

Dramatically enhanced effective electrostriction in ferroelectric polymeric composites

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This letter reports a ferroelectric polymeric composite concept with dramatically enhanced effective electrostriction, strain energy density, and electromechanical coupling factor, where high-dielectric-constant ceramics are arranged in series with ferroelectric polymers having large electrostrictive strain. We demonstrate the importance of the dielectric constant of the constituent phases and the microstructural geometry of the composite on the effective electrostriction of the material. © 2002 American Institute of Physics. [DOI: 10.1063/1.1505743]

Materials with large electromechanical coupling are attractive for a broad range of applications such as sensors and actuators. Recently, giant electrostriction and relaxor ferroelectric behavior have been discovered in electron-irradiated P(VDF-TrFE) polymers, where actuation strain as high as 4% has been obtained.¹ The irradiated polymers also demonstrate enhanced dielectric constant and slim polarization hysteresis, suggesting that the properties of P(VDF-TrFE) polymers can be improved by the introduction of “defect” structure through irradiation.² Motivated by these studies, we propose another mechanism that could enhance the electrostriction, the energy density, and the electromechanical coupling factor of ferroelectric polymers dramatically through the composite concept.

Electrostriction refers to the strain induced by an applied electric field and is proportional to the square of polarization.³ The effect is universal although it is negligibly small in most materials. One method to improve the electrostriction is to increase the dielectric constant of the material, so that the same electric field can induce higher polarization, and thus higher electrostrictive strain. This has been achieved in P(VDF-TrFE) polymers where the dielectric constant has been enhanced by electron irradiation.^{1,2} An alternative is to use the composite concept, where a second phase with much higher dielectric constant is embedded into the ferroelectric polymer to increase the dielectric constant of the composite. This is usually accompanied by an increase in stiffness, however, and caution must be exercised to maintain an elegant balance between the dielectric constant and the elastic stiffness since higher stiffness usually leads to lower actuation strain. Even more important is to optimize the electric field distribution in the composite since only the ferroelectric polymer is electrostrictive. Indeed, enhanced dielectric constant has been reported in composite consisting of P(VDF-TrFE) polymers and PMN-PT ceramic powders,⁴ but the particular microstructure constructed is not optimal for high electrostriction and thus no enhanced strain has been reported. In another word, an appropriate microstructure of the composite must be identified to take advantages of the high dielectric constant of ceramic phase, so that the en-

hanced electrostriction can be obtained in the composite.

To elaborate the concept we consider the electrostriction governed by the one-dimensional constitutive equations

$$\varepsilon = S\sigma + ME^2, \quad D = 2M\sigma E + \kappa E, \quad (1)$$

where ε and σ are the strain and stress, D and E are the electric displacement and field, S is the elastic compliance, κ is the dielectric constant, and M is the electrostrictive coefficient. The dielectric equation can also be written as

$$D = \kappa[\sigma]E \quad \text{with} \quad \kappa[\sigma] = \kappa + 2M\sigma \quad (2)$$

for simplification. This one-dimensional model captures the essence of our concept without introducing unnecessary three-dimensional complication. Notice that the electric field E rather than the polarization P is used as independent variable since it is experimentally controllable. As such Eq. (1) is only valid for linear dielectrics where the polarization P is proportional to the electric field E .

For a composite made of different phases where the electromechanical field is heterogeneous, we can define the effective moduli of the composite through the effective constitutive equation under the assumption of macroscopic homogeneity,⁵

$$\bar{\varepsilon} = S^* \bar{\sigma} + M^* \bar{E}^2, \quad \bar{D} = 2M^* \bar{\sigma} \bar{E} + \kappa^* \bar{E}, \quad (3)$$

where the overhead bar is used to indicate a volume-averaged quantity. Our goal is to enhance the effective electrostrictive coefficient M^* of the composite, but that is not the only measure of the electrostrictive property. Other measures include the effective strain energy density U^* and the electromechanical coupling factor k^* :

$$U^* = \frac{M^{*2} \bar{E}^4}{2S^*}, \quad k^* = \frac{M^{*2} \bar{E}^2}{\kappa^* S^*}. \quad (4)$$

The electromechanical coupling factor is derived following the procedure described by Hom *et al.*⁶ though the expression is different from theirs because we use E rather than P as the independent variable. Both U^* and k^* depend on the average electric field in the composite, again valid only in the linear dielectric regime. As such U^*/\bar{E}^4 and k^*/\bar{E}^2 are probably more meaningful measures of composite performance.

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TABLE I. The electromechanical properties of constituent materials in the composites.

	P(VDF-TrFE)	PZT-5	PZT-5H	PZT-7A
Y (GPa)	1.35	111	124	121
M (m^2/GV^2)	-2.40	0	0	0
κ/κ_0	68.5	830	1470	237

Now let us consider a composite made of two phases arranged in parallel with each other. This parallel model simulates the properties of fibrous composites along the fiber direction very well. In such configuration, the electric field and strain are uniform in the composite, and this leads to exact expressions for the effective properties of the composite

$$S^* = \frac{S_1 S_2}{f_1 S_2 + f_2 S_1},$$

$$M^* = \frac{f_1 M_1 S_2 + f_2 M_2 S_1}{f_1 S_2 + f_2 S_1}, \tag{5}$$

$$\kappa[\bar{\sigma}]^* = f_1 \kappa_1[\sigma_1] + f_2 \kappa_2[\sigma_2],$$

where subscripts 1 and 2 are used to indicate the quantities in polymeric or ceramic phase, and f_i is the volume fraction of the corresponding phase. An inspection on the effective moduli indicates that this composite is not very interesting. The second phase usually has smaller compliance and electrostriction, which tends to decrease the effective electrostriction of the composite. This is in contrast to the piezoelectric fibrous composites widely used in underwater sonar applications.⁷

Next let us consider a composite made of two phases arranged in series with each other. This model simulates the properties of composite laminates along laminating direction very well. In such configuration, the electric displacement and stress are uniform in the composite, and this leads to exact expressions for the effective properties of the composite

$$S^* = f_1 S_1 + f_2 S_2,$$

$$M^* = \frac{f_1 M_1 \kappa_2^2[\bar{\sigma}] + f_2 M_2 \kappa_1^2[\bar{\sigma}]}{(f_1 \kappa_2[\bar{\sigma}] + f_2 \kappa_1[\bar{\sigma}])^2}, \tag{6}$$

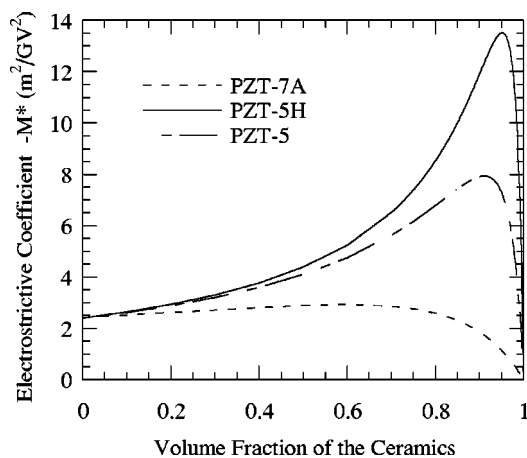


FIG. 1. The effective electrostrictive coefficient of the composites.

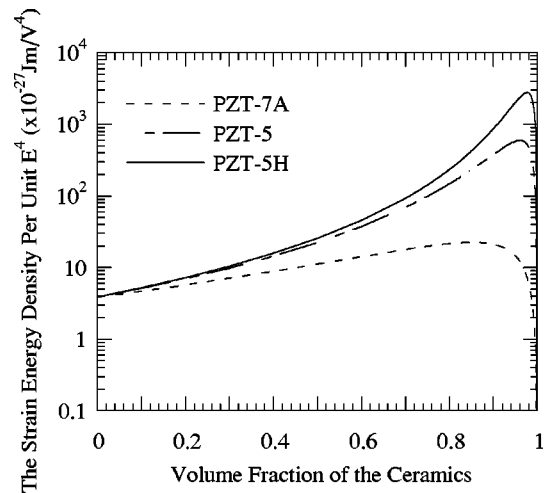


FIG. 2. The effective energy density of the composites.

$$\kappa^*[\bar{\sigma}] = \frac{\kappa_1[\bar{\sigma}]\kappa_2[\bar{\sigma}]}{f_1 \kappa_2[\bar{\sigma}] + f_2 \kappa_1[\bar{\sigma}]}$$

A inspection immediately reveals that this composite is very interesting in the sense that the effective electrostriction could be enhanced dramatically if an appropriate material is chosen as the second phase. Indeed, if we choose a ceramic with high dielectric constant such that $\kappa_1 \ll \kappa_2$, the effective electrostrictive coefficient can be simplified approximately as

$$M^* \approx \frac{M_1}{f_1}, \tag{7}$$

when f_1 is comparable to f_2 or larger. This suggests that the effective electrostriction can indeed be enhanced by incorporating a second phase with much larger dielectric constant than that of the ferroelectric polymer, even if the electrostriction of the second phase is zero. Meanwhile, both the strain energy density and the electromechanical coupling factor will also be improved, since the composite has larger electrostriction and elastic stiffness.

To demonstrate the concept we consider three composites made of PZT-5, PZT-5H, and PZT-7A ceramics embedded in P(VDF-TrFE) polymer, respectively. The polymer is isotropic, while the ceramics are transversely isotropic, and we choose the properties along the axis of the ceramic as the material properties in our one-dimensional model, which are listed in Table I. The materials properties for P(VDF-TrFE) are estimated from Zhang *et al.*,^{1,2} and the material properties for PZT are obtained from Dunn and Taya.⁸ We use the Young's modulus of 1.35 GPa for P(VDF-TrFE) to match the electromechanical coupling factor of 30% reported for P(VDF-TrFE)⁹ using our Eq. (4), and ignore the piezoelectricity of the ceramics because it is small compared to the electrostriction.

The effective electrostrictive coefficient, the effective energy density per unit E^4 , and the effective electromechanical coupling factor per unit E^2 of composites as function of the volume fraction of ceramics are shown in Figs. 1, 2, and 3, respectively. We notice that even small addition of PZT ceramics in P(VDF-TrFE) polymer enhances its electrostrictive properties, and the enhancement is most dramatic near

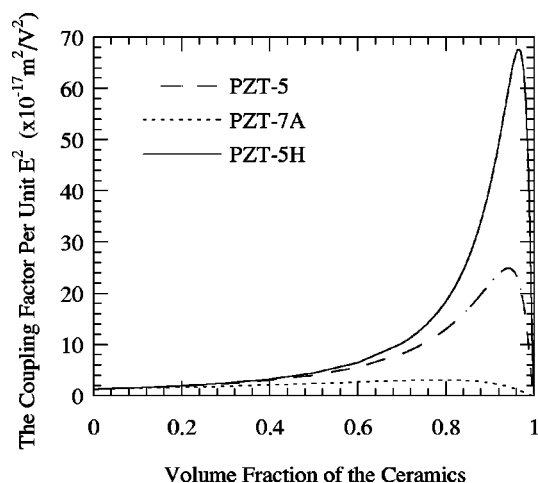


FIG. 3. The effective electromechanical coupling factor of the composites.

the high volume fraction limit. The three PZT ceramics we choose have similar Young's modulus Y , but quite different dielectric constant κ , which allows us to demonstrate the effect of dielectric constant of the ceramic phase on the overall behavior of the composites. Indeed, among three composites we considered, the PZT-5H reinforced one had the most enhancement, and the PZT-7A reinforced one had the least

improvement, reflecting the relative effect of the dielectric constant. For the PZT-5H reinforced composite, the electrostrictive coefficient can be increased as much as six times, and the enhancement in the strain energy density and the electromechanical coupling factor is even more dramatic. These results demonstrate that the electrostrictive properties can indeed be enhanced dramatically through the composite concept.

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- ¹Q. M. Zhang, V. Bharti, and X. Zhao, *Science* **280**, 2101 (1998).
- ²H. S. Xu, Z. Y. Cheng, D. Olson, T. Mai, Q. M. Zhang, and G. Kavarnos, *Appl. Phys. Lett.* **78**, 2360 (2001).
- ³V. Sundar and R. E. Newnham, *Ferroelectrics* **135**, 431 (1992).
- ⁴Y. Bai, Z. Y. Cheng, V. Bharti, H. S. Xu, and Q. M. Zhang, *Appl. Phys. Lett.* **76**, 3804 (2000).
- ⁵C. W. Nan and G. J. Weng, *Phys. Rev. B* **61**, 258 (2000).
- ⁶C. L. Hom, S. M. Pilgrim, N. Shankar, K. Bridger, and W. S. R. Massuda, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **41**, 542 (1994).
- ⁷M. L. Dunn and M. Taya, *Int. J. Solids Struct.* **30**, 161 (1993).
- ⁸M. L. Dunn and M. Taya, *J. Am. Ceram. Soc.* **76**, 1697 (1993).
- ⁹Q. M. Zhang and J. Scheinbeim, in *Electroactive Polymer (EAP) Actuators as Artificial Muscles*, edited by Y. Bar-Cohen (SPIE, Bellingham, WA, 2001), pp. 89–120.