Electromechanical Properties and Temperature Stability of 1-3 Type PZT/Epoxy Piezoelectric Composite

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Abstract. 1-3 type PZT5H/epoxy composites were fabricated via dice and fill method, by which the PZT5H ceramic blocks were processed into a series of rod arrays with kerf width of 120 µm ~ 260 µm and pillar width of 120 µm ~ 450 µm. Proper thickness was chosen to guarantee that the aspect ratio (height/width) is higher than 3. Piezoelectric properties of the 1-3 composites as a function of ceramic volume fraction and aspect ratio were investigated. The resultant composites show high piezoelectric coefficient $d_{33}>500$ pC/N, low mechanical quality factor $Q_m = 2.9 ~ 7.7$, enhanced electromechanical coupling coefficient $k_t=0.66$~0.74 and low acoustic impedance $Z = 9 ~ 17$ Mrayl, as well as a good temperature stability in the investigated temperature range from -50°C to 150°C.

1. Introduction

The 1-3 type piezoceramic/polymer composites are ideal functional materials to fabricate ultrasonic transducers for applications in medical imaging and underwater detection, because of the large merits of high sensitivity, wide band and narrow pulse [1,2,3]. This type of composites is formed in the way that inorganic piezoelectric ceramic rods are embedded in a three-dimensionally connected polymer matrix. Such composites maintain the high piezoelectric properties of ceramics and provide low acoustic impedances required for good matching with water and human tissue, in addition to the enhanced electromechanical coupling in thickness mode. Moreover, the piezoelectric properties of the 1-3 composites can also be tailored by varying the ceramic volume fraction, aspect ratio and periodicity to optimize the transducing performance. A large number of researches about the piezoelectric properties of 1-3 piezoelectric composites have been carried out in the past decades [4,5,6]. Nevertheless, studies on the temperature stability are still very limited. In this work, we systematically investigated the influences of ceramic volume fraction, aspect ratio and temperature on the piezoelectric properties of the 1-3 composites. Several 1-3 type piezoelectric composites with the characteristics of high $d_{33}$, large $k_t$, low $Z$, low $Q_m$ and good temperature stability were successfully fabricated by optimizing the ceramic volume fraction and aspect ratio.

2. Experimental procedure

Commercially available PZT5H ceramics (Zibo Yuhai Ceramic Co. Ltd, China) and Epoxy resin (EpoThin™ from BUEHLER Co. Ltd, USA) were used as the starting raw materials. The 1-3 type piezoceramic/epoxy composites were fabricated by the dice and fill method. Three types of dicing saws with different thickness (250 µm, 150 µm and 100 µm, respectively) were used to machine different PZT rod arrays. After forming the electrodes on the upper and bottom surfaces with silver
paint, plate-shaped composite samples were poled along the PZT rod direction at 100°C for 30 min under the electric field of 3 kV/mm.

Mass density was measured using the Archimedes method. Surface morphology and cross-sectional microstructure were observed by optical microscope. Piezoelectric coefficient $d_{33}$ was measured by a quasistatic piezoelectric constant testing meter ZJ-3A (Institute of Acoustics, Chinese Academy of Science). Ceramic volume fraction (CVR) was calculated from the pillar widths and the kerf widths of ceramic rod arrays. Piezoelectric characteristic was analysed with an Agilent 4294A impedance analyser. The electromechanical coupling coefficient and acoustic impedance were determined by resonance and anti-resonance method performed on the basis of IEEE standards. The composite density $\rho$ was calculated by Eq. (1). Planar coupling factor $k_p$ was evaluated by using IEEE standard curve of frequency separation $\gamma$ versus $k_p$ for thin discs, and $\gamma$ was calculated from Eq. (2). The thickness coupling factor $k_t$, longitudinal electromechanical coupling factor $k_{33}$ and mechanical quality factor $Q_m$ were determined from Eq. (3), (4), and (5), respectively. The quantities $v_c$, $\rho_c$ and $\rho_p$ are ceramic volume fraction, ceramic density, and polymer density, respectively. $f_r$ is the frequency at which electrical impedance shows a minimum in thickness resonance mode. $f_{-0.5}$ and $f_{+0.5}$ are the upper and lower frequencies with half of the conductance obtained at $f_r$ from the conductance versus frequency curve, respectively. $f_p$ and $f_s$ are the frequencies of a thin ceramic disc, at which electrical impedance show maximum and minimum in planar resonance mode, respectively.

\[ \rho = \rho_c v_c + (1 - v_c)\rho_p \]  
\[ \gamma = \frac{f_r - f_s}{f_s} \]  
\[ k_t^2 = \frac{\pi f_s}{2 f_p} \tan \left( \frac{\pi f_p f_s}{2 f_p} \right) \]  
\[ Q_m = \frac{f_r}{f_{-0.5} - f_{+0.5}} \]  
\[ k_{33}^2 = k_p^2 + k_t^2 - k_p^2 k_t^2 \]  
\[ V_{com} = 2 f_p t \]  
\[ Z = \rho_c V_{com} \]

3. Results and Discussion

Figure 1 is the X-ray diffraction (XRD) profile of an unpoled PZT5H ceramic recorded at room temperature. This XRD profile indicates that the ceramic is of pure perovskite structure without any secondary impurity phase. Peaks around $2\theta=45.5^\circ$, which correspond to $\{200\}$ reflections, are partially enlarged and can be well fitted with three Lorentz curves, as shown in the inset of Figure 1. Based on the peak intensities, we can judge that the PZT5H ceramic is in the $R$-$T$ phase coexistence at room temperature, and the volume fractional ratio of $R$-phase to $T$-phase is approximately 1:3.

Table 1 shows the various physical properties of the PZT5H ceramic. It possesses a high $d_{33}$ of 740 pC/N, a large longitudinal electromechanical coupling factor $k_{33}$ of 0.82 and a low dielectric loss tan$\delta$ of 0.02. As demonstrated in Figure 2, the temperature stabilities of electromechanical coupling factors are quite good in the investigated temperature range from -50°C to 150°C. Thus, this commercial PZT is considered as an ideal ceramic material for fabricating the 1-3 type piezoceramic/polymer composites.
Figure 1. XRD pattern of unpoled PZT5H ceramic. Inset is the enlargement of {200} peak and fitted with Lorentz curve.

Table 1 Various physical properties of PZT5H ceramic

| Property | Value |
|----------|-------|
| $\rho$ (g/cm$^3$) | 7.50 |
| $\varepsilon_r$ | 3200 |
| $\tan\delta$ (%) | 2.0 |
| $T_c$ ($^\circ$C) | 230 |
| $d_{33}$ (pC/N) | 740 |
| $k_t$ | 0.56 |
| $k_{33}$ | 0.82 |
| $Q_m$ | 70 |
| $Z$ (Mrayl) | 32 |

Figure 2. Temperature stabilities of $k_t$, $k_p$ and $k_{33}$ of PZT5H ceramic.

Figure 3 shows the optical microscope images of microstructure for the 1-3 type composites with CVRs of 25% and 41%, respectively. As can be seen from it, arrays of periodically ordered structure with defect-free ceramic rods and pore-free epoxy were successfully fabricated. The aspect ratio (= thickness/pillar width) is calculated to be higher than 8, according to Figure 3(c). In addition, a fact that the ceramic rods and epoxy matrix are well bonded can be also understood. A series of 1-3 type PZT5H/epoxy composites with varied CVRs from 21% to 51% were prepared by varying the pillar width and kerf width in this study.
Figure 3. Optical microscopic images of microstructure of 1 - 3 type PZT5H/epoxy composites. (a) Surface image of a composite with CVR=25%, (b) Surface image of a composite with CVR=44%, and (c) cross-sectional image of a composite with CVR=25%.

Figure 4. Impedance and phase vs. frequency spectra. (a) monolithic PZT5H ceramic, (b) a 1-3 type PZT5H/epoxy composite with CVR=31%

The impedance and phase vs. frequency spectra of PZT5H ceramic and a 1-3 type PZT5H/epoxy composite with CVR= 31% are shown representatively in Figure 4(a) and 4(b), respectively. The PZT5H ceramic exhibits vibrant planar mode at lower frequencies. The second largest peak near 1.0 MHz is the thickness mode. In contrast, the 1-3 type PZT5H/epoxy composite reveals a neat thickness mode near 2.0 MHz and trivial planar mode. It means, compared with pure PZT5H ceramic, $k_p$ of the 1-3 composite is dramatically decreased and $k_t$ is increased.
Figure 5(a) shows the dielectric constant $\varepsilon'$ and piezoelectric coefficient $d_{33}$ of the 1-3 type PZT5H/epoxy composites as a function of CVR. Clearly, $\varepsilon'$ changes nearly linearly with the increase of CVR. However, the change of $d_{33}$ with CVR is a little bit complicated. In the range of small CVR values, $d_{33}$ increases rapidly with the increase of CVR and reaches 425 pC/N at CVR=20%. Then, $d_{33}$ increases slowly but continuously with the further increase of CVR, and reaches 625 pC/N at CVR=48%. Thus, even when CVR is only 25%, $d_{33}$ can be as large as 500 pC/N. Figure 5(b) shows longitudinal piezoelectric voltage coefficient $g_{33}$ and electromechanical coupling coefficient $k_t$ of the 1-3 type PZT5H/epoxy composites as a function of CVR. It is well known that $d_{33}$ characterizes the ultrasonic beam transmission capability of a transducer while its echo receiving sensitivity is directly related to its $g_{33}$. Thus, we consider it is very important to know how $g_{33}$ changes with the change of CVR. According to Figure 5(b), $g_{33}$ and $k_t$ show the same changing trend, i.e., they increase first, and then decrease with the increase of CVR. The maxima of $g_{33}=0.091$ Vm/N and $k_t=0.71$ are observed at CVR=25% and 48%, respectively. A large $g_{33}$ implies a high ability to detect the low intensity ultrasonic vibration, leading to improved detecting sensitivity of the transducers. As expected, $k_t$ can be enhanced effectively by using the 1-3 connectivity, as indicated in Figure 5(b). It is interesting that all of the 1-3 PZT5H/epoxy composites with different CVRs show higher $k_t$ than the PZT5H ceramic. In particular, the one with CVR=48% show a $k_t$ maximum of 0.71, which is significantly higher than the PZT5H ceramic, which has $k_t$ of 0.56.

Figure 5. (a) Changes of $d_{33}$ and $\varepsilon'$ as a function of CVR (b) Changes of $k_t$ and $g_{33}$ as a function of CVR in the 1-3 type PZT5H/epoxy composites.

Figure 6. Thickness dependence of $k_t$ of 1-3 type PZT5H/epoxy composites. (a) a composite with kerf = 175 $\mu$m and CVR=25%, and (b) a composite with kerf = 260 $\mu$m and CVR=25%.
Figure 6 present the $k_t$ change of the 1-3 type PZT5H/epoxy composites as a function of thickness. As can be seen from these figures, $k_t$ first increases and then decreases slowly with the increase of thickness. For these two 1-3 type PZT5H/epoxy composites, maximum $k_t$ is obtained at the thicknesses of 0.60 mm and 0.80 mm, respectively. Interestingly, these thicknesses correspond to aspect ratios (thickness/pillar width) of about 3.0.

Table 2 lists the various physical properties relevant to ultrasonic transducing for a series of 1-3 type PZT5H/Epoxy composites with different CVRs. As can be seen from the table, all these composites possess relatively low loss $\tan \delta$ (≤0.051) and low acoustic impedance $Z$ (9.1~17.1 Mrayl), which is favorable for matching that of the load (such as water or human tissue) to minimize reflection losses at the interface. Meanwhile, low $Q_m$ (2.9~7.7) is good for transducers with wide bandwidth and low pulse.

As shown in Figure 6, the performance of a 1-3 type composite is affected by thickness. For the 1-3 type PZT5H/epoxy composite with CVR=25% and kerf = 260 $\mu$m, the maximum $k_t$ of 0.71 is obtained at the thickness of 0.80 mm, which corresponds to an aspect ratio of 3.1. The obtained physical properties of this 1-3 piezoelectric composite at the optimum thickness of 0.80 mm are summarized in Table 3. The temperature stability of its $k_t$ is shown in Figure 7. As can be seen, $k_t$ maintains a high level of 0.68~0.74 with a weak temperature dependence in the whole measured temperature range from -50°C to 150°C.

![Figure 7. Temperature stability of $k_t$, obtained for a 1-3 type PZT5H/epoxy composite with CVR=25% and aspect ratio=3.1](image-url)
Table 3 Performance of an optimized 1–3 type PZT5H/epoxy composite

| $\rho$ (g/cm$^3$) | $\varepsilon_r$ | $\tan\delta$ (%) | $d_{33}$ (pC/ N ) | $k_t$ | $Q_m$ | $Z$ (Mrayl) |
|------------------|--------------|-----------------|-----------------|------|------|------------|
| 2.70             | 670          | 4.7             | 515             | 0.73 | 3.7  | 9.8        |

4. Conclusion
A series of 1-3 type PZT5H/epoxy piezoelectric composites were fabricated by the cut and fill method. The influences of ceramic volume fraction, aspect ratio and thickness on those physical properties relevant to ultrasonic transducing were systematically investigated. Compared to PZT5H ceramic, the 1-3 type composites show generally increased $k_t$ but decreased $k_p$. A high-performance 1-3 type PZT5H/epoxy piezoelectric composite was successfully prepared by optimizing the ceramic volume fraction and the aspect ratio. This composite possesses the excellent ultrasonic transducing properties of $d_{33} =515$ pC/N, $k_t=0.73$, $Z=9.8$ Mrayl and $Q_m=3.7$. Moreover, its $k_t$ shows a very desirable temperature-stable character in the wide temperature range between -50$^\circ$C and 150$^\circ$C.

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