Dielectric and Piezoelectric Properties of 0-3 PZT/PVDF Composite Doped with Polyaniline*

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Abstract: Lead zirconate titanate (PZT)/polyvinylidene fluoride (PVDF) 0-3 piezoelectric composites doped with polyaniline (PANI) were obtained by hot-press method. The polarization properties of the composites were characterized by XRD and P-E hysteresis loops at room temperature. And the dielectric and piezoelectric properties were also measured. The results show that the poling of PZT could be effectively carried out and the dielectric constant ε_r and dissipation $\tan\delta$ increase monotonously by increasing the volume fraction of PANI in the composite. The piezoelectric constant d_{33}, and the planar electromechanical coupling factor k_p increase while the mechanical quality factor Q_m decreases with the increase in the content of PANI. The d_{33}, k_p and Q_m show the extremum values at 8 vol%-10 vol% PANI.

Key words: piezoelectric composite;   polyaniline;   dielectric properties;   piezoelectric properties

1   Introduction

Ferroelectric ceramic/polymer composites with different connectivities have been widely used as piezoelectric sensor because of their high value of piezoelectric coefficient and the formability and flexibility, which are not attainable in a single-phase piezoelectric material, $i\ e$, an electroceramic or a polymer. Although 0-3 piezoelectric ceramic/polymer composite[1-4] has advantages over other composites, particularly in terms of cost and ease of manufacture, the design of a composite with optimum properties is still a challenge. For a composite with 0-3 connectivity the electric field E_c acting on an individual piezoelectric grain is given by[5]

$$E_c = 3\varepsilon^P E_0/(\varepsilon^c + 3\varepsilon^P) \qquad (1)$$

where ε_c and ε_p are the dielectric constants of ceramic and polymer, respectively. E_0 is the applied external electric field. Since most polymer have a lower dielectric constant ($i\ e$, < 10) compared to piezoelectric ceramics ($i\ e$, > 10^3), most of the applied electric field will be concentrated in the polymer (the analog electrical circuit is two resistances in series for the composite), and efficient poling of ceramic dipoles is very difficult. One way to effectively pole 0-3 composites is to introduce a small volume fraction of a conductive third phase such as carbon and germanium[5,6]. By controlling conductivities of the polymers, the poling can be efficiently carried out. Similar to the inorganic conductor, the conducting polymer may also be expected to reduce the resistivity of the matrix. However, little has been reported about the results of the composite doped with the conducting polymer.

The present paper reports the results of dielectric and piezoelectric characterization of 0-3 PZT/PVDF composite doped with polyaniline (PANI). The effect of the conductive phase on the polarization, dielectric and piezoelectric properties is discussed.

2   Experimental

PZT ceramics prepared by a conventional mixed oxide technique were bought from local market (d_{33} = 400 pC/N, ε_r = 1650, $\sigma \approx 10^{-8}$ S·m^{-1}). The ceramic powders with an average size of 3 μm were made from fired ceramics by grinding and milling. The PANI with a conductivity of 0.1 S·m^{-1} was prepared by chemical oxidation polymerization method[7]. The PVDF was bought from local market and used without further purification. The required amounts of PVDF and PANI powders were dissolved in N-methyl pyrrolidone (NMP) and PZT powders were uniformly dispersed in the polymer solution using an agitator. After evaporation of the solvent at 60-70 ℃, the dried mixture was put into an oven at 120 ℃ for 24 h to remove the solvent completely. Then the composite powders were pressed at 200 ℃ for 10 min under 150 MPa, in a steel die with a diameter of 12 mm. Finally the die was cooled to room temperature under the applied pressure, and the composites with a thickness of 0.3-0.4 mm were obtained. The volume fraction of ceramics in all the samples was 50%. The PANI contents in different samples were ranged from 0 to 14 vol% while the corresponding PVDF loading ranged from 50 vol% to 36 vol%. After the air-dry silver electrodes were spreaded on both polishing surfaces, the samples were poled in silicon oil with an applied electric field of 10 kV/mm at 120 ℃ for 1 h.

Dielectric and piezoelectric properties were measured

by means of the resonace-anti-resonance method using a precision impedance analyzer (HP4294A). The conductivities of the polymer blends were measured by two-probe method using LCR at 1 kHz. X-ray patterns of the poled composite samples were taken on a D/MAX-III X-ray diffractometer with Cu K_a radiation ($\lambda = 1.5418$ Å) and a graphite monochrometer. The diffraction data were recorded for 2θ between 10 to 80° with a resolution of 0.02°. The *P-E* hysteresis loops were obtained by a Radient Precision ferroelectric testing system with a frequency of 50 Hz. Piezoelectric constants d_{33} of the samples were measured by a quasi-static d_{33} meter (ZJ-3A) based on Berlincourt method with a frequency of 110 Hz. The planar electromechanical coupling factor K_p was calculated from the resonance and anti-resonance frequencies based on the Onoe's formula[8].

3 Results and Discussion

3.1 Dielectric properties

The relative dielectric constant and dielectric loss of PZT/PVDF composites with PZT of 50 vol% and PANI ranging from 0 to 14 vol% are shown in Fig.1. It can be seen that the dielectric constant and dielectric loss increase monotonously with increasing the content of PANI in the composites. One can be sure that the contribution of the space charges in the PANI/PVDF blends confirmed by Radhakrishnan *et al*[9] to dielectric constant and dielectric loss can be neglected at the applied frequency of 1 kHz. The enhancement in dielectric loss is mainly related with the increase of the electrical conductivity of the com-
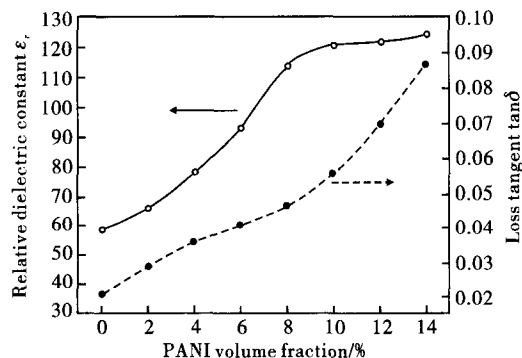
posite due to the presence of PANI. The dielectric constant and conductivities of the polymer blends at frequency of 1 kHz are shown in Table 1. The rapid increase in electrical conductivity of the polymer with increasing PANI loading in PVDF was also reported by Wang *et al*.[10] The increase in dielectric constants may be mostly correlated with the PANI with high dielectric properties in the composite films. As Radhakrishnan's result the PANI formed large numbers of particles and dispersed uniformly in the PVDF[9]. These particles can effectively increase the dielectric constant in polymer blends by forming numerous fine capacitors.

Fig.2 shows the frequency (10^2-10^6 Hz) dependence of the relative dielectric constants (ε_r) and loss tangents ($\tan\delta$) in the composites. It can be seen that the dielectric properties change greatly with frequency. At low frequencies ($< 10^3$ Hz) the ε_r and $\tan\delta$ in the composites with more PANI reduce more quickly with frequency. The facts causing this variation in these composites are that the space charges can not be neglected in this frequency range. The more PANI in the polymer blend induce more space charges which can increase the dielectric constant and dielectric loss at a low frequency[9]. At high frequencies the ε_r decreases while the $\tan\delta$ increases with a frequency similar to those found in PVDF and its composite with PZT by Hilczer *et al*.[11]. These changes are mainly caused by the dielectric relaxation in PVDF. It should be mentioned that the faster enhancement in $\tan\delta$ for the composites with more PANI at high frequencies ($> 10^4$ Hz) may be concerned with the rapid increase of conductivities in PANI blends with frequency[12].

Fig.1   Variation of dielectric properties in the composites with the PANI volume fraction
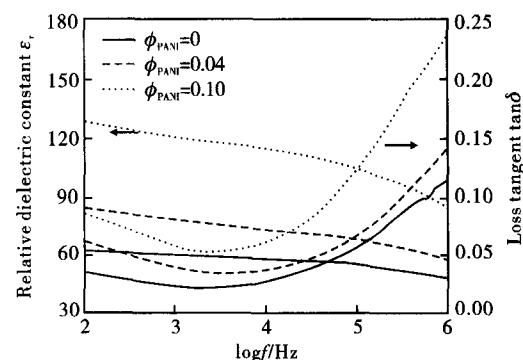

Fig.2   Frequency dependence of the relative dielectric constant and dielectric loss in the composites with different PANI content

Table 1   Dielectric constant and conductivities of blends with different PANI content in PVDF at 1 kHz

PANI content in polymer/vol%	0	4	8	12	16	20	24	28
Dielectric constant	8.6	10.4	13.6	15.7	19.5	26.2	46.7	100.4
Log(σ) (S/m) (25℃)	-14.1	-13.8	-13.2	-12.9	-12.2	-11.1	-9.7	-7.8
Log(σ) (S/m) (120℃)	-13.7	-12.8	-12.1	-11.2	-9.5	-8.3	-7.2	-5.9

3.2 Polarization properties

Fig.3 shows X-ray diffraction (XRD) patterns of the poled samples with different PANI content. From Fig. 3 it can be seen that the XRD patterns show the characteris-

tics of perovskite structure, and there was no obvious difference in the three patterns. However, the diffraction peaks with 2θ of 43-46° of the composites are different as shown in the insert part of Fig. 3. The intensities of

(002) peaks in PANI-doped samples are obviously stronger than that in the one without PANI phase. And the intensity of (002) peak in 14% PANI-doped samples is weaker than the one with 10% PANI. Domains of PZT with their c-axis (polar axis) perpendicular to the XRD planes, referred as c-domains, were responsible for the (002) diffraction peak. And domains with their a-axis perpendicular to the XRD planes, referred as a-domains, were responsible for the (200) peak. The intensities of the (002) and (200) peaks can be correlated with the
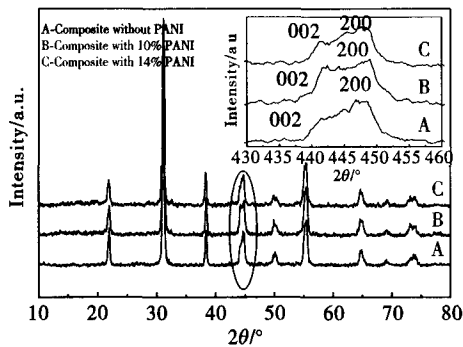

Fig.3 XRD patterns of the composites with different PANI
volume fraction with 2θ of 10-80°. The inset
at the right top is the XRD patterns of the
corresponding composites with 2θ of 43-46°

The P-E hysteresis loops of the composites without and with 10 vol% PANI at room temperature are presented in Fig.4. The sample with 10 vol% PANI was chosen to study the characteristics of hysteresis loops for their good piezoelectric properties discussed later. From Fig.4 it is seen that the maximum and remanent polarizations of 10% PANI-doped composite are clearly larger than those of the composite without PANI in the same applied electric field ($E = 10$ kV/mm). The remanent polarization P_r was altered from 2.91 $\mu C/cm^2$ of sample without PANI to 5.04 $\mu C/cm^2$ of PANI-doped one. This clearly indicates the addition of an appropriate amount of PANI can markedly affect the polarization property of the composite. The increased remanent polarization means the poling of the piezoelectric phase can be efficiently carried out. This result can be proved by XRD patterns with 2θ of 43-46° presented in the inset part of Fig.3. The sufficient poling of piezo-phases is related with the high dielectric constant of the polymer blends discussed above. In accordance with Equation 1 the higher dielectric constant of polymer can increase the electrical field acting on the piezoelectric grains to pole them effectively. Another reason for the increase in the remanent polarization in composite may be that the higher dielectric constant of the polymer matrix can provide larger retention of the polarization of the ceramic particles[14].

3.3 Piezoelectric properties

The piezoelectric properties of PANI-doped PZT/PVDF composites are shown in Fig.5 and Fig.6. It can

volumes of the c- and a-domains in the samples. From the variation in the intensities of the (002) and (200) peaks, one can infer the change in the populations of the two kinds of domains[13]. The variation of the (002) and (200) peaks illustrates that an appropriate amount of PANI in composite favors the c-domains of PZT and induces more a-domains to switch to c-domains in the external applied electric field. In other words, the poling of PZT can be easily carried out with an appropriate amount of PANI.
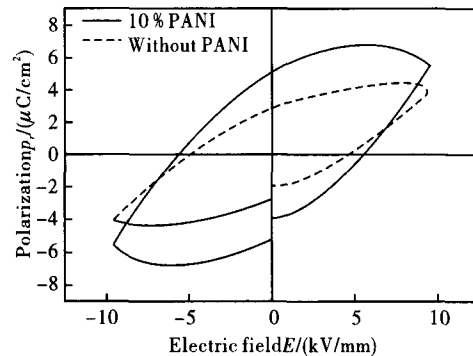

Fig.4 P-E hystersis loops of the composites without and
with 10 vol% PANI at room temperature

be found that the piezoelectric constant d_{33} and the planar electromechanical coupling factor k_p show a maximum value while the mechanical quality factor Q_m shows the minimum value at PANI volume fraction of 0.08-0.10. At 10 vol% PANI, an obvious improvement on the piezoelectric constant in composite can be seen and the value of d_{33} increased by more than 80% in comparison with the composite without PANI phase. The variation in piezoelectric and electromechanical properties in this experiment may be mostly related with the remanent polarization of the piezoelectric ceramic. In accordance with the above discussion the dielectric constant of the matrix markedly affects the polarization in composite. It should be noted that, except for the dielectric constant, the conductivity of the polymer matrix also affects the poling of the composite. The increase in conductivities of polymer can enhance the polarization of ceramics in composite when the conductivity of polymer is less than that of PZT[15]. However, the higher conductivity of polymer which exceeds the ceramics' can lead the samples to break easily in the poling electrical field because of a large leak current. Thus the ceramics in composite can not be poled effectively. As the result in this experiment the conductivity of PVDF-containing 20 vol% PANI was very close to the value of the piezoelectric ceramic at 120 °C (Table 1). The PZT ceramics and their composites with polymer were usually be poled at this temperature. This fact may interpret why the d_{33} and k_p of the composite film show the maximum values at PANI volume fraction of 10%. The variation of me-

chanical quality factor in PANI-doped composite can be explained as that the distinction of inner friction contributing to Q_m arising from the interface and polymer is not obvious because of similar composition and structure in PANI-doped PZT/PVDF composite. The variation of Q_m in composite is mainly related with the mechanical energy
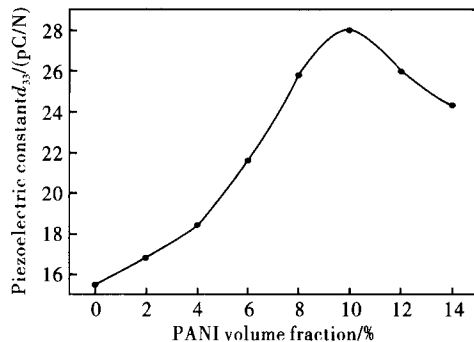

Fig.5   Variation of the piezoelectric constant d_{33} in the composite with PANI content

consumed in the friction of movement in ceramic dipoles in the AC electric field. The mechanical energy consumed in a resonance period can increase with the degree of orientation in dipoles. Thus the fully poled sample doped by an appropriate mount of PANI shows a low Q_m.
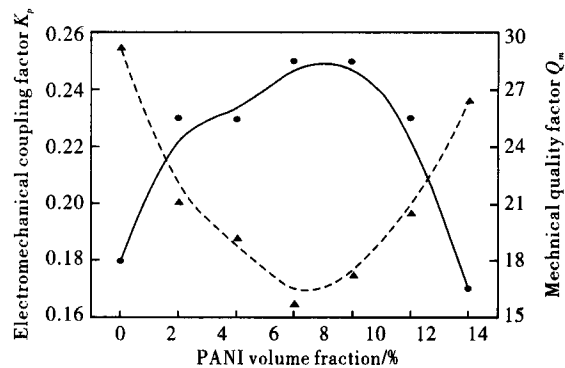

Fig.6   Variation of the electromechnical couping and mechanical quality factor, k_p and Q_m, with PANI content

4   Conclusions

The presence of an appropriate amount of PANI in 0-3 PZT/PVDF composite with PZT volume fraction of 0.5 can increase the polarization and piezoelectric properties obviously. Under the same poling condition, the remanent polarization P_r in PANI-doped composite is much larger than that in the one without PANI. At 8 vol%-10 vol% PANI, the d_{33} coefficient, k_p and Q_m show the extremum values of 28 pC/N, 0.25 and 15.6 respectively. The d_{33} coefficient increases by more than 80% in comparison with the composite without PANI at the dopant content of 10 vol%. The dielectric constant and loss tangent increase monotonously with the increase of dopant.

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