Journal of the Mechanics and Physics of Solids
52 (2004) 591 – 615

JOURNAL OF THE
MECHANICS AND
PHYSICS OF SOLIDS

www.elsevier.com/locate/jmps

Micromechanics of ferroelectric polymer-based electrostrictive composites

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Received 8 January 2003; received in revised form 24 July 2003; accepted 31 July 2003

Abstract

Electrostriction refers to the strain induced in a dielectric by electric polarization, which is usually very small for practical application. In this paper, we present a micromechanical analysis on the effective electrostriction of a ferroelectric polyvinylidene fluoride trifluoroethylene [P(VDF-TrFE)] polymer-based composite, where the exact connections between the effective electrostrictive coefficients and effective elastic moduli are established, and numerical algorithm for the prediction of the effective electrostrictive coefficients of the composite in terms of its microstructural information is developed. From our calculations, enhanced electrostriction in the composite has been demonstrated, and optimal microstructure for electrostriction enhancement has been identified. Our analysis provides a mechanism for the electrostriction enhancement, where the electrostrictive strain several times higher than that of polymer matrix can be obtained, if the microstructure of the composites can be carefully tailored.

Keywords: Micromechanics; P(VDF-TrFE) polymer; Electrostriction; Electrostrictive composite

1. Introduction

Electrostriction refers to the strain induced in a dielectric material by electric polarization (Sundar and Newnham, 1992). It depends on the polarization quadratically,

$$\varepsilon_{ij} = Q_{ijkl}P_kP_l, \tag{1.1}$$

thus exists in all insulating materials and does not require lack of a symmetry center, as piezoelectric materials do. In Eq. (1.1), ε_{ij} is the strain tensor and P_k is the polarization

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doi:10.1016/S0022-5096(03)00117-0

vector, and Q_{ijkl} is the fourth-rank charge-related electrostrictive tensor. For linear dielectrics where the polarization is proportional to the electric field

$$P_i = \chi_{ij} E_j, \tag{1.2}$$

we have

$$\varepsilon_{ij} = M_{ijkl} E_k E_l, \tag{1.3}$$

where χ_{ij} is the susceptibility tensor and M_{ijkl} is the fourth-rank electric field related electrostrictive tensor (Newnham et al., 1997).

The electrostriction is attractive for actuators, sensors, and transducers applications. However, the electrostrictive strain demonstrated in most dielectric materials is very small. For example, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) ceramics, which have one of the largest electrostriction among inorganic materials, exhibit electrostrictive strain in the order of 0.1% (Sundar and Newnham, 1992). As is clear from Eqs. (1.1) and (1.2), it is necessary for materials with large electrostriction to have relatively large susceptibility χ_{ij}. In fact, the high electrostriction in PMN ceramics is due to its large dielectric constant, since its charge-related electrostrictive coefficient is very modest. This suggests that the electrostriction of a material can be enhanced if its dielectric constant can be increased, so that the same electric field can induce higher polarization, thus higher electrostrictive strain. Indeed, this has been recently demonstrated in electron-irradiated polyvinylidene fluoride trifluoroethylene [P(VDF-TrFE)] polymers (Zhang et al., 1998; Cheng et al., 1999; Bharti et al., 1999; Xu et al., 2001), where a dielectric constant one order higher than that of untreated P(VDF-TrFE) polymers has been observed, resulting dramatically enhanced electrostriction as high as 4%.

Encouraged by this development, alternative methods to enhance the dielectric constant of materials for electrostriction enhancement have been proposed, among them the composite concept, where a second phase with much higher dielectric constant is embedded in the P(VDF-TrFE) polymer matrix to increase the overall dielectric constant of the composite. The essence of the composite concept is that the electric field in the P(VDF-TrFE) polymer could be enhanced, if the microstructure of the composites can be carefully tailored. The idea has recently been demonstrated by Li and Rao (2002) using a simple one-dimensional model, and has been accomplished by Zhang et al. (2002) in a P(VDF-TrFE) polymer-based all-organic composite, where the organic second phase, copper-phthalocyanine (CuPc), has the relative dielectric constant as high as 10^5. As a result, the electrostrictive strain in the order of 2% has been obtained in the all-organic composite at a much lower electric field, suggesting a dramatically improved electrostrictive coefficient.

While the development is exciting and promising, there are some issues that need to be addressed. The increase in the dielectric constant of the composites is usually accompanied by an increase in stiffness, and caution must be exercised to maintain an elegant balance between the softening of dielectric constant and the stiffening of the elastic constant, since higher stiffness usually leads to lower actuation strain. On the other hand, higher stiffness also gives higher actuation energy density and force, thus may be desirable, especially when the polymer phase is soft. As a matter of fact, the figures of merit for the electrostriction are the electromechanical coupling factors (Hom et al., 1994)

$$k_{31} = \frac{M_{13}E_3^2}{\kappa_{33}S_{11}}, \quad k_{33} = \frac{M_{33}E_3^2}{\kappa_{33}S_{33}},$$

which measure the portion of electric energy converted to mechanical energy. In the equation, M, κ and S are electrostrictive, dielectric, and elastic compliance constants, and E is the applied electric field; the notation adopted will be discussed in detail in the next section. As such, it is very important to tailor the microstructure of the composites to balance different requirements. Ideally, the optimal microstructure should lead to optimized electric field enhancement in the P(VDF-TrFE) polymer phase, yet relaxed mechanical constraint from the dielectric ceramic phase. Indeed, enhanced dielectric constant has been reported in the composites consisting of P(VDF-TrFE) polymers and $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PMN-PT) ceramic powders (Bai et al., 2000), but the particular microstructure constructed was not optimal for high electrostriction and thus no enhanced strain was reported. One of the reasons that dramatically enhanced electrostriction has been observed in CuPc reinforced P(VDF-TrFE) polymers is because CuPc is very soft elastically (Zhang et al., 2002; Li, 2003), so that the mechanical constraint on the P(VDF-TrFE) polymers is relaxed. In summary, microstructure plays a key role in the enhancement and optimization of electrostriction in the P(VDF-TrFE) polymer-based electrostrictive composites, and appropriate microstructure must be identified in order to take advantage of the high dielectric constant of the reinforcing phase for enhanced electrostriction.

Motivated by those studies, we intend to investigate the effective electrostriction in the P(VDF-TrFE) polymer-based electrostrictive composites systematically, with the objective to predict the macroscopic behavior of the composites from their microstructure information, which could be used for the design and optimization of the P(VDF-TrFE) polymer-based composites with enhanced electrostriction. Besides the obvious technological importance, this class of composites demonstrates many interesting features arising from the nonlinear electromechanical coupling, which are worthy of investigation. For example, the stress modulated linear dielectric response in a pure electrostrictive phase leads to nonlinear dielectric response in composites, which may find application in microwave devices (Gevorgian et al., 1998). Although significant progress has been made in the last decade on the micromechanics modelling of electromechanical composites (Dunn and Taya, 1993a; Benveniste, 1993; Chen, 1993; Bisegna and Luciano, 1996; Aboudi, 1998; Avellaneda et al., 1998; Hori and Nemat-Nasser, 1998; Qin and Yu, 1998; Li, 2000; Fang et al., 2001, Guinovart-Diaz et al., 2001), these models are essentially linear in nature, thus cannot be applied to the nonlinear electrostrictive composites. Significant progress has also been made in nonlinear micromechanical analysis, though they are essentially uncoupled, concerning either the mechanical (Talbot and Willis, 1985; Willis, 1991; Ponte Castañeda, 1996; Ponte Castañeda and Suquet, 1998) or dielectric behaviors (Talbot and Willis, 1996) of the composites. There are only a few exceptions very recently, where either composites with simple geometries were considered (Tan and Tong, 2001), or approximation was made to decouple the electrostriction from the mechanical field (Nan and Weng, 2000), which is appropriate when the polarization of the composite saturates under the high electric field.

In this paper, we develop a nonlinear micromechanics model that relates the macroscopic behavior of electrostrictive composites to their microstructural features. We are concerning the bulk composites without addressing the size effects and interface coupling, which play important roles in the electrostriction enhancement of the all-organic composite (Zhang et al., 2002; Li, 2003). The basic constitutive equations governing electrostriction will be presented in Section 2, followed by a detailed analysis of electrostrictive composites in Section 3, where the effective electrostrictive moduli will be defined in Section 3.1, exact connections between the effective elastic moduli and the effective electrostrictive coefficients will be established using the uniform field concept (Dvorak, 1990; Benveniste and Dvorak, 1992) in Section 3.2, and nonlinear micromechanics model and numerical algorithm will be developed in Section 3.3. We then present some numerical results and discussion regarding the P(VDF-TrFE) polymer-based composites in Section 4 and conclude the paper.

2. The electrostriction

We consider the electrostriction governed by the nonlinearly coupled electromechanical constitutive equations

$$\begin{aligned} \varepsilon_{ij} &= S_{ijkl}\sigma_{kl} + M_{ijkl}E_kE_l, \\ D_i &= \kappa_{ij}E_j + 2M_{klij}\sigma_{kl}E_j, \end{aligned} \tag{2.1}$$

where ε_{ij} and σ_{kl} are strain and stress, respectively; D_i and E_j are electric displacement and electric field, respectively; and S_{ijkl}, κ_{ij}, and M_{ijkl} are elastic compliance, dielectric constant, and electrostrictive coefficient, respectively. The summation convection is adopted for the repeated subscript. The constitutive equations can be derived from the potential energy

$$V[\sigma, \mathbf{E}] = -\tfrac{1}{2}S_{ijkl}\sigma_{ij}\sigma_{kl} - M_{ijkl}\sigma_{ij}E_kE_l - \tfrac{1}{2}\kappa_{ij}E_iE_j, \tag{2.2}$$

where both subscripted and bold symbols are used for tensor representation to simplify the notation. It is noted that Eq. (2.2) requires the fourth-rank electrostrictive tensor to satisfy the following symmetry conditions:

$$M_{ijkl} = M_{jikl} = M_{jilk},$$

but not necessarily the main diagonal symmetry

$$M_{ijkl} = M_{klij},$$

which is different from the requirement on the elastic compliance tensor. We also assumed the existence of a symmetry center in the materials, so that the linear coupling term disappears, which is different from piezoelectricity. For simplification, we introduce a second-rank tensor

$$\mathbf{E}^2 = \mathbf{E} \otimes \mathbf{E} \quad \text{or} \quad E^2_{ij} = E_iE_j, \tag{2.3}$$

where $\otimes$ is used to represent the tensor product. We also adopt the well-known matrix notation for the tensor, so that the constitutive equation (2.1) can be rewritten as

$$\begin{aligned} \varepsilon_I &= S_{IJ}\sigma_J + M_{IJ}E_J^2, \\ D_i &= \kappa_{ij}E_j + 2M_{Kij}\sigma_K E_j, \end{aligned} \tag{2.4}$$

where the upper case subscripts range from 1 to 6 and repeated upper case subscripts are summed from 1 to 6. In (2.4_2), only the last two indices of M_{ijkl} are contracted.

The electrostrictive strain is inelastic, thus can be treated as an eigenstrain (Mura, 1987; Nemat-Nasser and Hori, 1993)

$$\varepsilon_I^{\mathrm{T}}[\mathbf{E}^2] = M_{IJ}E_J^2, \tag{2.5}$$

which is a function of the electric field. We can also introduce the stress-dependent dielectric constant

$$\kappa_{ij}^{\sigma} = \kappa_{ij} + 2M_{Kij}\sigma_K, \tag{2.6}$$

which is modulated by the stress and needs to be positive definite; this gives a range of stresses under which the constitutive equation is valid. The constitutive equation (2.4) can then be reformulated as

$$\begin{aligned} \varepsilon_I &= S_{IJ}\sigma_J + \varepsilon_I^{\mathrm{T}}[\mathbf{E}^2], \\ D_i &= \kappa_{ij}^{\sigma}E_j, \end{aligned} \tag{2.7}$$

where the electric displacement is proportional to the electric field, though the proportionality is stress dependent. The constitutive equations (2.7) formally resemble the linear elastic constitutive equation with eigenstrain and linear dielectric equation, though they are actually coupled nonlinearly. The resemblance, however, allows us to carry out the micromechanical analysis, as detailed in the next section.

To proceed we consider the static behavior of electrostrictive materials with no body force and free charge, so that the stress and electric displacement satisfy the equilibrium equations

$$\begin{aligned} \sigma_{ij,i} &= 0, \\ D_{i,i} &= 0, \end{aligned} \tag{2.8}$$

where the subscript i, is used to represent a partial differentiation with resect to x_i. The strain and electric field, on the other hand, can be derived from elastic displacement u_i and electric potential ϕ,

$$\begin{aligned} \varepsilon_{ij} &= u_{(i,j)}, \\ E_i &= -\phi_{,i}, \end{aligned} \tag{2.9}$$

where subscript (i,j) is used to represent symmetrization operation on the second-rank tensor. Complemented by appropriate boundary conditions, those equations need to be solved to determine the electromechanical field distribution in the electrostrictive solid.

3. The electrostrictive composites

3.1. The effective moduli

To fix the idea we consider a multi-phase composite made of electrostrictive materials, where the constitutive equations for each phase are given by

$$\begin{aligned} &\varepsilon_r = \mathbf{S}_r\sigma_r + \varepsilon_r^{\mathrm{T}}[\mathbf{E}_r^2], \\ &\mathbf{D}_r = \kappa_r^{\sigma}\mathbf{E}_r \end{aligned} \tag{3.1}$$

with

$$\begin{aligned} &\varepsilon_r^{\mathrm{T}}[\mathbf{E}_r^2] = \mathbf{M}_r\mathbf{E}_r^2, \\ &\kappa_r^{\sigma} = \kappa_r + 2\mathbf{M}_r\sigma_r. \end{aligned} \tag{3.2}$$

The subscript r in this context refers to the quantities for phase r, and $r=1$ is reserved for the matrix. Each phase has distinct material properties $\mathbf{S}_r$, $\mathbf{M}_r$, and κ_r, resulting in heterogeneous electromechanical field ε_r, σ_r, $\mathbf{E}_r$, and $\mathbf{D}_r$.

We assume that a uniform traction and linear electric potential are applied at the boundary of the composite

$$\begin{aligned} &\mathbf{t} = \sigma^0\mathbf{n}, \\ &\phi = -\mathbf{E}^0\mathbf{x}, \end{aligned} \tag{3.3}$$

where $\mathbf{t}$ is the traction, $\mathbf{n}$ is the unit outward normal, $\mathbf{x}$ is the position vector, and σ^0 and $\mathbf{E}^0$ are constant stress tensor and electric field vector. The specified boundary conditions lead to

$$\begin{aligned} &\bar{\sigma} = \sigma^0, \\ &\bar{\mathbf{E}} = \mathbf{E}^0 \end{aligned} \tag{3.4}$$

according to the average field theorem (Dunn and Taya, 1993b), where the overhead bar is used to denote the volume-averaged field variables over the composite, $\bar{f} = ⨍_V f(\mathbf{x})\,\mathrm{d}\mathbf{x}$. Eqs. (3.4) are derived from the boundary conditions (3.3) using equilibrium equation (2.8_1) and gradient equation (2.9_2), regardless of the constitutive equations.

We are interested in determining the macroscopic properties of the electrostrictive composites in terms of their microstructures, and propose that the electromechanical behaviors of multi-phase electrostrictive composites with macroscopic homogeneity are governed by the effective constitutive equations

$$\begin{aligned} &\bar{\varepsilon} = \mathbf{S}^*\bar{\sigma} + \varepsilon^*[\bar{\mathbf{E}}^2], \\ &\bar{\mathbf{D}} = \kappa^{\sigma *}\bar{\mathbf{E}}, \end{aligned} \tag{3.5}$$

where $\mathbf{S}^*$ is the effective compliance of the composites, with the effective eigenstrain $\varepsilon^*[\bar{\mathbf{E}}^2]$ and the effective stress-dependent dielectric constants $\kappa^{\sigma *}$ given by

$$\varepsilon^*[\bar{\mathbf{E}}^2] = \mathbf{M}^*\bar{\mathbf{E}}^2,$$

$$\kappa^{\sigma *} = \kappa^* + 2\mathbf{M}^*\bar{\sigma}, \tag{3.6}$$

where $\bar{\mathbf{E}}^2 = \bar{\mathbf{E}} \otimes \bar{\mathbf{E}}$, and $\mathbf{M}^*$ and κ^* are the effective electrostrictive tensor and effective dielectric tensor, respectively. In another word, the effective behaviors of the composites are represented by an effective potential energy

$$V^*[\bar{\sigma}, \bar{\mathbf{E}}] = -\tfrac{1}{2}S^*_{ijkl}\bar{\sigma}_{ij}\bar{\sigma}_{kl} - M^*_{ijkl}\bar{\sigma}_{ij}\bar{E}_k\bar{E}_l - \tfrac{1}{2}\kappa^*_{ij}\bar{E}_i\bar{E}_j. \tag{3.7}$$

Notice that the effective compliance $\mathbf{S}^*$ is a material constant independent of the applied stress or electric field, since the applied stress alone will not induce the electric field in the composites, and the stress–strain relationship is linear. However, $\mathbf{M}^*$ and κ^* are stress and electric field dependent in general, as opposed to the linear piezoelectric composites, due to the nonlinear electromechanical coupling. As a result, we need to determine the electromechanical distribution in composites for given combination of stress and electric field.

To proceed, let us assume that the yet unknown average stress and average electric field in each phase are found to be σ_r and $\mathbf{E}_r$, and try to determine their relations with the average stress and electric field in the composites, σ^0 and $\mathbf{E}^0$. Since σ_r is given, κ_r^σ is known, and the dielectric equation is linear, such that

$$\mathbf{E}_r = \alpha_r\mathbf{E}^0, \tag{3.8}$$

where α_r is the electric field concentration factor depending on the stress-dependent dielectric constant κ_r^σ of each phase and the microstructure of the composites. As a result, the eigenstrain for each phase, $\varepsilon_r[\mathbf{E}_r]$, can also be determined, and the stress in each phase is then obtained as

$$\sigma_r = \mathbf{B}_r\sigma^0 + \sigma_r^{\mathrm{T}}[\mathbf{E}_r^2], \tag{3.9}$$

where the first term is due to the applied traction at the boundary, with $\mathbf{B}_r$ being the stress concentration factor of phase r, depending on the elastic compliance $\mathbf{S}_r$ of each phase and the microstructure of composites. The second term is the eigenstress induced by the electrostriction

$$\sigma_r^{\mathrm{T}}[\mathbf{E}_r^2] = \mathbf{b}_r(\varepsilon_r^{\mathrm{T}}[\mathbf{E}_r^2] - \varepsilon_1^{\mathrm{T}}[\mathbf{E}_1^2]) \tag{3.10}$$

with $\mathbf{b}_r$ being the eigenstress concentration factor depending on the compliance $\mathbf{S}_r$ of each phase and the microstructure of the composites. Eq. (3.10) reflects the fact that the eigenstress is induced in the composites only when there is a mismatch between eigenstrain in constituent phases. From the average field theorem (Dunn and Taya, 1993b), we then conclude that

$$\sum_{r=1}^{N} f_r\mathbf{B}_r = \mathbf{I},$$

$$\sum_{r=1}^{N} f_r \sigma_r^{\mathrm{T}} = \mathbf{0},$$

$$\sum_{r=1}^{N} f_r \alpha_r = \mathbf{i}, \tag{3.11}$$

where f_r is the volume fraction of phase r, N is the number of phase present in the composite, $\mathbf{I}$ is the fourth-rank unit tensor, $\mathbf{0}$ is the second-rank null tensor, and $\mathbf{i}$ is the second-rank unit tensor. Using Eqs. (3.8)–(3.10) along with constitutive equations (3.1) for phase r, we obtain the effective compliance

$$\mathbf{S}^* = \sum_{r=1}^{N} f_r \mathbf{S}_r \mathbf{B}_r, \tag{3.12}$$

which bears no influence from the electrostriction thus is electromechanical field independent, as we discussed earlier. It is identical to that of linear elastic composites. The effective stress-dependent dielectric constant is determined as

$$\kappa^{\sigma *} = \sum_{r=1}^{N} f_r \kappa_r^{\sigma} \alpha_r, \tag{3.13}$$

which is coupled with the stress field. It recovers that of linear dielectric composites if κ_r^{σ} is independent of stress. The effective eigenstrain is determined similarly as

$$\varepsilon^*[\bar{\mathbf{E}}^2] = \sum_{r=1}^{N} f_r (\mathbf{S}_r \sigma_r^{\mathrm{T}}[\mathbf{E}_r^2] + \varepsilon_r^{\mathrm{T}}[\mathbf{E}_r^2]), \tag{3.14}$$

which leads to the effective electrostrictive coefficient

$$\mathbf{M}^* = \sum_{r=1}^{N} f_r \{(\mathbf{S}_r \mathbf{b}_r + \mathbf{i}) \mathbf{M}_r (\alpha_r \otimes \alpha_r) - \mathbf{S}_r \mathbf{b}_r \mathbf{M}_1 (\alpha_1 \otimes \alpha_1)\}. \tag{3.15}$$

In general, they are stress and electric field dependent, due to the stress dependence of α_r. As a result, the strain in the electrostrictive composites is no longer quadratic in the electric field. Eq. (3.14) recovers that of linear elastic composites with eigenstrain, if $\varepsilon_r^{\mathrm{T}}$ is stress independent. A similar manipulation on Eq. (3.13) leads to the observation that the effective dielectric constant

$$\kappa^* = \kappa^{\sigma *} - 2\mathbf{M}^* \bar{\sigma} \tag{3.16}$$

also depends on the stress and electric field, suggesting a dielectric nonlinearity induced in the composites by the heterogeneity, as we will show later. In another word, for multi-phase composites consisting of piecewise uniform phases, each having linear dielectric relationship with the dielectric constant modulated by the stress, the electric displacement versus the electric field becomes nonlinear, induced by the mismatch between the material properties. This leads us to question whether the nonlinear dielectric relationship observed in the electrostrictive ceramics is intrinsic due to the nonlinearity at grain level, or extrinsic due to the inter-granular constraint; this investigation will be reported elsewhere.

All the derivations in this subsection rely on the assumption that the electromechanical field distribution in the electrostrictive composites has already been determined, so that the relationship between them can be established. The question remains on how to solve the electromechanical field distribution to determine the effective electrostriction and effective dielectric constant. We will address this issue in the following two subsections.

3.2. The exact connections

In this subsection, we establish some exact relations governing the effective moduli of electrostrictive composites, using the uniform field concept developed by Dvorak (1990) and extended to piezoelectric composites by Benveniste and Dvorak (1992). To this end, we again notice that the effective compliance of the composite is decoupled from the electric field. As a result, all the exact relations governing the effective elastic moduli of an elastic composite are still applicable to the electrostrictive composite, and we will focus on the effective electrostrictive coefficients.

The essence of the uniform field concept is that the existence of a uniform field in a composite imposes some constraints on its effective moduli, from which the exact connections can be established. So the first step is to characterize the uniform field. We consider two-phase composites first. For a given electric field $\mathbf{E}^0$, the following stress will ensure a uniform strain field in the composites

$$\sigma^0 = (\mathbf{S}_1 - \mathbf{S}_2)^{-1}(\mathbf{M}_2 - \mathbf{M}_1)\mathbf{E}^{0^2}, \tag{3.17}$$

which is derived from (3.1_1), where superscript -1 is used to denote tensor inversion. With the stress so specified, the electric field is determined by solving

$$\kappa_1 - \kappa_2 = 2(\mathbf{M}_2 - \mathbf{M}_1)(\mathbf{S}_1 - \mathbf{S}_2)^{-1}(\mathbf{M}_2 - \mathbf{M}_1)\mathbf{E}^{0^2} \tag{3.18}$$

to ensure a uniform electric displacement in the composite, derived from (3.1_2); we ignored the trivial solution where the electric field is zero. To ensure real solutions for Eqs. (3.17) and (3.18), both $\mathbf{S}_2 - \mathbf{S}_1$ and $\mathbf{M}_2 - \mathbf{M}_1$ need to be invertible, thus have nonzero determinant, and $\kappa_1 - \kappa_2$ and $\mathbf{S}_1 - \mathbf{S}_2$ are either both positive definite or both negative definite; otherwise the analysis breaks down. Notice that the existence of a uniform field imposes no constraint on the symmetry of the constituent phases or composites. It does not even require the macroscopic homogeneity at this point.

Now we consider a macroscopic homogeneous two-phase composite of orthorhombic symmetry consisting of orthorhombic phases, but with otherwise arbitrary geometry. This leads to the following elastic compliance and electrostrictive coefficient:

$$\mathbf{S} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{22} & S_{23} & 0 & 0 & 0 \\ S_{13} & S_{23} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{bmatrix},$$

$$\mathbf{M} = \begin{bmatrix} M_{11} & M_{12} & M_{13} & 0 & 0 & 0 \\ M_{21} & M_{22} & M_{23} & 0 & 0 & 0 \\ M_{31} & M_{32} & M_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & M_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & M_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & M_{66} \end{bmatrix}.$$

Notice that we assume no diagonal symmetry for $\mathbf{M}$ in general. In order to determine M_{11}^*, M_{21}^*, and M_{31}^*, we assume that the only nonzero electric field component is

$$E_1|_1 = E_1|_2 = E_1^0,$$

such that the applied stress σ_{11}^0, σ_{22}^0 and σ_{33}^0 need to satisfy

$$\begin{bmatrix} \sigma_{11}^0 \\ \sigma_{22}^0 \\ \sigma_{33}^0 \end{bmatrix} = \begin{bmatrix} F_{11} & F_{12} & F_{13} \\ F_{12} & F_{22} & F_{23} \\ F_{13} & F_{23} & F_{33} \end{bmatrix}^{-1} \begin{bmatrix} M_{11}|_2 - M_{11}|_1 \\ M_{21}|_2 - M_{21}|_1 \\ M_{31}|_2 - M_{31}|_1 \end{bmatrix} E_1^0,$$

to ensure a uniform strain field, where

$$\begin{bmatrix} F_{11} & F_{12} & F_{13} \\ F_{12} & F_{22} & F_{23} \\ F_{13} & F_{23} & F_{33} \end{bmatrix} = \begin{bmatrix} S_{11}|_1 - S_{11}|_2 & S_{12}|_1 - S_{12}|_2 & S_{13}|_1 - S_{13}|_2 \\ S_{12}|_1 - S_{12}|_2 & S_{22}|_1 - S_{22}|_2 & S_{23}|_1 - S_{23}|_2 \\ S_{13}|_1 - S_{13}|_2 & S_{23}|_1 - S_{23}|_2 & S_{33}|_1 - S_{33}|_2 \end{bmatrix}$$

and $|_r$ is used to denote components in phase r. With the stress so specified in terms of the electric field, we can solve Eq. (3.1_2) for E_1^0 to ensure the uniform electric displacement in the composite. If the moduli of the constituent phases guarantee the existence of nontrivial real solutions, we have

$$E_1^0 = \pm \frac{1}{N_{11}} (\kappa_{11}|_1 - \kappa_{11}|_2)$$

with

$$N_{11} = 2 \begin{bmatrix} M_{11}|_2 - M_{11}|_1 \\ M_{12}|_2 - M_{12}|_1 \\ M_{13}|_2 - M_{13}|_1 \end{bmatrix}^t \begin{bmatrix} F_{11} & F_{12} & F_{13} \\ F_{12} & F_{22} & F_{23} \\ F_{13} & F_{23} & F_{33} \end{bmatrix}^{-1} \begin{bmatrix} M_{11}|_2 - M_{11}|_1 \\ M_{21}|_2 - M_{21}|_1 \\ M_{31}|_2 - M_{31}|_1 \end{bmatrix},$$

where the superscript t is used to denote matrix transpose. The uniform electromechanical field needs to satisfy the constitutive equations for both constituent phases and composites, as a result, we obtain the exact relations between the effective electrostrictive coefficients and the effective compliance of the composites using Eqs. (3.5_1)

and (3.1_1),

$$\begin{bmatrix} M_{11}^* - \bar{M}_{11} \\ M_{21}^* - \bar{M}_{21} \\ M_{31}^* - \bar{M}_{31} \end{bmatrix} = \begin{bmatrix} \bar{S}_{11} - S_{11}^* & \bar{S}_{12} - S_{12}^* & \bar{S}_{13} - S_{13}^* \\ \bar{S}_{12} - S_{12}^* & \bar{S}_{22} - S_{22}^* & \bar{S}_{23} - S_{23}^* \\ \bar{S}_{13} - S_{13}^* & \bar{S}_{23} - S_{23}^* & \bar{S}_{33} - S_{33}^* \end{bmatrix}$$

$$\times \begin{bmatrix} F_{11} & F_{12} & F_{13} \\ F_{12} & F_{22} & F_{23} \\ F_{13} & F_{23} & F_{33} \end{bmatrix}^{-1} \begin{bmatrix} M_{11}|_2 - M_{11}|_1 \\ M_{21}|_2 - M_{21}|_1 \\ M_{31}|_2 - M_{31}|_1 \end{bmatrix}. \qquad (3.19)$$

Similarly we can assume that the only nonzero applied electric field is given by

$$E_2|_1 = E_2|_2 = E_2^0$$

to determine M_{12}^*, M_{22}^* and M_{32}^*, or

$$E_3|_1 = E_3|_2 = E_3^0$$

to determine M_{13}^*, M_{23}^* and M_{33}^*. They are summarized as the following:

$$\begin{bmatrix} M_{12}^* - \bar{M}_{12} \\ M_{22}^* - \bar{M}_{22} \\ M_{32}^* - \bar{M}_{32} \end{bmatrix} = \begin{bmatrix} \bar{S}_{11} - S_{11}^* & \bar{S}_{12} - S_{12}^* & \bar{S}_{13} - S_{13}^* \\ \bar{S}_{12} - S_{12}^* & \bar{S}_{22} - S_{22}^* & \bar{S}_{23} - S_{23}^* \\ \bar{S}_{13} - S_{13}^* & \bar{S}_{23} - S_{23}^* & \bar{S}_{33} - S_{33}^* \end{bmatrix}$$

$$\times \begin{bmatrix} F_{11} & F_{12} & F_{13} \\ F_{12} & F_{22} & F_{23} \\ F_{13} & F_{23} & F_{33} \end{bmatrix}^{-1} \begin{bmatrix} M_{12}|_2 - M_{12}|_1 \\ M_{22}|_2 - M_{22}|_1 \\ M_{32}|_2 - M_{32}|_1 \end{bmatrix}, \qquad (3.20)$$

and

$$\begin{bmatrix} M_{13}^* - \bar{M}_{13} \\ M_{23}^* - \bar{M}_{23} \\ M_{33}^* - \bar{M}_{33} \end{bmatrix} = \begin{bmatrix} \bar{S}_{11} - S_{11}^* & \bar{S}_{12} - S_{12}^* & \bar{S}_{13} - S_{13}^* \\ \bar{S}_{12} - S_{12}^* & \bar{S}_{22} - S_{22}^* & \bar{S}_{23} - S_{23}^* \\ \bar{S}_{13} - S_{13}^* & \bar{S}_{23} - S_{23}^* & \bar{S}_{33} - S_{33}^* \end{bmatrix}$$

$$\times \begin{bmatrix} F_{11} & F_{12} & F_{13} \\ F_{12} & F_{22} & F_{23} \\ F_{13} & F_{23} & F_{33} \end{bmatrix}^{-1} \begin{bmatrix} M_{13}|_2 - M_{13}|_1 \\ M_{23}|_2 - M_{23}|_1 \\ M_{33}|_2 - M_{33}|_1 \end{bmatrix}. \qquad (3.21)$$

In another word, the effective electrostrictive coefficients are determined by the effective compliance in two-phase electrostrictive composites, regardless of the micro-geometry other than the requirements on the macroscopic homogeneity and symmetry. We can also verify that in general the effective electrostrictive tensor does not have main diagonal symmetry, even if that of the constituent phases does. We need to point out though, that the exact connections only apply to the effective electrostrictive coefficients at those particular electromechanical loadings that guarantee the existence of a uniform field. This is due to the nonlinear nature of the electrostriction, which makes the exact relations much less useful than those in elastic or piezoelectric composites. Nevertheless, we can use those exact connections to validate our micromechanical approximation and numerical algorithm, as we do later.

Some of these exact relations governing the effective electrostrictive coefficients can be derived using an alternative method for fibrous and laminated composites, which provides a consistency check. To this end, we first recall the exact relation between the effective eigenstrain and the stress concentration factor

$$\varepsilon^*[\bar{\mathbf{E}}^2] = \sum_{r=1}^{N} f_r \mathbf{B}_r^t \varepsilon_r^{\mathrm{T}}[\mathbf{E}_r^2], \tag{3.22}$$

which was first established by Levin (1967) for thermal expansion coefficients. For two-phase composites, we have

$$\mathbf{S}^* = \mathbf{S}_1 + f_2(\mathbf{S}_2 - \mathbf{S}_1)\mathbf{B}_2 \tag{3.23}$$

derived from Eqs. (3.12) and (3.11). Solving $\mathbf{B}_2$ in terms of $\mathbf{S}^*$ yields

$$\mathbf{B}_2 = \frac{1}{f_2}(\mathbf{S}_2 - \mathbf{S}_1)^{-1}(\mathbf{S}^* - \mathbf{S}_1). \tag{3.24}$$

As a result, if $\mathbf{E}_r$ can be determined, then the exact connection between the effective compliance and the effective electrostrictive coefficient can be established through (3.22) and (3.24),

$$\varepsilon^*[\bar{\mathbf{E}}^2] = \varepsilon_1^{\mathrm{T}}[\mathbf{E}_1^2] + (\mathbf{S}^* - \mathbf{S}_1)(\mathbf{S}_2 - \mathbf{S}_1)^{-1}(\varepsilon_2^{\mathrm{T}}[\mathbf{E}_2^2] - \varepsilon_1^{\mathrm{T}}[\mathbf{E}_1^2]). \tag{3.25}$$

We first consider a two-phase fibrous composite, where the fiber direction is chosen as x_3-axis. In order to determine the effective electrostrictive constant M_{13}^*, M_{23}^* M_{33}^*, we apply an arbitrary electric field E_3^0 to the composite, which results in

$$E_3|_1 = E_3|_2 = E_3^0$$

due to the continuity of the tangent of the electric field. As a result, we obtain

$$M_{I3}^* = M_{I3}|_1 + (S_{IK}^* - S_{IK}|_1)(S_{JK}|_2 - S_{JK}|_1)^{-1}(M_{J3}|_2 - M_{J3}|_1) \tag{3.26}$$

using Eqs. (3.22) and (3.24), which is consistent with Eq. (3.21). We then consider a two-phase laminated composite, where the normal of the laminates is chosen as x_3-axis. In order to determine the effective electrostrictive constant M_{11}^*, M_{21}^*, M_{31}^*, we apply the electric field E_1^0 to the composite, which results in

$$E_1|_1 = E_1|_2 = E_1^0$$

due to the continuity condition. As such, we obtain

$$M_{I1}^* = M_{I1}|_1 + (S_{IK}^* - S_{IK}|_1)(S_{JK}|_2 - S_{JK}|_1)^{-1}(M_{J1}|_2 - M_{J1}|_1), \tag{3.27}$$

which is consistent with Eq. (3.19). Similarly, we have

$$M_{I2}^* = M_{I2}|_1 + (S_{IK}^* - S_{IK}|_1)(S_{JK}|_2 - S_{JK}|_1)^{-1}(M_{J2}|_2 - M_{J2}|_1) \tag{3.28}$$

in consistency with Eq. (3.20). It is worthwhile to notice that Eqs. (3.20)–(3.28) hold regardless of the magnitude of the applied electric field, though they are only applicable to the particular fibrous or laminated micro-geometry, unlike Eqs. (3.19)–(3.21), which are valid for arbitrary micro-geometry but only at the specified electromechanical load.

For multi-phase fibrous or laminated composites, we were unable to determine the stress concentration factor $\mathbf{B}_r$ in terms of $\mathbf{S}^*$. However, we can still use Eq. (3.22) to determine certain components of the effective electrostrictive coefficients, due to the existence of a uniform field. For multi-phase fibrous composites we can determine M_{13}^*, M_{23}^* and M_{33}^* in such way as

$$M_{I3} = \sum_{r=1}^{N} f_r B_{KI}|_r M_{K3}|_r, \quad I = 1,2,3. \tag{3.29}$$

which are well-defined material constants independent of the applied electric field E_3^0. For laminated composites, we have

$$M_{IJ} = \sum_{r=1}^{N} f_r B_{KI}|_r M_{KJ}|_r, \quad I = 1,2,3, \;\; J = 1,2, \tag{3.30}$$

which are also well-defined independent of the applied electric fields E_1^0 or E_2^0. Neither equations require any constraint on the symmetry of constituent phases and composites.

3.3. Micromechanical approximation

For general loading conditions and micro-geometry, the exact connections usually are not applicable, and approximations must be made regarding the distribution of electromechanical field in the composites in order to determine the effective moduli $\mathbf{S}^*$, $\kappa^{\sigma *}$, and $\mathbf{M}^*$. We turn to a micromechanical model for this purpose. For linear elastic or piezoelectric composites, the Mori–Tanaka approach is very successful in predicting the effective elastic, piezoelectric and dielectric moduli of the composites (Mori and Tanaka, 1973; Dunn and Taya, 1993a), which is essentially a mean field method (Benveniste, 1987). Using this approach, the stress concentration factor of electrostrictive composites can be determined directly from linear elasticity as (Li, 1999)

$$\mathbf{B}_r = \mathbf{B}_r^{\text{dil}} \left(\sum_{i=1}^{N} f_i \mathbf{B}_i^{\text{dil}} \right)^{-1}, \tag{3.31}$$

because it is decoupled from the electric field, with the dilute stress concentration factor given by

$$\mathbf{B}_r^{\text{dil}} = \{\mathbf{I} + \mathbf{S}_1^{-1}(\mathbf{I} - \mathbf{S}_r^{\text{Esh}})(\mathbf{S}_r - \mathbf{S}_1)\}^{-1}, \tag{3.32}$$

where $\mathbf{S}_i^{\text{Esh}}$ is the elastic Eshelby tensor for phase r (Eshelby, 1957), which depends on the elastic moduli of the matrix and the shape aspect ratio of phase r. It is clear that the normalization condition is automatically satisfied by Eq. (3.31). The Mori–Tanaka approach cannot be applied directly to determine the effective electrostrictive coefficients though, due to the nonlinear electromechanical coupling of the electrostriction. However, if the stress σ_r is known for each phase, then we can determine the electric field concentration factor as

$$\alpha_r = \alpha_r^{\mathrm{dil}} \left(\sum_{i=1}^{N} f_i \alpha_i^{\mathrm{dil}} \right)^{-1} \tag{3.33}$$

using the Mori–Tanaka approximation, with the dilute field concentration factor given by

$$\alpha_r^{\mathrm{dil}} = \{\mathbf{i} + \mathbf{s}_r (\kappa_1^{\sigma})^{-1} (\kappa_r^{\sigma} - \kappa_1^{\sigma})\}^{-1}, \tag{3.34}$$

where $\mathbf{s}_r$ is the dielectric Eshelby tensor, which is dependent on κ_1^{σ} of the matrix and the shape aspect ratio of phase r. It is clear that the electric field concentration factor is coupled with the elastic field through the stress-dependent dielectric constant κ_r^{σ}. If the electric field concentration factor is determined as such, we can then determine the eigenstrain $\varepsilon_r^{\mathrm{T}}[\alpha_r \mathbf{E}^0]$, and use the exact connection between the eigenstress and the stress concentration factor (Benveniste et al., 1991)

$$\begin{aligned} \sigma_r^{\mathrm{T}}[\mathbf{E}_r^2] = {} & (\mathbf{I} - \mathbf{B}_r)(\mathbf{S}_1 - \mathbf{S}_r)^{-1} (\varepsilon_r^{\mathrm{T}}[(\alpha_r \mathbf{E}^0) \otimes (\alpha_r \mathbf{E}^0)] \\ & - \varepsilon_1^{\mathrm{T}}[(\alpha_1 \mathbf{E}^0) \otimes (\alpha_1 \mathbf{E}^0)]), \end{aligned} \tag{3.35}$$

to determine the eigenstress for phases 2 to N. For the matrix, the eigenstress is solved from (3.11_2) as

$$\sigma_1^{\mathrm{T}} = -\frac{1}{f_1} \sum_{i=2}^{N} f_i \sigma_r^{\mathrm{T}}. \tag{3.36}$$

Clearly we have coupled electromechanical equations (3.33)–(3.36), where the electric field concentration factor depends on the stress distribution in the composites through the stress-dependent dielectric constants, and the eigenstress depends on the electric field distribution in the composites through the electric field-dependent eigenstrain. In general, it is difficult to solve these nonlinearly coupled electromechanical equations analytically, and we turn to the numerical method for solution. What we developed is an iterative scheme, starting with an initial guess on the electric field, and calculate the stress and the electric field distributions accordingly. The iteration stops when convergence criteria on both electric field and stress distributions are satisfied. The numerical algorithm is summarized as follows:

1. Input the material properties, volume fractions, and shape aspect ratio for all phases, as well as the applied stress σ^0 and electric field $\mathbf{E}^0$;
2. evaluate the elastic Eshelby tensor $\mathbf{S}_r^{\mathrm{Esh}}$ for phase r using the elastic properties of matrix and shape aspect ratio of phase r;
3. evaluate the stress concentration factor $\mathbf{B}_r$ according to Eqs. (3.31) and (3.32);
4. assign $\mathbf{E}_r = \mathbf{E}^0$ for phase r as an initial guess;
5. evaluate the eigenstrain $\varepsilon_r^{\mathrm{T}}[\mathbf{E}_r^2]$ according to Eq. (3.2_1);

6. evaluate the eigenstress $\sigma_r^{\mathrm{T}}[\mathbf{E}_r^2]$ according to Eqs. (3.35) and (3.36);
7. evaluate the stress σ_r in phase r according to Eq. (3.9);
8. evaluate the stress-dependent dielectric constant κ_r^{σ} according to Eq. (3.2$_2$),
9. evaluate the dielectric Eshelby tensor $\mathbf{s}_i$, and electric field concentration factor α_r according to Eqs. (3.34) and (3.33);
10. evaluate the updated electric field $\mathbf{E}_r$ according to Eq. (3.8), and check the convergence of both electric field and stress; go to step 5 until converging;
11. evaluate the effective compliance $\mathbf{S}^*$ according to Eq. (3.12), the effective electrostrictive coefficient $\mathbf{M}^*$ according to Eq. (3.15), the effective stress-dependent dielectric constant $\kappa^{\sigma *}$ according to Eq. (3.13), and the effective dielectric constant κ^* according to Eq. (3.16).

This algorithm allows us to determine the effective muduli of multi-phase electrostrictive composites with various micro-geometry, as we demonstrate in the next section.

4. Numerical results and discussion

In this section, we consider the effective electrostriction of P(VDF-TrFE) polymers reinforced by $\mathrm{Pb(Zr}_x\mathrm{Ti}_{1-x})\mathrm{O}_3$ (PZT) ceramics with various micro-geometries using the nonlinear micromechanics model we developed, implemented in an FORTRAN program. The algorithm has been validated using the exact relations governing the effective moduli. The electron-irradiated P(VDF-TrFE) polymer has dramatically enhanced electrostriction compared to the typical polymers without electron irradiation (Zhang et al., 1998), where it is shortened in the longitudinal direction along the applied electric field, and stretched in the lateral direction perpendicular to it. With the addition of PZT ceramics of high dielectric constant, the electrostriction can be further improved, if the microstructure of the composite is carefully tailored. It is the objective of this study to identify the optimal microstructure of composites with optimized effective electrostriction, which could be used to guide the design and optimization of P(VDF-TrFE) polymer-based composites.

We assume that the P(VDF-TrFE) polymer is isotropic, with Young's modulus, the electrostrictive coefficients M_{11} and M_{12}, and the dielectric constants estimated from plots in Zhang et al. (1998). The material properties of PZT ceramics, which are transversely isotropic, are obtained from Dunn and Taya (1993a), with the exception that the piezoelectric constants are assumed to be zero, justified by the fact that the piezoelectric strain of ceramics is much smaller than electrostrictive strain of polymers. The material properties of constituent phases are listed in Table 1. It is noted that PZT ceramics are much softer dielectrically, and much stiffer elastically than P(VDF-TrFE) polymers, thus an optimal microstructure must take advantage of its high dielectric constants, yet relax its mechanical constraint on the polymers, as we demonstrate here. In the following calculations, we consider two-phase composites subject to the traction free boundary conditions such that $\bar{\sigma} = \mathbf{0}$, where aligned ellipsoidal ceramics are embedded in P(VDF-TrFE) matrix, with the aspect ratio given by $\alpha = a_3/a_1 = a_3/a_2$.

Table 1
The electromechanical properties of constituent materials in the composites

Material	S_{11}	S_{12}	S_{13}	S_{33}	S_{44}
P(VDF-TrFE)	0.74	-0.22	-0.22	0.74	1.92
PZT	$1.44\ 10^{-2}$	$-4.45\ 10^{-3}$	$-7.71\ 10^{-3}$	$2.00\ 10^{-2}$	$4.35\ 10^{-2}$
	M_{11}	M_{12}	κ_{11}	κ_{33}	
P(VDF-TrFE)	-2.40	1.20	68.5	68.5	
PZT	0	0	1700	1470	

Units: $\mathbf{S}: 10^{-9}$, $\mathbf{M}: 10^{-18}\ \mathrm{m}^2/\mathrm{V}^2$, $\kappa : \kappa_0$.

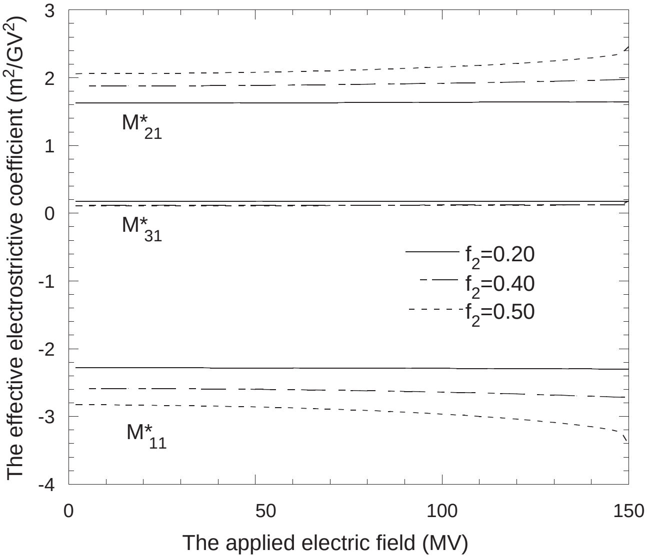

Fig. 1. The effective electrostrictive coefficients of fibrous composites versus the applied electric field.

4.1. The effect of electric field

We first consider the variation of the effective electrostrictive coefficients with respect to the applied electric field induced by the nonlinear electromechanical coupling, where M_{11}^*, M_{21}^* and M_{31}^* of fibrous composites, M_{13}^* and M_{33}^* of particulate composites, and M_{33}^* of laminated composites with different volume fraction of ceramics are shown in Figs. 1–3, respectively. It is observed that although the effective electrostrictive coefficients increase with the applied electric field, the dependence is weak in general. The variation of the electrostrictive coefficients with respect to the applied electric field is larger when the applied electric field and the volume fraction of the ceramic are higher, due to the increased interaction between the ceramics and polymers. For

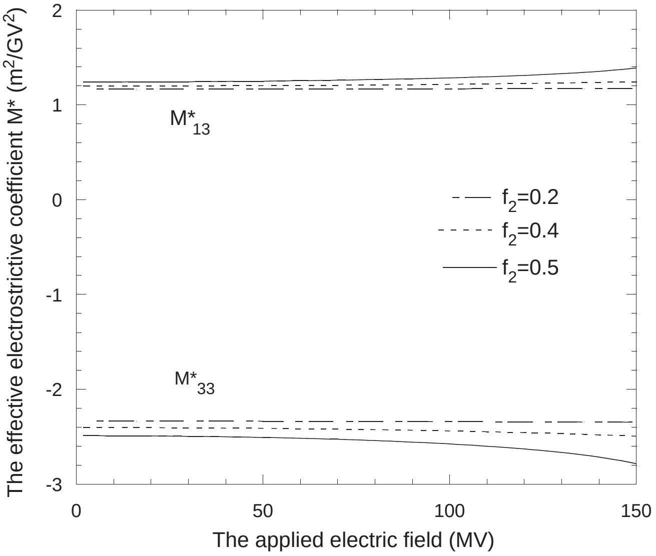

Fig. 2. The effective electrostrictive coefficients of particulate composites versus the applied electric field.

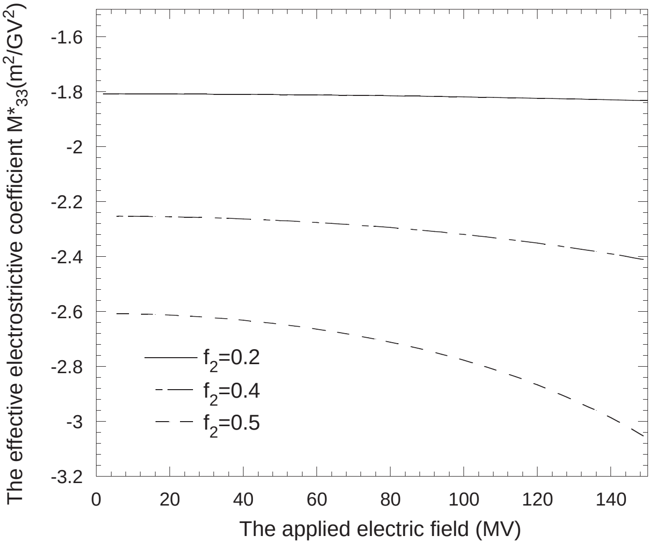

Fig. 3. The effective electrostrictive coefficients of laminated composites versus the applied electric field.

fibrous composites, M_{31}^* shows least variation with respect to the electric field, due to the severe mechanical constraint from the ceramics along the fibrous direction. For the longitudinal compression along the field direction, M_{33}^* of laminated composites shows the largest variation compared to M_{11}^* of fibrous composites and M_{33}^* of particulate

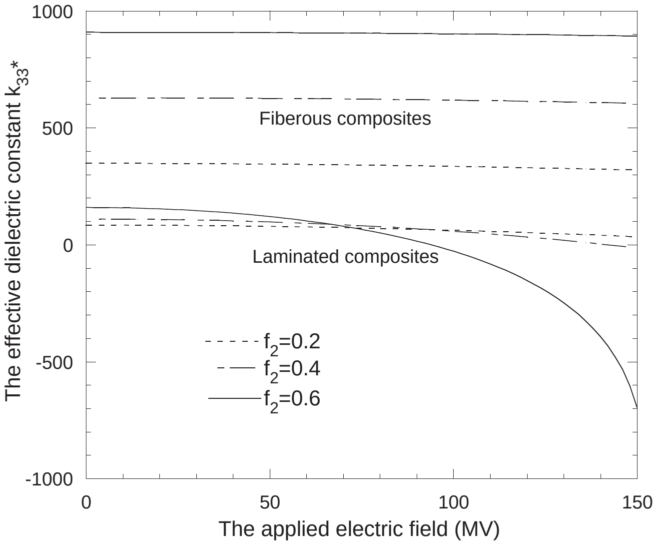

Fig. 4. The effective dielectric constant of fibrous and laminated composites versus the applied electric field.

composites, due to the least mechanical constraint along the field direction for the laminated configuration.

Owing to the internal stress induced by the electric field and the stress-dependent dielectric constant of P(VDF-TrFE), the variation of the effective dielectric constant κ_{33}^* with respect to the electric field is larger, especially for the high electric field and large volume fraction of the ceramics, as shown in Figs. 4 and 5. It is observed that κ_{33}^* decreases with the applied electric field, because compressive stress is induced in the polymers in the x_1 and x_2 directions due to the constraint of ceramics, and such compressive stress tends to decrease the stress-dependent dielectric constant of P(VDF-TrFE), $\kappa_{33}^\sigma = \kappa_{33} + 2(M_{13}\sigma_1 + M_{23}\sigma_2 + M_{33}\sigma_3)$, where M_{13} and M_{23} are positive. The variation is largest in the laminated composites and smallest in the fibrous composites, because the lateral constraint is most severe in laminated composites and least severe in fibrous composites. For laminated composites with 60% of ceramic, κ_{33}^* even becomes negative at high electric field due to the large compressive stress σ_{11} and σ_{22}, which suggests that the linear dielectric constitutive equation may no longer be applicable.

4.2. *The effect of volume fraction of ceramic*

We then investigate the effect of volume fraction on the effective electrostriction, where the effective electrostrictive coefficients $M_{13}^* = M_{23}^*$ and M_{33}^* of fibrous composites and M_{11}^*, M_{21}^*, and M_{31}^* of laminated composites are shown in Figs. 6 and 7, respectively, which are independent of the applied electric field, due to the existence of the uniform electric field under the particular micro-geometries and loading conditions.

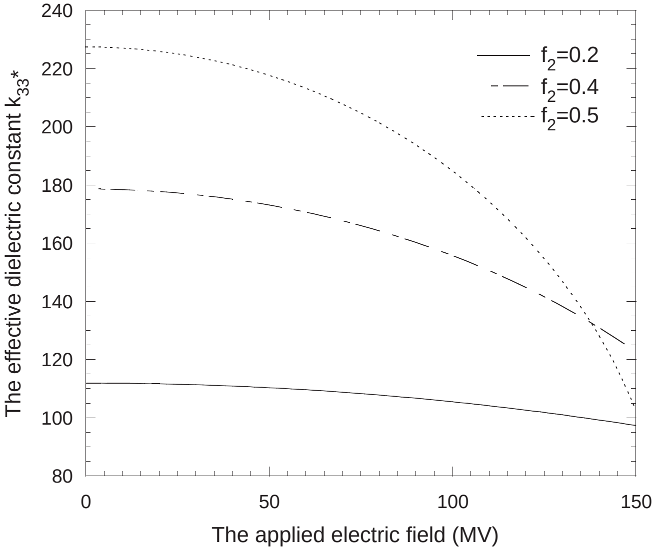

Fig. 5. The effective dielectric constant of particulate composites versus the applied electric field.

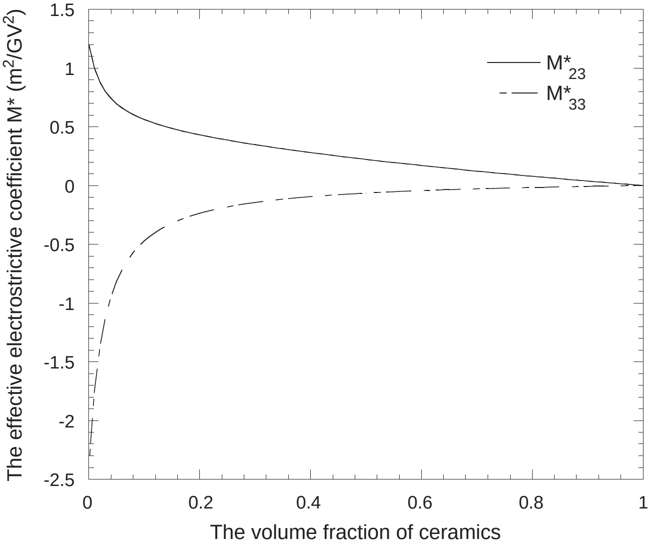

Fig. 6. The effective electrostrictive coefficients of fibrous composites versus the volume fraction of ceramics.

They are very similar, both decreasing with the addition of the ceramic phase, thus are not attractive for electrostriction enhancement, in consistency with the one-dimensional model where each phase is arranged in parallel with each other (Li and Rao, 2002). It is also observed that for the laminated composites, M_{21}^* is much smaller than M_{31}^* due

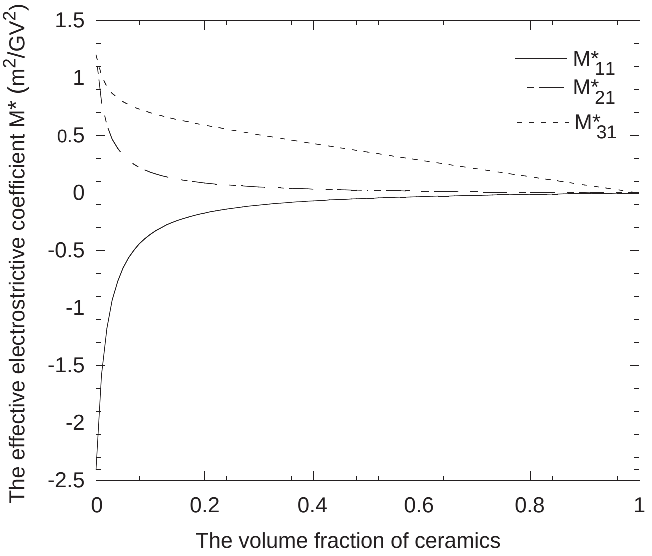

Fig. 7. The effective electrostrictive coefficients of laminated composites versus the volume fraction of ceramics.

to the much more severe lateral mechanical constraint along x_2 direction than that along x_3 direction, suggesting that the micro-geometry is very important for the macroscopic behaviors of the composites.

The variation of M^*_{33} versus the volume fraction of the ceramic, calculated at $E_0 = 75$ MV/m, is shown in Fig. 8 for composites with different aspect ratio of ceramics. The dependence of the electrostrictive coefficients with respect to the applied electric field is weak, as we demonstrated before. It is observed that the electrostriction can indeed be enhanced by the composite concept, where the electrostrictive coefficients three times higher than that of polymer can be obtained. Meanwhile, not all the micro-geometries lead to the enhanced electrostriction; with the increase of the volume fraction of ceramics, the effective electrostriction increases for aspect ratio of 1, 0.1, and 10^{-6}, but decrease for the aspect ratio of 10. In addition, we notice that laminated composite is not optimal as far as the electrostriction enhancement is concerned; the composite with aspect ratio of 0.1 has larger electrostriction than that of composite with aspect ratio of 10^{-6}, due to the relaxed mechanical constraint. As such, we need to investigate the effect of the aspect ratio on the effective electrostriction to identify the optimal micro-geometry.

4.3. *The effect of aspect ratio of ceramic*

We finally consider the variation of the effective electrostriction with respect to the aspect ratio of the ceramic, shown in Figs. 9–11, where the effective electrostrictive coefficients are calculated under E_0=75MV/m. In general, it is observed that fibrous com-

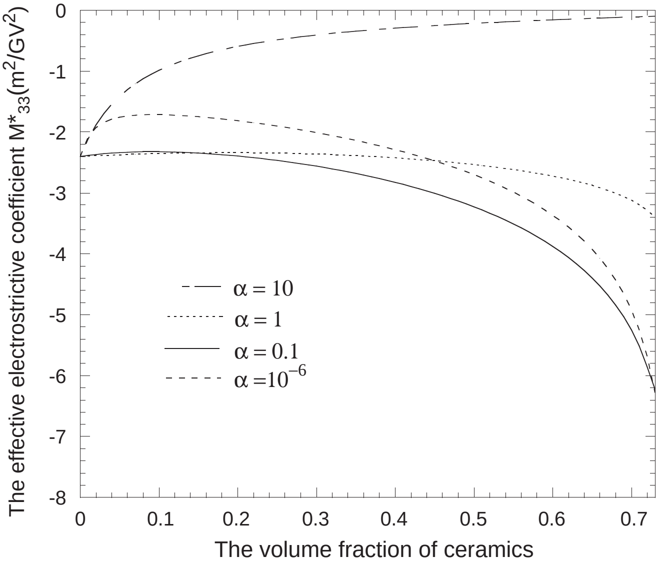

Fig. 8. The effective electrostrictive coefficients of composites with different aspect ratio of ceramics versus the volume fraction of ceramics.

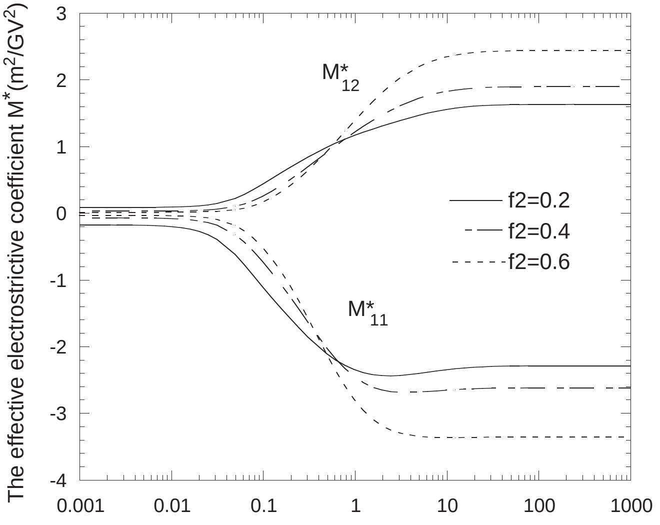

Fig. 9. The effective electrostrictive coefficients M_{11}^* and M_{12}^* of composites versus the aspect ratio of the ceramics.

posites have enhanced M_{11}^* and M_{12}^*, while laminated composites have enhanced M_{33}^*, in consistency with the one-dimensional analysis (Li and Rao, 2002), since the electric field is magnified in the polymer phase for the particular micro-geometry considered, leading to higher electrostrictive strain. However, neither fibrous (M_{11}^*) nor laminated

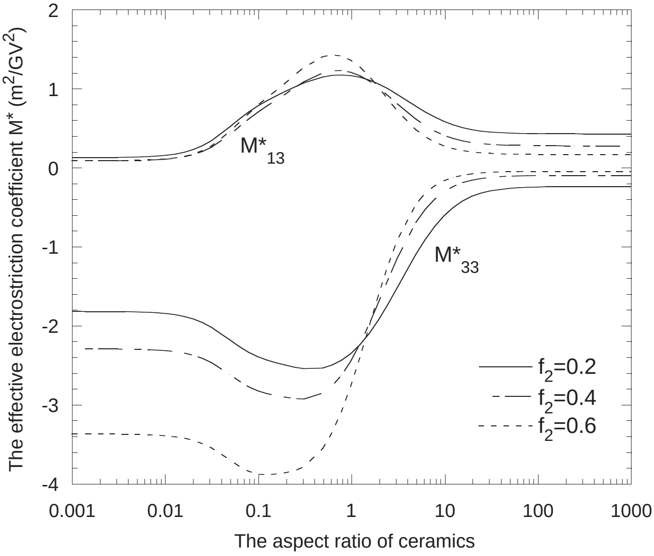

Fig. 10. The effective electrostrictive coefficients M_{13}^* and M_{33}^* of composites versus the aspect ratio of the ceramics.

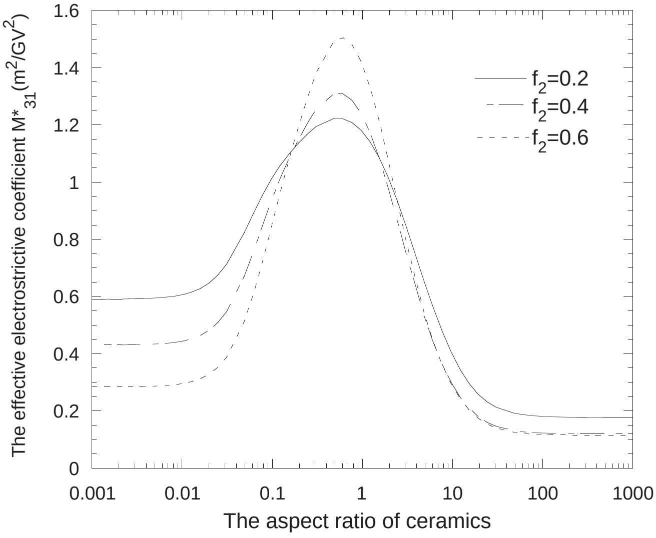

Fig. 11. The effective electrostrictive coefficient M_{31}^* of composites versus the aspect ratio of the ceramics.

composites (M_{33}^*) are optimal for the longitudinal electrostriction along the field direction, because of the severe lateral mechanical constraint. As such, it is observed that there are peaks in the curves of M_{33}^*, M_{13}^*, M_{31}^* and M_{11}^* near aspect ratio of 1.

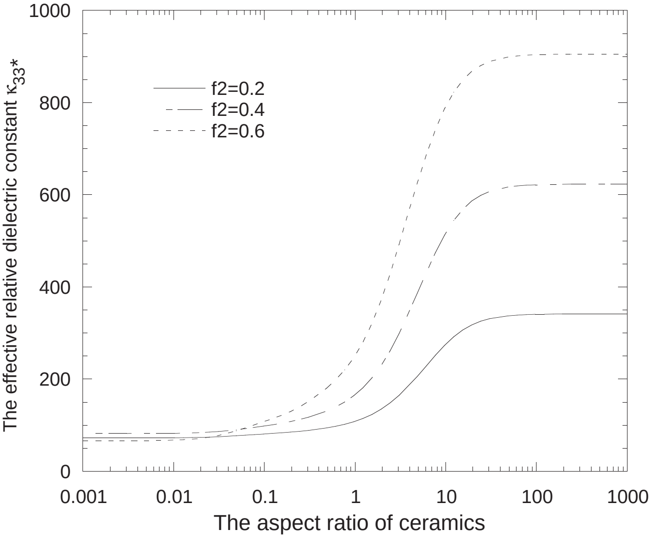

Fig. 12. The effective dielectric constant of composites versus the aspect ratio of the ceramics.

To understand this phenomenon, we recall that P(VDF-TrFE) polymer not only gets shortened along the longitudinal direction under an electric field, it also gets stretched along the lateral directions, which is severely constrained by the ceramic phase. As a result, the optimal microstructure should have the maximum electric field magnification for P(VDF-TrFE) polymer, yet relaxed mechanical constraint, suggesting an aspect ratio close to 0.1 for M_{33}^* and close to 10 for M_{11}^* as shown in the figures. The peak of M_{33}^* near aspect ratio of 0.1 is more significant than that of M_{11}^*, due to the relaxation of more severe lateral constraint. For the same reason, there are peaks in the curves of M_{13}^* and M_{31}^*, which are not equal to each other and thus $\mathbf{M}^*$ is not diagonally symmetric. It is also noticed that away from the peak where the effective electrostriction is not enhanced compared to that of pure polymer, the composites with lower volume fraction of ceramic often have higher electrostriction than composites with higher volume fraction of ceramic, due to the dilution effect. This suggests again that the enhancement of electrostriction in the composites is due to the interaction between the P(VDF-TrFE) polymers and the dielectric ceramic, which results in the electric field magnification in the polymer phase, and is more effective at higher volume fraction regime of ceramic.

The dielectric constant κ_{33}^* versus the aspect ratio of ceramic particles is also shown in Fig. 12 for different volume fractions. It is observed that the dielectric constant increases with the aspect ratio, and the difference between different volume fraction is very small for laminated composites where the aspect ratio is small, and is very large for fibrous composites where the aspect ratio is large. This is because for laminated composites κ_{33}^* is mainly determined by that of polymer which is relatively small, while for fibrous composites it is mainly determined by that of ceramics which is relatively large.

5. Concluding remarks

In summary, we developed a nonlinear micromechanics model to study the effective electrostriction of the P(VDF-TrFE) polymer-based composites in terms of their microstructural information. Exact connections between the effective electrostrictive coefficients and the effective elastic moduli were established, and a numerical algorithm for the effective electrostriction calculations was developed. Enhanced electrostriction in the composites has been demonstrated, and the optimal microstructure of the composites has been identified.

Acknowledgements

We gratefully acknowledge the support of the National Science Foundation Nanomanufacturing Program (DMI-0300014), Strategic Research Cluster Grant from the University of Nebraska-Lincoln, and the Type G Grant of Petroleum Research Fund from American Chemical Society (PRF# 39526-G5B).

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