Polymer/Piezoelectric Ceramic Composites: Polystyrene and Poly(methyl Methacrylate) with PZT

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Synopsis

Lead zirconate–titanate (PZT)/polymer composites have been prepared by *in situ* polymerization of styrene and methyl methacrylate around aligned, thin PZT rods. Hydrostatic piezoelectric coefficients ($\bar{d}_h$ and $\bar{g}_h$) measured by a dynamic technique yielded figures of merit ($\bar{d}_h\bar{g}_h$) roughly four times that of homogeneous PZT for as-polymerized composites. When these composites were annealed at a temperature slightly below the glass transition temperature of the matrix polymer and repoled, $\bar{d}_h\bar{g}_h$ increased nearly twofold due primarily to a reduction of the composite dielectric constant. The piezoelectric response was found to be essentially independent of frequency from 30 to 160 Hz.

INTRODUCTION

Piezoelectric composites have been the center of much recent study[1] because of their possible advantages over single phase piezoelectrics [e.g., poly(vinylidene fluoride) (PVDF) and lead zirconate–titanate (PZT)] for hydrophone applications. The phase connectivity[2] is a particularly important parameter, which ultimately determines the properties of a composite solid. For piezoelectric composites made from PZT and polymers, designs which allow the ceramic to be poled to saturation produce relatively large piezoelectric coefficients even for low PZT concentrations.

One such motif studied by Klicker et al.[3] consisted of slender PZT rods aligned perpendicular to the electrode surface and surrounded by a thermosetting polymer (epoxy). These diphasic materials are designated 1–3 composites in the notation adopted by Newnham et al.[2] The numbers refer to the total orthogonal directions in which each phase is continuous throughout the object. In this case the active phase (PZT) extends continuously in one direction, while the polymer matrix spans the composite in all three orthogonal directions. Klicker et al.'s PZT/epoxy composites have hydrostatic "figures of merit" about an order of magnitude larger than homogeneous PZT.[3] In addition, these materials have low densities ($\rho < 1.8$ g/cm^3), which provide for better acoustic coupling to water than PZT ($\rho = 7.8$ g/cm^3), and are flexible relative to PZT ceramics.

Even though the major improvements in properties for these composites over PZT ceramics can be traced to the polymeric phase, few polymer systems have been studied as possible matrix materials. Furthermore, only thermosetting polymers (e.g., epoxies and polyurethanes) have been employed previously in

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1–3 composites. Because the mechanical and physical properties of polymers can vary widely, and because theory[4] suggests that matrix mechanical properties should strongly affect composite piezoelectric response, we have fabricated composites with a variety of thermoplastic polymers. This paper describes our initial studies on polystyrene (PS)/PZT and poly(methyl methacrylate) (PMMA)/PZT 1–3 composites.

BACKGROUND—THEORY

Piezoelectric materials experience a polarization (P) due to an applied stress (σ). The piezoelectric coefficient (d) is a measure of the polarization produced per unit stress. Under hydrostatic conditions, the piezoelectric coefficient is given by

$$d_h = d_{33} + 2d_{31} \tag{1}$$

where the subscripts are the reduced notation for designated directions in an orthogonal axis system. The d_{33} and d_{31} coefficients refer to polarizations which develop along the poling axis (i.e., the 3-direction) due to applied stresses parallel and transverse to the poling direction, respectively. For PZT, d_{31} is opposite in sign to and approximately one-half of d_{33}; therefore, d_h is small. The hydrostatic voltage coefficient (g_h) is related to d_h by

$$g_h = d_h/\epsilon_{33} \tag{2}$$

where ϵ_{33} is the dielectric permittivity. Since d_h is low and the permittivity is high for PZT, the voltage coefficient, which is important for hydrophone applications, is very low. For a hydrostatic transducer material the $d_h g_h$ product is considered to be an all-encompassing "figure of merit."

A simple theory to describe the piezoelectric coefficients of composites with 1–3 connectivity has been described by Skinner et al.[4] The theoretical piezoelectric and dielectric coefficients are given by

$$\bar{d}_{33} = \frac{{}^1v \, {}^1d_{33} \, {}^2J_{33} + {}^2v \, {}^2d_{33} \, {}^1J_{33}}{{}^1v \, {}^2J_{33} + {}^2v \, {}^1J_{33}} \tag{3}$$

$$\bar{d}_{31} = {}^1v \, {}^1d_{31} + {}^2v \, {}^2d_{31} \tag{4}$$

$$\bar{\epsilon}_{33} = {}^1v \, {}^1\epsilon_{33} + {}^2v \, {}^2\epsilon_{33} \tag{5}$$

where v and J are the volume fraction and elastic compliance, respectively. The superscripts refer to phase 1 (PZT) or phase 2 (polymer), and the bar represents the average composite coefficient.

Equations (3)–(5) can be reduced by considering that most polymers are nonpiezoelectric (i.e., ${}^2d_{33} = {}^2d_{31} = 0$), and possess relatively low dielectric permittivities (${}^1\epsilon_{33} \gg {}^2\epsilon_{33}$). Therefore, eqs. (3)–(5) become

$$\bar{d}_{33} = \frac{{}^1v \, {}^1d_{33} \, {}^2J_{33}}{{}^1v \, {}^2J_{33} + {}^2v \, {}^1J_{33}} \tag{6}$$
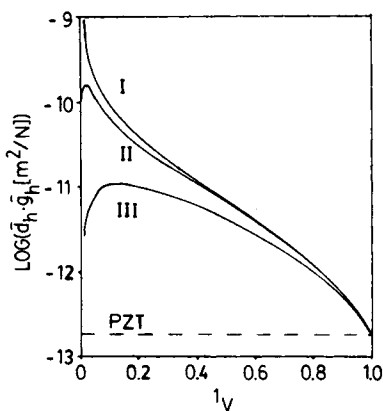
$$\bar{d}_{31} = {}^1v \, {}^1d_{31} \tag{7}$$

Fig. 1. Theoretical plot of log $(\bar{d}_h \bar{g}_h)$ as a function of volume fraction of PZT (^1v). Curve I corresponds to $^2J_{33} = 10^{-7}$ m²/N; for curve II, $^2J_{33} = 10^{-9}$ m²/N; and for curve III, $^2J_{33} = 10^{-10}$ m²/N. The broken line represents the $d_h g_h$ for homogeneous PZT.

$$\bar{\epsilon}_{33} = {}^1v \; {}^1\epsilon_{33} \tag{8}$$

Since most polymers are much more compliant than PZT (i.e., $^2J_{33} \gg {}^1J_{33}$), eq. (6) further reduces to

$$\bar{d}_{33} = {}^1d_{33} \tag{9}$$

In this case, all of the force in the fiber direction is borne by the ceramic rod elements. However, if $^1v \ll {}^2v$, this approximation to eq. (6) is invalid.

By combining eqs. (1), (6), and (7), the hydrostatic piezoelectric coefficient is obtained

$$\bar{d}_h = \frac{{}^1v \; {}^1d_{33} \; {}^2J_{33}}{{}^1v \; {}^2J_{33} + {}^2v \; {}^1J_{33}} + 2 \; {}^1v \; {}^1d_{31} \tag{10}$$

Figure 1 shows how $\bar{d}_h \bar{g}_h$ varies as a function of ^1v according to eqs. (2), (8) and (10) for several values of matrix compliance. For low concentrations of PZT, $\bar{d}_h \bar{g}_h$ is predicted to vary significantly as the matrix compliance changes.

Several modifications to the model of Skinner et al. have been suggested.[5,6] Klicker[6] has shown that $\bar{d}_{33}$ is not necessarily equal to the d_{33} of PZT, but is a function of the PZT rod diameter and volume fraction, composite thickness, and matrix compliance. Additionally, the internal forces arising from a difference in constriction between the phases through Poisson's ratio produce an enhancement of $|\bar{d}_{31}|$ over that predicted by eqs. (4) or (7).[5] These considerations lead to the conclusion that $\bar{d}_h$ predictions based on the Skinner et al. approach are overestimates for 1–3 PZT/polymer composites.

Another important internal stress is that which is due to a mismatch in thermal expansion (or contraction) between the constituent phases.[7,8] Polymers have coefficients of thermal expansion which are at least an order of magnitude larger than PZT ceramics. Therefore, large compressive stresses can develop at the interface of the resin and the PZT rods. These stresses may alter the piezoelectric and dielectric response of composite piezoelectrics. Furthermore, stresses related to curing or polymerization may also be of consequence.

EXPERIMENTAL

The preparation of the PZT rods used in this study has been described else-where.[3] All rods were 12-mil (305-μm) in diameter and were prepared from PZT 501A (Ultrasonic Powders, Inc. South Plainfield, N. J.). The sintered rods were aligned in racks which consisted of two parallel plates of aluminum foil separated by ~2 cm. Each plate had an array of perforations through which the rods were inserted to be held in place during polymerization of the matrix in order to insure the proper volume fraction (4%) of PZT for all composites.

In situ polymerization of liquid monomers was the most convenient method to prepare composites because of the fragile nature of the PZT rods. The liquid monomers (styrene and methyl methacrylate) were purified by vacuum distillation prior to use. Polymerization was initiated by 0.5 wt % benzoyl peroxide. Prepolymer syrups (polymer in monomer) were prepared by heating the monomer–initiator systems at 80°C for 15 min and then cooling the mixture to room temperature. By using a prepolymer, the resulting composites were found to be essentially void free.

Composites were then fabricated by placing filled racks of PZT rods into glass molds and pouring a given prepolymer into the mold until the rods were submerged in the liquid and covered over by ~1 cm. The molds were then placed in an oven maintained at 50°C until the polymer solidified. Additional heating to 90°C for 1 h completed the polymerizations. After the molds were removed from the oven and allowed to cool, the glass mold was broken and the composites were sectioned perpendicular to the rod axis using an electric diamond saw or a hacksaw. The as-cut slugs were then sanded with 60-grit garnet paper followed by polishing using 200-grit garnet paper. All composites were 4 mm thick in the fiber direction. The glass transition temperatures (T_g) of the matrices were determined with a Perkin–Elmer DSC-2 equipped with a Thermal Analysis Data Station. The T_g of both the PS and PMMA was found to be approximately 100°C.

Air-dry silver electrodes were applied to the two faces perpendicular to the rods, and the composites were poled at 75°C in an oil bath with a field of 22 kV/cm for 5 min. After the composites were removed from the bath, they were allowed to cool in air under a field of 7.5 kV/cm for 10 min to prevent depoling during cooling. The poled composites were aged for at least 24 h prior to piezoelectric and dielectric measurements.

Dielectric measurements were performed with a Hewlett-Packard 4270A Automatic Capacitance Bridge at 1 kHz and 1 V. $\bar{d}_{33}$ was measured using a Berlincourt Piezo d_{33}-Meter with rounded rams. The ratio of the diameter of the rams to the center-to-center distance of the PZT rods was 0.74. The $\bar{d}_{33}$ was taken as the average of 20 random measurements (10 on each electroded surface of the composite) at a ram pressure of approximately 55 psi. The hydrostatic piezoelectric coefficients ($\bar{d}_h$ and $\bar{g}_h$) were measured by a dynamic[9] method. The apparatus consisted of an oil-filled chamber in which the samples and a PZT standard of known d_h and g_h were immersed. The pressure inside the vessel was raised to 100 psi and alternating sinusoidal pressure cycles (amplitude ±0.1 psi) were imposed using an AC stress generator driven by a function generator adjusted to the proper frequency. The sample (or standard) voltage was recorded on an oscilloscope display.

TABLE I
Piezoelectric Properties of 1–3 Composites and Single Phase Materials

Material	Density (g/cm^3)	$\overline{K}_{33}$	$\overline{d}_{33}$[a] (10^{-12} C/N)	$\overline{d}_h$[b] (10^{-12} C/N)	$\overline{g}_h$[b] (10^{-3} V·m/N)	$\overline{d}_h\overline{g}_h$[b] (10^{-15} m^2/N)
PZT/PS	1.32	70	110 ± 16	22	36	790
PZT/PS (annealed)	1.32	54	130 ± 18	26	54	1400
PZT/PMMA	1.46	131	110 ± 18	28	25	700
PZT/PMMA (annealed)	1.46	100	125 ± 21	35	39	1370
PZT	7.9	1600	400	50	4	200
PVDF	1.8	12	30	11	104	1140
PZT/epoxy (Ref. 9)	1.4	97	—	32	51	1630

[a] Errors are ± 1 standard deviation.
[b] Estimated errors are $\overline{d}_h$ ± 12%, $\overline{g}_h$ ± 16%, and $\overline{d}_h\overline{g}_h$ ± 20%.

After the composites were tested, they were annealed at 95°C for 15 h under vacuum followed by slow cooling to room temperature. The annealed composites were repoled in order to ensure saturation poling of the PZT rods and then re-tested as described above.

RESULTS AND DISCUSSION

The dielectric and piezoelectric properties of the PZT/PS and PZT/PMMA composites are summarized in Table I. As expected, the composite dielectric constants ($\overline{K}_{33}$) were considerably less than that of PZT ($K_{33} \approx 1600$). The value of $\overline{K}_{33}$ predicted by the simple parallel model for a 4% PZT/polymer, 1–3 composite is 64. The PZT/PS composites approached the theoretical value; however, the PZT/PMMA materials far exceeded the prediction. One possible explanation for this discrepancy may involve cracking or crazing of the PS matrix. Examination of unannealed PZT/PS composites under a light microscope revealed crazes (or cracks) emanating radially away from each rod into the PS matrix at the electrode surface. No such cracks were observed in PZT/PMMA samples. Since applied compressive stress is known to increase the dielectric constant of PZT,[10] one would expect $\overline{K}_{33}$ of the PZT/PS composites to be less than $\overline{K}_{33}$ of the PZT/PMMA materials if the cracks acted to relieve interfacial compressive stresses.

The presence of internal stresses in these composites is further supported by the decrease in the dielectric constant after they were annealed. If the annealing process acts to relieve some radial compression between the rods and the matrix, then the dielectric constant would be expected to be lower than the $\overline{K}_{33}$ before annealing. Presumably, the radial stresses resulted from thermal expansion mismatches, mechanical processing (cutting and polishing), or polymerization shrinkage.

The simple Skinner et al. model predicts that the $\overline{d}_{33}$ for composites with matrices of the same stiffness should be the same. Since PS and PMMA have roughly the same elastic modulus ($\sim 3 \times 10^9$ N/m^2), it is not surprising that $\overline{d}_{33}$ is similar for both composite materials. However, the predicted $\overline{d}_{33}$ values are three times greater than those observed. Clearly, transfer of applied stress from matrix to rods is more complex than allowed for by the simple parallel model. If the effective matrix region of influence on the rods is less than the total matrix
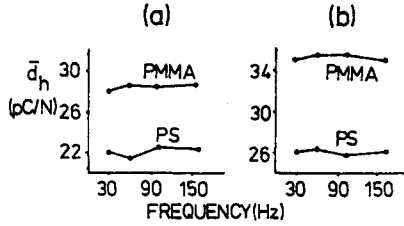
Fig. 2. Piezoelectric response of PZT/PS and PZT/PMMA composites as a function of frequency: (a) unannealed; (b) annealed.

area, then the amount of stress experienced by the rods would be less than predicted by the Skinner et al. model.[6] This would act to decrease $\bar{d}_{33}$ relative to the predicted value.

The standard deviations of $\bar{d}_{33}$ values obtained from a d_{33}-meter using rounded probes gives an indication of the relative piezoelectric homogeneity of the composites. For the composites tested here the standard deviations of the $\bar{d}_{33}$ measurements were similar. Again, considering that the matrices used in this work have similar mechanical properties, this result is not unexpected.

The hydrostatic piezoelectric coefficients ($\bar{d}_h$) reported in Table I are smaller than those of PZT but similar to that observed by Lynn[9] for the PZT/epoxy system. The voltage coefficients are roughly an order of magnitude larger than PZT because the permittivities of the composites are much lower than the values for PZT alone. This results in $\bar{d}_h\bar{g}_h$ being significantly larger than that of PZT and comparable to that of PVDF. Also, no frequency dependence of $\bar{d}_h$ was observed from 30 to 160 Hz (Fig. 2). Annealing was found to improve the piezoelectric coefficients (especially $\bar{g}_h$) due to a significant decrease in $\bar{K}_{33}$.

Composite densities are roughly 1.4 g/cm^3 (calculated), which is considerably lower than the 7.8 g/cm^3 of PZT. Low density materials provide better acoustic coupling to an aqueous environment than ones of high density. Therefore, these types of composites may be useful as shallow-water hydrophones or for medical ultrasound applications.

CONCLUSIONS

Composites of uniaxially oriented, continuous PZT rods embedded in polystyrene or poly(methyl methacrylate) matrices possess hydrostatic piezoelectric coefficients somewhat lower than that of homogeneous PZT. However, hydrostatic voltage coefficients for these materials are approximately an order of magnitude larger than the ceramic element. Enhancement of $\bar{g}_h$ is primarily due to the reduction of $\bar{K}_{33}$ over PZT. Further enhancement of the piezoelectric response can be accomplished by annealing which further reduces $\bar{K}_{33}$. The $\bar{d}_{33}$ values and the standard deviation of the $\bar{d}_{33}$ measurements are similar for both types of composites. Predictions of the composite piezoelectric coefficients based on the Skinner et al. model are qualitatively correct but quantitatively overestimated.

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