Exchange Coupling in P(VDF-TrFE) Copolymer Based All-Organic Composites with Giant Electrostriction

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In this Letter, we discuss the dramatically enhanced electrostriction and dielectric constant in an all-organic composite consisting of polyvinylidene fluoride trifluoroethylene [P(VDF-TrFE)] copolymer matrix and copper-phthalocyanine (CuPc) particles, which could not be explained by traditional composite theory. Using a Landau-type potential energy combined with energy minimization, we demonstrate that the dramatic property enhancement is due to the exchange coupling between the dielectrically hard P(VDF-TrFE) and dielectrically soft CuPc, which becomes dominant when the heterogeneity size of the composite is comparable to the exchange length. The exchange coupling is a very effective mechanism for the enhancement of functional properties in ferroelectric and dielectric systems, and its variation with various material parameters is demonstrated and discussed.

Materials with large electromechanical coupling are attractive for a broad range of applications such as sensors and actuators. Recently, giant electrostriction and large dielectric constants have been demonstrated in a polyvinylidene fluoride trifluoroethylene [P(VDF-TrFE)] copolymer based all-organic composite [1], where the electrostrictive strain as high as 2% has been obtained at an applied electric field about 13 MV/m. In contrast, an electric field 1 order higher in magnitude is required to achieve the same amount of strain in the electron-irradiated P(VDF-TrFE) copolymers [2], suggesting that the effective electrostrictive coefficient of the all-organic composite is 2 orders higher than its matrix. While it is generally believed that the much enhanced electrostriction is related to the large dielectric constant of the second phase in the composite, copper-phthalocyanine (CuPc), which can be as high as 10^5 [1], the exact nature of the enhancement is not clear, which we hope to clarify.

Electrostriction refers to the strain ε induced by an applied electric field E and is proportional to the square of the polarization P [3], $\varepsilon = QP^2$, where Q is the charge related electrostrictive coefficient. Alternatively, we have $\varepsilon = ME^2$, where $M = Q\chi^2$ is the field related electrostrictive coefficient [4] and χ is the susceptibility. While Q is strictly a material constant, M could be field dependent due to the dielectric nonlinearity of materials. The electrostriction is universal in dielectrics although it is negligibly small in most materials. One way to improve the electrostriction of a material is to enhance its dielectric constant, so that the same electric field can induce higher polarization, thus higher electrostrictive strain. This has recently been accomplished in the P(VDF-TrFE) copolymer based all-organic composites [1].

The electric field enhancement in P(VDF-TrFE) copolymers due to the presence of a dielectrically soft second phase has been proposed as one mechanism for the electrostriction enhancement [5], but it cannot be used to explain the large increase of the electrostriction in the all-organic composite, since the enhancement is limited by $1/c_f$ under this mechanism [5], thus it cannot provide more than a factor of 2 in the magnification of the electrostriction, far less than those observed in experiment. Here c_f, the volume fraction of the P(VDF-TrFE) copolymer, is about 60% in the all-organic composite [1], and we use subscripts f and d to represent quantities in hard and soft phases. In the context of dielectrics, hard phase refers to materials with a small dielectric constant, while soft phase refers to materials with a large dielectric constant.

We propose that the large electrostriction enhancement in the all-organic composite is due to the exchange coupling between the P(VDF-TrFE) copolymer matrix and CuPc particles, which is a short range interaction between dipoles, thus effective only at the matrix-particle interface. As the heterogeneity in the composite becomes smaller and smaller, the influence of the exchange layer, an interface layer in which the polarization is strongly affected by both phases, becomes more and more important, and eventually dominates when the heterogeneity size and the exchange length become comparable. This phenomena is well known in exchange spring magnets [6,7], where the exchange coupling between the soft and hard magnetic phases results in dramatically enhanced remnant magnetization and energy product. Although it has not been explored in ferroelectrics and dielectrics intentionally, we believe that the greatly enhanced electrostriction and dielectric constant in the all-organic composite are due to the exchange coupling between the dielectrically hard P(VDF-TrFE) copolymers and dielectrically soft CuPc.

To support our argument, we consider the Landau-type potential energy [8] of a one-dimensional periodic composite with hard ferroelectric phase located in $x \in (-L_f, 0)$ and soft dielectric phase located in $x \in (0, L_d)$, where the first integral represents the potential energy of

ferroelectric phase with spontaneous polarization P_s, and the second integral represents that of the dielectric phase,

$$\Phi = \int_{-L_f}^{0} \left[\frac{a}{2}\left(\frac{dP}{dx}\right)^2 + \frac{1}{2\chi_f}(P - P_s)^2 - E_0 P \right] dx$$
$$+ \int_{0}^{L_d} \left[\frac{a}{2}\left(\frac{dP}{dx}\right)^2 + \frac{1}{2\chi_d}P^2 - E_0 P \right] dx.$$

In both integrals, the second term is the stored energy density, and the third term is the potential with the applied electric field E_0. The first term is the exchange energy penalizing the polarization gradient, with a being the exchange constant, which leads to the appearance of a polarization gradient rather than a sharp discontinuity at the ferroelectric-dielectric interface. The polarization gradient in the energy density of a dielectric was first postulated by Mindlin [9], who also indicated the relationship between polarization gradient and the shell-shell and core-shell interactions of the lattice theory of crystals. The equation relating exchange constant to the microscopic lattice properties in cubic ionic crystals was later derived by Askar et al. [10] using long-wave approximation. Furthermore, polarization gradients were observed in both atomic simulation of ferroelectric superlattices [11] and structural characterization of ferroelectric domain walls [12]. As such, our inclusion of exchange energy in the phenomenological continuum theory is justified, without attempting to address it from a microscopic point of view. We have ignored the depolarization energy, since CuPc is a semiconductor [1], thus can provide charges to neutralize the poles arising from the polarization distribution. The equilibrium state of the composite minimizes its potential energy [8], $\delta\Phi/\delta P = 0$, which leads to

$$a \frac{d^2 P}{dx^2} - \frac{1}{\chi_f}(P - P_s) + E_0 = 0,$$
$$a \frac{d^2 P}{dx^2} - \frac{1}{\chi_d} P + E_0 = 0$$

for the ferroelectric and dielectric phases, where δP is assumed to be continuous. Solving these two equations with appropriate boundary conditions at infinity, and continuity of P and dP/dx at the interface, we obtain the field dependent polarization as a function of position

$$\frac{P[E_0]}{\chi_f[E_m]E_m} = \{(\alpha^2 - 1)\gamma - \beta\}/(1 + \alpha)e^y + \gamma + \beta$$

for the ferroelectric and

$$\frac{P[E_0]}{\chi_f[E_m]E_m} = -\alpha\{(\alpha^2 - 1)\gamma - \beta\}/(1 + \alpha)e^{-(y/\alpha)} + \alpha^2 \gamma$$

for the dielectric, where $E_m = 13\ \mathrm{MV/m}$ is a fixed reference electric field, and $\alpha = \sqrt{\chi_d/\chi_f[E_0]}$, $\beta = P_s/(\chi_f[E_m]E_m)$, and $\gamma = (\chi_f[E_0]E_0)/(\chi_f[E_m]E_m)$ are dimensionless parameters. $y = x/\lambda$ is the scaled position

and $\lambda = \sqrt{a\chi_f}$ is the exchange length of the ferroelectric phase. The polarization profiles across the hard-soft interface under $E_0 = 13\ \mathrm{MV/m}$ are shown in Fig. 1 for different χ_d, where $\chi_f[E_0] = 60$, $\chi_f[0] = 42$, and $P_s = 0\ \mathrm{C/m^2}$ have been used in the calculation, all obtained from experiment data for the P(VDF-TrFE) copolymer [1], which loses ferroelectricity after being treated by electron irradiations. Clearly, we observe the existence of an exchange layer at the interface with characteristic lengths λ and $\alpha\lambda$ for hard and soft phases, where the exchange length in the dielectric phase is much longer due to its dielectric softness. In addition, we notice that, while the polarization in the exchange layer of P(VDF-TrFE) copolymer is only modestly enhanced when $\chi_d = 10^3$, it is about 40 times higher than that far away from the interface when $\chi_d = 10^5$, suggesting that $P = 0.28\ \mathrm{C/m^2}$, which is larger than $0.1\ \mathrm{C/m^2}$, the spontaneous polarization of ferroelectric P(VDF-TrFE) [13]. One possible microscopic mechanism for such polarization enhancement is charge injection, which was observed at the all-organic composite interface [14]. Since the electrostrictive strain is proportional to the square of the polarization, we have reason to believe that the much enhanced polarization in the exchange layer could lead to the greatly enhanced electrostriction of the composites.

To support our claim, we consider the electrostrictive strain due to the polarization distribution in the composite. Only P(VDF-TrFE) is considered electrostrictive, since the electrostriction of CuPc is negligibly small. As such, the effective electrostriction of the composite is given by the average electrostriction in P(VDF-TrFE) weighted by its volume fraction, because there is no mechanical constraint in this one-dimensional composite,
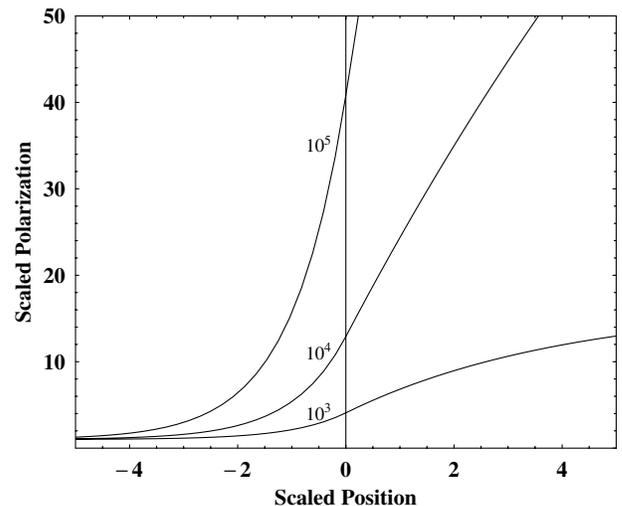
FIG. 1. The polarization $P/(\chi_f[E_m]E_m)$ as a function of scaled position x/λ under the applied electric field for different χ_d.
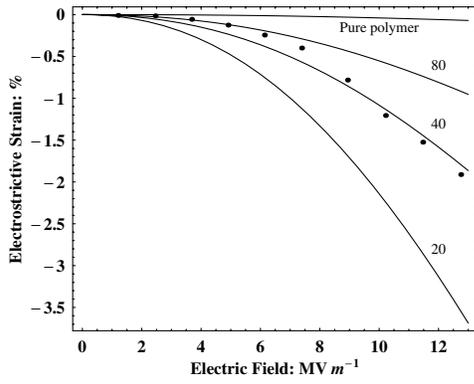
FIG. 2. The electrostrictive strain as a function of the electric field for different sizes of the P(VDF-TrFE) phase, L_f/λ; the dots are experimental data from [1].

$$\frac{\varepsilon_c}{Q(\chi_f[E_m]E_m)^2} = \frac{2c_f}{\nu}\int_{-\nu/2}^{0}\left(\frac{P[E_0]}{\chi_f[E_m]E_m}\right)^2 dy,$$

where $\nu = L_f/\lambda$ is the dimensionless heterogeneity size, and we consider only the half length of P(VDF-TrFE) because of symmetry. The mechanical constraint in the three-dimensional composite is expected to be insignificant also, because the elastic stiffness of CuPc is very close to that of P(VDF-TrFE) [1]. The electrostrictive strain of composites is shown in Fig. 2 as a function of the applied electric field for different ν. In the calculation, the strain is calibrated with respect to that of copolymer to obtain Q,

$$\frac{\varepsilon_p}{Q(\chi_f[E_m]E_m)^2} = (\beta + \gamma)^2 - \beta,$$

which is about 0.07% at $E_0 = 13$ MV/m, and $\chi_f[E_0]$ is obtained from experimental data as [1]

$$\chi_f[E_0] = 42.19 + 2.73E_0 - 0.10E_0^2,$$

with E_0 given in MV/m. Clearly, as $\nu = 40$, the calculated strain-electric field curve approximates the experimental data very well. The enhancement of electrostriction with respect to the P(VDF-TrFE) copolymer as a function of the P(VDF-TrFE) size is shown in Fig. 3, which clearly demonstrates the importance of the softness of the dielectric phase and the size of the hard phase.

Our claim is further supported by the large increase of the dielectric constant κ^* of the all-organic composite, which reaches as high as 1000 at 10^{-2} Hz [1], about 20 times higher than that of the P(VDF-TrFE) copolymer. In contrast, the mean field-type composite theory, which is very reliable when the size effect is not important, predicts the effective dielectric constant of the composite as [15]

$$\kappa^* = \frac{2\kappa_f + \kappa_d - 2c_d(\kappa_f - \kappa_d)}{2\kappa_f + \kappa_d + c_d(\kappa_f - \kappa_d)}\kappa_f,$$

which is approximately $(1 + 2c_d)/(1 - c_d)\kappa_f$ since κ_d is
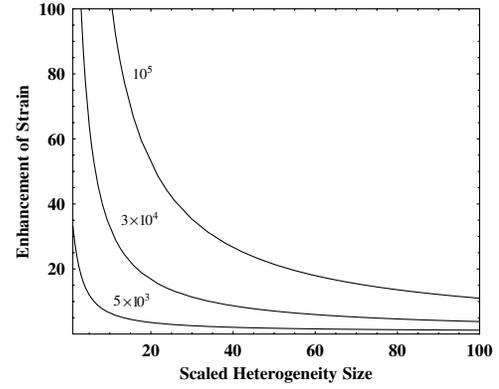
FIG. 3. The enhancement of the electrostrictive strain $\varepsilon_c/\varepsilon_p$ as a function of L_f/λ, the size of P(VDF-TrFE) phase, for different χ_d.

much larger than κ_f, thus is only about 3 times that of P(VDF-TrFE) for $c_d = 40\%$, and cannot be used to explain the large increase of the dielectric constant of the composites. This increase, however, is consistent with the polarization enhancement in the exchange layer of the P(VDF-TrFE) phase. Indeed, the effective susceptibility of P(VDF-TrFE) with the exchange coupling considered is given by

$$\frac{\chi_f^*[E_0]}{\chi_f[E_0]} = \frac{2}{\nu}\int_{-\nu/2}^{0}\left(\frac{P}{\gamma\chi_f[E_m]E_m}\right) dy,$$

and its variation with respect to ν for different χ_d is shown in Fig. 4, where the experimental value $E_0 = 0.01$ MV/m is used in the calculation [1]. As ν approach 40, a fourfold enhancement of susceptibility in the P(VDF-TrFE) phase with respect to that of pure copolymer is observed. Combined with the threefold enhancement in the composite predicted by the mean field theory, we conclude that the effective dielectric constant is about 12 times that of pure P(VDF-TrFE) copolymer, consistent with the experiment observed 20-fold enhancement [1]. As a result, both electrostrictive
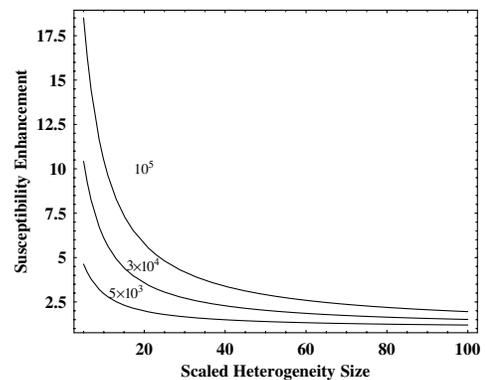
FIG. 4. The enhancement of the dielectric constant of P(VDF-TrFE) due to the exchange coupling as a function of L_f/λ, the size of P(VDF-TrFE), for different χ_d.
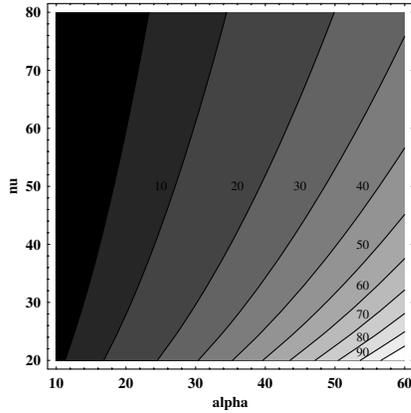
FIG. 5. The contour plot of the electrostrictive enhancement $\varepsilon_c/\varepsilon_p$ in terms of α and ν.

and dielectric enhancement can be explained by the exchange coupling, with the size of P(VDF-TrFE) approximately equalling 40 times the exchange length λ.

For the exchange coupling mechanism to be effective, the second phase must be very soft (with dielectric constant as high as 10^5), and the size of the P(VDF-TrFE) phase must be comparable to its exchange length λ. Otherwise, the influence of the exchange layer will be negligible. Because of the critical role of the size effect, it is worthwhile to estimate the effective length of P(VDF-TrFE) in the composite. To this end, we consider a composite sphere of radius r_o consisting of P(VDF-TrFE) at the outer shell and a CuPc particle of radius r_i at the inner shell; the volume fraction of CuPc is thus $c_d = r_i^3/r_o^3$. For the composite with 40% of CuPc, we have $r_o = 1.35r_i$, suggesting that the P(VDF-TrFE) shell is $0.35r_i$ thick. The particle size in the all-organic composite is less than 1 μm [1], indicating 175 nm as an upper limit of P(VDF-TrFE) thickness. As a result, the exchange length, estimated by $\lambda = L_f/\nu = 175/40$, is approximately 4 nm, about five unit cells thick, consistent with both experimental observations and first principle calculations of domain wall thickness in ferroelectrics [16,17]. From this exchange length, we can estimate the exchange constant as $a = \lambda^2/\chi_f[E_0] = 4.7 \times 10^{-8}$ V m^3/C. In comparison, the exchange constant of the KCl crystal determined from the shell model is 1.2×10^{-9} V m^3/C [10].

Finally, we discuss how the electrostriction enhancement varies with the size of the hard phase and dielectric constant of the soft phase by a contour plot of $\varepsilon_c/\varepsilon_p$ as a function of α and ν, presented in Fig. 5, because they both play critical roles in the property enhancement. It shows the enhancement increases with α/ν, which suggests that a larger χ_d or smaller χ_f will result in larger electrostriction. But a smaller χ_f might not be desirable, since it leads to smaller exchange length, thus requires a smaller heterogeneity size for the exchange coupling to be effective. It also excludes perovskite ferroelectrics as a candidate constituent for the electrostrictive composites, since

they have much larger dielectric constants than P(VDF-TrFE).

In summary, we demonstrate that the exchange coupling between the dielectrically hard P(VDF-TrFE) and dielectrically soft CuPc can lead to the much enhanced polarization in the exchange layer, thus dramatically enhancing the electrostriction and dielectric constant of the all-organic composites when the heterogeneity size is comparable to the exchange length. Excellent agreement between the analysis and experiment has been observed, and exchange constant and exchange length have been determined. The exchange coupling is a very effective mechanism and has potential for the enhancement of other functional properties related to the polarization in addition to the electrostriction and dielectric constant, such as the piezoelectric and pyroelectric coefficients and the remnant polarization of the materials.

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