

Enhanced electromechanical properties in all-polymer percolative composites

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In this letter, we discuss the enhanced electrostriction and dielectric constant in an all-polymer percolative composite consisting of poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE)] terpolymer matrix and polyaniline (PANI) conductive particles. Using a self-consistent approach, we calculate the dielectric constant and dielectric loss tangent of the composite in excellent agreement with experiments, and demonstrate that the electrostriction enhancement is due to the electric field fluctuation in P(VDF-TrFE-CTFE) matrix, which becomes dominant when the dielectric constant of the second phase is much larger than that of the matrix. The inhomogeneous field distribution in the matrix has also been used to estimate the breakdown field of the composite, which agrees well with experimental measurement. The study could be used to design and optimize electrostrictive composites with optimal electromechanical properties. © 2004 American Institute of Physics. [DOI: 10.1063/1.1702127]

Materials with large electromechanical coupling are attractive for a broad range of applications such as sensors and actuators. Recently, enhanced dielectric constant and giant electrostriction have been demonstrated in an all-polymer percolative composite consisting of poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE)] terpolymer matrix and polyaniline (PANI) conductive particles,^{1,2} where the dielectric constant as high as 6000 and the electrostrictive strain as high as 2.5% have been obtained at a modest applied electric field about 10 MV/m. In contrast, electric field one order higher in magnitude is required to achieve the same amount of strain in P(VDF-TrFE-CTFE) terpolymers, suggesting that the effective electrostrictive coefficient of the all-polymer composite is almost two orders higher than its matrix. While it is generally believed that the much enhanced electrostriction is related to the enhanced dielectric constant of the composite near percolation limit, the exact nature of the enhancement is not clear, which we seek to clarify in this letter.

Electrostriction refers to the strain ε in materials induced by polarization, which is proportional to the square of the electric field E , $\varepsilon = ME^2$, where M is the field related electrostrictive coefficient.³ The electrostrictive effect is universal in dielectrics although it is negligibly small in most materials. To overcome this difficulty, composite concept has been proposed to enhance the electrostriction of materials, where a dielectrically soft second phase is embedded in a dielectrically hard electrostrictive matrix to magnify the electric field^{4,5} or polarization^{6,7} in the matrix. The polarization enhancement has recently been demonstrated in a poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer based all-organic composites,⁷ where electrostrictive

strain as high as 2% has been obtained. However, the exchange-coupling based mechanism⁶ is not applicable for this percolative composite, since no polarization can be induced in the conductive particles. This suggests that the electrostriction enhancement in the percolative composite is due to the electric field enhancement in the P(VDF-TrFE-CTFE) matrix, but the uniform field enhancement proposed in Ref. 4 cannot be used to explain the large increase of the electrostriction in the all-polymer composite, since the enhancement is limited by $1/c_1$ under this mechanism, and thus cannot provide more than a factor of 2 in the magnification of the electrostriction, far less than those observed in the experiment. Here c_1 , the volume fraction of the P(VDF-TrFE-CTFE) terpolymer, is less than 25% in the all-polymer composite.^{1,2} As such, we have to look into the electric field fluctuation in the matrix.

We propose that the large electrostriction enhancement in the all-polymer percolative composite is due to the inhomogeneous field distribution in P(VDF-TrFE-CTFE) terpolymer matrix, which on average is much larger than the applied field at the boundary. In another word, the field fluctuation in the matrix lead to much higher enhancement than would be obtained if the electric field in matrix is uniform. To support this claim, we consider the effective dielectric constant κ of the composite first, which can be derived using the self-consistent approach as⁸

$$\kappa = \frac{1}{4} \{ (2 - 3c_2)\kappa_1 + (3c_2 - 1)\kappa_2 + \sqrt{8\kappa_1\kappa_2 + [(3c_2 - 2)\kappa_1 + (1 - 3c_2)\kappa_2]^2} \}, \quad (1)$$

where κ_1 and κ_2 are the dielectric constants of matrix and particle, and c_2 is the volume fraction of the particles. Spherical particle is assumed in the derivation. From Eq. (1), it is clear that if $\kappa_2 \gg \kappa_1$, there would be a critical volume

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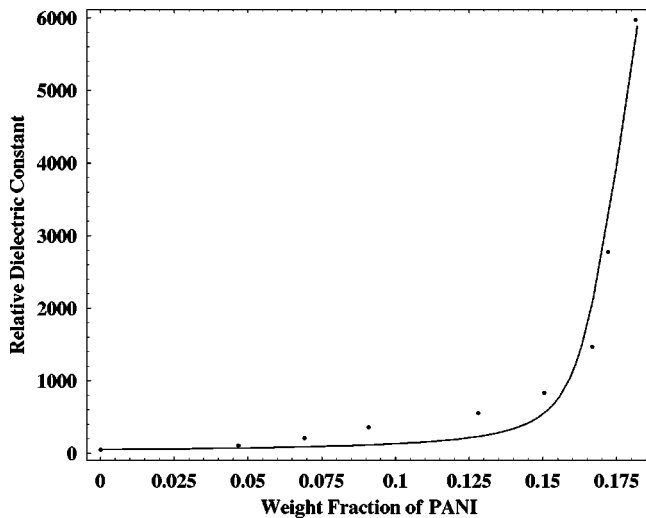


FIG. 1. Effective dielectric constant κ of the percolative composite as function of the weight fraction of PANI; the dots are experimental data.

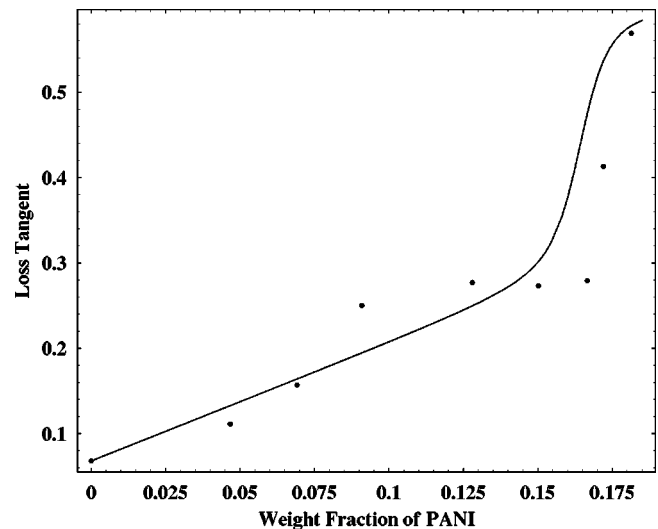


FIG. 2. Loss tangent of the percolative composite as function of the weight fraction of PANI; the dots are experimental data.

fraction $c_2=1/3$ beyond which the dielectric constant of the composite will increase dramatically, corresponding to a percolation transition. This is indeed observed in our calculation as shown in Fig. 1, which agrees with experimental measurement very well. Similar experimental data have also been reported by other authors.⁹ In the calculation, we used the volume fraction of the particles as $c_2=1.4\alpha w$, where w is the weight fraction of PANI measured from the experiment, 1.4 is the conversion factor between volume fraction and weight fraction calculated from densities of P(VDF-TrFE-PTFE) and PANI, and $\alpha=1.45$ is a dimensionless parameter used to account for the charge injection near the interface between the matrix and particles,¹ which corresponds to an interface thickness of 33 nm for particle size of 1 μm . In principle α should be determined from the microscopic model, but due to the lack of information, we just take an empirical value. The complex dielectric constant $\kappa_1=52[1+0.68(1+c_2\beta)i]$ is measured from the experiment, with the exception that $c_2\beta$ is used to account for the dielectric loss at the interface, where β is taken to be 10. The complex dielectric constant of PANI was measured in Refs. 10 and 11, which was reported to be sensitive to doping and frequency. In particular, dielectric constant over 10^5 with large loss tangent has been observed. Here, the complex dielectric constant is assumed to be $\kappa_2=(1+0.6i)10^5$, which is consistent with experiment measurements. The dielectric loss tangent as a function of the weight fraction of PANI is shown in Fig. 2, as evaluated from $\tan \delta=\kappa''/\kappa'$, where superscript r and i are used to denote the real and imaginary part of the dielectric constant. Again, good agreement between our calculation and experiment is observed. From Figs. 1 and 2, it is clear that there is a percolation transition near $w=0.15$ for both dielectric constant and dielectric loss tangent, and our self-consistent approach is able to predict this transition. We need to point out that the quantitative agreement between the self-consistent model and experiments relies on the parameters α and β we choose, and the model should not be applied beyond the percolation transition.

The dielectric constant κ of composite also allows us to determine the electric field concentration factor a of the matrix⁸

$$a = \frac{\kappa - \kappa_2}{c_1(\kappa_1 - \kappa_2)}, \tag{2}$$

from which the average field in the matrix, \bar{E}_1 , can be determined as $\bar{E}_1 = aE_0$, where E_0 is the applied electric field at the boundary, and the overhead bar is used to denote volume averaged variables. Since $\kappa > \kappa_1$, a is greater than 1, and the electric field in the P(VDF-TrFE-CTFE) matrix is indeed magnified compared to the applied field. However, as we mentioned, a homogeneous magnification of electric field in the matrix is not sufficient to explain the dramatic electrostriction enhancement in the composite, and we must look into the fluctuation of electric field in the matrix. To this end, we recall that the second moment of the electric field in the matrix, $\langle E_1^2 \rangle$, can be determined from the variation of the dielectric constant of the composite as¹²

$$\langle E_1^2 \rangle = \frac{1}{c_1} \frac{\delta \kappa}{\delta \kappa_1} E_0^2, \tag{3}$$

which was established rigorously for a more general heterogeneous piezoelectric solid with macroscopic homogeneity.¹² The average electrostrictive strain of the matrix, $\bar{\epsilon}_1$, is then determined from the second moment of the field

$$\bar{\epsilon}_1 = M_1 \langle E_1^2 \rangle, \tag{4}$$

where M_1 is the electrostrictive coefficient of P(VDF-TrFE-CTFE). Notice that our previous model ignored the fluctuation of electric field in the matrix⁴ and used the square of the average electric field, \bar{E}_1^2 , rather than the second moment of the electric field, $\langle E_1^2 \rangle$, in the calculation. When there is a large contrast of dielectric constant between two phases, this approximation may lead to a large error. The calculated strain-electric field curves for the composite with 12.7% of PANI are shown in Fig. 3, where both average field and second moment of field are used in the calculations. It is clear that the calculations using the average field underestimate the electrostriction significantly, while those using second moment have much better agreement with experiments. This suggests that the electrostriction enhancement is due to the inhomogeneous electric field enhancement in the matrix. AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

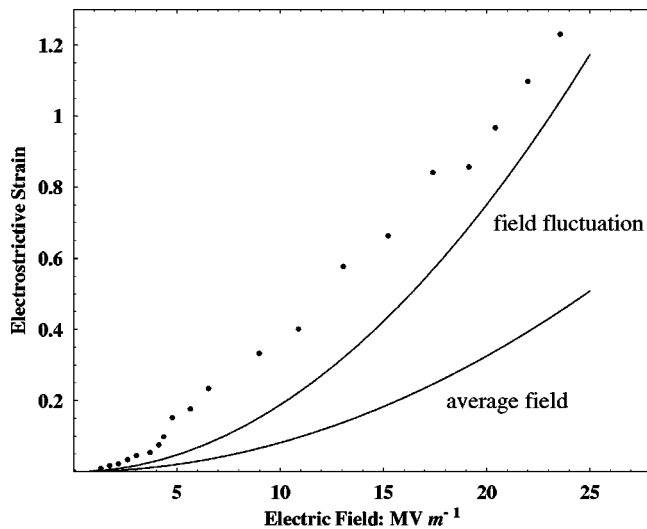


FIG. 3. Electrostrictive strain of the percolative composite as function of the electric field; the dots are experimental data.

Our calculation still underestimates the strain, probably due to the fact that we ignored piezoelectric effect and Maxwell stress. In the calculations, M_1 is taken to be $3.62 \times 10^{-4} \text{ m}^2/\text{MV}^2$, as measured from the experiment.

Our argument is further supported by the analysis on the breakdown field of the percolative composites. If the average field in the matrix, $\bar{E}_1 > E_b$, is used as the breakdown criterion, where E_b is the breakdown field of single phase P(VDF-TrFE-PTFE), the breakdown strength will be overestimated significantly. This is not surprising, since the breakdown starts from the local field concentration. As such, we propose to include the field fluctuation in the breakdown criterion

$$\bar{E}_1 + \sqrt{\langle E_1^2 \rangle - \bar{E}_1^2} > E_b, \quad (5)$$

which provides breakdown predictions in good agreement with experiments, much better than those using average field, as shown in Fig. 4. It is noted that in the low weight fraction of PANI, our calculations underestimate the breakdown field, since at the low volume fraction of PANI, the local breakdown as predicted using Eq. (5) does not necessarily lead to global breakdown. On the other hand, at higher weight fraction, our model overestimates the breakdown strength, since it is necessary to consider higher order moment of the electric field in the matrix when the volume fraction of PANI increases. Local inhomogeneity and defects also play a role in the breakdown of the composite.²

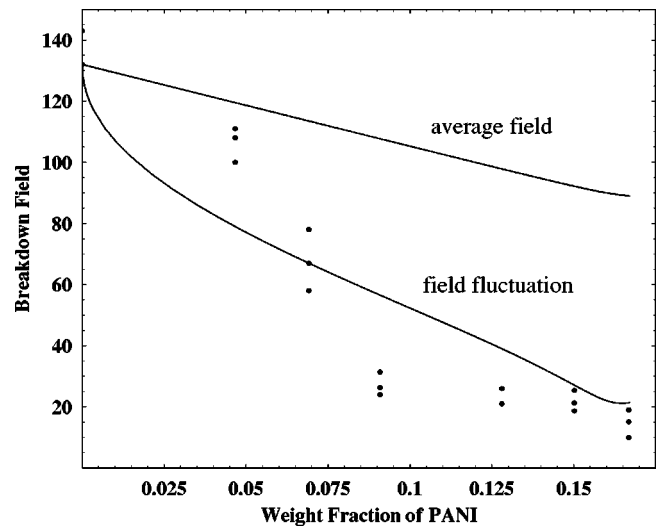


FIG. 4. Breakdown field of the percolative composites as function of the weight fraction of PANI; the dots are experimental data.

In summary, we demonstrated that the inhomogeneous electric field distribution in P(VDF-TrFE-PTFE) terpolymer matrix can lead to much enhanced electrostriction and dielectric constant in the all-polymer percolative composites, and we obtained good agreement between our analysis and experimental measurements for dielectric constant, dielectric loss, breakdown field, and electrostrictive strain of the percolative composites.

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