ELSEVIER

International Journal of Solids and Structures 41 (2004) 2995–3011

INTERNATIONAL JOURNAL OF SOLIDS and STRUCTURES

www.elsevier.com/locate/ijsolstr

The electrostriction of P(VDF-TrFE) copolymers embedded with textured dielectric particles

Nagadip Rao, Jiang Yu Li *

Department of Engineering Mechanics, University of Nebraska-Lincoln, W317.5 Nebraska Hall, Lincoln, NE 68588-0526, USA

Received 11 August 2003; received in revised form 10 December 2003

Available online 21 February 2004

Abstract

Electrostriction refers to the nonlinear electromechanical coupling in materials, where the strain depends on the electric field quadratically. In this paper we present a micromechanical analysis on the effective electrostriction of a polyvinylidene fluoride trifluoroethylene [P(VDF-TrFE)] copolymer embedded with textured dielectric particles, where the effective constitutive equations are established using a nonlinear micromechanics model, and a numerical algorithm is developed to calculate the effective electrostrictive coefficients of the composite in terms of its microstructural features. The effects of particle shape and orientation distribution have been investigated, enhanced electrostriction in the composite has been demonstrated, and optimal microstructure for electrostriction enhancement has been identified. Our analysis provides a guideline for the design and optimization of electrostrictive composites for optimal electromechanical properties.

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

1. Introduction

Polyvinylidene fluoride trifluoroethylene [P(VDF-TrFE)] copolymers are attractive for sensors, actuators, and transducers applications, thanks to their relatively large electrostrictive strain induced by electric polarization (Garrett et al., 2003). The large electrostriction is obtained, however, at the expense of high electric field, and great effort has been devoted to increase the dielectric constant of the polymers, so that the magnitude of the applied field required for the large electrostrictive strain can be reduced. For example, electron irradiation has been used to treat P(VDF-TrFE) copolymers (Zhang et al., 1998; Cheng et al., 1999; Bharti et al., 1999; Xu et al., 2001), resulting in a dielectric constant one order higher in magnitude and a dramatically enhanced electrostriction of 4%. Alternatively, composite concept has been proposed to enhance the electrostriction of polymers from both experimental (Bai et al., 2000; Zhang et al., 2002; Dang et al., 2002; Huang et al., 2003) and theoretical point of views (Li and Rao, 2002, 2004; Li, 2003), where a

* Corresponding author. Tel.: +1-402-472-1631; fax: +1-402-472-8292.
E-mail addresses: jli2@unl.edu, jiangyuli@unlnotes.unl.edu (J.Y. Li).

0020-7683/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijsolstr.2003.12.021

second phase with much larger dielectric constant is embedded in the P(VDF-TrFE) matrix to increase the effective dielectric constant of the composite.

The essence of the composite concept is that the electric field in a P(VDF-TrFE) copolymer can be magnified with respect to the applied one, if the microstructure of the composite is carefully tailored, leading to larger dielectric constant and higher electrostriction. While the idea is exciting and promising, there are some issues that need to be addressed. For example, the increase in the dielectric constant of the composite is often accompanied by 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 of the composite, since higher stiffness usually leads to lower actuation strain. On the other hand, higher stiffness also results in larger actuation energy density and force, thus may be desirable for actuator applications, especially when the polymer phase is soft. Ideally, the optimal microstructure should lead to the optimized electric field magnification in the P(VDF-TrFE) copolymers, yet relaxed mechanical constraint from the second dielectric phase, as we demonstrated for a two-phase composite consisting of aligned dielectric second phase embedded in a P(VDF-TrFE) matrix (Li and Rao, 2004). Clearly, microstructure plays a key role in the optimization of electrostriction in the P(VDF-TrFE) copolymer based electrostrictive composites, and appropriate microstructure must be identified in order to take advantage of the high dielectric constant of the second phase for the enhanced electrostriction.

Motivated by those studies, we will investigate the effective electrostriction of the P(VDF-TrFE) copolymers embedded with textured dielectric particles in this paper, with the objectives to predict the macroscopic behavior of the composites from their microstructure information, and to identify the appropriate microstructure for the optimal electrostriction enhancement. In particular, we will study the effect of particle orientation distribution on the electrostriction of the composites, which has not been addressed in our previous papers. This effect is important, since it is difficult to align all particles in the matrix. Besides the obvious technological importance, this class of composites also demonstrates many interesting features arising from the nonlinear electromechanical coupling, which are worthy investigation. For example, the stress modulated linear dielectric behavior in a pure electrostrictive phase will lead to nonlinear dielectric response in composites, which may find applications in tunable microwave devices (Gevorgian et al., 1998). Although significance 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; Hori and Nemat-Nasser, 1998; Li, 2000a), 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 stress (Nan and Weng, 2000), which is appropriate when the polarization of the composite saturates under a 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 essential roles in the electrostriction enhancement in an all-organic composite (Zhang et al., 2002; Li, 2003). Particularly, we are interested in the effects of particle shape and orientation distribution on the overall electrostriction of the composites, generalizing the micromechanics model we developed for two-phase electrostrictive composites containing aligned dielectric second phase (Li and Rao, 2004). Unlike our previous papers, we have to carry out orientational averaging in order to account for particle orientation distributions, and we have developed a numerical scheme to do that. The basic constitutive equations governing electrostriction will be presented in Section 2, followed by a detailed analysis of electrostrictive composites in Section 3, where a nonlinear

micromechanics model will be established, particle orientation distribution and orientational averaging will be discussed, and a numerical algorithm will be developed to predict the effective moduli of the electrostrictive composites. We then present some numerical results and discussion regarding P(VDF-TrFE) copolymers embedded with textured dielectric particles in Section 4 and conclude the paper.

2. The electrostrictive effect

We consider the electrostrictive effect of materials governed by the nonlinearly coupled electromechanical energy (Newnham et al., 1997)

$$V[\sigma, \mathbf{E}] = -\frac{1}{2} S_{ijkl}\sigma_{ij}\sigma_{kl} - M_{ijkl}\sigma_{ij}E_kE_l - \frac{1}{2}\kappa_{ij}E_iE_j, \tag{2.1}$$

which leads to the electrostrictive constitutive equations

$$\begin{aligned} \varepsilon_{ij} &= S_{ijkl}\sigma_{kl} + M_{ijkl}E_kE_l, \\ D_i &= \kappa_{ij}E_j + 2M_{klij}\sigma_{kl}E_j, \end{aligned} \tag{2.2}$$

where ε_{ij} and E_i are strain and electric field, respectively, derivable from the elastic displacement u_i and electric potential ϕ,

$$\begin{aligned} \varepsilon_{ij} &= u_{(i,j)}, \\ E_i &= -\phi_{,i}, \end{aligned} \tag{2.3}$$

with the comma representing a partial differentiation with respect to x_i and subscript (i,j) representing a symmetrization operation on the second rank tensor; σ_{ij} and D_i are stress and electric displacement, respectively, satisfying the equilibrium equations

$$\begin{aligned} \sigma_{ij,i} &= 0, \\ D_{i,i} &= 0. \end{aligned} \tag{2.4}$$

In (2.2), the constitutive moduli S_{ijkl}, κ_{ij}, and M_{ijkl} are elastic compliance, dielectric constant, and electrostrictive coefficient, respectively, and we adopt the summation convention for the repeated subscript unless pointed out otherwise. We notice that the elastic and electric fields are coupled nonlinearly through the electrostrictive tensor M_{ijkl}, which does not necessarily have the main diagonal symmetry, as is clear from (2.1). The strain depends on the electric field quadratically, while the electric displacement can be changed by stress only if the material is also subject to an electric field. In another word, the electric displacement is proportional to the electric field, with the coefficient modulated by the stress. We ignore the dielectric nonlinearity here, such as polarization saturation at high electric field.

For simplicity, we adopt the well-known matrix notation for the tensor, and introduce a second rank tensor

$$\mathbf{E}^2 = \mathbf{E} \otimes \mathbf{E} \quad \text{or} \quad E^2_{ij} = E_iE_j, \tag{2.5}$$

where $\otimes$ is used to represent the tensor product. The constitutive equation (2.2) can then be rewritten as

$$\begin{aligned} \varepsilon_I &= S_{IJ}\sigma_J + M_{IJ}E^2_J, \\ D_i &= \kappa_{ij}E_j + 2M_{Kij}\sigma_K E_j, \end{aligned} \tag{2.6}$$

where upper case subscripts range from 1 to 6 and repeated upper case subscripts are summed from 1 to 6. In $(2.6)_2$, only the first two indices of M_{ijkl} are contracted. We regard the electrostrictive strain as an eigenstrain (Mura, 1987; Nemat-Nasser and Hori, 1993)

$$\varepsilon_I^{\mathrm{T}}[\mathbf{E}^2] = M_{IJ}E_J^2 \tag{2.7}$$

and introduce a stress-dependent dielectric constant

$$\kappa_{ij}^{\sigma} = \kappa_{ij} + 2M_{Kij}\sigma_K, \tag{2.8}$$

so that the constitutive equation (2.6) can be be reformulated as

$$\begin{aligned} \varepsilon_I &= S_{IJ}\sigma_J + \varepsilon_I^{\mathrm{T}}[\mathbf{E}^2], \\ D_i &= \kappa_{ij}^{\sigma}E_j, \end{aligned} \tag{2.9}$$

which formally resembles the linear elastic equation with eigenstrain and linear dielectric equation, though they are actually coupled nonlinearly.

3. The electrostrictive composite

3.1. The effective moduli and average field

For a multi-phase composite made of electrostrictive materials, the constitutive equations of 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

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

where the subscript r in this context refers to the quantities in phase r, and $r = 1$ is reserved for the matrix. When the composite is subject to a uniform traction and linear electric potential at the boundary

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

we have

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

according to the average field theorem (Dunn and Taya, 1993b), where $\mathbf{t}$ is the traction, $\mathbf{n}$ is the unit outward normal, $\mathbf{x}$ is the position vector, σ^0 and $\mathbf{E}^0$ are constant stress and electric field, and the overhead bar is used to denote the volume averaged field variables in the composite. The electromechanical behaviors of the multi-phase electrostrictive composites are governed by the effective constitutive equations

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

with the effective eigenstrain $\varepsilon^*[\overline{\mathbf{E}}^2]$ and the effective stress-dependent dielectric constants $\kappa^{\sigma *}$ given by

$$\begin{aligned} \varepsilon^*[\overline{\mathbf{E}}^2] &= \mathbf{M}^*\overline{\mathbf{E}}^2, \\ \kappa^{\sigma *} &= \kappa^* + 2\mathbf{M}^*\bar{\sigma}, \end{aligned} \tag{3.6}$$

where $\mathbf{S}^*$, $\mathbf{M}^*$ and κ^* are the effective compliance, effective electrostrictive tensor, and effective dielectric tensor of the composite, respectively, and $\overline{\mathbf{E}}^2 = \overline{\mathbf{E}} \otimes \overline{\mathbf{E}}$.

In order to determine the effective constitutive moduli, let us assume for the time being that the yet unknown average stress in each phase is found to be σ_r. Since σ_r is given, κ_r^σ is known, and the linear dielectric equation leads to

$$\mathbf{E}_r = \alpha_r \mathbf{E}^0, \tag{3.7}$$

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 composite. The eigenstrain for each phase, $\varepsilon_r^{\mathrm{T}}[\mathbf{E}_r^2]$, can then be determined, leading to the average stress in each phase

$$\sigma_r = \mathbf{B}_r \sigma^0 + \sigma_r^{\mathrm{T}}[\mathbf{E}_r^2], \tag{3.8}$$

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, dependent on the elastic compliance $\mathbf{S}_r$ of each phase and the microstructure of the composite; the second term is the eigenstress induced by the electrostriction

$$\sigma_r^{\mathrm{T}}[\mathbf{E}_r^2] = \mathbf{b}_r(\varepsilon_r^{\mathrm{T}}[\mathbf{E}_r^2] - \varepsilon_1^{\mathrm{T}}[\mathbf{E}_1^2]), \tag{3.9}$$

where $\mathbf{b}_r$ is the eigenstress concentration factor. There is an exact connection between the eigenstress and the stress concentration factor (Benveniste et al., 1991)

$$\sigma_r^{\mathrm{T}}[\mathbf{E}_r^2] = (\mathbf{I} - \mathbf{B}_r)(\mathbf{S}_1 - \mathbf{S}_r)^{-1}(\varepsilon_r^{\mathrm{T}}[(\alpha_r \mathbf{E}^0) \otimes (\alpha_r \mathbf{E}^0)] - \varepsilon_1^{\mathrm{T}}[(\alpha_1 \mathbf{E}^0) \otimes (\alpha_1 \mathbf{E}^0])] \tag{3.10}$$

for phases 2 to N. For matrix, we have

$$\sigma_1^{\mathrm{T}} = -\frac{1}{f_1} \sum_{i=2}^{N} f_i \sigma_r^{\mathrm{T}} \tag{3.11}$$

obtained from $(3.12)_2$

$$\begin{aligned} &\sum_{r=1}^{N} f_r \mathbf{B}_r = \mathbf{I}, \\ &\sum_{r=1}^{N} f_r \sigma_r^{\mathrm{T}} = \mathbf{0}, \\ &\sum_{r=1}^{N} f_r \alpha_r = \mathbf{i}, \end{aligned} \tag{3.12}$$

which are derived from the average field theorem (Dunn and Taya, 1993b), where f_r is the volume fraction of phase r, N is the number of phases 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. (3.7)–(3.9) along with constitutive equations (3.1) for phase r, we obtain the effective compliance

$$\mathbf{S}^* = \sum_{r=1}^{N} f_r \mathbf{S}_r \mathbf{B}_r \tag{3.13}$$

identical to that of linear elastic composites. The effective stress-dependent dielectric constant is determined as

$$\kappa^{\sigma*} = \sum_{r=1}^{N} f_r \kappa_r^{\sigma} \alpha_r, \tag{3.14}$$

recovering that of linear dielectric composites if κ_r^{σ} is independent of stress. The effective eigenstrain is determined similarly as

$$\varepsilon^*[\overline{\mathbf{E}}^2] = \sum_{r=1}^{N} f_r (\mathbf{S}_r \sigma_r^{\mathrm{T}}[\mathbf{E}_r^2] + \varepsilon_r^{\mathrm{T}}[\mathbf{E}_r^2]) \tag{3.15}$$

from which the effective electrostrictive coefficient can be obtained

$$\mathbf{M}^* = \sum_{r=1}^{N} f_r \{(\mathbf{S}_r \mathbf{b}_r + \mathbf{i})\mathbf{M}_r(\alpha_r \otimes \alpha_r) - \mathbf{S}_r \mathbf{b}_r \mathbf{M}_1(\alpha_1 \otimes \alpha_1)\}. \tag{3.16}$$

Combining (3.14) and (3.16), we obtain the effective dielectric constant

$$\kappa^* = \kappa^{\sigma*} - 2\mathbf{M}^* \bar{\sigma}. \tag{3.17}$$

Clearly, we need to determine the concentration factors in order to calculate the effective constitutive moduli of the composite.

3.2. Orientation distribution and orientational averaging

We now focus on an electrostrictive composite consisting of ferroelectric polymers embedded with textured dielectric particles. Because of anisotropy, the particles at different orientations will have different constitutive moduli in a global coordinate system, and thus will be regarded as different phases. As a result, orientational averaging over all particles at different orientations is necessary in order to determine the effective constitutive moduli of the composite. To this end, we adopt two kinds of coordinate systems to describe the orientation of particles, one is global fixed on the matrix, and the other is local attached to individual particles. The orientation of the particles in the global system can then be specified by three Euler angles (θ, ψ, ϕ), and their electromechanical properties in the global coordinate system can be obtained using the tensor transformation rules

$$\begin{aligned} S_{ijkl}(\theta,\psi,\phi) &= T_{im}T_{jn}T_{ko}T_{lp}S_{mnop}, \\ M_{ijkl}(\theta,\psi,\phi) &= T_{im}T_{jn}T_{ko}T_{lp}M_{mnop}, \\ \kappa_{ij}(\theta,\psi,\phi) &= T_{im}T_{jn}\kappa_{mn}, \end{aligned} \tag{3.18}$$

where the transformation matrix is a function of Euler angles

$$T^{-1}(\theta,\psi,\phi) = \begin{bmatrix} \cos\psi\cos\theta\cos\phi - \sin\psi\sin\phi & \sin\psi\cos\theta\cos\phi + \cos\psi\sin\phi & -\sin\theta\cos\phi \\ -\cos\psi\cos\theta\sin\phi - \sin\psi\cos\phi & -\sin\phi\cos\theta\sin\phi + \cos\psi\cos\phi & \sin\theta\sin\phi \\ \cos\psi\sin\theta & \sin\psi\sin\theta & \cos\theta \end{bmatrix}.$$

The effective electrostrictive moduli can then be expressed as

$$\mathbf{S}^* = f_1\mathbf{S}_1\mathbf{B}_1 + f_2\langle \mathbf{S}_2(\theta,\psi,\phi)\mathbf{B}_2(\theta,\psi,\phi)\rangle, \tag{3.19}$$

$$\kappa^{\sigma^*} = f_1\kappa_1^{\sigma}\alpha_1 + f_2\langle \kappa_2^{\sigma}(\theta,\psi,\phi)\alpha_2(\theta,\psi,\phi)\rangle, \tag{3.20}$$

$$\varepsilon^*[\overline{\mathbf{E}}^2] = f_1(\mathbf{S}_1\sigma_1^{\mathrm{T}} + \varepsilon_1^{\mathrm{T}}) + f_2\langle \mathbf{S}_2(\theta,\psi,\phi)\sigma_2^{\mathrm{T}}(\theta,\psi,\phi) + \varepsilon_2^{\mathrm{T}}(\theta,\psi,\phi)\rangle \tag{3.21}$$

derived from Eqs. (3.13)–(3.15), where the orientational averaging over all particles, represented by $\langle\cdot\rangle$, is carried out first, and the volume averaging in the composite is then conducted using the volume fractions of

matrix and particles, f_1 and f_2. Notice that the electromechanical field and the corresponding concentration factors of particles are all orientation dependent, and (3.12) becomes

$$\begin{aligned} &f_1\mathbf{B}_1 + f_2\langle \mathbf{B}_2(\theta,\psi,\phi)\rangle = \mathbf{I},\\ &f_1\sigma_1^{\mathrm{T}} + f_2\langle \sigma_2^{\mathrm{T}}(\theta,\psi,\phi)\rangle = \mathbf{0},\\ &f_1\alpha_1 + f_2\langle \alpha_2(\theta,\psi,\phi)\rangle = \mathbf{i}. \end{aligned} \tag{3.22}$$

We adopt the orientation distribution function (ODF) $W(\theta,\psi,\phi)$ to describe the probability of locating a particle at orientation (θ,ψ,ϕ), which is analog to the volume fraction, and leads to the following orientational averaging:

$$\langle H(\theta,\psi,\phi)\rangle = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} H(\theta,\psi,\phi)W(\theta,\psi,\phi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\psi\,\mathrm{d}\phi.$$

In general the orientational averaging is difficult to evaluate analytically, and we adopt Gaussian quadrature method for numerical integration (Press et al., 1992), where the integral is approximated by the sum of the value of its integrand at a set of points called abscissa, multiplied by weighting coefficient w_{ijk}

$$\langle H(\theta,\psi,\phi)\rangle = \sum_{i=1}^{I}\sum_{j=1}^{J}\sum_{k=1}^{K} \sin\theta_i H(\theta_i,\psi_j,\phi_k)W(\theta_i,\psi_j,\phi_k)w_{ijk}.$$

Our goal is to determine the effect of orientation distribution of particles, given in terms of $W(\theta,\psi,\phi)$, on the effective electrostriction of composites. One possibility is the random orientation distribution of particles, $W(\theta,\psi,\phi) = 1$, and the other is the fiber texture where all the particles are aligned along x_3-axis of the global coordinate, $W(\theta,\psi,\phi) = \delta(\theta)$. Both cases can be approximated by the Gaussian distribution function

$$W(\theta,\psi,\phi) = \frac{1}{\mu\sqrt{2\pi}}\mathrm{e}^{-(\theta^2/2\mu^2)}, \tag{3.23}$$

where the parameter μ can be adjusted to approximate a wide range of ODF for composites with overall transverse isotropy. For example, fiber texture is represented by $\mu \to 0$ while random orientation distribution is represented by $\mu \to \infty$. As μ increases from 0 to ∞, the particles become increasingly misaligned from $\theta = 0$, and eventually become randomly oriented. As such, we call μ the orientation distribution coefficient of particles. We have used this ODF to study the textured piezoelectric ceramics before (Li, 2000b).

3.3. Micromechanics approximation

In order to determine the effective moduli $\mathbf{S}^*$, κ^*, and $\mathbf{M}^*$ of the composites, we need to determine various concentration factors, which are related to the electromechanical field distribution in the composites. We will address this issue here using micromechanics approximation regarding the distribution of electromechanical field in the composites. For linear elastic and piezoelectric composites, the mean field Mori–Tanaka approximation is very successful in predicting the effective elastic, piezoelectric and dielectric moduli of the composites (Mori and Tanaka, 1973; Benveniste, 1987; Dunn and Taya, 1993a), which we adopt here. Under the mean field approximation, the stress concentration factors of electrostrictive composites can be determined directly from linear elasticity as (Li, 1999)

$$\mathbf{B}_2(\theta,\psi,\phi) = \mathbf{B}_2^{\mathrm{dil}}(\theta,\psi,\phi)[f_1\mathbf{I} + f_2\langle \mathbf{B}_2(\theta,\psi,\phi)^{\mathrm{dil}}\rangle]^{-1} \tag{3.24}$$

and

$$\mathbf{B}_1(\theta,\psi,\phi) = [f_1\mathbf{I} + f_2\langle \mathbf{B}_2(\theta,\psi,\phi)^{\mathrm{dil}}\rangle]^{-1} \tag{3.25}$$

with the dilute stress concentration factor given by

$$\mathbf{B}_2^{\mathrm{dil}}(\theta,\psi,\phi) = \{\mathbf{I} + \mathbf{S}_1^{-1}(\mathbf{I} - \mathbf{S}^{\mathrm{esh}}(\theta,\psi,\phi))(\mathbf{S}_2(\theta,\psi,\phi) - \mathbf{S}_1)\}^{-1}, \tag{3.26}$$

where $\mathbf{S}^{\mathrm{esh}}(\theta,\psi,\phi)$ is the elastic Eshelby tensor for particles at orientation (θ,ψ,ϕ) (Eshelby, 1957). It depends on the elastic moduli of the matrix and the shape aspect ratio of the particle. Clearly the normalization condition $(3.22)_1$ is automatically satisfied. 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 factors as

$$\alpha_2(\theta,\psi,\phi) = \alpha_2^{\mathrm{dil}}(\theta,\psi,\phi)[f_1\mathbf{i} + f_2\langle\alpha_2^{\mathrm{dil}}(\theta,\psi,\phi)\rangle]^{-1} \tag{3.27}$$

and

$$\alpha_1 = [f_1\mathbf{i} + f_2\langle\alpha_2^{\mathrm{dil}}(\theta,\psi,\phi)\rangle]^{-1} \tag{3.28}$$

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

$$\alpha_2^{\mathrm{dil}}(\theta,\psi,\phi) = \{\mathbf{i} + \mathbf{s}(\theta,\psi,\phi)(\kappa_1^\sigma)^{-1}(\kappa_2^\sigma(\theta,\psi,\phi) - \kappa_1^\sigma)\}^{-1}, \tag{3.29}$$

where $\mathbf{s}(\theta,\psi,\phi)$ is the dielectric Eshelby tensor for particles at orientation (θ,ψ,ϕ), which is dependent on κ_1^σ of the matrix and the shape aspect ratio of the particle. If the electric field concentration factor is determined as such, we can then determine the eigenstrain $\varepsilon^{\mathrm{T}}(\theta,\psi,\phi)[\alpha_2(\theta,\psi,\phi)\mathbf{E}^0]$, and use the exact connection between the eigenstress and the stress concentration factor, (3.10), to determine the eigenstress in particles.

Clearly we have nonlinearly coupled electromechanical equations, where the electric field concentration factor depends on the stress distribution in the composite through the stress-dependent dielectric constants, and the eigenstress depends on the electric field distribution in the composite through the electric field dependent eigenstrain. In general, it is difficult to solve these nonlinearly coupled electromechanical equations analytically, and we turn to 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 following:

1. Input the materials properties, volume fractions, and shape aspect ratio of the matrix and particles, as well as the applied stress σ^0 and electric field $\mathbf{E}^0$.
2. Evaluate the elastic Eshelby tensor $\mathbf{S}^{\mathrm{esh}}(\theta,\psi,\phi)$ for particle at (θ,ψ,ϕ) using the elastic properties of the matrix and shape aspect ratio of the particle.
3. Evaluate the stress concentration factors $\mathbf{B}_2(\theta,\psi,\phi)$ and $\mathbf{B}_1$ according to (3.24)–(3.26).
4. Assign $\mathbf{E}_1 = \mathbf{E}_2(\theta,\psi,\phi) = \mathbf{E}^0$ for the matrix and particles as an initial guess.
5. Evaluate the eigenstrain $\varepsilon_1^{\mathrm{T}}[\mathbf{E}_1^2]$ and $\varepsilon_2^{\mathrm{T}}(\theta,\psi,\phi)[\mathbf{E}_2^2(\theta,\psi,\phi)]$ according to $(3.2)_1$.
6. Evaluate the eigenstress $\sigma_1^{\mathrm{T}}[\mathbf{E}_1^2]$ and $\sigma_2^{\mathrm{T}}(\theta,\psi,\phi)[\mathbf{E}_2^2(\theta,\psi,\phi)]$ according to (3.10) and (3.11).
7. Evaluate the stress σ_1 and $\sigma_2(\theta,\psi,\phi)$ in matrix and particles according to (3.8).
8. Evaluate the stress-dependent dielectric constant κ_1^σ and $\kappa_2^\sigma(\theta,\psi,\phi)$ according to $(3.2)_2$, and evaluate the dielectric Eshelby tensor $\mathbf{s}(\theta,\psi,\phi)$.
9. Evaluate the electric field concentration factor α_1 and $\alpha_2(\theta,\psi,\phi)$ according to (3.27)–(3.29).
10. Evaluate the updated electric field $\mathbf{E}_1$ and $\mathbf{E}_2(\theta,\psi,\phi)$ according to (3.7), 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 (3.19), the effective stress-dependent dielectric constant $\kappa^{\sigma*}$ according to (3.20), and the effective eigenstrain according to (3.21); the effective electrostrictive coefficient $\mathbf{M}^*$ and the effective dielectric constant κ^* are then evaluated according to (3.6).

This algorithm allows us to determine the effective constitutive moduli of electrostrictive polymers embedded with textured dielectric particles, as we demonstrate in the next section.

4. Numerical results and discussion

In this section we investigate the effective electrostriction of P(VDF-TrFE) copolymers embedded with barium titanate particles of various shape aspect ratios and orientation distributions using the nonlinear micromechanics model we developed, implemented in a FORTRAN code. The code has been validated using the exact relations governing the effective moduli of the electrostrictive composite, established by Li and Rao (2004). In particular, the effective moduli calculated by this code satisfy all the known exact relations, and recover that of two-phase composite with aligned second phase, when $\mu \to 0$, or when the particles are spherical and isotropic.

The P(VDF-TrFE) copolymers, if treated by electron irradiation, demonstrate much enhanced electrostriction (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 the field. With the addition of barium titanate particles of high dielectric constant and large dielectric anisotropy, we hope to further enhance the electrostriction and reduce the magnitude of the applied electric field, by tailoring the microstructure of the composite carefully. We are interested in the effect of particle aspect ratio represented by $\alpha = \frac{a_3}{a_1} = \frac{a_3}{a_2}$, and the effect of the particle ODF represented by the orientation distribution coefficient μ; $a_1 = a_2$ and a_3 are the dimensions of particles along the principal axes of ellipsoidal particles. A wide range of microstructures can be simulated by adjusting α and μ, with particle shapes ranging from fiber ($\alpha \to \infty$) to penny shape ($\alpha \to 0$), and particle orientation distributions ranging from perfectly aligned along x_3-axis ($\mu \to 0$) to completely random ($\mu \to \infty$). With ODF given by (3.23), the particles are randomly oriented in x_1–x_2 plane, and the composites are transversely isotropic.

The constitutive moduli of P(VDF-TrFE) copolymer, which is assumed to be isotropic, are estimated from plots in Zhang et al. (1998). The material properties of barium titanate, which is tetragonal, is obtained from Zgonik et al. (1994), with the exception that the piezoelectric constants are taken to be zero, since the piezoelectric strain of the particle is much smaller than the electrostrictive strain of copolymers. There is no difficulty in including piezoelectric coupling, but we would like to focus on the electrostrictive effect, which is our main interest here. The materials constants of constituent phases are listed in Table 1. In the following calculations, we apply the traction free boundary condition to composites subject to an electric field of 75 MV/m, and the volume fraction of particles is taken to be 50%.

It is noted that barium titanate is much softer dielectrically, and much stiffer elastically than P(VDF-TrFE) copolymers, thus an optimal microstructure must take advantage of its high dielectric constant, yet relax its mechanical constraint on the copolymer matrix. Otherwise, no electrostriction enhancement will be

Table 1
The electromechanical properties of constituent materials in the composites

Material	S_{11}	S_{12}	S_{13}	S_{33}	S_{44}	S_{66}	M_{11}	M_{12}	κ_{11}	κ_{33}
P(VDF-TrFE)	0.74	−0.22	−0.22	0.74	1.92	1.92	−2.40	1.20	68.5	68.5
$BaTiO_3$	7.38×10^{-3}	-1.39×10^{-3}	-4.41×10^{-3}	1.31×10^{-2}	1.64×10^{-2}	7.46×10^{-3}	0	0	2200	56

Units: $\mathbf{S}$: 10^{-9}, $\mathbf{M}$: 10^{-18} m^2/V^2, κ: κ_0.

achieved. For example, the P(VDF-TrFE) copolymers embedded with randomly oriented barium titanate particles exhibit smaller electrostrictive strain than pure copolymers, regardless of the particle aspect ratio, as shown in Fig. 1. It is also interesting to notice that when they are randomly oriented, spherical particles lead to the highest electrostrictive strain in the composites. As such, in order to get the enhanced electrostriction in the composites, we must identify the optimal combination of particle shape and orientation distribution.

4.1. The effect of particle shape

We first consider the effect of particle shape. The effective dielectric constants of the composites with three different orientation distributions versus the aspect ratio of particles, α, are shown in Figs. 2 and 3. In both cases, we observe much higher dielectric constants of the composites than those of copolymer, due to the large dielectric constant of barium titanate particles. Three regimes are observed. At relatively small α, the dielectric constants are largest and insensitive to particle shape. They start to decrease with the increase of α at $\alpha = 10$, reaching minimum at $\alpha = 1000$, and become insensitive to α again. κ_{11}^* is largest in the composites with aligned particles, while κ_{33}^* is largest in the composites with randomly oriented particles, due to the strong anisotropy of the embedded barium titanate particles. This suggests a strong dependence of composite properties on their microstructures, and it remains to be seen whether this enhanced dielectric constants will lead to larger electrostriction.

The effective electrostrictive coefficients of the composites with three different particles orientation distributions versus the aspect ratio of the particles are shown in Figs. 4 and 5. Interestingly, the highest electrostriction does not occur in the composites with highest dielectric constant. In both cases, there is a peak in the effective electrostrictive coefficients near $\alpha = 1000$, where the effective dielectric constants are relatively small. This is because at this aspect ratio, the mechanical constraint on copolymers from the

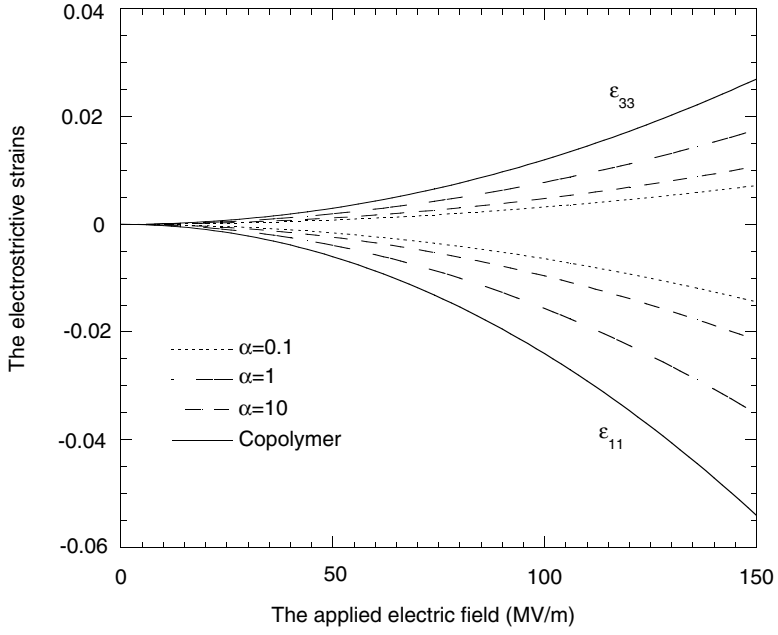

Fig. 1. The electrostrictive strain of composites with different particle shapes versus the applied electric field E_1^0; the orientation distribution of particle is random.

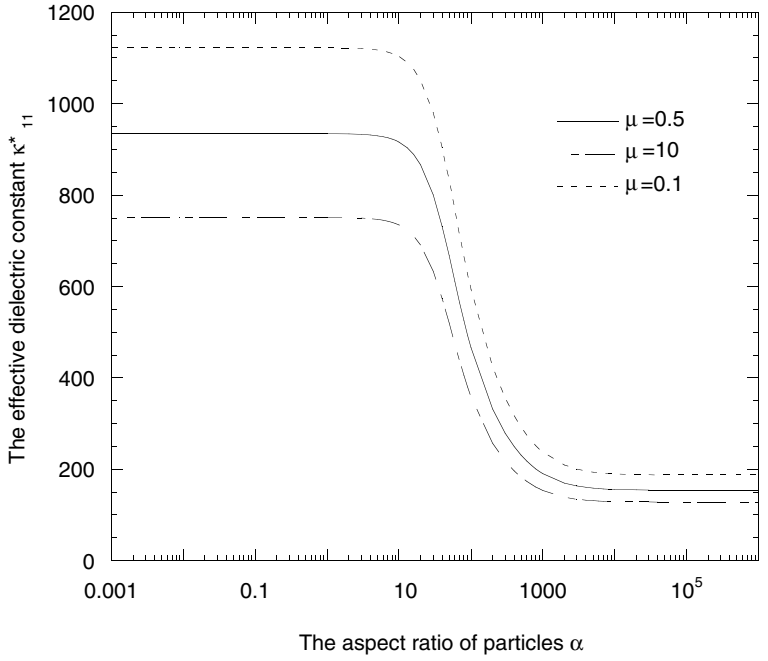

Fig. 2. The effective dielectric constant κ_{11}^{*} of composites with different particle orientation distributions versus the aspect ratio of particles α.

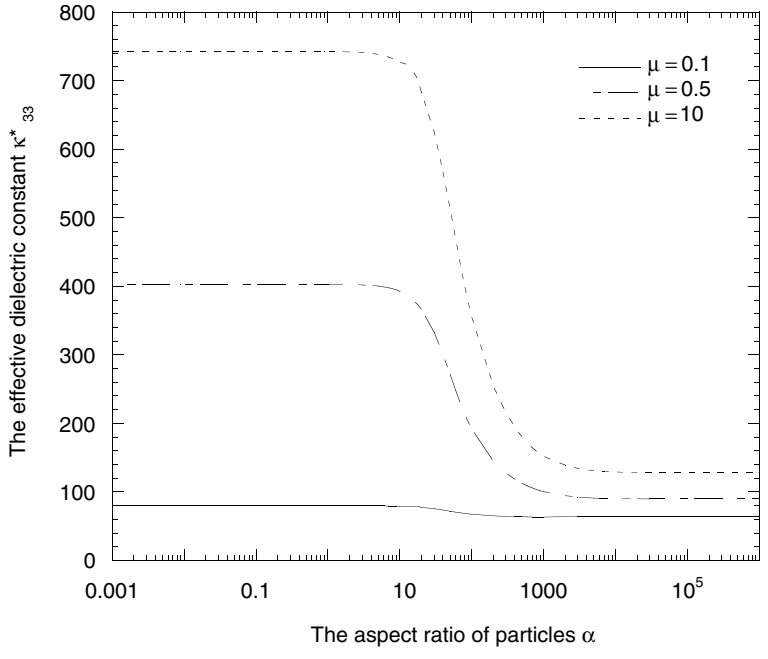

Fig. 3. The effective dielectric constant κ_{33}^{*} of composites with different particle orientation distributions versus the aspect ratio of particles α.

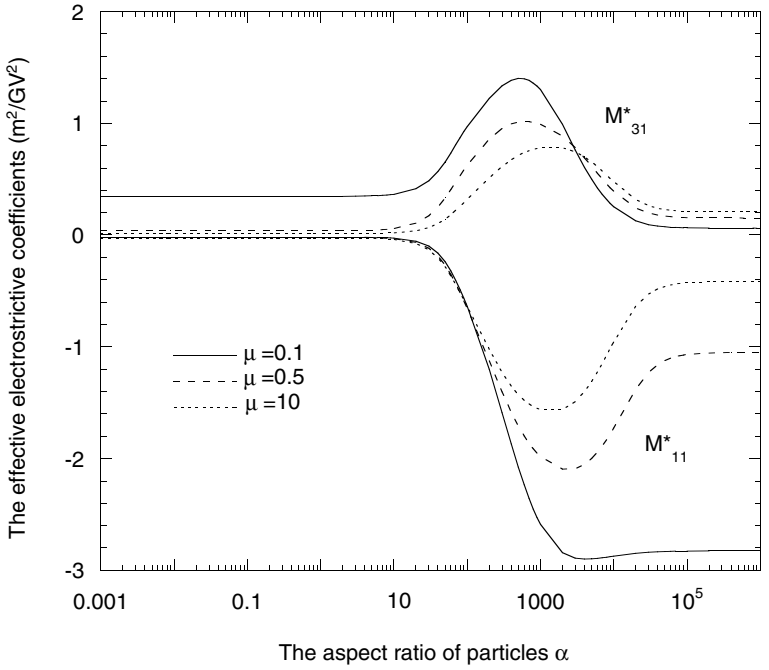

Fig. 4. The effective electrostrictive coefficients M_{11}^{*} and M_{31}^{*} of composites with different particle orientation distributions versus the aspect ratio of particles α.

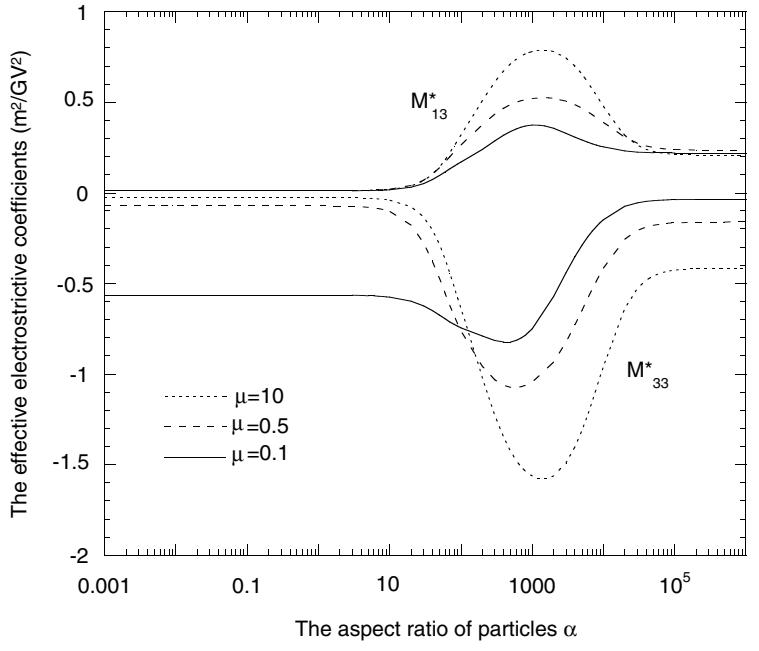

Fig. 5. The effective electrostrictive coefficients M_{13}^{*} and M_{33}^{*} of composites with different particle orientation distributions versus the aspect ratio of particles α.

dielectric particles is minimized. For example, particles with small α will severely constrain the mechanical deformation of copolymers in x_1 direction, while particles with large α will severely constrain the mechanical deformation of copolymer in x_3 direction. For M_{11}^* and M_{31}^*, the composite with aligned short fiber ($\mu = 0.1$, $\alpha = 1000$) has highest electrostrictive coefficients, larger than those of copolymer, suggesting that the effective electrostriction can indeed be enhanced. On the other hand, for M_{13}^* and M_{33}^*, the composite has lower electrostriction than those of copolymer, due to the small dielectric constant κ_{33} of the particle. Among different orientation distribution of particles, the composites with aligned particles $\mu = 0.1$ have highest M_{11}^* and M_{31}^*, while those with randomly oriented particles ($\mu = 10$) have the highest M_{13}^* and M_{33}^*, consistent with the trend in the dielectric constants. Clearly, the material properties of the composites are sensitive to the combination of particle shapes and orientation distribution.

4.2. The effect of particle orientation distribution

We then consider the effect of particle orientation distributions. The effective dielectric constants of the composites versus the orientation distribution coefficient μ are shown in Figs. 6 and 7. It is observed that κ_{11}^* decreases, while κ_{33}^* increases with the increasing μ, due to the large anisotropy of barium titanate particles, where κ_{11} is two orders larger than κ_{33}. This also leads to small κ_{33}^* at small μ where the second phase is aligned. Among different particle shapes, the composites with smaller particle aspect ratio has higher dielectric constant, due to the larger electric field enhancement in the copolymer matrix.

The effective electrostrictive coefficients of the composites versus μ are given in Figs. 8 and 9, where it is observed that higher dielectric constants usually lead to higher electrostriction. In general, the highest M_{11}^* and M_{31}^* occur at small μ where the dielectric particles aligned, corresponding to largest κ_{11}^*, while the highest M_{13}^* and M_{33}^* occur at large μ where the dielectric particles are randomly oriented, corresponding to largest κ_{33}^*. There are exceptions, though, where the trend is reversed for M_{31}^* with $\alpha = 10$, and M_{33}^* with $\alpha = 0.1$. This can be understood by considering the difference in mechanical constraint and electric field

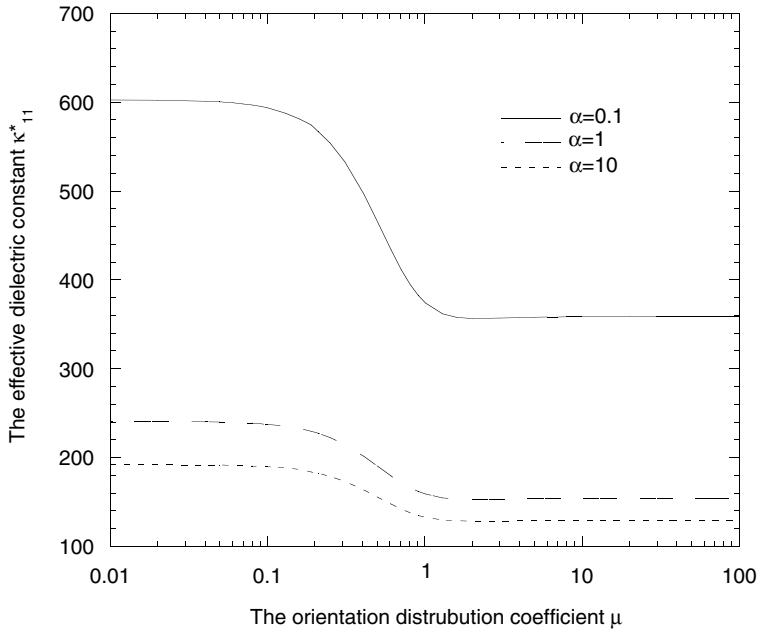

Fig. 6. The effective dielectric constant κ_{11}^* of composites with different particle shapes versus the orientation distribution coefficient μ.

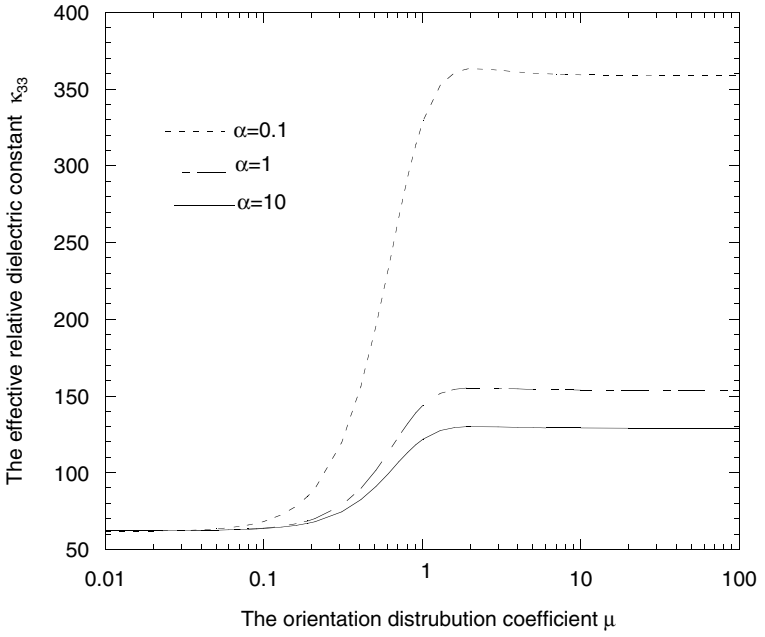

Fig. 7. The effective dielectric constant κ^*_{33} of composites with different particle shapes versus the orientation distribution coefficient μ.

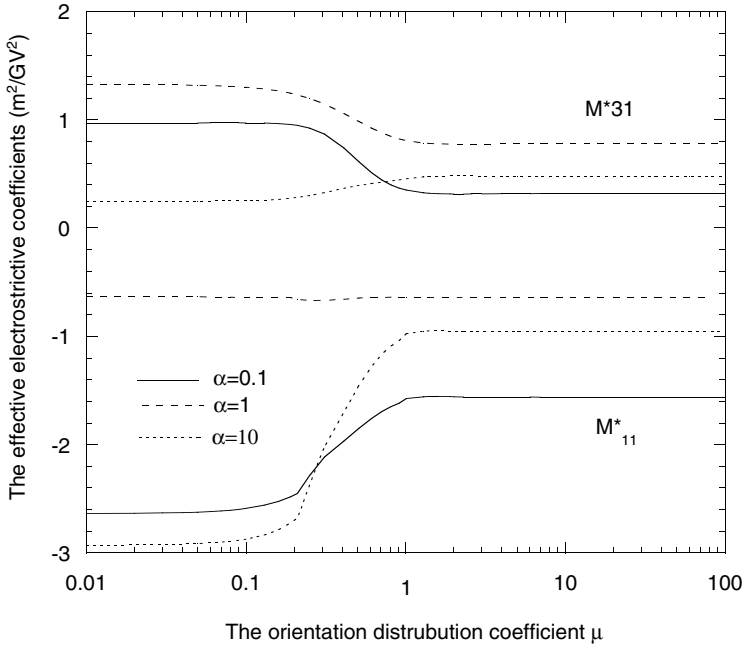

Fig. 8. The effective electrostrictive coefficients M^*_{11} and M^*_{31} of composites with different particle shape versus the particle orientation distribution coefficient μ.

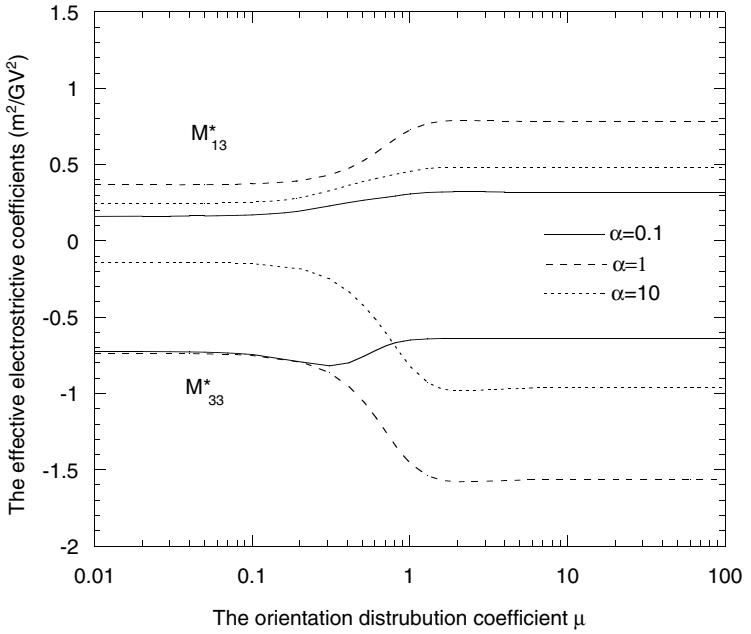

Fig. 9. The effective electrostrictive coefficients M_{13}^* and M_{33}^* of composites with different particle shapes versus the particle orientation distribution coefficient μ.

magnification for different particle orientation distributions. For example, with small α, the mechanical constraint in x_3 direction is relaxed if the particles are aligned, leading to higher M_{33}^*, while for large α, the electric field magnification is largest when the particles are aligned, leading to higher M_{31}^*.

5. Concluding remarks

In summary, we have developed a nonlinear micromechanical model to analyze the effective electrostriction of P(VDF-TrFE) copolymer based composites containing textured particles. The effects of particle shape and orientation distribution have been revealed, enhanced electrostriction in the composite has been demonstrated, and optimal microstructure for electrostriction enhancement has been identified. We expect that our analysis can provide a guideline for the design and optimization of electrostrictive composites with enhanced electrostriction.

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).

References

Bai, Y., Cheng, Z.Y., Bharti, V., Xu, H.S., Zhang, Q.M., 2000. High-dielectric-constant ceramic-powder polymer composites. Appl. Phys. Lett. 76, 3804–3806.

Benveniste, Y., 1987. A new approach to the application of Mori–Tanaka's theory in composite materials. Mech. Mater. 6, 147–157.
Benveniste, Y., 1993. Exact results in the micromechanics of fibrous piezoelectric composites exhibiting pyroelectricity. Proc. R. Soc. London A 441, 59–81.
Benveniste, Y., Dvorak, G.J., Chen, T., 1991. On diagonal and elastic symmetry of the approximate effective stiffness tensor of heterogeneous media. J. Mech. Phys. Solids 39, 927–946.
Bharti, V., Cheng, Z.Y., Gross, S., Xu, T.B., Zhang, Q.M., 1999. High electrostrictive strain under high mechanical stress in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer. Appl. Phys. Lett. 75, 2653–2655.
Bisegna, P., Luciano, R., 1996. Variational bounds for the overall properties of piezoelectric composites. J. Mech. Phys. Solids 44, 583–602.
Chen, T.Y., 1993. Piezoelectric properties of multiphase fibrous composites—some theoretical results. J. Mech. Phys. Solids 41, 1781–1794.
Cheng, Z.Y., Bharti, V., Xu, T.B., Wang, S.X., Zhang, Q.M., Ramotowski, T., Tito, F., Ting, R., 1999. Transverse strain responses in electrostrictive poly(vinylidene fluoride-trifluoroethylene) films and development of a dilatometer for the measurement. J. Appl. Phys. 86, 2208–2214.
Dang, Z.M., Shen, Y., Nan, C.W., 2002. Dielectric behavior of three-phase percolative Ni–$BaTiO_3$/polyvinylidene fluoride composites. Appl. Phys. Lett. 81, 4814–4816.
Dunn, M.L., Taya, M., 1993a. Micromechanics predictions of the effective elctroselastic moduli of piezoelectric composites. Int. J. Solids Struct. 30, 161–175.
Dunn, M.L., Taya, M., 1993b. An analysis of piezoelectric composite materials containing ellipsoidal inhomogeneities. Proc. R. Soc. London A 443, 265–287.
Eshelby, J.D., 1957. The determination of the elastic field of an ellipsoidal inclusion and related problem. Proc. R. Soc. London A 241, 376–396.
Garrett, J.T., Roland, C.M., Petchsuk, A., Chung, T.C., 2003. Electrostrictive behavior of poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene). Appl. Phys. Lett. 83, 1190–1192.
Gevorgian, S., Carlsson, E., Wikborg, E., Kollberg, E., 1998. Tunable microwave devices based on bulk and thin film ferroelectrics. Integrat. Ferroelectr. 22, 765–777.
Huang, C., Zhang, Q.M., Su, J., 2003. High-dielectric-constant all-polymer percolative composites. Appl. Phys. Lett. 82, 3502–3504.
Hori, M., Nemat-Nasser, S., 1998. Universal bounds for effective piezoelectric moduli. Mech. Mater. 30, 1–19.
Li, J.Y., 1999. On micromechanics approximation for the effective thermoelastic moduli of multi-phase composite. Mech. Mater. 31, 149–159.
Li, J.Y., 2000a. Magnetoelectroelastic multi-inclusion and inhomogeneity problems and their applications in composite materials. Int. J. Eng. Sci. 38, 1993–2011.
Li, J.Y., 2000b. The effective electroelastic moduli of textured piezoelectric polycrystalline aggregates. J. Mech. Phys. Solids 48, 529–552.
Li, J.Y., 2003. Exchange coupling in P(VDF-TrFE) copolymer based all-organic composite with giant electrostriction. Phys. Rev. Lett. 90 (article number 217601).
Li, J.Y., Rao, N., 2002. Dramatically enhanced effective electrostriction in ferroelectric polymeric composites. Appl. Phys. Lett. 81, 1860–1862.
Li, J.Y., Rao, N., 2004. Micromechanics of ferroelectric copolymer based electrostrictive composites. J. Mech. Phys. Solids 52, 591–615.
Mori, T., Tanaka, K., 1973. Average stress in matrix and average elastic energy of materials with misfitting inclusions. Acta Metall. 21, 571–574.
Mura, T., 1987. Micromechanics of Defects in Solids, second ed. Martinus Nijhoff, The Netherlands.
Nan, C.W., Weng, G.J., 2000. Theoretical approach to effective electrostriction in inhomogeneous materials. Phys. Rev. B 61, 258–265.
Nemat-Nasser, S., Hori, M., 1993. Micromechanics: Overall Properties of Heterogeneous Materials. Elsevier, New York.
Newnham, R.E., Sundar, V., Yimnirun, R., Su, J., Zhang, Q.M., 1997. Electrostriction: nonlinear electromechanical coupling in solid dielectrics. J. Phys. Chem. B 101, 10141–10150.
Ponte Castañeda, P., 1996. Exact second-order estimates for the effective mechanical properties of nonlinear composite materials. J. Mech. Phys. Solids 44, 827–862.
Ponte Castañeda, P., Suquet, P., 1998. Nonlinear composites. Adv. Appl. Mech. 34, 171–302.
Press, W.H., Teukolsky, S.A., Vetterling, W.T., Flannery, B.P., 1992. Numerical Recipes in FORTRAN, second ed. Cambridge University Press.
Talbot, D.R.S., Willis, J.R., 1985. Variational principles for inhomogeneous non-linear media. IMA J. Appl. Math. 35, 39–54.
Talbot, D.R.S., Willis, J.R., 1996. Three-point bounds for the overall properties of a nonlinear composite dielectric. IMA J. Appl. Math. 57, 41–52.
Tan, P., Tong, L., 2001. Micromechanics models for non-linear behavior of piezoelectric fiber reinforced composite materials. Int. J. Solids. Struct. 38, 8999–9032.
Willis, J.R., 1991. On methods for bounding the overall properties of nonlinear composites. J. Mech. Phys. Solids 39, 73–86.

Xu, H.S., Cheng, Z.Y., Olson, D., Mai, T., Zhang, Q.M., Kavarnos, G., 2001. Ferroelectric and electromechanical properties of poly(vinylidene-fluoride-trifluoroethylene-chlorotrifluoroethylene) terpolymer. Appl. Phys. Lett. 78, 2360–2362.

Zgonik, M., Bernasconi, P., Duelli, M., Schlesser, R., Günter, P., Garrett, M.H., Rytz, D., Zhu, Y., Wu, X., 1994. Dielectric, elastic, piezoelectric, electro-optic, and elasto-optic tensors of $BaTiO_3$ crystals. Phys. Rev. B 50, 5941–5949.

Zhang, Q.M., Bharti, V., Zhao, X., 1998. Giant electrostriction and relaxor ferroelectric behavior in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer. Science 280, 2101–2104.

Zhang, Q.M., Li, H.F., Poh, M., Xia, F., Cheng, Z.Y., Xu, H.S., Huang, C., 2002. An all-organic composite actuator material with a high dielectric constant. Nature 419, 284–287.