PZT/P(VDF/TrFE) Nanocomposite Hydrophones for Ultrasonic Measurements

H.L.W. Chan, S.T. Lau , K.W. Kwok, and C.L. Choy

Department of Applied Physics and Materials Research Centre,
The Hong Kong Polytechnic University,
Hunghom, Kowloon, Hong Kong.

Abstract – Needle-type hydrophones for the calibration of medical ultrasonic transducers have been fabricated using lead zirconate titanate/vinylidene fluoride-trifluoroethylene [PZT/P(VDF-TrFE)] 0-3 nanocom-posite films. The 0-3 nanocomposite film has been prepared by incorporating nanosized PZT powder (derived from a sol-gel process) in a P(VDF-TrFE) matrix. Since the piezoelectric coefficients of PZT and P(VDF-TrFE) have opposite signs, the PZT and P(VDF-TrFE) phases in the nanocomposites have been poled in opposite directions in order to give enhanced piezoelectric activity. A nanocomposite hydrophone with 0.2 volume fraction of PZT has been characterized and found to be more sensitive than a P(VDF-TrFE) hydrophone of similar structure.

INTRODUCTION

Piezoelectric hydrophones are widely used for measuring the acoustic outputs from medical imaging/therapeutic ultrasonic equipment. Knowledge of the acoustic output from medical ultrasonic equipment is important in the optimization of treatment and the improvement of imaging effectiveness, as well as for ensuring safety. Polyvinylidene fluoride (PVDF) and vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) copolymers have good mechanical flexibility and acoustic impedances close to those of water and human tissues and give a uniform response over a wide frequency range when used as sensing element in hydrophones. [1-3] Single element PVDF hydrophones with element sizes in the range of 0.2 – 0.5 mm are available commercially but as the PVDF element of this size has small capacitance, their sensitivities are greatly affected by cable shunting.

Piezoelectric 0-3 composites consist of piezoelectrically active ceramic particles dispersed in a 3-dimensionally connected polymer matrix. Although non-piezoelectric polymer matrices have mostly been used in previous works, 0-3 composites in which both the ceramic and polymer phases are piezoelectric have also attracted some interest. [4-6] When a P(VDF-TrFE) copolymer is used as the matrix, as the piezoelectric coefficients of the ceramic and copolymer have opposite signs, it is necessary to pole the two phases in opposite directions in order to obtain reinforced piezoelectric responses. To produce a homogeneous hydrophone element with a small thickness, it is imperative to use ceramic powder with size in the nanometer range. The nanocomposite has an advantage over the copolymer P(VDF-TrFE) in that it has higher permittivity, hence circumventing the cable shunting problem encountered in copolymer hydrophone.

FABRICATION OF PZT/P(VDF-TrFE) 0-3 NANOCOMPOSITES

The procedure for preparing PZT powder by the sol-gel method has been described in our previous report. [7] The powder used in this study has been annealed at 800°C and has an average crystallite diameter of about 80 nm. The P(VDF-TrFE) 70/30 mol% copolymer supplied by Piezotech has a Curie temperature of 102°C upon heating and a melting temperature of 150°C as determined by differential scanning calorimetry (DSC). To prepare 0-3 nanocomposite thin films, 2 g of the copolymer was dissolved in 10 ml of methyl-ethyl-ketone (MEK) and PZT nanocrystalline powder was then blended into the solution to form a mixture. The ceramic volume fraction of the composite is 0.2. To fabricate a capacitor structure for poling, an aluminum lower electrode was thermally evaporated on a glass slide. Then the composite was spin-coated onto the Al/glass substrate using a photoresist spinner. To produce a film of thickness about 6 μm, a rotation speed of 1600 RPM and duration of 1 min were used. After the spin-coating procedure, the film was kept overnight at room temperature and then annealed at 120°C for

0-7803-4095-7/98/$10.00

2 h to remove the solvent. An Al top electrode was then thermally evaporated on the surface of the composite film to produce the desired capacitor structure. A P(VDF-TrFE) film of similar thickness and structure was also prepared.

To pole the ceramic inside the composite, the sample was heated in an oven to a temperature of 115°C, which was above the Curie temperature (T_c) of the copolymer. A DC voltage of 30 kV/mm was applied across the electrodes for 60 min., then the electric field was switched off and the sample was cooled slowly to room temperature. As the electric field was switched off when the copolymer was in a paraelectric phase, only the ceramic inside the composite was poled. The copolymer phase was then poled in a direction opposite to that of the ceramic at room temperature by applying an electric field of ~ 60 kV/mm at room temperature. For comparison, another P(VDF-TrFE) film was prepared and was also poled at room temperature by applying an electric field of ~ 60 kV/mm. After poling, both the nanocomposite and copolymer films were peeled off from the glass slides and the Al electrodes were etched away in KOH. Circular elements of diameter ~ 0.7mm were cut out from these films for subsequent hydrophone fabrication.

CONSTRUCTION OF HYDROPHONES

The construction of a needle-type hydrophone is shown schematically in Fig. 1. The center wire in the stainless-steel tubing was held in position by epoxy. After the epoxy had set, the tip of the needle was polished to expose the tip of the wire. A circular element prepared as described in the last section was glued to the tip of the exposed wire by silver-filled conductive epoxy (Ablestik). Three types of hydrophone elements were used: (a) P(VDF-TrFE), (b) PZT/P(VDF-TrFE) nanocomposite with only the ceramic phase poled, (c) P(VDF-TrFE) with the ceramic and copolymer poled in opposite directions. A chromium-gold electrode was evaporated onto the needle tip which connects the top surface of the film to the steel tubing, served as the ground electrode. The cable length of the hydrophone was about 0.3 m, which was the shortest practical length required to connect the hydrophone output signal into an amplifier.

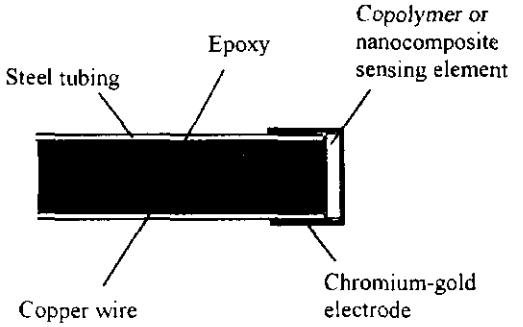

Figure 1 (a) Schematic diagram of the nanocomposite needle-type hydrophone.

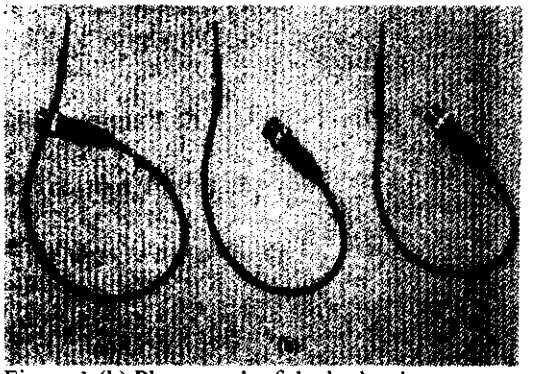

Figure 1 (b) Photograph of the hydrophones.

PERFORMANCE OF THE HYDROPHONES

Testing of the hydrophones was carried out in a water tank. Two plane transducers, with centre frequency of 5 MHz and 7.5 MHz and of diameter d = 12.4 mm were used to generate acoustic waves in water. The hydrophone was positioned at the near field –far field transition point T ($T = d^2/4\lambda$ where λ is the acoustic wavelength in water) of the transducers. A bilaminar membrane hydrophone with element size 0.5 mm (manufactured by GEC-Marconi and calibrated at National Physical Laboratory, United Kingdom) together with an amplifier was used to measured the acoustic pressure P at position T from 1 to 10 MHz. Then the needle hydrophone to be characterized was placed at the same field point. The end-of-cable loaded sensitivity of the hydrophone M_L can be calculated from:

$$M_L=(V_L/V_s)M_s \qquad (1)$$

where V_L and V_s are the measured voltage output from the needle and membrane hydrophone, respectively, and M_s is the end-of-cable loaded sensitivity of the standard membrane hydrophone. If an amplifier is used, the sensitivity (M_a) at the output of an amplifier which is connected to the hydrophone can be related to the end-of –cable loaded sensitivity of the hydrophone (M_L) as follows:

$$M_a = GM_L \quad (2)$$

where G is the gain of the amplifier. The input impedance of the HP54504A digitizing oscilloscope is 7 pF// 1MΩ. As the impedance of both the hydrophone and the load can be assumed to be capacitive, hence, using the end-of-cable capacitance C of the hydrophone measured at different frequencies (Fig. 2), and the load capacitance C_{el} = 7 pF, the end-of-cable open-circuit sensitivity M_o can be calculated from:

$$M_L = M_o [C/(C + C_{el})] \quad (3)$$

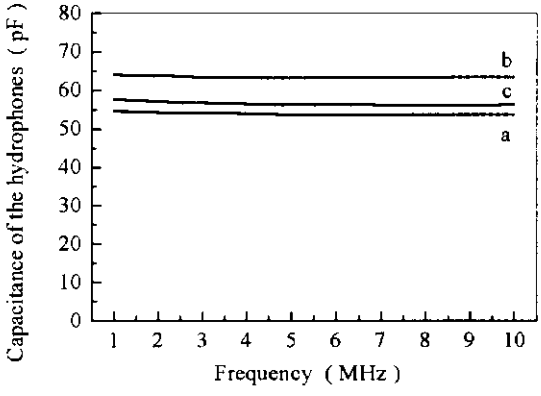

Figure 2 End-of-cable capacitance C of the hydrophones with different sensing elements as a function of frequency.

- a P(VDF-TrFE),
- b PZT/P(VDF-TrFE) with only the ceramic phase poled, and
- c PZT/P(VDF-TrFE) with the ceramic and the copolymer phase poled in opposite directions.

EXPERIMENTAL RESULTS

Fig. 2 shows the end-of-cable capacitance C of the three different types of hydrophones as a function of frequency and it can be seen that the nanocomposite hydrophone with only the ceramic phase poled has the highest capacitance. After both phases were poled in opposite directions, the capacitance of the hydrophone decreases. This is mainly due to the decrease in relative permittivity in the copolymer phase caused by better dipole alignment. The end-of-cable loaded sensitivity (with the amplifier) M_a of the hydrophones as a function of frequency is shown in Fig. 3. After correcting for amplifier gain using eq. (2), the end-of-cable open-circuit sensitivities M_o of the three hydrophones are shown in Fig. 4. Both Figs. 3 & 4 show that the hydrophone with the nanocomposite element containing ceramic and copolymer phases poled in opposite directions has the highest sensitivity.

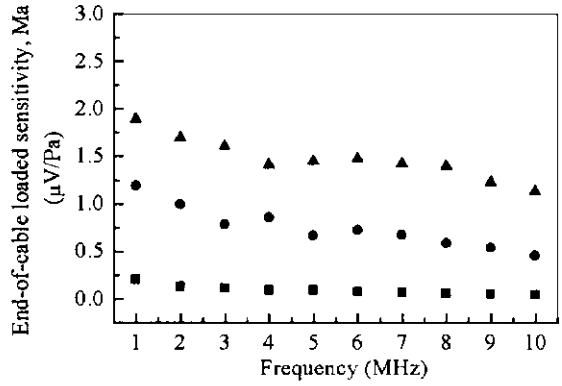

Figure 3 End-of-cable loaded sensitivity (with the amplifier) M_a of the hydrophones with different sensing elements.

- ● P(VDF-TrFE),
- ■ PZT/P(VDF-TrFE) with only the ceramic phase poled, and
- ▲ PZT/P(VDF-TrFE) with the ceramic and the copolymer phases poled in opposite directions.

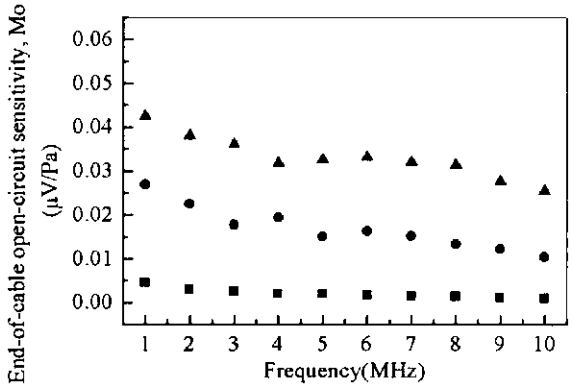

Figure 4 End-of-cable open-circuit sensitivity M_o of the hydrophones with different sensing elements.

- ● P(VDF-TrFE),
- ■ PZT/P(VDF-TrFE) with only the ceramic phase poled, and
- ▲ PZT/P(VDF-TrFE) with the ceramic and the copolymer phases poled in opposite directions

CONCLUSION AND DISCUSSION

Needle-type hydrophones with P(VDF-TrFE) copolymer and PZT/P(VDF-TrFE) 0-3 nanocomposites as sensing elements have been fabricated and characterized. The hydrophone with the ceramic and the copolymer phases poled in opposite directions is found to have the highest

sensitivity. Work is in progress to fabricate hydrophones by dip-coating a nanocomposite on a fine pin tip and then poling the sensing element by corona discharge. The results will be reported in due course.

ACKNOWLEDGEMENTS

The work described in this paper was substantially supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region (Project No. PolyU5159/98P) and also supported by the PolyU Centre for Smart Materials.

REFERENCES

[1] M.C. Ziskin and P.A. Lewin ed., *Ultrasonic Exposimetry*, Ann Arbor, CRC Press, 1993.

[2] P.A. Lewin, "Miniature Piezoelectric Polymer Hydrophones in Biomedical Ultrasonics", *Ferroelectrics*, vol. 60, pp.127-139, (1984).

[3] G.R. Harris, "Hydrophone Measurements in Diagnostic Ultrasound Fields", IEEE *Trans. Ultrasonics, Ferroelectrics and Frequency Control, UFFC* vol. 35, pp. 87-101, 1988.

[4] D.P. Skinner, R.E. Newnham and L.E. Cross, "Flexible Composite Transducers", *Mater. Res. Bull.*, vol. 13, pp.599-607, 1978.

[5] T. Furukawa, K. Ishida and E. Fukada, "Piezoelectric properties in the composite systems of polymers and PZT ceramics", *J. Appl. Phys.*, vol. 50, pp 4904-4912, 1979.

[6] D.K. Das-Gupta ed., *Ferroelectric Polymers and Ceramic Polymer Composites*, Aedermannsdorf, Trans Tech. Pub., 1994.

[7] Q.F. Zhou, H.L.W. Chan and C.L. Choy, "Nanocrystalline Powder and Fibres of Lead Zirconate Titanate Prepared by the Sol-Gel Process", *J. Materials Processing Technology*, vol. 63(1-3), pp. 281-285, 1997.