Piezoelectric Properties of 1-3 Composites of PZT in P(VDF-TrFE) Copolymer

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ABSTRACT

PZT/P(VDF-TrFE) 1-3 composites were fabricated by embedding pre-sintered PZT rods in a pre-poled copolymer matrix. The rods were then poled using an electric field much lower than the coercive field of the copolymer. The electromechanical coupling factor k_t, and the resonance characteristics of the composites were measured. The resonance characteristics of the composites were found to be dominated by the individual PZT rods. Poling of the copolymer matrix results in broadening of the main resonance peak. For transducer applications, it is advisable to pole the copolymer and the PZT rods in the same direction as this gives a higher k_t value.

INTRODUCTION

1-3 composite piezoelectric materials have attracted considerable interest recently because of their relatively high electromechanical coupling factor and low impedance as compared with the constituent materials. However, most of the composites were made of piezoelectrically active ceramic and piezoelectrically passive polymer. Since piezoelectricity can be activated in bulk unstretched samples of P(VDF-TrFE), it is now feasible to prepare composites with both phases piezoelectrically active. Moreover, the piezoelectric constants of PZT and P(VDF-TrFE) have opposite sign, so it is of interest to investigate how the piezoelectricity as well as the direction of dipole alignment of each phase affect the resultant piezoelectric properties of the composites.

In this work, 1-3 composite samples were fabricated by embedding PZT ceramic rods in a pre-poled P(VDF-TrFE) copolymer matrix. Previous experimental results [1] showed that electrical breakdown occurred across the PZT phase when trying to pole the copolymer matrix insitu, thereby making it impossible to pole both phases simultaneously. The impedance characteristics of the composites were investigated by using an impedance analyzer (HP4194A), and their k_t values were calculated by the method of Sherrit et al [2]. Stopband structures of these composites were found and also discussed.

SAMPLE PREPARATION

PZT powder of grain size between 1 and 3 μm was used in this work to make rods of 1 mm diameter. The powder was supplied by the Shanghai Institute of Ceramics, and has properties similar to the Vernitron (Morgan Matroc Ltd) PZT-4 composition. The rods were extruded through a home-made die and sintered at 1300°C for about 6 hours. To measure the piezoelectric properties of the ceramic component, a rod sample of length 0.78 mm was cut from a long fired rod (sample A).

An extruded unpoled vinylidene fluoride-trifluoroethylene (80/20) copolymer sheet supplied by Atochem North America Inc. was used as the composite matrix. The sheet was 0.8 mm thick, and its Curie transition temperature for the first heating ($Tc\uparrow$) and melting temperature were 124.4°C and 149.0°C respectively, indicating a TrFE content of slightly higher than 20% [3]. In order to optimize the piezoelectric properties of the thick sheet samples, they were poled by using a two-step poling process at 115°C under an electric field of 30 MV/m [4]. A disked-shaped sample (Sample B) was then made from the poled copolymer.

A series of holes of 1 mm diameter were drilled in the pre-poled copolymer sheets, in a square pattern with 3 mm center-to-center periodicity, and the fired PZT rods were inserted into these holes. To glue the PZT rods to the copolymer, the composites were immersed into epoxy (Shell 815 + hardener C), and then degassed for 15 minutes. After curing of the epoxy, the composites were cut into disks about 0.7 mm thick and 12 mm in diameter. The ceramic volume percentage was about 8%. The composite was re-poled again at 85°C under an electric field of 3 MV/m for half an hour in order to align the PZT dipoles. Sample E was re-poled in a direction parallel

CH3416-5 0-7803-1847-1/95/$4.00©1995IEEE

to the poling direction of the matrix, while sample F was re-poled in an anti-parallel direction. As the poling temperature was well below the matrix Curie temperature, and 3 MV/m was too low to disrupt the polarization in the copolymer, the pre-existed piezoelectric properties of the matrix was retained. Sample C was a composite sample without re-poling. Sample D was prepared by using a similar method, but the copolymer matrix was not pre-poled. All the samples used in this work are summarized in Table 1.

To confirm the assumption that repoling the composite at 85°C under an electric field of 3 MV/m for half an hour will not lead to any piezoelectric activity in the copolymer, a copolymer sample was poled using the above conditions and no resonance was observed.

TABLE 1
Description of the samples.

Sample	Constitutes
A	poled PZT rod
B	poled copolymer
C	pre-poled copolymer, unpoled PZT
D	unpoled copolymer, poled PZT
E	copolymer and PZT poled in the same direction
F	copolymer and PZT poled in the opposite direction

EXPERIMENTAL RESULTS

An impedance analyzer (HP4194A) was used to measure the impedance characteristics of the samples. The electromechanical coupling factor k_t was determined by the method of Sherrit et al [2] which took into account the mechanical and dielectric loss in the copolymer matrix. The k_t value was evaluated from the strongest resonance of each sample. Since the second harmonic for the radial mode resonance was very weak for most of the samples, the electromagnetic coupling factor k_p were not determined.

1. Thickness mode resonance

The impedance vs frequency plots of the samples are shown in Figs. 1 to 6, and the values of k_t are given in Table 2. The poled PZT rod (sample A, Fig.1) has a strong resonance at 2 MHz and two weak resonances at 2.7 MHz and 3.9 MHz. These three resonances, although weaker, can still be found in sample D (Fig.2), i.e. after the ceramic rods have been inserted into the unpoled copolymer matrix, showing that the soft copolymer matrix does not greatly modify the resonances of the individual rods.

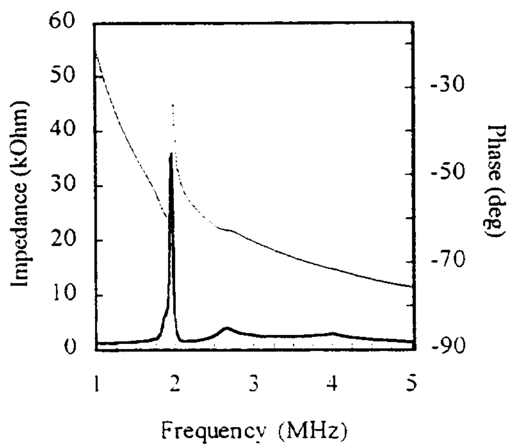

Fig.1 Impedance (--) and phase (—) plot for sample A.

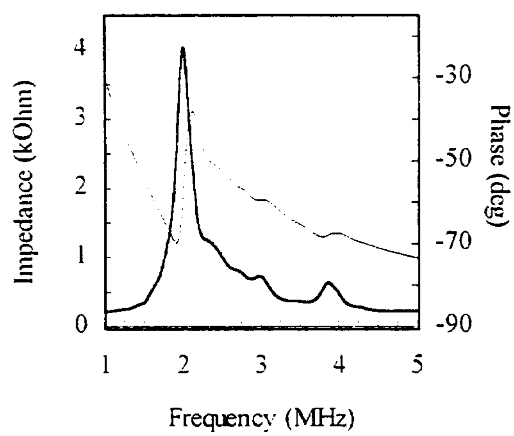

Fig.2 Impedance (--) and phase (—) plot for sample D.

The thickness resonance of the poled copolymer sample B (Fig.3) is observed at 1.4 MHz. After inserting the unpoled PZT rods (sample C), the thickness resonance of the matrix becomes weaker and occurs at a slightly higher frequency of 1.5 MHz (Fig.4). This is because sample C is thinner. The k_t value of sample C is lower than that of sample B (Table 2).

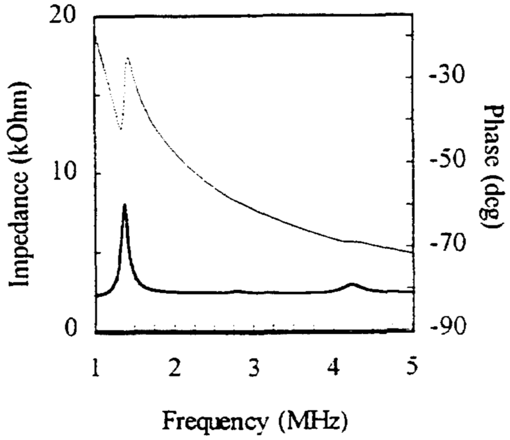

Fig.3 Impedance (--) and phase (—) plot for sample B.

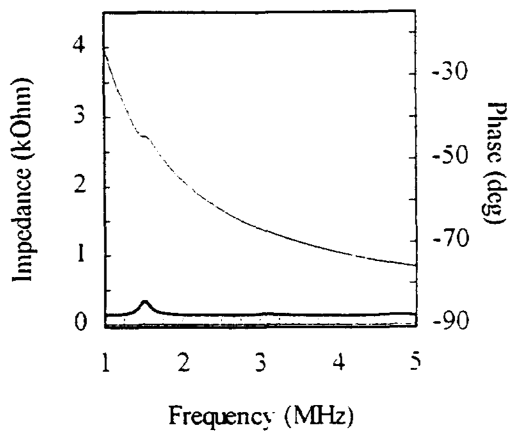

Fig.4 Impedance (--) and phase (—) plot for sample C.

Comparing samples E and F (Figs 5 & 6), the weak copolymer resonance is still observable in both samples. The PZT rod resonances can also be seen. Due to the fact that the diameter of the rod is very close to its thickness, the different resonance modes of the rods and the copolymer merge together to form a resonance with a broad shoulder. Whether this material is suitable for fabricating wide band transducer is worth pursuing and will be left for future study. It is important to note that poling of the matrix in a direction parallel or anti-parallel to the PZT rods does not give rise to distinct difference in the thickness resonance characteristics. This is because the PZT rod is much stiffer than the copolymer and thus dominates the composites resonances. However, k_t of sample E (PZT and copolymer poled in the same direction) is higher than that of sample F (with the two phases poled oppositely). Hence, in transducer applications, it is advisable to pole the copolymer and PZT in the same direction to give a high k_t.

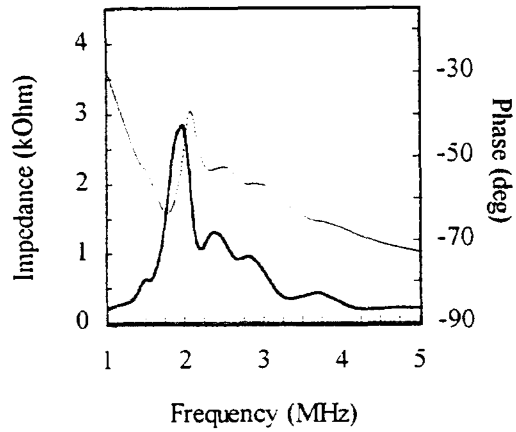

Fig.5 Impedance (--) and phase (—) plot for sample E.

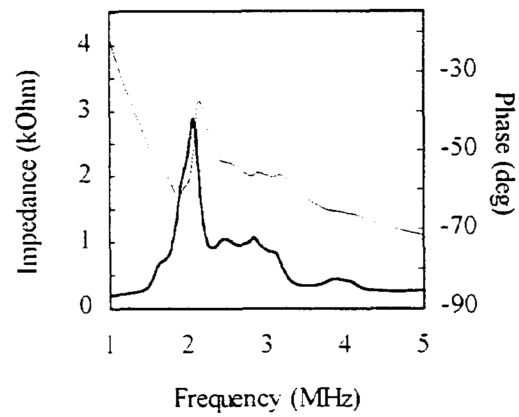

Fig.6 Impedance (--) and phase (—) plot for sample F.

TABLE 2
The thickness and electromechanical coupling factor for the samples.

Samples	Thickness (mm)	k_t
B	0.78	0.22
C	0.71	0.13
D	0.70	0.36
E	0.71	0.45
F	0.68	0.30

2. Planar mode resonance

The fundamental planar mode resonance was found at 85 kHz. The resonance frequency depends only on the diameter of the sample and is the same for samples B to F. The second harmonic of the radial mode is very weak and can hardly be observed.

3. Stopband resonance

In addition to the characteristic resonances of the PZT rods and the copolymer matrix, 1-3 composites also have stopband resonances due to Bragg reflection in the periodic array of PZT rods [5]. Two weak stopband resonances at frequencies about 490 kHz and 730 kHz were found in sample D (with unpoled copolymer matrix). When the rods and the copolymer were poled in the same direction (sample E), the stopband resonances were slightly enhanced and were found at 500 kHz and 780 kHz. However, in sample F where the rods and the copolymer were poled oppositely, the stopband resonances shifted to higher frequencies (660 kHz and 810 kHz).

CONCLUSION AND DISCUSSION

The resonance characteristics of PZT/P(VDF-TrFE) 1-3 composites with two piezoelectric phases were studied. The followings were observed :

1. In all of the 1-3 composites studied, the characteristic resonances of the individual PZT rods are clearly observable. The copolymer matrix does not significantly modify the characteristic resonances of the individual PZT rods, because the soft copolymer matrix does not impose an appreciable clamping on the rods. Detailed calculations of the resonance frequencies of the individual rods will be reported later.

2. The thickness resonance of the poled copolymer matrix is very weak and, in the present sample geometry, merges with the PZT resonances to form a broad resonance peak. Whether this material can be used to make broadband transducer will need further investigation.

3. The resonance characteristics of the samples with PZT and copolymer poled in the same direction and poled oppositely are quite similar. The electromechanical coupling constant k_t is higher if the two phases are poled in the same direction.

4. The radial mode resonance of the 1-3 composites depends only on the diameter of the sample and is independent of sample poling history.

5. Stopband resonances are observed; and when the two piezoelectric phases are poled oppositely, they shifted to higher frequencies.

ACKNOWLEDGMENTS

The authors would like to thank Prof. Q. Yin of the Shanghai Instate of Ceramics for supplying the ceramic powder. Financial support from the Hong Kong Research Grants Council (RGC) is also acknowledged.

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