Influence of Al Particle Size and Lead Zirconate Titanate (PZT) Volume Fraction on the Dielectric Properties of PZT-Epoxy-Aluminum Composites

S. Banerjee
Mechanical and Aerospace Engineering Department, Rutgers, The State University of New Jersey, Piscataway, NJ 08854-8058

K. A. Cook-Chennault
Mechanical and Aerospace Engineering Department, Rutgers, The State University of New Jersey, Piscataway, NJ 08854-8058; Center of Advanced Energy Systems, Rutgers, The State University of New Jersey, Piscataway, NJ 08854-8058

Two-phase PZT-epoxy piezoelectric composites and three phase PZT-epoxy-Al compositions were fabricated using a poling voltage of 0.2 kV/mm. The influence of aluminum inclusion size (nano and micron) and (lead zirconate titanate) PZT volume fraction on the dielectric properties of the three phase PZT-epoxy-aluminum composites were experimentally investigated. In general, dielectric and piezoelectric properties of the PZT-epoxy matrix were improved with the addition of aluminum particles. Composites that were comprised of micron scale aluminum inclusions demonstrated higher piezoelectric d_{33}, strain-coefficients, and higher dielectric loss compared to composites that were comprised of nanosize aluminum inclusions. Specifically, composites comprised of micron sized aluminum particles and PZT volume fractions of 20%, 30%, and 40% had dielectric constants equal to 405.7, 661.4, and 727.8 (pC/N), respectively, while composites comprised of nanosize aluminum particles with the same PZT volume fractions, had dielectric constants equal to 233.28, 568.81, and 657.41 (pC/N), respectively. The electromechanical properties of the composites are influenced by several factors: inclusion agglomeration, contact resistance between particles, and air voids. These composites may be useful for several applications: structural health monitoring, energy harvesting, and acoustic liners. (DOI: 10.1115/1.4004812)

Keywords: composite, PZT-epoxy, PZT-Al-epoxy, dielectric loss

1 Introduction

Two-phase composite piezoelectric polymers (CPPs), so-called 0-3 composites comprised of piezoelectric particles embedded within a continuous matrix, have attracted much attention due to their flexibility, ease of processing and use in embedded passive devices [1–12], such as capacitors. Integration of embedded passive components into printed circuit boards generally results in enhanced electrical performance of the device, improved reliability, reduction of device size, faster switching speed, and lower production costs [3,4,9]. Two-phase composites: metal-polymer and ceramic-polymer have been extensively studied [1,10,11,13–22] for application to coupling or by-pass capacitor technology, wherein emphasis has been placed on achievement of high effective dielectric constants via analysis based on percolation theory and mixing rules. However, as dielectric materials, these two-phase composites have relatively low values of dielectric constant compared to three phase 0-3-0 composite piezoelectric materials comprised of piezoelectric and electrically conductive particles embedded within a continuous matrix [1,2,23]. Thus, in order to enhance the dielectric properties of two-phase polymer-based composites, workers have investigated three phase composites consisting of a piezoelectric ceramic, metal, and polymer. Choi et al. [24] found that BaTiO_{3}-PMMA-Ni composites comprised of 10% volume fraction of nickel (40 μm in size) had dielectric constants equal to ~110 pC/N compared to the two-phase CPP, BaTiO_{3}-PMM, which had a dielectric constant equal to ~14.4 pC/N [25]. In addition to higher dielectric constants, these three phase composites have lower processing temperatures [24] and improved loss factors, which make them suitable for damping materials [1,16,19,20,23,26].

Inclusion of conductive fillers within polymer matrixes has been demonstrated by several other workers [16,23,24,27,28]. All have reported that the polymer matrix conductivity was enhanced by the electrically conductive filler. Ma and Wang [19] compared the microstructure and dielectric properties of epoxy-based damping composites that contained carbon nanotubes (CNTs) and PMN PZT piezoceramics. They concluded that the composites exhibited a percolation threshold in the range of 1.0–1.5 g CNTs per 100 g epoxy. They also concluded that in the region of the percolation threshold, a continuous electroconductive network was formed, and that beyond the percolation threshold, these materials demonstrated dynamic mechanical loss factors that were superior to those below the percolation threshold, and those without semiconductive inclusions. Tian and Wang [20] also examined the performance of epoxy/multiwalled carbon nanotube/piezoelectric ceramic composites as rigid damping materials. Their results were similar to Ma and Wang [19], where the percolation threshold was found to be in the range of 1.0–1.5 g CNTs per 100 g epoxy. They too concluded that loss factors were improved with the incorporation of CNT and (PZT), where the amount of CNT was above the critical electrical percolation loading. Hori et al. [26] found that three phase composites produced superior damping loss values in comparison to two-phase composites for specific volume fractions of piezoelectric and conductive material. They fabricated samples that were comprised of PZT, carbon black and epoxy. The three phase composite achieved a maximum value of damping loss.
substantial increase from the single phase composites. The dielectric constant of the three-phase CPP has an influence on the dielectric constant of the three-phase composite, which resulted in enhanced damping loss values. The size of the piezoelectric particles within the composite also has an influence on the dielectric constant of the three-phase composites. The dielectric constant of the three-phase CPP [7,8,27], BaTiO$_3$-PMMA-Ni comprised of micron size BaTiO$_3$ particles was found to be $\sim$150 pC/N in comparison to 100 pC/N for three-phase composites with nanosize BaTiO$_3$ particles. The effects of the piezoelectric particle size on the bulk properties of the composite were attributed to the increase in percolation threshold of nickel that was caused when individual or aggregate BaTiO$_3$ particles surrounded the nickel particles [27].

Hence, the dielectric behavior of the composite is dependent upon the size, shape, and spatial distribution of the filler particles within the host matrix, the adhesion and the interaction between the phases, and the processing method [17,22,24,27,29–31]. In this paper, we report on the effects of the size of the conductive particle on the dielectric properties of the piezoelectric-epoxy-conductor composite. Specifically, the influence of the size of the Al particle on the dielectric constant, strain coefficient and tan $\delta$ is observed. The PZT-epoxy-Al composites examined comprised of micron and nanosize aluminum particles.

2 Experimental

PZT powder manufactured by READE International (CAS #12626-81-2, EC-76) and epoxy resin (DGEBA, Epofix$^{TM}$ Cold-Setting Embedding Resin) manufactured by Electron Microscopy Sciences were mixed by hand using a stainless steel rod and stirred for 15 min. The mixture of PZT and epoxy was then ball milled for 1 h. Aluminum particles: nanosize, 99.95% purity, spherical morphology (APS: 18 nm) and micron, 99.97% purity spherical morphology, 200 mesh were supplied by MTI and Acros-Fisher Scientific, respectively. The volume fraction of aluminum was held constant at 20%. The aluminum particles were dispersed in ethanol and then stirred with a mechanical stirrer for 15 min. The mixture of PZT and epoxy was then added to the Al dispersion in ethanol mixture. An epoxy hardener was added, after the ethanol was evaporated at room temperature for approximately 12 min. The final mixture was then poured into a circular mold that was 6 mm thick with a radius equal to 7 mm. The mold, containing the sample, was placed in between the top and bottom platens of a Carver Hydraulic press, and subjected to 500 psi for 5 min at room temperature. The samples were cured at 75°C for 8 h. The samples were polished and subsequently painted on the top and bottom surfaces with conductive silver paint. The samples were then poled at 0.2 kV/mm at 1200°C for 10 min in silicone oil. After poiling, the sample was wrapped in Al foil for 24 h to get rid of residual charges. The dielectric constant, dielectric loss tangent, and piezoelectric strain coefficient at 110 Hz were recorded using a commercial $d_{33}$-meter from Piezotest, and the impedance from 100 to 1500 kHz was recorded for each sample using a HP 4194 A Impedance analyzer. The fractured surface morphology of the samples was studied with the help of a scanning electron microscope (FESEM ZEISS 982). Two samples were prepared for each volume fraction of PZT, e.g., 10%, 20%, 30%, 40%, 50%, 60%, and 70%. The values presented in the figures are the average values from the two samples prepared.

3 Results and Discussion

Two-phase PZT-epoxy composites were fabricated using the methodology described above (without inclusion of aluminum particles), where the volume fraction of PZT was varied from 10% to 70%. The dielectric constant of the two-phase composite is plotted as a function of volume fraction of PZT in Fig. 1. As expected, the dielectric constant of the composite increased with the volume fraction of PZT. The dielectric constant plot as a function of piezoelectric volume fraction followed the same trend as Refs. [27] and [30], wherein the plotted results fall between the Maxwell Garnett approximation

$$\varepsilon = \varepsilon_{\text{环氧}} \left[ \frac{1 + 3 \phi_{\text{PZT}} \beta}{1 - \phi_{\text{PZT}} \beta} \right]$$

and the Bruggeman’s effective medium approximation [27]

$$\left(1 - \phi_{\text{PZT}}\right) \frac{\delta_{\text{环氧}} - \varepsilon}{\delta_{\text{环氧}} + 2 \varepsilon} + \phi_{\text{PZT}} \frac{\delta_{\text{PZT}} - \varepsilon}{\delta_{\text{PZT}} - \varepsilon} = 0$$

In Eqs. (1) and (2), $\phi_{\text{PZT}}$ is the volume fraction of PZT, $\beta = (\varepsilon_{\text{环氧}} - \varepsilon_{\text{环氧}})/(\varepsilon_{\text{PZT}} + 2 \varepsilon_{\text{环氧}})$, and $\varepsilon$, $\varepsilon_{\text{PZT}}$, and $\varepsilon_{\text{环氧}}$ represent the dielectric constant of the two-phase composite, PZT and epoxy, respectively. Both analytical models can be used to determine the effective dielectric constant of a matrix-based composite with embedded inclusions [27]. In general, the Maxwell expression underestimates [27] the effective dielectric constant,
while Bruggeman’s expression overestimates this value as the volume fraction of the piezoelectric material increases. For our data, the Maxwell expression underestimates and Bruggeman’s expression overestimates the empirical results for $\phi_{PZT} > 30\%$. This is due to the aggregation of PZT and epoxy particles in the composite along with the increase in PZT volume fraction, which results in continuous percolation clusters in the composites [27]. A SEM image that details the distribution of PZT within the epoxy matrix is provided in Figs. 2(a) and 2(b). The SEM micrographs of the PZT-epoxy composite are magnified 1000 and 5000 times, respectively. The arrows indicate the PZT and epoxy matrix. In Fig. 2(b), evidence of PZT clustering is seen, which supports the explanation for the underestimation of the Maxwell Garnett approximation.

In Fig. 3, a plot of the effective dielectric constant as a function of PZT volume fraction is provided for the PZT-epoxy and the three phase composites with micron and nanosize Al inclusions. The volume fraction of the Al inclusions is held constant at 20% for all three phase composites. As expected, the dielectric constants of the three phase composites are greater than those of the PZT-epoxy. This is attributed to the addition of the aluminum particles. This enhancement can be explained by the following power law [24,27]:

$$e_{\text{3-Phase}} = \left| \frac{\phi_e - \phi_c}{\phi_c} \right|^{-q}$$  \hspace{1cm} (3)

where $e$ is the dielectric constant of the PZT-epoxy two-phase composite, $\phi_e$ is the percolation threshold volume fraction, $\phi_c$ is the volume fraction of the aluminum, and $q$ is the critical exponent. A value of 1.3 was determined for the critical exponent, $q$, when a value of 16% [27,30] for the percolation threshold of aluminum, $\phi_c$, and the experimental values for the dielectric constant were substituted into Eq. (3).

The effective dielectric constant for the composite that incorporates micronsize aluminum particles presents higher effective dielectric constants for equivalent volume fractions of PZT than the composites with nanosize aluminum particles. For example, at volume fractions of 20%, 30%, and 40% of PZT, the dielectric constants of the microcomposites are 405.74, 661.38, and 727.78 (pC/N) as compared to 233.28, 568.81, and 657.41 (pC/N), respectively, for the nanocomposite. Differences in the piezoelectric strain coefficient and loss factor, $\tan \delta$, are also observed when aluminum particles are added to the two-phase composite, and when the size of the aluminum particles is varied. $\tan \delta$ is an important parameter in the characterization of the macromolecular viscoelasticity of the material. It represents the damping capacity of the material and describes the ability of the material to convert mechanical energy into heat energy, when subjected to an external load. In general, $\tan \delta = \frac{E''}{E'}$, where $\tan \delta$ is the phase angle between the stress and strain [20], while $E'$ and $E''$ are the elastic storage modulus and elastic loss modulus, respectively. The results provided in Fig. 4 indicate that all of the composites show an increase in loss factor at higher concentrations of PZT. This

![Fig. 2 SEM micrographs of two-phase (PZT/epoxy) composite with PZT volume fraction of 50% and magnifications of (a) 1000 and (b) 5000](image)

![Fig. 3 A comparison of the dielectric constants of the two-phase and three phase microcomposite and nanocomposite](image)
trend agrees well with those noted by Refs. [19] and [20]. The experimental values also follow the power law [24]:

$$\tan \delta = \tan \delta_0 \left| \frac{\phi_0 - \phi}{\phi_0} \right|^{-r} \quad (4)$$

In Eq. (4), \(\tan \delta_0\) is the loss tangent of the two-phase matrix and \(r\) is direct current conductivity of the composites. The experimental values of the dielectric loss tangent are in good agreement with Eq. (4) and follow the same trend as Refs. [27] and [30]. \(r\) may be determined from the empirical data provided. The composites that have the micron size aluminum particles present higher values of \(\tan \delta\) than the composites that incorporate nanosize aluminum constituents. For example, the \(\tan \delta\) values for a PZT volume fraction equal to 70% are 0.014, 0.0273, and 0.0457 for the PZT-epoxy, PZT-epoxy-Al= nano, and PZT-epoxy-Al/microcomposites, respectively.

In Fig. 5, a plot of the piezoelectric strain coefficient, \(d_{33}\), as a function of PZT volume fraction is presented. As evidenced by other workers [32,33], \(d_{33}\) increases with the volume fraction of PZT in composite piezoelectric materials. Similar to the loss factor results presented in Fig. 4, the strain coefficient of the composites containing nanosize particles of aluminum is lower than those containing micron size particles of aluminum. The strain coefficient is a function of the capacitance of the material, which is proportional to the number of charges that are stored on the surface of the sample under an applied electric field. The inclusion of dielectric fillers result in higher permittivity of the composite and ultimately higher piezoelectric coefficients. In fact, the \(d_{33}\) coefficient of the microcomposite is almost three times that of the nanocomposite for PZT volume fractions of 40% and 50%.

In Figs. 6(a) and 6(b), the distribution of the Al microparticles in the PZT-epoxy matrix can be observed. In these figures, clustering of the Al is observed. In Figs. 7(a) and 7(b), the three phase composite comprised of nanosize Al inclusions are provided at magnifications of 1000 and 5000. The aluminum particles in the nanometer range have more surface area to interact with the PZT-epoxy matrix than that of the microsized Al inclusions. Thus, the interfacial effect [27] between the materials becomes more prominent as the size of the conductive inclusion diminishes. Agglomeration of Al nanoparticles is circled in the SEM micrographs. Both interfacial effects and agglomeration are important factors governing the dielectric and piezoelectric characteristics of the composite.

The difference in performance of the composites comprised of nano and micron size aluminum particles is the result of several factors. Contact resistance between the conductive material and the polymer matrix and dielectric material reduce the conductivity of the conductive materials themselves. Smaller size conductive materials provide higher contact surface area per unit volume of

![Fig. 4](image1.png)  
**Fig. 4** A comparison of the dielectric loss of the three phase microcomposite and nanocomposite with the two-phase PZT-epoxy composite with increasing PZT volume fraction shows that microcomposites have the highest dielectric loss as compared to the nanocomposite and two-phase composite.

![Fig. 5](image2.png)  
**Fig. 5** A comparison of the piezoelectric strain coefficient \(d_{33}\) of the three phase microcomposite and nanocomposite with the two-phase PZT-epoxy composite with increasing PZT volume fraction. Microcomposites have the highest dielectric loss as compared to the nanocomposite and two-phase composite.
composite material than composites comprised of micron sized materials. This results in reduced values in strain coefficient for composites comprised of nanoconductive particles in comparison to those comprised of micron size particles. Also, composite homogeneity is a critical parameter in achieving optimal performance and is a challenge to achieve due to space charge effects. Adequate dispersion of PZT and conductive filler within the polymer matrix, and minimal air voids are desirable. However, agglomeration of PZT and conductive filler material within the matrix is common as evidenced by the SEM images. The agglomeration of the constituent materials can lead to reduced mechanical, electrical, and conductive properties in the materials. Agglomeration was observed in all of the sets of composite materials, in particular those containing nanosize aluminum constituents. Also, addition of ceramic materials tends to introduce flaws, in the form of agglomerations that contribute to scattering of results.

4 Conclusions

Piezoelectric composites comprised of PZT, epoxy, and Al were fabricated, and the size of the aluminum particles was varied from nano to micro in size. The dependence of the dielectric and piezoelectric characteristics of the composite on the volume fraction of PZT has been established. The enhancement of dielectric and piezoelectric properties resulting from the addition of Al inclusions and increase of PZT volume fraction has been shown. A comparative study on the microcomposite and nanocomposite showed that the influence of the interfacial effect and Al nanoparticle agglomeration on the dielectric and piezoelectric characteristics of the bulk three phase composite. The difference in properties of the microcomposite and nanocomposite proves that the dielectric and piezoelectric properties of these particulate composites can be tailored by varying inclusion particle size, while the other parameters remain fixed. The ease of processing, flexibility, and good dielectric behavior of the three-phase piezoelectric particulate composites potentially makes the composites suitable for practical applications in energy harvesting, acoustic dampening, and structural health monitoring.

Acknowledgment

We appreciate partial support of the research by the New Jersey Space Grant Consortium, a NASA-sponsored program.

References

