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Nonlinear behavior of 0-3 type ferroelectric composites with polymer matrices

DAI-NING FANG
Department of Engineering Mechanics, Tsinghua University, Beijing 100084, People's Republic of China
E-mail: fangdn@mail.tsinghua.edu.cn

AI. KAH. SOH
Department of Mechanical Engineering, The University of Hong Kong, Hong Kong, People's Republic of China

CHANG-QING LI, BING JIANG
Department of Engineering Mechanics, Tsinghua University, Beijing 100084, People's Republic of China

The nonlinear electric and mechanical behavior of 0-3 type (particle-reinforced) ferroelectric composites with different viscoelastic and dielectric relaxation polymer-matrixes was observed experimentally. The analysis of the experimental results was carried out in the present study by examining the effects of the viscoelasticity and dielectric relaxation of the polymer matrices, the loading rate and the volume fraction of the PZT particles on the nonlinear behavior of the composites. The composite sample was isolated from the test frame to prevent high voltage arcing in the setup, which was employed to make precise measurement to systematically provide experimental results. Using a high voltage amplifier and a servo-hydraulic test frame, the hysteresis loops of electric displacement versus electric field at different loading amplitudes and rates, and the piezoelectric curves of the ferroelectric composites were measured. The results show that the effects of viscoelasticity and dielectric relaxation of the matrices on the electric and mechanical behavior of the ferroelectric composites are significant. The nonlinear behavior of ferroelectric composites with a viscoelastic and dielectric relaxation matrix is also related to the frequency of the applied loads.

1. Introduction

In general, ferroelectric composites are made of ferroelectric inclusions and non-piezoelectric matrix. These composites can be used as sensors in many fields such as smart materials and structures [1–8]. The most commonly employed matrix material for making ferroelectric composites is polymer. The molecule chains of polymers, some of which have polarities, are very long and are, thus, flexible. Therefore, polymers exhibit viscoelasticity and dielectric relaxation in mechanical and electric behavior, respectively, which can affect the electromechanical behavior of ferroelectric composites significantly. Since Newnham *et al.* [5] put forward the concept of connectivity in 1978, a lot of theoretical and experimental work has been carried out. However, most of the work was on the prediction of the effective electroelastic properties of piezoelectric composites based on the hypothesis of series or parallel connection. Due to the complexity of nonlinear electromechanical behavior related to viscoelasticity and dielectric relaxation, and the lack of acceptable theoretical modeling on constitutive relations, the experimental study becomes very important. For example, the experimental studies on the effective electroelastic moduli and the polarization problem of 0-3 type ferroelectric composites were carried out by Furukawa *et al.* [9, 10] and Yamada *et al.* [11]. Chan *et al.* [12] have also studied experimentally the effective properties of 1-3 type ferroelectric composites. Moreover, the piezoelectric and dielectric properties of piezoelectric composites were observed experimentally by many others [13–16]. However, the experimental investigations on ferroelectric composites were limited to the linear properties of ferroelectric composites except for the polarization problems. In other words, little attention has been paid to the non-linear properties induced by domain switching in ferroelectric composites. Furthermore, a polymer such as Epoxy resin, which has no polarization and has very small dielectric relaxation, was often used as matrix materials for making ferroelectric composites in the past years. Therefore, the effect of dielectric relaxation of the matrix on the electromechanical properties was not well studied. It is worth noting that the dielectric relaxation of some polymers such as F-24 is very strong. Hence, the electromechanical coupling behavior of ferroelectric composites with such polymer matrix is very complicated. To-date, systematically experimental investigations on the nonlinear behavior of such ferroelectric composites has not been reported.

In the present investigation, an experimental study was carried out on the nonlinear electric and mechanical behavior of four kinds of 0-3 type ferroelectric composites, in which the polymer-matrices with viscoelasticity and dielectric relaxation were reinforced by different PZT particles. The detailed analysis of the experimental results is presented in this paper. The effects of the viscoelasticity and the dielectric relaxation of the polymer matrices, the loading rate and the volume fraction of the PZT particles on the nonlinear behavior of the composites are examined.

2. Experimental procedure
2.1. Specimen preparation
The material chosen for this investigation was the 0-3 type ferroelectric composite. Two kinds of ferroelectric ceramic powders, i.e., PZT-5A and PZT-2, were employed to make the ferroelectric phase of the composites. Three kinds of polymers, which are the non-piezoelectric epoxy resin, F-24 (PVDF + PTFE) and the unpoled PVDF, were employed as matrix materials. Note that the poled PVDF is a piezoelectric polymer, but it can be poled only under a strict condition with an extremely high electric field. Under our testing conditions, it cannot be poled and, therefore, it did not have piezoelectricity.

Five different kinds of 0-3 type ferroelectric composites, i.e., the PVDF matrix with 17% PZT-5A particles, the epoxy resin with 17% PZT-5A particles and the F-24 matrix with 10%, 30% and 65% PZT-2 particles. The composites were produced in a rolling process by a heat-rolling machine. Note that the particles are randomly distributed in the matrix. The specimens, with nominal dimensions 10 mm × 10 mm × 16 mm, were cut from the bulk ferroelectric composites, and all faces were polished. The upper and lower faces of the specimens with an area of 10 mm × 10 mm were electroded with sputtered Ag. That is, the poling direction is vertical to the upper and lower faces and parallel to the long side of the cubed specimen.

2.2. Experimental setup
The electric hysteresis loop and the butterfly-shape curve are two main nonlinear characteristics of ferroelectric materials. The hysteresis loops of strain versus electric field and electric field versus electric displacement were recorded using a modified Sawyer-Tower circuit, as shown in Fig. 1. A servo-hydraulic loading fixture was set up for applying stresses to a polarized sample. Since the thickness of the samples was large (about 15 mm), a very high voltage was required in order to reach the coercive electric field of the ferroelectric inclusion. Hence, the samples were placed in a silicone oil bath to prevent high voltage arcing.

With reference to Fig. 2, the sample was isolated from the fixture by two alumina and one ethoxyline blocks. The high voltage arcing was prevented effectively by the silicon oil bath and a ringed ethoxyline block in the middle of the sample. For protecting the strain gauges from the high voltage arcing, these gauges must be bonded to the area near the ground electrode and covered by a special isolated-glue. To avoid the bending stress and the inhomogeneous distribution of the stress, the upper and lower faces of both the aluminum and the ethoxyline blocks were kept parallel (misalignment <0.01 mm). Besides, one spherical cone was incorporated in the setup. Moreover, to ensure that the upper and lower faces were parallel to each other, the sample was polished again after the two faces were electroded. A 50 KN load sensor was installed on the test fixture to monitor the applied force on the specimen. The load sensor output was recorded through the A/D circuit, which was connected to the computer. The stress was determined from the force and the cross sectional area of the specimen.

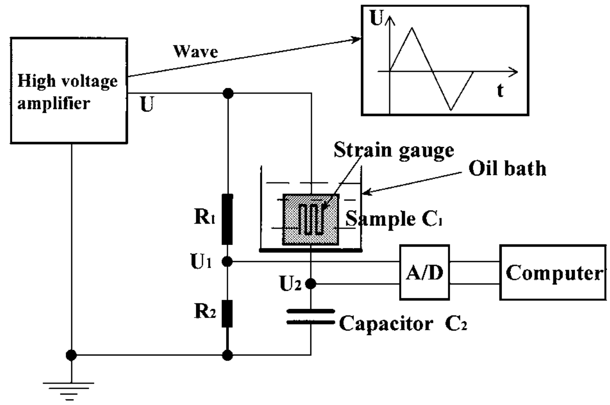

Figure 1 Approach of taking test measurements. The electric displacement is monitored by voltage U2 and the electric field is measured by voltage U1.

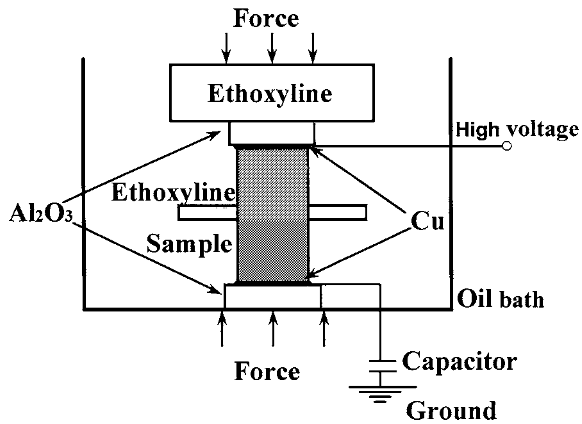

Figure 2 Schematic of the electric-mechanical loading system.

2.3. Experimental procedure
2.3.1. Measurement of electric displacement
A high voltage source was connected to the upper electrode of the specimen. This voltage source created a triangular wave of ±30 KV with frequency from 1 HZ to 0.003 HZ. A reference signal (1/10000 times the output) was provided by the source. This reference signal was recorded through the A/D circuit connected to the computer. By multiplying this signal by 10000 times and divide it by the thickness, the applied electric field can be

obtained. The charge per unit area on the electrode was equal to the normal component of the electric displacement. The charge on the electrode was measured by monitoring the voltage of a capacitor (10 μF) connected from the lower electrode of the specimen to the ground. The voltage of the capacitor was monitored by means of a high input impedance electrometer and the A/D circuit connected to the computer. Thus, the hysteresis loops of electric field versus electric displacement for ferroelectric composites can be obtained. Many important parameters, such as the remanent polarization and coercive field, can then be obtained from the hysteresis loops.

2.3.2. Measurement of strain

Strain gauges were bonded to the center of the area near the lower electrode to measure the strains parallel and perpendicular to the polarization direction. The strain gauges were connected to a Wheastone Bridge and an A/D circuit that was connected to the computer.

2.3.3. Measurement of piezoelectric curve

When the specimen was subjected to compressive stress, the 90° domain switching occurred in the ferroelectric phase of the composite. This phenomenon led to the decrease of the overall remanent polarization of the composite and finally gave rise to the lost of the electromechanical coupling properties of the composite. The stress versus electric displacement curve is called the piezoelectric curve. To avoid the bending stress and the inhomogeneous distribution of stresses, a specially designed loading setup was employed in which one spherical cone was incorporated. Moreover, to ensure that the upper and lower faces were parallel to each other, the sample was polished again once the two faces have been electroded.

3. Experimental results and analysis

By subjecting the specimen to an electric field with different frequencies, the hysteresis loops of electric displacement versus electric field were recorded, and

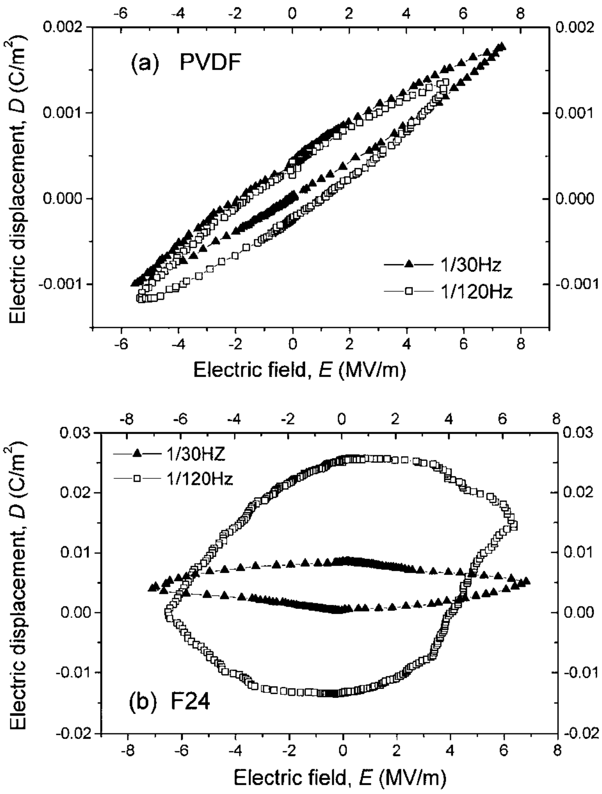

Figure 3 Plots of electric field versus electric displacement for matrix materials at an applied cyclic electric field of 7 MV/m with two loading frequencies of 1/30 Hz and 1/120 Hz: (a) PVDF matrix; (b) F24 matrix.

when a compressive stress was applied, the piezoelectric curves of stress versus electric displacement were also recorded. All experimental results are presented in Figs 3 through 10. The measured electric and mechanical properties of the materials are presented in Table I, which shows that both F24 and PVDF are not piezoelectric.

3.1. Behavior of the matrix materials

Firstly, the behavior of two matrix materials, i.e., the unpoled PVDF and F-24, was observed. The stable curves

TABLE I Electric and mechanical properties of materials[a]

Electromechanical properties		PZT-2	PZT-5A	F-24	PVDF
Elastic moduli	C_{1111} (Gpa)	135	121	8.0	8.0
	C_{1122} (Gpa)	84.1	75.4	4.4	4.4
	C_{1133} (Gpa)	83.9	75.2	4.4	4.4
	C_{3333} (Gpa)	113	111	8.0	8.0
	C_{1313} (Gpa)	23.5	21.1	1.8	1.8
Piezoelectric constants	e_{311} (C/m^2)	−1.9	−5.4	0	0
	e_{333} (C/m^2)	9.0	15.8	0	0
	e_{131} (C/m^2)	9.8	12.3	0	0
Dielectric constants	k_{11}^{ε}/k_o	504	916		
of PZT particles	k_{33}^{ε}/k_o	260	830		
	k_{11}^{σ}/k_o	990	1730		
	k_{33}^{σ}/k_o	450	1700		
Dielectric constants	κ^0/k_o			660	50.5
of matrixes	κ^1/k_o			−660	−34.2
Spontaneous strain	$\varepsilon_{11}^{\#}=\varepsilon_{22}^{\#}$	-2.52×10^{-4}	-2.52×10^{-4}		
	$\varepsilon_{33}^{\#}$	5.04×10^{-4}	5.04×10^{-4}		
Spontaneous polarization	$P_3^{\#}$ (C/m^2)	0.253	0.253		
Coercive field	E_c (MV/m)	0.75	0.75		
Dielectric relaxation time	$\tau=1/\nu$ (s)			48.2	8.03

[a]the permittivity of the free space, $k_o = 8.85\times10^{-12}$ C/Vm^2.

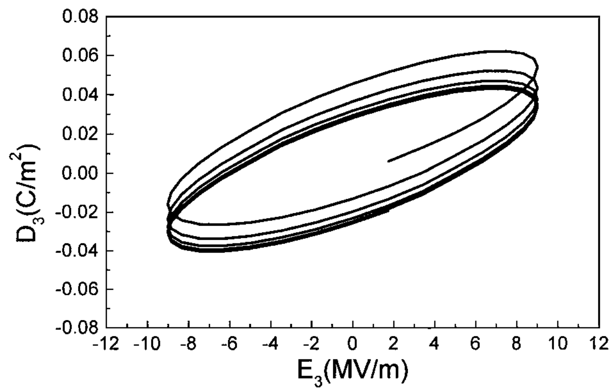

Figure 4 Actual hysteresis loops of dielectric relaxation materials.

of electric displacement versus electric field for these two materials, subjected to an applied electric field of amplitude 7 MV/m with two loading frequencies, were recorded as shown in Fig 3a and b, respectively. In fact, for the dielectric relaxation material, the real hysteresis loops are as shown in Fig. 4. At the initial loading stage, the hysteresis loops are like screw loops, but they become stable once the loading time is larger than the relaxation time of the material. In the subsequent analyses, only the stable curves were studied. From the experimental results, some conclusions for the two matrix materials can be drawn as follows:

(a) The strength of the relaxation property of the material is mainly related to the dielectric relaxation time, τ. The larger the τ, the stronger is the relaxation property of the material.

(b) The saturation polarization and coercive field of both PVDF and F24 are very large. It is very difficult to establish an experimental setup to completely pole these two kinds of polymer matrices so that they do not possess piezoelectricity under our testing conditions.

(c) The electric displacement is dependent upon the loading frequency. The smaller the frequency, the larger is the electric displacement.

(d) The stronger the relaxation property of the material, the more significant is the effect of the loading frequency on the hysteresis loops. The relaxation property of F-24 is stronger than that of PVDF, therefore, F-24 is more sensitive to the loading frequency than PVDF.

3.2. Electric field versus electric displacement hysteresis loops

In the case of F-24 matrix ferroelectric composite reinforced with PZT-2 particles of three different volume fractions of 10%, 30% and 65%, the curves of electric displacement versus electric field, due to the applied electric field of different amplitudes with frequency 1/100 Hz, are shown in Fig. 5a through c. It can be seen from Fig. 5 that the hysteresis loops are affected by both the volume fractions of the PZT particles and the applied electric field amplitude. The saturation polarization and coercive field of the composites are extremely large since the size of the loops increase with the increase of the applied electric field amplitude. The hysteresis loops for the PVDF matrix composite with

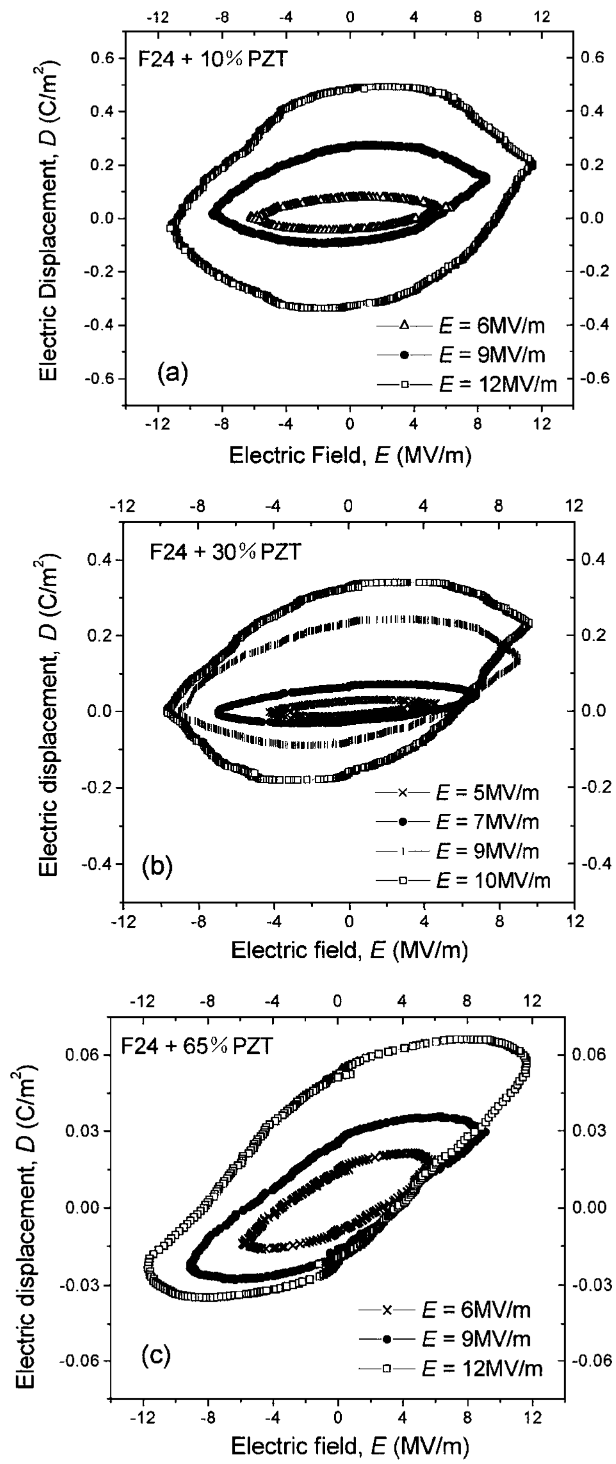

Figure 5 Hysteresis loops of electric field versus electric displacement for the F-24 matrix composites subjected to different applied electric field amplitudes with a constant loading frequency of 1/100 Hz: (a) with 10% PZT-2 particles; (b) with 30% PZT-2 particles; (c) with 65% PZT-2 particles.

17% PZT-5 particles and the epoxy matrix composite with 17% PZT-5 particles due to different applied electric field amplitudes with frequency 1/100 Hz are presented in Fig. 6a and b, respectively. By comparing Figs 5 and 6, one can clearly see that for the composite with F24 matrix, the remanent polarization is still increasing even when the applied electric field is reduced from its maximum value. Moreover, the maximum value of the remanent polarization is increased when the electric field is reduced to zero, which means that this type of ferroelectric composite has a strong dielectric

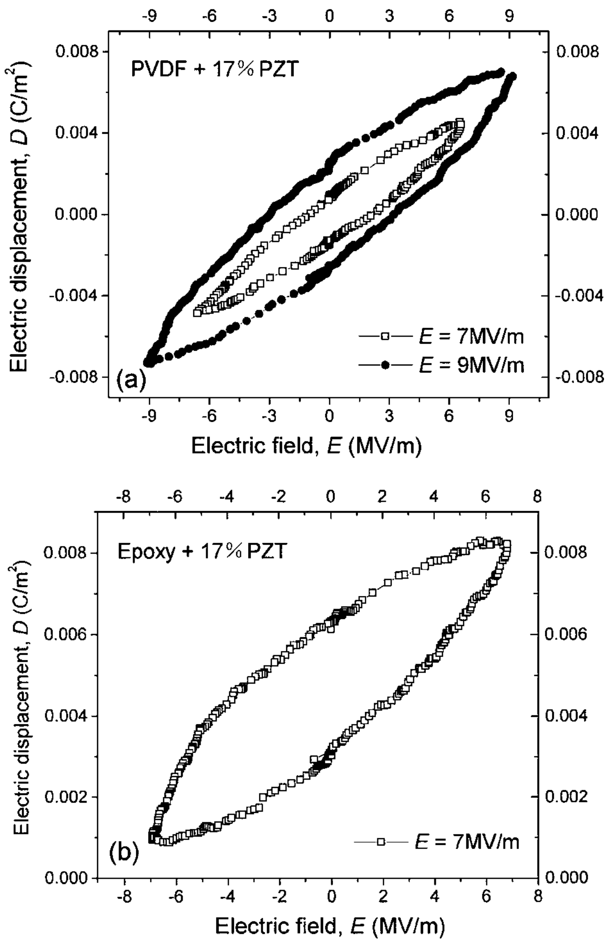

Figure 6 Hysteresis loops of electric field versus electric displacement subjected to different applied electric field amplitudes with a constant loading frequency of 1/100 Hz: (a) the PVDF matrix composite with 18% PZT-5A particles; (b) the epoxy matrix composite with 17% PZT-5A particles.

relaxation. However, one cannot find such characteristics from the hysteresis loops of both the PVDF and the epoxy matrix composites, as shown in Fig. 6. This shows that these two composites did not have significant dielectric relaxation, which was due to the fact that the strength of the relaxation property of the material is closely related to the dielectric relaxation time, τ. It can be seen from Table I that the dielectric relaxation time, τ, of the F24 matrix is one order larger than that of the PVDF matrix. However, our experimental results show that when the amplitude of the applied electric field was very large, the PVDF-matrix composite also clearly exhibited dielectric relaxation.

Fig. 5 shows that the remanent polarization decreased with the increase of the volume fraction of the PZT-2 particle, which means that the dielectric property of the F24 matrix is even stronger than that of the PZT-2. However, by comparing Figs 6a and 3a, we found that the remanent polarization increased with the increase of the volume fraction of the PZT-5 particle. This may be because the dielectric property of PZT-5 is even stronger than that of the PVDF matrix. The same conclusion might be made from the dielectric constants listed in Table I. It has been mentioned above that the dielectric relaxation of the F24 matrix is considerably strong, refer to Fig. 3b. But, the increase of the volume fraction of the PZT-2 particle will reduce the dielectric relaxation of the ferroelectric composite, which can be seen from Fig. 5a through c. The shape change of the hysteresis loops in Fig. 5 caused by the increase of the PZT volume fraction evidently reflects the change of the dielectric relaxation. Finally, Figs 5 and 6 show that under the conditions of same volume fraction and loading frequency, the larger the electric field, the larger is the coercive field of the composite. The reason is that due to the dielectric relaxation of the matrix, when the applied electric field is reversed in direction, the positive electric field still work on the ferroelectric inclusions, which makes the local field on the ferroelectric inclusions smaller than the applied electric field. The larger the applied electric field, the more obvious is the phenomenon of the counter-interaction between the positive and the negative electric fields.

Fig. 7 illustrates the hysteresis loops of the composites with different matrices subjected to an applied electric filed of amplitude 7 MV/m and loading frequency 1/100 Hz. It can be seen from Fig. 7 that at the same loading amplitude and frequency, the remanent polarization of the F24-matrix composite is far larger than that of the PVDF-matrix and epoxy-matrix composites. This is due to the fact that the dielectric constant of the F24 matrix is one order higher than that of the PVDF and the epoxy matrices, as shown in Table 1. Fig. 7b shows that the hysteresis loop of the PVDF matrix

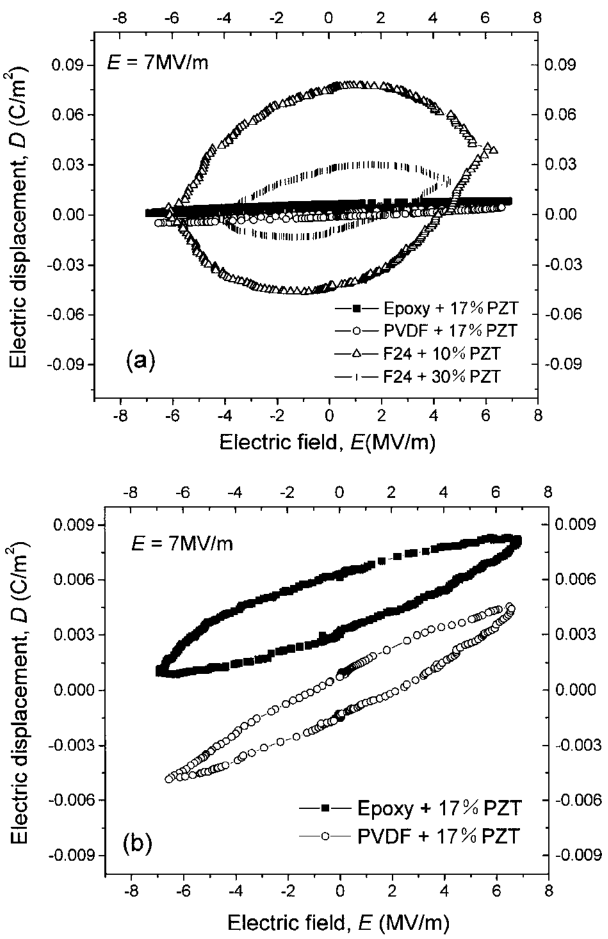

Figure 7 Comparison of the matrix materials for the hysteresis loops of electric field versus electric displacement subjected to an applied electric field of amplitude 7 MV/m and loading frequency 1/100 Hz: (a) different composites with four kinds of the matrix materials; (b) the PVDF-matrix and epoxy-matrix composites with 17% PZT-5A particles.

composite is similar to that of the epoxy matrix composite and both of them do not exhibit significant dielectric relaxation. However, the electric displacement of the former is less than that of the later. This is due to the fact that the dielectric constant of PVDF is smaller than that of the epoxy resin. It can be clearly seen from Fig. 7 that the property of the matrix significantly affects the nonlinear behavior of the composite.

Due to the viscoelasticity of the polymer matrices, the loading rate will affect the remanent polarization and coercive field of the composites. In order to examine the effect of the loading rate upon the hysteresis behavior, three loading frequencies of 1/20 Hz, 1/60 Hz and 1/360 Hz were selected to test the F24-matrix composites with two PZT volume fractions. It can be observed from Fig. 8a and b that for the composite with 10% PZT-2 particles, when the frequency is small, that is, when the loading rate is low, the electric displacement increases even when the electric field reduces from its maximum point. This shows that the dielectric relaxation is significant. Because of the small volume fraction of the PZT-2 particle, the shape of the hysteresis loop of the composite is similar to that of the F-24 matrix material. This means that the property of the matrix dominates the behavior of the composite when both the volume fraction of the PZT particle and the loading frequency are low. Moreover, it is worth noting that the electric displacement in the case of fast loading is much smaller than that of slow loading. This indicates the strong influence of the viscoelasticity of the matrix on the hysteresis behavior. With reference to Fig. 8, when the loading rate is increased from that of 1/360 Hz, the hysteresis loop changes from that of slow loading. It is reasonable to assume that domain switching occurs at the faster loading rate. In other words, the faster the loading rate, the more significant is the effect of the properties of the ferroelectric phase on the electromechanical behavior of the composite. In addition, the loading rate also affects the coercive field of the composite. This can be clearly seen from Fig. 8a and b in which the current coercive field of the composite increases with the increase of the loading rate.

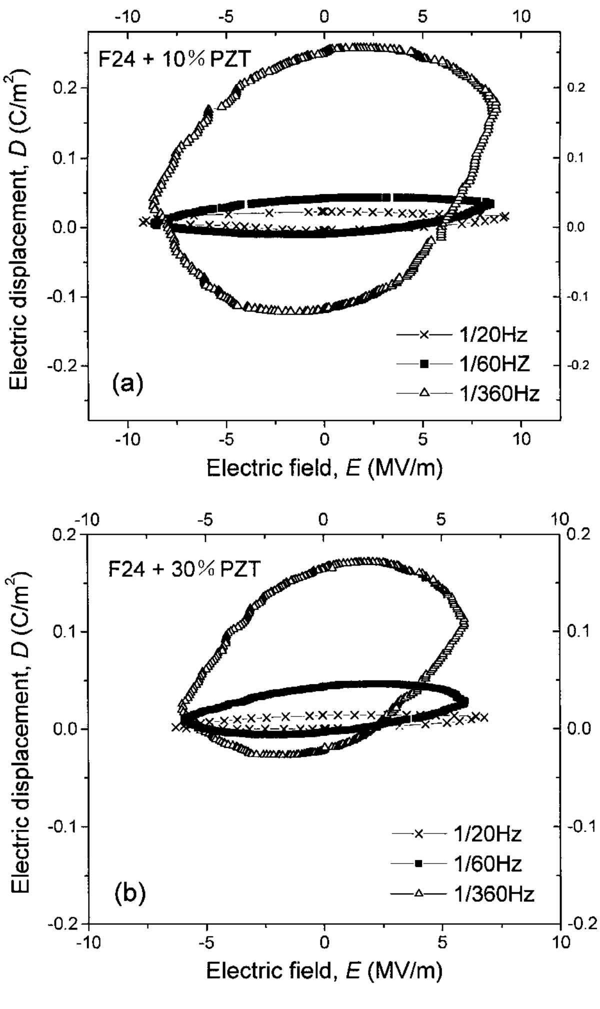

Figure 8 Effects of the loading frequency on the hysteresis loops of electric field versus electric displacement for the F24 matrix composites subjected to an applied electric field of amplitude 7 MV/m with three different loading frequencies of 1/20 Hz, 1/60 Hz and 1/360 Hz: (a) with 10% PZT-2 particles; (b) 30% PZT-2 particles.

3.3. Piezoelectric curves

Figs 9 and 10 show the measured piezoelectric curves, i.e., axial compressive stress versus electric displacement, for four kinds of composites, namely, the PVDF

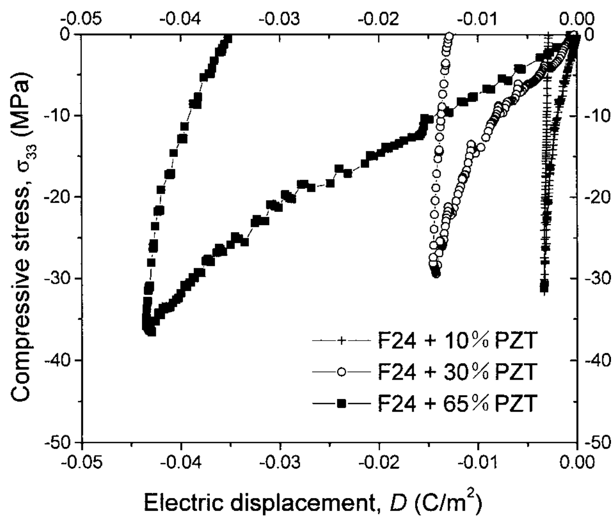

Figure 9 Piezoelectric curves of the F24 matrix composites with 10% , 30% and 65% PZT-5A particles.

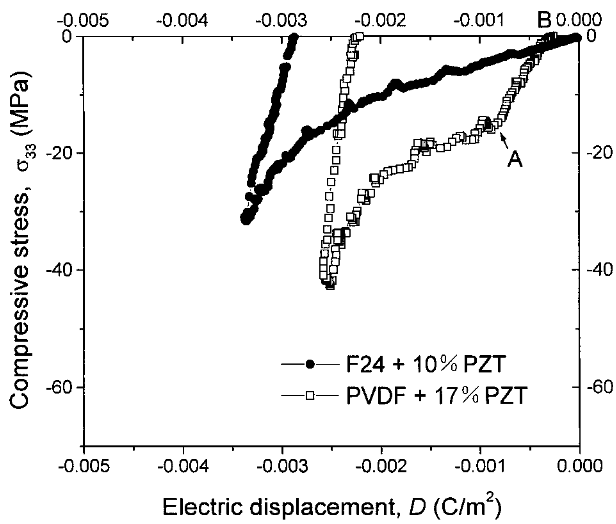

Figure 10 Piezoelectric curves of the PVDF and F24 matrix composites with 18% PZT-5A and 10% PZT-2 particles, respectively.

matrix with 17% PZT-5A particles and the F-24 matrix with 10%, 30% and 65% particles. With reference to Fig. 9, for the composite with F24 matrix, the remanent electric displacement increases with the increase of the volume fraction of the ferroelectric inclusions. Moreover, for the composite with a larger volume fraction of PZT particle, a larger compressive stress is required in order to obtain the piezoelectric curve. In addition, unlike the piezoelectric curves of the PZT ceramics, there is neither a linear region nor a clear turning point corresponding to the coercive stress in the three curves shown in Fig. 9. This may be due to the effects of dielectric relaxation and/or the viscoelasticity of the matrix. It has been mentioned above that the dielectric relaxation of the F-24 material is strong and so is its viscoelasticity. Whereas, the dielectric relaxation of the PVDF material is quite weak and so is its viscoelasticity. Therefore, the coercive stress in the piezoelectric curve of the composite of PVDF + 17% PZT shows both a linear loading region (segment AB) and an obvious turning point A, as shown in Fig. 10. Hence, it is obvious that the effects of the viscoelasticity and dielectric relaxation of the matrix material on the electromechanical behavior should be taken into account carefully, in the design and analysis of the ferroelectric composites with a polymer matrix.

4. Conclusions

In this paper, the experimental analysis of the electric and mechanical behavior of ferroelectric composites with a viscoelastic and dielectric relaxation matrix was carried out. It was found that the hysteresis loops and the piezoelectric curves depend not only on the volume fraction of the PZT inclusions, but also on the loading frequency. This was due to the dielectric relaxation and the viscoelasticity of the polymer matrix. The analysis shows that the effects of viscoelasticity and dielectric relaxation of the matrix on the electromechanical coupling behavior of ferroelectric composites are significant and, therefore, can not be neglected in engineering applications. Some specific conclusions are as follows:

(1) The strength of the dielectric relaxation property of both the composites and the matrix materials are mainly related to the dielectric relaxation time, τ. The larger the τ, the stronger is the relaxation property of the materials.

(2) In the case of same volume fraction and loading frequency, the larger the electric field, the larger is the coercive field of the composite. The saturation polarization and coercive field of both the composite and matrix materials are very large. It is very difficult to establish an experimental setup to completely poled the F24 and PVDF polymer matrices, so that they do not possess piezoelectricity under our testing conditions.

(3) At the same loading amplitude and frequency, the remanent polarization of the F24-matrix composite is much larger than that of both the PVDF-matrix and epoxy-matrix composites. This is due to the fact that the dielectric constant of the F24 matrix is one order higher than that of the PVDF and the epoxy matrices.

(4) The effect of the PZT volume fraction on the nonlinear behavior of the composite is dependent on the ratio of the dielectric property of the matrix to that of the PZT particle. For example, the remanent polarization decreases with the increase of the volume fraction of the PZT-2 particle. This means that the dielectric property of the F24 matrix is even stronger than that of the PZT-2 particle. But, the remanent polarization increases with the increase of the volume fraction of the PZT-5 particle because the dielectric property of PZT-5 particle is even stronger than that of the PVDF matrix.

(5) The electric displacement is dependent upon the loading frequency. The smaller the loading frequency, i.e., the slower the loading rate, the larger is the electric displacement. The stronger the relaxation property of the material, the more significant is the effect of the loading frequency on the hysteresis loops. The relaxation property of the F-24 material is stronger than that of the PVDF material, therefore, the composite with F-24 matrix is more sensitive to the loading frequency than that with the PVDF matrix. In addition, the faster the loading rate, the more significant is the effect of the properties of the ferroelectric phase on the electromechanical behavior of the composite.

(6) The piezoelectric curve is affected both by the relaxation property of the matrix and the volume fractions of the PZT particle. The remanent electric displacement increases with the increase of the volume fraction of the ferroelectric inclusions. One needs to apply a larger compressive stress to the composite with a larger volume fraction of PZT particle to obtain the piezoelectric curve. If the dielectric relaxation and viscoelasticity of the polymer matrix are weak, the coercive stress shows both a linear loading region and a turning point in the piezoelectric curve of the ferroelectric composite.

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