite: (a) BEI micrographs of cross section (×100), (b) EDS of polymer phase and (c) EDS of ceramic phase.

Fig. 7 showed the fracture strength values as a function of ceramic volume fraction of ceramics and composite. It was obvious that the fracture strength of ceramics deceased accompanied by a decrease of ceramic volume fraction. Fig. 8 showed the variation of stress with displacement. In comparison with the porous PZT, the composites had higher fracture strength and elastic constant. The fracture strength of composite was 50% larger than porous PZT with a ceramic volume fraction of 68%, for example. These results demonstrated that infiltrating polymer into the pores of porous ceramic could lead to great enhancement of mechanical properties.

3.2. Piezoelectric properties

It is well known that dielectric constant of ceramics is significantly larger than that of the polymer. Therefore, the ceramic phase fraction dominates the dielectric constant of composite. Fig. 9 showed the relative dielectric constant of ceramics and composite as a function of ceramic volume fraction. With the decrease of piezoelectric phase, the dielectric constant ε_{33}^{T} of composite decreased, which could be attributed to the increased vertical volume of polymer phase with low dielectric constant.

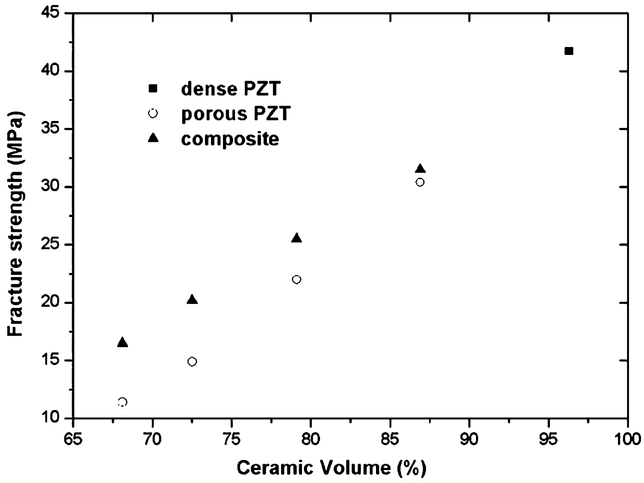


Fig. 7. Variation of the fracture strength with ceramic volume fraction.

The effect of ceramic volume fraction on longitudinal piezoelectric coefficient was shown in Fig. 10. The internal pores lead to microscopic stress and strain near the pores, which prevent grain grown, inhibit the movement of domain walls and then reduce the piezoelectric coefficient [17]. If an external force was applied, the stress produced by ceramic phase of PZT/polymer composite was less than that of porous PZT. Hence the piezoelectric coefficient of composite was less than that of porous PZT. The decrease of the piezoelectric phase made the transverse piezoelectric coefficient ($-d_{31}$) decrease more drastically than the longitudinal one (d_{33}), which produced an increase in the hydrostatic strain coefficient. The hydrostatic voltage coefficient is related to the hydrostatic charge coefficient ($d_h = d_{33} + 2d_{31}$) and the relative dielectric constant under constant stress (ε_{33}^{T}): $g_h = d_h/\varepsilon_{33}^{T}$. Therefore, the lower dielectric constant of porous PZT and composite resulted in a higher hydrostatic voltage constant as shown in Fig. 11. The hydrostatic figure of merit ($d_h g_h$) with ceramic volume fraction was shown in Fig. 12 and the $d_h g_h$ of composite was close to that of porous PZT. The hydrostatic figure of merit with a ceramic volume fraction of 68% was more than 5000×10^{-15} m^2/N, while the $d_h g_h$ of other PZT/polymer composite reported with the same volume fraction was about 3000×10^{-15} m^2/N

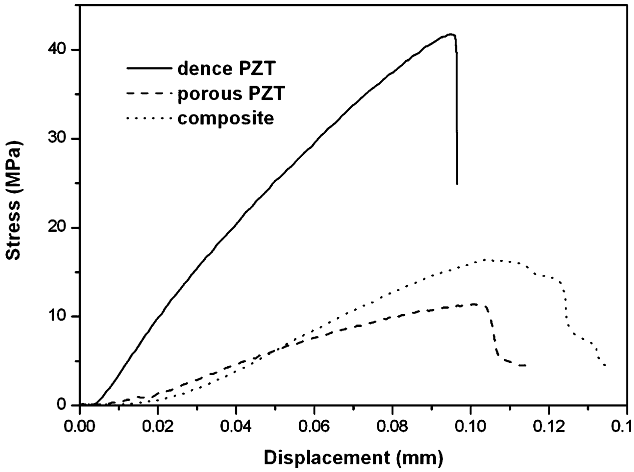


Fig. 8. Stress/displacement curves for the dense PZT, porous PZT and composite (68% ceramics volume fraction).

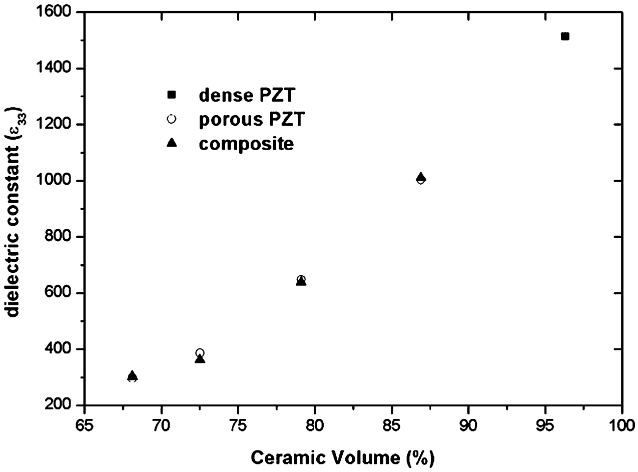


Fig. 9. Variation of dielectric constant with the ceramic volume fraction.

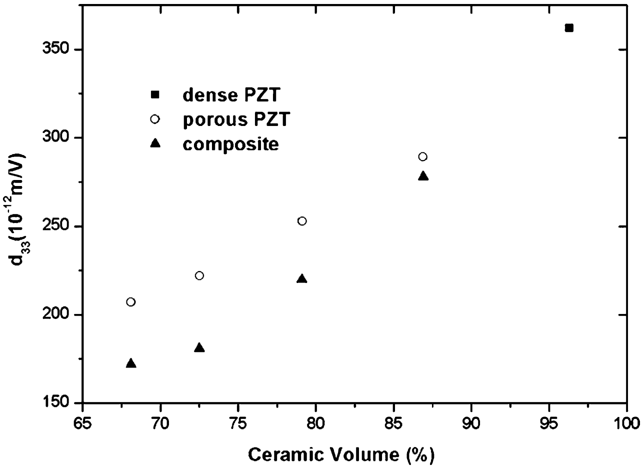


Fig. 10. Variation of the longitudinal piezoelectric constant with ceramic volume fraction.

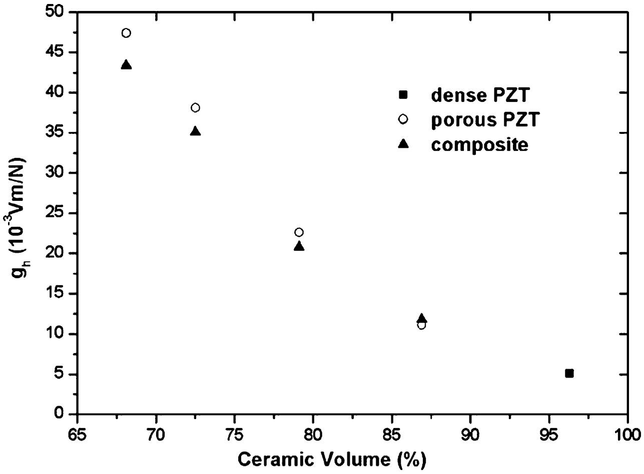


Fig. 11. Variation of hydrostatic voltage coefficient with the ceramic volume.

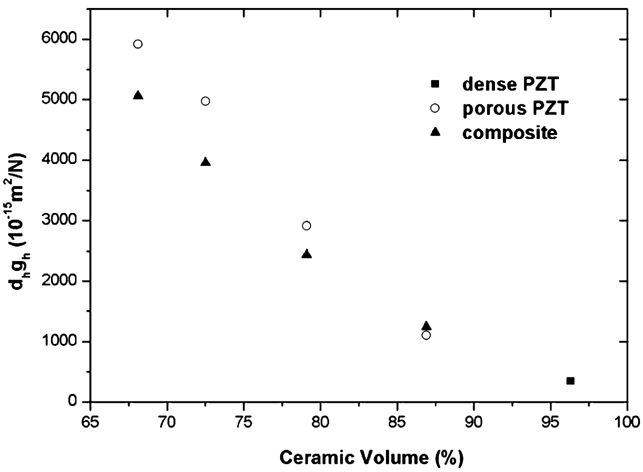


Fig. 12. Variation of hydrostatic figure of merit with the ceramic volume.

[15,16]. We propose two possible explains for such high hydrostatic figure of merit obtained. One is that the hydrostatic resin used in the experiment has a low hardness. With a decrease of the hardness of polymer phase, the hydrostatic figure of merit decreases. The results shows that hydrocarbon resin has more advantages to be a composition of PZT/polymer composite compared with other polymer. The other is due to the processing of fabricating composite. In this work, the processing of poling is before infiltrating polymer. The prior polarization made the ceramic pole more sufficiently, which caused better piezoelectric characteristics.

4. Conclusions

PZT/polymer composite were fabricated by infiltrating hydrocarbon resin into porous PZT ceramic over a range of ceramic volume fraction (68–87%). With the decrease in ceramic volume fraction, the density of porous ceramic and composite decreased. The fracture strength and the elastic coefficient of composites were larger than those of the porous PZT due to the polymer infiltration. The longitudinal piezoelectric coefficient and dielectric constant of composite decreased with the decreasing ceramic phase, while the hydrostatic voltage coefficient and the hydrostatic figures of merit increased. The hydrostatic figure of merit of the composite with a ceramic volume fraction of 68% was over 5000×10^{-15} m^2/N. This value was much higher than that ever reported with the same ceramic volume fraction. The kind of PZT/polymer composite could have promising applications in sensors and actuators.

Acknowledgement

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