PZT/P(VDF-TrFE) Nanocomposites for Ultrasonic Hydrophone Application

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Abstract

0-3 composites with nanosized lead zirconate titanate (PZT) powder imbedded in a vinylidene fluoride-trifluoroethylene copolymer (P(VDF-TrFE)) matrix have been fabricated. Since the piezoelectric coefficients of PZT and P(VDF-TrFE) have opposite signs, the PZT and P(VDF-TrFE) phases in the nanocomposites were poled in opposite directions in order to enhance the piezoelectric activity. The PZT powder, prepared by a sol-gel process, has a tetragonal structure. The ratio of the (002) and (200) X-ray diffraction peaks was used as a measure of the degree of poling in the ceramic phase. The piezoelectric coefficient of the nanocomposite film was measured by a laser interferometry technique. A needle type hydrophone for the calibration of medical ultrasonic transducers was fabricated using the nanocomposite as the sensing element and its performance was evaluated.

1. Introduction

Piezoelectric ceramic/polymer 0-3 composites consisting of piezoelectric ceramic particles imbedded in a polymer matrix have been extensively studied over the past decade for the use as piezoelectric sensors and actuators [1,2]. They have relatively high hydrostatic coefficient (d_h) and low acoustic impedance as compared with the constituent ceramic. Recently, 0-3 composites with both phases piezoelectrically active have also attracted some interest [3-5]. Previous works [6,7] show that the two phases of a piezoelectric ceramic/piezoelectric polymer 0-3 composite can be poled either in the same or opposite directions. As the piezoelectric coefficients of the ceramic and the copolymer are opposite in sign, the composite with both phases poled in opposite directions will have piezoelectric activities of the two phases reinforced and pyroelectric activities partially canceled each other. As a result, the composite will have high piezoelectric but low pyroelectric activities, thereby reducing the electric noise due to temperature fluctuation. In the present work, we aim at fabricating PZT/P(VDF-TrFE) 0-3 nanocomposite thin films with both phases poled in opposite directions, and studying their piezoelectric properties and hydrophone performances.

2. Sample Preparation

The procedure for preparing nanosized lead zirconate titanate (PZT) ceramic powder by the sol-gel method has been described in our previous report [8]. The powder used in this study has a Zr/Ti ratio of 48/52 and has a tetragonal structure. It has been annealed at 900°C for 1 h, and has an average crystallite diameter of about 80 nm. The vinylidene fluroide-trifluoroethylene copolymer (P(VDF-TrFE)) was obtained in pellet form from Piezotech in France. It contains ~30 mol% of TrFE as confirmed by differential scanning calorimeter (DSC) measurements. The Curie temperature of the copolymer upon heating was 102°C and the melting temperature was 150°C. In the preparation of PZT/P(VDF-TrFE) 0-3 composite films, the copolymer was first dissolved in methyl-ethyl-ketone (MEK) at room temperature and an appropriate amount of PZT powder was gradually introduced into the solution with constant stirring. The composite solution was then spin-coated on an Al/glass substrate of which the aluminum layer serving as bottom electrode was thermally evaporated. The film was kept overnight at 40°C and then annealed at 120°C for 2 h to remove the solvent and to increase the crystallinity of the copolymer phase. Another thin layer of aluminum was thermally

evaporated on the film to serve as a top electrode. The ceramic volume fraction of the composite film is about 0.2, and the thickness is about 6 μm.

3. Sample Poling

In the present study, three types of sample were prepared: sample A (only the PZT phase poled), sample B (both phases poled in the same direction), and sample C (both phases poled in opposite directions). To prepare sample A, the composite film was heated to 120°C and a DC electric field of 35 MV/m was applied across the electrodes for 3 h. Then the electric field was switched off and the sample was cooled slowly to room temperature. As the electric field is applied only at temperature higher than the Curie temperature of the copolymer, only the dipoles in PZT were aligned. To prepare samples B and C, the poled composite film (sample A) was re-poled at room temperature under an AC electric field of 50 MV/m in order to align the dipoles in the copolymer. Sample B was re-poled such that the copolymer phase was polarized in a direction parallel to the polarization of the PZT phase, while the copolymer phase in sample C was polarized in a direction opposite to that of the PZT phase.

The intensities $I_{(002)}$ and $I_{(200)}$ of the (002) and (200) peaks in the X-ray diffraction pattern were used to evaluate the degree of poling of the PZT in the composites. The polarization ratio α is defined as [9]

$$\alpha = 1 - \frac{I_{(002)}}{I_{(200)}} \frac{I'_{(200)}}{I'_{(002)}} \tag{1}$$

where $I'_{(002)}$ and $I'_{(200)}$ are the intensities after poling, and $I_{(002)}$ and $I_{(200)}$ are the intensities before poling. The α values of all samples are very close, about 0.26, indicating that the pre-existed polarization in the PZT phase has not been disrupted by the AC electric field in polarizing the copolymer phase. As compared with the α value of a fully poled PZT sample (0.55), the smaller α values of the composites indicate that the PZT particles inside the composites are not fully polarized. Attempts have been made, but α cannot be improved significantly.

4. Piezoelectric Coefficient d_{33}

A Mach-Zehnder type heterodyne interferometer (SH-120 from B.M. Industries, France) was used to measure the surface displacement of the composite film (Fig.1). A linearly polarized laser beam, L (frequency f_L, λ = 632.8 nm for a He-Ne Laser) is split into a reference beam, R, and a probe beam, P. R is directed through a Dove prism and a polarizing beam splitter into a photodetector. The frequency of P is shifted by a frequency f_B (70 MHz) in a Bragg cell, and then this beam (now labeled S) is phase modulated by the surface displacement of the film sample, $x = u \cos(2\pi f_u t)$ (vibration frequency f_u, displacement amplitude u). For small vibration displacement, only the components of the detected signal at f_B and f_B+f_u are significant, and the ratio of their amplitudes R gives the displacement amplitude u [10]:

$$R = J_1(4\pi u/\lambda)/J_0(4\pi u/\lambda) \sim 2\pi u/\lambda = u/1007 \tag{2}$$

where J_0 and J_1 are the Bessel function of the zeroth and the first order, respectively. The ratio R is measured using a spectrum analyzer (HP 3589A). The piezoelectric coefficient d_{33} (strain/applied field) of the film can then be calculated as

$$d_{33} = (u/t)/(V/t) = u/V \tag{3}$$

where V is the voltage applied across the film.

The measured d_{33} values for the composite samples are given in Table 1. As mentioned in section 3, the PZT particles inside the composites are not fully polarized, so the d_{33} value of sample A is small, about 1.82 pm/V. The d_{33} value of sample C is about 40 % larger than that of sample B, indicating that the piezoelectric activity of the composite is enhanced by the oppositely oriented dipoles in the two phases. It should be noted that as

the film is laterally clamped on the glass substrate, the measured d_{33} value is smaller than the value of the bulk sample [11].
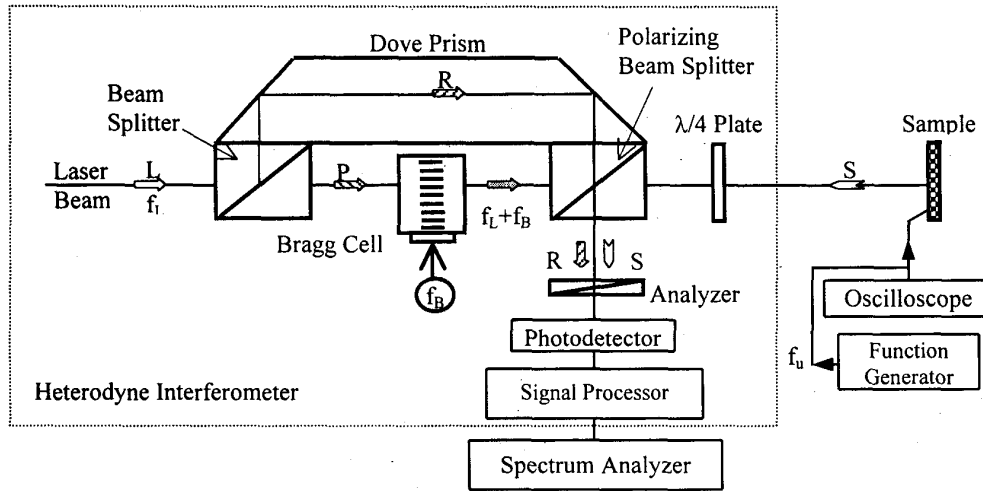

Figure 1. A Mach-Zehnder type heterodyne interferometer.

Table 1: Piezoelectric coefficients of the samples

Sample	d_{33} (pm/V)
A (only the PZT ceramic phase poled)	1.82
B (both phases poled in the same direction)	5.2
C (both phases poled in opposite directions)	8.0

5. Hydrophone Performance Evaluation

Sample C, in the form of circular disk of diameter 1mm, was fabricated into a needle type hydrophone (Fig. 2). To evaluate the performance of the hydrophone, its receiving sensitivity was measured as a function of frequency. A commercial transducer (10 MHz, 0.25 inch diameter, Panametrics V312) is used to generate acoustic waves in water. The acoustic waves are received by the needle type hydrophone placed at the far-field near-field transition point T ($T = a^2/4\lambda$ where a is the radius of the transducer and λ is the acoustic wavelength in water) for the transducer, and the signal from the hydrophone is measured by a digitizing oscilloscope (HP 54504A). For comparison, a standard PVDF bilaminar shielded membrane hydrophone with an active element of diameter 0.5 mm (GEC-Marconi, Type Y-34-3598) is also used to measure the acoustic waves at the same field point T. The end-of-cable loaded receiving sensitivity (M_L) of the needle type hydrophone is then calculated from:

$$M_L = \frac{V_L}{Vs} Ms \qquad (4)$$

where V_L and V_S are the measured voltage output using the needle-type and membrane hydrophones, respectively, and M_S is the end-of-cable loaded receiving sensitivity of the membrane hydrophone.

Fig. 3 shows the variation of the receiving sensitivity of the hydrophones with frequency. It can be seen that the composite hydrophone has better sensitivity than the standard PVDF bilaminar shielded membrane hydrophone.
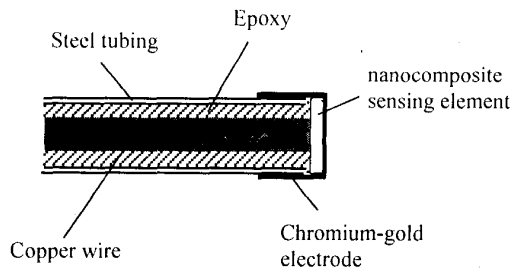
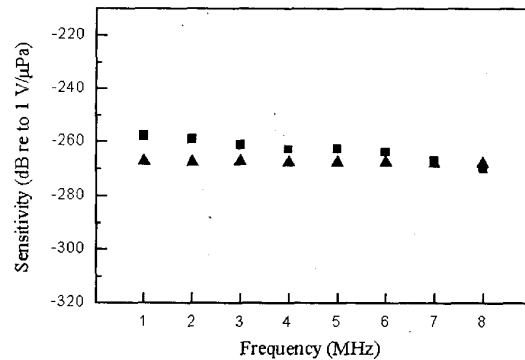Figure 2. Schematic diagram of the nanocomposite needle.

Figure 3. End-of–cable loaded sensitivity of the hydrophones: 0-3 composite with both phases poled in opposite directions, ■; standard PVDF membrane ▲.

6. Conclusion

PZT/P(VDF-TrFE) 0-3 nanocomposite thin films with 0.2 ceramic volume fraction have been prepared and characterized. The piezoelectric coefficient of the composite with both phases poled in opposite directions is enhanced. Needle-type hydrophone with the composite as the sensing element has been fabricated and shown to have good receiving sensitivity.

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8. References

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