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Electric properties of single-crystal PMN-31% PT/epoxy 1–3 piezoelectric composites

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PMN-31% PT/expoxy 1–3 piezoelectric composites with a different volume fraction of PMN-31% PT single crystals from 0.4 to 0.7 have been studied as regards fabrication and electric properties. The ⟨001⟩ oriented piezoelectric composites exhibit functional properties of low dielectric constant, high electromechanical coupling coefficient (0.80), and low acoustic impendence compared to the ⟨110⟩ oriented ones. The vibration characteristics of the piezoelectric composites strongly depend on the rod geometry and the volume fraction. The results obtained indicate that these piezoelectric composites with better global properties are promising candidates for biomedical imaging and underwater transducer applications.

1 Introduction

The functional advantages of 1–3 connectivity piezoelectric composites, i.e. piezoelectric rods or fibers in a passive matrix, are now widely recognized [1]. The use of this type of material helps to improve the resolution and bandwidth of transducers, and is growing in the areas of underwater sonar, biomedical imaging and therapy, and non-destructive testing, with its manufacture taking place in many commercial organizations. The vast majority of these devices incorporate polycrystalline PZT piezoelectric ceramics. Recently, the relaxor-based ferroelectric crystals lead magnesium niobate–lead titanate (PMN-PT) and lead zinc niobate–lead titanate (PZN-PT) have been found to have ultrahigh piezoelectric properties and electromechanical coupling properties [2–4]. They have proved be efficient and powerful materials for ultrasonic transducers [5, 6]. However, a drawback of these materials is the relatively high acoustic impedance (approximately 30 Mrayls) resulting in a problem of acoustic impedance mismatch with that of human tissue (1.54 Mrayls) and water (1.49 Mrayls). In order to improve performance, the piezoelectric materials are often incorporated into a polymer matrix to form 1–3 composites, resulting in increased thickness electromechanical coupling and reduced acoustic impedance. These composites are produced with the aim of obtaining a combination of piezoelectric and mechanical properties that would be useful in electromechanical transducer applications.

Research has shown that piezoelectric PMN-PT single crystals near their morphotropic phase boundary (MPB; with the content of PT ranging from 30 to 35%) have an interesting property used as a 1–3 piezocomposites, and coupling factors as high as 0.9 could be achieved [7, 8]. When used in ultrasonic

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probes the pulse-echo impulse response of single-crystal PMN-PT/epoxy 1–3 composite transducers improved by factor of 5 compared with that of single-crystal PMN-PT transducers [9]. We believe it is clear that single-crystal piezocomposites should provide significant improvements in transducer performance and are worth further investigation. The present work involved the fabrication and characterization of ⟨001⟩ oriented and ⟨110⟩ oriented single-crystal PMN-31% PT/epoxy 1–3 composites. The measured dielectric, piezoelectric, and electromechanical coupling properties with tailored volume fraction are presented and applications considered.

2 Experimental

The PMN-PT crystals were grown by the modified Bridgman method [10]. The single crystals were oriented using an X-ray diffractometer, then cut into dimensions of $10 \times 10 \times 2$ mm^3 and $10 \times 10 \times 3$ mm^3 along the $\langle 001\rangle_{\mathrm{cub}}$ and $\langle 110\rangle_{\mathrm{cub}}$ directions, respectively. The crystals were coated by a silver electrode and were poled under a 0.7 kV/mm electric field at 110 °C.

The $\langle 001\rangle_{\mathrm{cub}}$ oriented and $\langle 110\rangle_{\mathrm{cub}}$ oriented PMN-31% PT single crystals with generally piezoelectric properties were selected. Rectangular piezocomposites with different PMN-PT volume fraction and the dimensions of rods were achieved using the dice and fill method [11]. Because of the fragile nature, the cutting velocity was slowed by 0.06 mm/s using a blade with cut width of 0.30 mm. 4-Minute Epoxy with a hardener (4:1) supplied by Bondo/Mar-Hyde Co., USA, was used to fill the kerfs. Two sets of closely spaced cuts were made: parallel cuts were made in a sample, the second set being perpendicular to the first. After a first dicing, the polymer was cast in the grooves in the samples and cured at 40 °C for a week. A second dicing was then done and the polymer also filled the crevices among the crystal rods. A small number of bubbles were trapped in the crevices although the majority were removed by running a fine wire through the grooves, while observing the sample under a microscope. The samples were also cured at 40 °C for a week in order to develop the homogenous and optimum electric properties of piezocomposites, and then excess polymer was removed. The samples were polished and a silver polymer electrode was applied at room temperature. The PMN-PT/epoxy 1–3 composites were poled in oil again at temperature of 30 °C under a 1.4 kV/mm field.

3 Results and discussion

The composites were fabricated with a fine polymer width so that they can be considered as homogeneous piezoelectric materials. The PMN-PT single crystals used for cutting had piezoelectric coefficient d_{33} ~1800 pC/N, as measured by a model ZJ-3A d_{33} meter supplied by Beijing Institute of Acoustics, Chinese Academy of Sciences, along thickness direction. The density of the composites was measured according to the Archimedes law. The electromechanical coupling properties of PMN-PT crystals and PMN-PT/epoxy 1–3 composites were determined at room temperature following the IEEE Standards on Piezoelectricity [12]. The experimental results were obtained by the resonance method using an HP 4285A (Agilent, Japan) impedance analyzer. The thickness electromechanical coupling coefficient k_{t} in the composites can be evaluated experimentally using the relation

$$k_{\mathrm{t}} = \frac{\pi}{2}\frac{f_{\mathrm{s}}}{f_{\mathrm{p}}}\tan\left(\frac{\pi}{2}\frac{f_{\mathrm{p}} - f_{\mathrm{s}}}{f_{\mathrm{p}}}\right), \tag{1}$$

where f_{s} and f_{p} are the series and the parallel resonance frequencies of the 1–3 piezocomposite plate, respectively. It was assumed that f_{s} is the frequency of minimum impedance and f_{p} is the frequency of maximum impedance. In order to avoid mode coupling, which adversely affects the measurement, the aspect ratio of the PMN-PT rods inside the composite samples was higher than 3. Other parameters such as mechanical quality factor Q_{m}, the longitudinal wave velocity V_{33}^{D} and stiffness constant C_{33}^{D} under constant electric displacement vector (D) conditions, and the acoustic impedance Z were also determined.

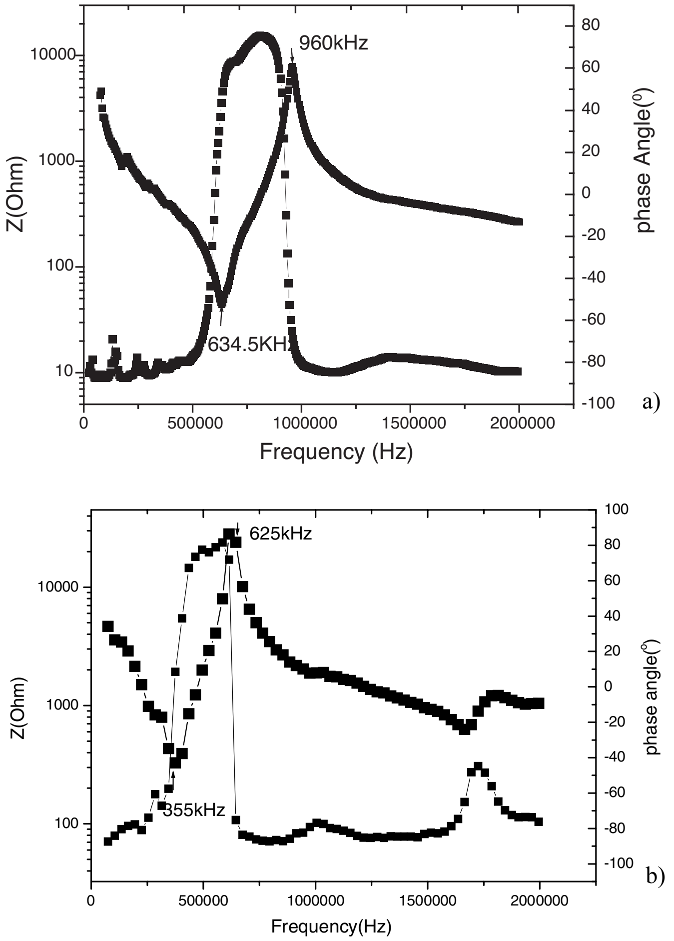

Fig. 1 Frequency dependence of the electric impedance and the phase angle in the PMN-31% PT/epoxy 1–3 piezocomposites: a) ⟨001⟩ oriented; b) ⟨110⟩ oriented.

The thickness electromechanical coupling coefficient k_t in 1–3 composites, as discussed experimentally and theoretically, can be enhanced using PMN-PT columns embedded in the epoxy matrix. Figure 1 shows the plots of electrical impedance and phase angle vs. frequency for single-crystal PMN-31% PT/epoxy 1–3 composites (a silver polymer electrode). The corresponding plot of ⟨001⟩ orientated single-crystal PMN-31% PT/epoxy 1–3 composites (a silver polymer electrode) with 0.45 volume fraction and 1.8 mm thickness is shown in Fig. 1(a). The electromechanical coupling coefficient k_t of the ⟨001⟩ oriented single-crystal PMN-PT/epoxy composite with different volume fraction of PMN-PT as shown in Fig. 2(a) can reach as high as 0.8, which is higher than that of ⟨001⟩ orientated PMN-PT crystal. From the result, k_t appears lower than the longitudinal electromechanical coupling coefficient k_{33} (~0.9) of a single-crystal rod. This may arise from the partial breakdown of crystal rods during the processing procedures and also at the polymer/PMN-PT interface when polymer cured. It is possible that those pieces successfully cut actually contained damage that reduced the piezoelectric performance. It can be deduced from the low frequency constant that poled single-crystal material is less stiff than an unpoled one. In addition, it is possible that more compliant epoxy filler is required to achieve higher coupling factors.

With the exception of the k_t value, the fact that the measured d_{33} value (shown in Fig. 2(f)) is lower than the predicted one is somewhat anomalous. Figure 3 shows the strain vs. electric field (unipolar) curves

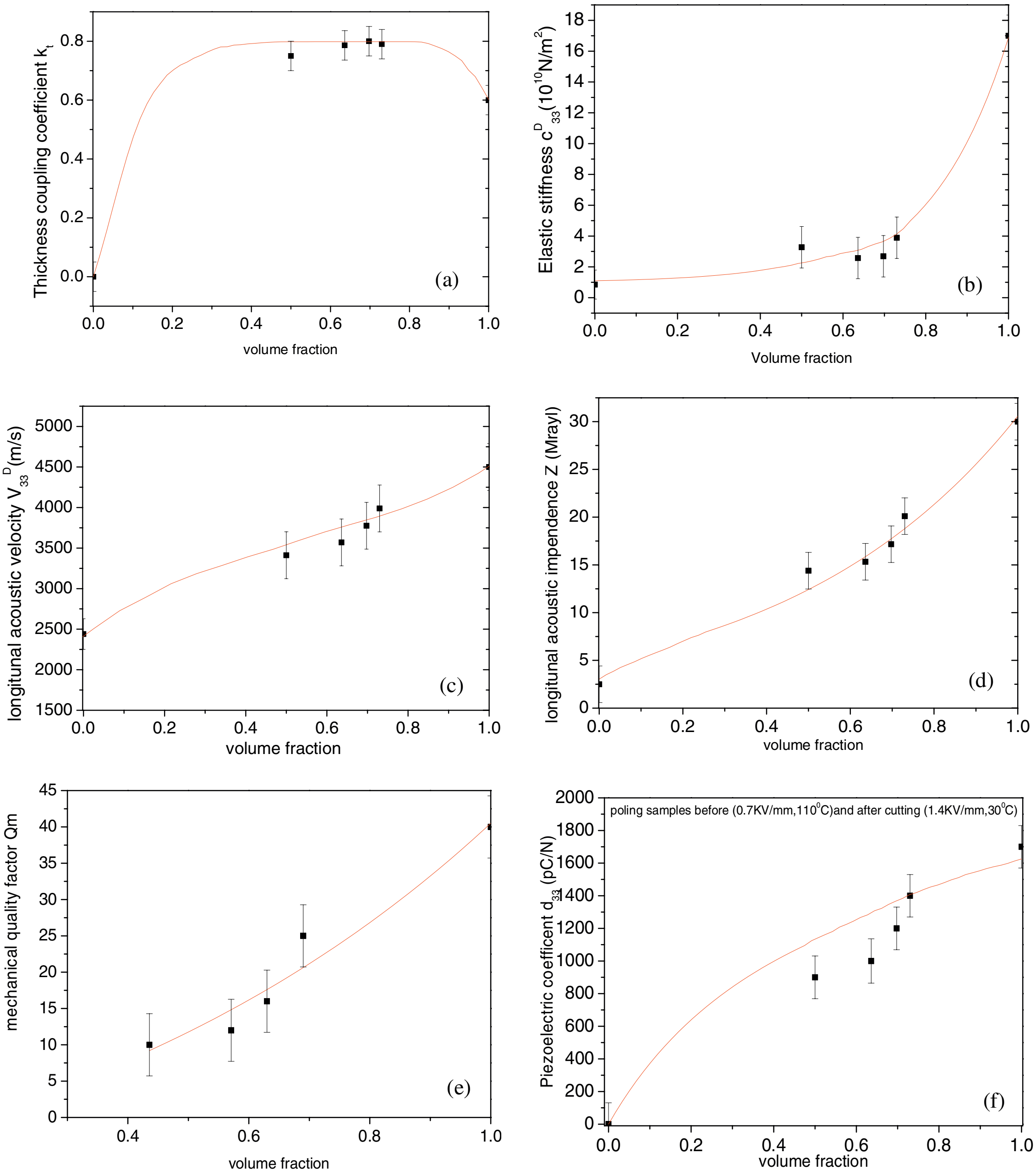

Fig. 2 (online colour at: www.pss-a.com) Comparison between model predictions (solid lines) and measured values (points) of the ⟨001⟩ PMN-31% PT/epoxy 1–3 piezocomposite properties as a function of PMN-31% PT crystal volume fraction: a) thickness electromechanical coupling coefficient (k_t); b) elastic stiffness (C_{33}^D); c) acoustic velocity (V_{33}^D); d) acoustic impendence (Z); e) mechanical quality factor (Q_m); f) piezoelectric coefficient (d_{33}). The error bars are guides for the eye.

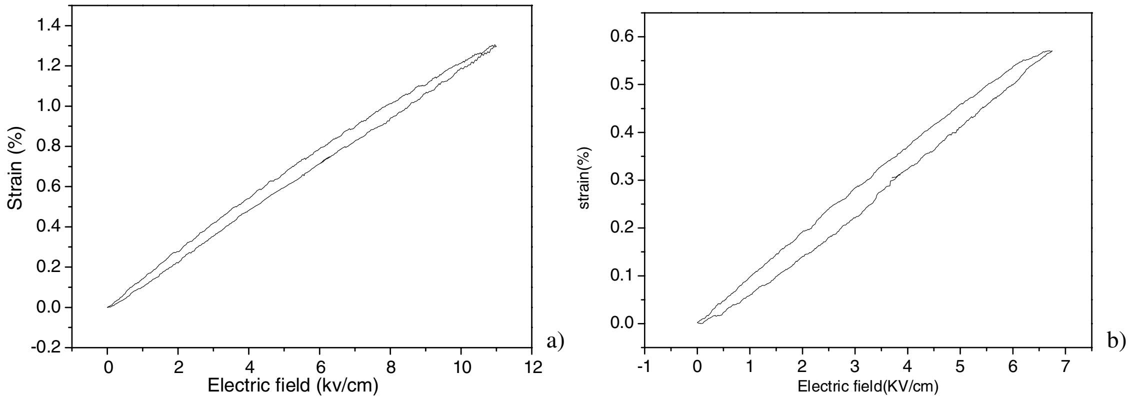

Fig. 3 Electric field dependence of the strain in the PMN-31% PT/epoxy 1–3 piezocomposites: a) ⟨001⟩ oriented; b) ⟨110⟩ oriented.

for PMN-PT/epoxy 1–3 piezocomposites made up of ⟨001⟩ oriented PMN-PT and ⟨110⟩ oriented PMN-PT single crystals. The piezoelectric coefficient d_{33} under constant stress is defined by formula

$$d_{33} = \left(\frac{\partial S}{\partial E}\right)_T ,$$

where S, E, and T are the strain, electric field, and stress, respectively, so its value can be derived from the strain vs. electric field curves. From Fig. 3 the d_{33} value obtained is about 2400 pC/N at 7 kV/cm which is much higher than the measured d_{33} value. Because these dice-and-fill samples proved difficult to pole due to breakdown at the polymer/PMN-PT interface and PMN-PT rods, this is probably the major problem to be overcome if this type of composite is to achieve its potential. If the low d_{33} was due to inadequate poling, it would be expected that both d_{33} and k_t would be low. The k_t value of PMN-PT/epoxy composites appears higher than that of PMN-31% PT crystal but the d_{33} value is lower than that of PMN-31% PT crystal. The reason may also relate to the different measurement frequency [13].

The modified series and parallel model [7, 14] could be applied to describe the properties of PMN-PT/epoxy piezoelectric composites. The composites can be considered as a piezoelectric rod embedded with a non-piezoelectric matrix. A comparison between the properties of ⟨001⟩ orientated and ⟨110⟩ orientated PMN-31% PT crystals and PMN-31% PT/epoxy 1–3 composites is given in Table 1. The main parameters including resonant frequency f_s and f_p, frequency constant N_t, thickness electromechanical coupling coefficient k_t, volume fraction of crystal, dielectric constant ε_r, dielectric loss tan δ, and measured d_{33} value are presented in Table 1 for selected crystals and composites. From Fig. 2 and Table 1 the ⟨001⟩ oriented single-crystal PMN-PT/epoxy composites have functional advantages with moderate

Table 1 Comparison between the properties of ⟨001⟩ orientated and ⟨110⟩ orientated PMN-31% PT crystals and PMN-31% PT/epoxy 1–3 composites.

sample	f_s (kHz)	f_p (kHz)	N_t (kHz mm)	k_t (%)	volume fraction	ε_r (kHz)	tan δ (kHz)	d_{33}
⟨001⟩ PMN-PT/epoxy piezocomposite	634.5	960	1142.1	78.2	0.45	1390.2	0.0175	1600
⟨110⟩ PMN-PT/epoxy piezocomposite	355	625	1057.9	84.8	0.58	1580.9	0.0173	1500
⟨001⟩ PMN-PT crystal	846.3	972	1773.23	53	1	6074.9	0.0251	1800
⟨110⟩ PMN-PT crystal	584	663	1822.08	51	1	5838.6	0.0389	2000

acoustic impedance, low mechanical quality, and low dielectric constant. Composites made up of the ⟨110⟩ oriented PMN-PT single crystals, if properly designed, would also provide excellent electric properties. Composites with 0.58 volume fraction and 2.98 mm thickness consisted of the ⟨110⟩ oriented PMN-PT single crystals which had an electromechanical coupling factor as high as 0.84 (shown in Fig. 1(a)). Therefore, the vibrational characteristics of the composites were strongly influenced by the rod geometry and the rod arrangement, i.e. volume fraction. According to the modeling approach of Smith [7], the predicted parameters of thickness electromechanical coupling coefficient, elastic stiffness, acoustic impedance, acoustic velocity, mechanical quality factor, and piezoelectric coefficient of piezocomposites varying with the volume fraction of piezoelectric crystals are presented as solid lines in Fig. 2. The modeling results were compared with experimental data and the error bars between them are guides to the eyes. Plot of the elastic stiffness C_{33}^{D} in Fig. 2(b) shows it increases slowly with volume fraction. The acoustic velocity V_{33}^{D} was measured by an ultrasonic method and also increased with volume fraction as shown in Fig. 2(c). The acoustic impedance Z is given by $Z = \rho V_{33}^{D}$, where ρ is the density of the piezocomposite. The acoustic impedance (as shown in Fig. 2(d)) varies within the range 10–20 Mrayls and appears lower than that of PMN-PT crystal. For our 1–3 composites, other parasitic resonances were well separated from thickness mode resonance, so the mechanical quality factor Q_{m} was approximately measured by the conductance vs. susceptance circle method. We can measure the conductance and susceptance at many frequencies near the resonance frequency, thus Q_{m} is calculated by

$$Q_{\mathrm{m}} = \frac{f_{\mathrm{s}}}{f_{+1/2} - f_{-1/2}}\,, \tag{2}$$

where the series resonance frequency f_{s} is equal to the frequency at maximum of conductance, and $f_{+1/2}$ and $f_{-1/2}$ are frequencies at half of conductance. It is seen that Q_{m} (shown in Fig. 2(e)) of the composites of all the volume fractions was about 10–20, which is close to that of the polymer. From the results obtained, the properties of single-crystal PMN-31% PT/epoxy 1–3 composites are basically coincident with the prediction tendency of modeling theory and obviously prior to those of PMN-31% PT single crystals and PZT ceramic/polymer 1–3 composites. These results are necessarily optimized, that is, further changes could be made in each of these designs that may improve performance for particular applications. This indicates that PMN-PT/epoxy 1–3 composites would help transducers of similar structure to obtain broader bandwidth and high sensitivity compared to PMN-PT single crystals.

4 Conclusions

The single-crystal PMN-31% PT/epoxy 1–3 composites with various volume fractions of PMN-PT were produced using the dice-and-fill method, and their electromechanical properties were measured using the resonance method. The tendency of the properties of the piezoelectric composites agreed well with the modeled performance of the composites. The ⟨001⟩ oriented single-crystal PMN-31% PT/epoxy 1–3 composites have excellent properties with higher thickness electromechanical coupling coefficient, lower dielectric constant, and moderate acoustic impendence compared to those of PMN-PT single crystals and conventional PZT ceramic piezocomposites. Also, ⟨110⟩ oriented single-crystal PMN-31% PT/epoxy composites can be designed appropriately in this way. This material is likely to provide better properties and also expected to make a more dramatic improvement in transducer applications. It is expected that more work will be done on the development and introduction of these single crystals into a wider variety of transducer designs.

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