附件一

行政院國家科學委員會補助專題研究計畫 □期中進度報告 v 期末報告

壓電壓磁複合材料電磁耦合效應之提升

計畫類別：v 個別型計畫　□整合型計畫
計畫編號：NSC 100－2628－E－009－022－MY2
執行期間：100 年 8 月 1 日至 102 年 7 月 31 日

執行機構及系所：國立交通大學土木工程學系

計畫主持人：郭心怡
共同主持人：
計畫參與人員：郭祐旻、彭晟祐、凌毓翔、游舒含

本計畫除繳交成果報告外，另含下列出國報告，共 _1_ 份：
□移地研究心得報告
v 出席國際學術會議心得報告
□國際合作研究計畫國外研究報告

處理方式：除列管計畫及下列情形者外，得立即公開查詢
□涉及專利或其他智慧財產權，□一年□二年後可公開查詢

中　華　民　國 102 年 10 月 10 日

附件二

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

   V 達成目標

   □ 未達成目標（請說明，以 100 字為限）

   □ 實驗失敗

   □ 因故實驗中斷

   □ 其他原因

   說明：

2. 研究成果在學術期刊發表或申請專利等情形：

   論文：v 已發表 □未發表之文稿 □撰寫中 □無

   專利：□已獲得 □申請中 □無

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   其他：（以 100 字為限）

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以 500 字為限）

   多鐵複合材料近十年來成為微觀力學的新興課題，然而過去的研究材料極化方向假設與纖維方向同向，而對於任意極化方向與三相複合材料的課題，著墨甚少。本研究探討極化方向與三相組合對於圓柱狀內含物複合材料的磁電彈多重物理耦合場之影響，並預測最佳之磁電耦合效應所對應的極化方向或組合方式，提供材料學家製造多鐵材料的設計依據。

Effective magnetoelectricity of coated fibrous composites of piezoelectric and piezomagnetic phases

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Abstract

This paper studies the effective magnetoelectric behaviors of three-phase, core-shell-matrix fibrous composites of piezoelectric and piezomagnetic phases. A micromechancial model, the two-level recursive scheme together with the Mori-Tanaka's method, is proposed to investigate the magnetoelectricity of the coated fibrous multiferroic composites. The magnitudes and trends of the solutions are in good agreement with the calculations by the finite element analysis. Based on this micromechanical approach, we find that, for the case of PE/PM/PM (core/shell/matrix) multiferroic compoiste, with a coating ap-

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propriate for the inhomogeneity, the effective magnetoelecitrc coupling can be enhanced many-fold as compared to the noncoated counterpart.

1 Introduction

This work is concerned with the magnetoelectric (ME) effect of a coated fibrous composite made of piezoelectric and piezomagnetic phases. ME materials are particular exciting since they posess the coupling between the electric and magnetic fields. This make them appealing and promising for a wide range of applications, such as ME data storage and switching, magnetic field detectors, and electric control of magnetism, etc. (Fiebig, 2005; Spaldin and Fiebig, 2005; Eerenstein et al., 2006;) However, the ME effect in natural materials is rather weak and is often observed at low temperature (Astrov, 1960; Rado and Folen, 1961). Therefore, various researchers have turned to composites made of piezoelectric and piezomagnetic media to enhance the magnetoelectricity, as explained in recent reviews by Nan et al. (2008) and Srinivasan (2010). This much stronger ME effect could be realized using product properties: an applied magnetic field creates a strain in the piezomagnetic material which in turn creates a strain in the piezoelectric material, resulting in an electric polarization.

The promise of applications, and the indirect coupling through strain have also made ME composites the topic of a number of theoretical and experimental studies (Nan et al., 2008; Zheng et al., 2004). Among them, the classical Eshelby's equivalent inclusion approach and the Mori-Tanaka mean-field model have been generalized to multiferroic composites by Li and Dunn (1998a, b), Huang (1998), Wu and Huang (2000), Huang and Zhou (2004) and Srinivas et al. (2006). The analysis for local fields is available for simple microstructures such as a single inclusion (Huang and Kuo, 1997), laminates (Srinivasan et al., 2001; Bichurin et al., 2003; Kuo et al., 2010), and

periodic array of circular/ellptic fibrous ME composites (Kuo, 2010; Kuo and Pan, 2011; Dinzart and Sabar, 2011). Homogenization methods were also proposed for periodic ME fibrous composites (Aboudi, 2001; Camacho-Montes et al., 2009), while numerical methods based on the finite element analysis have also been developed to address ME composites with more general microstructures (Liu et al., 2004; Lee et al., 2005).

Recently, some three-phase multiferroic composites were made experimentally to enhance the ME coupling. Nan et al. (2002, 2003) made a Terfenol-D/PZT/PVDF mixture, and the measured ME coefficient was enhanced to 45mV/cm. Dong et al. (2006) prepared a $MnZnFe_2O_4$/Terfenol-D/PZT laminate, and found the enhanced ME field coefficients of up to 8-28 times of those of Terfenol-D/PZT counterpart. Gupta and Chatterjee (2009) prepared a three-phase $BaTiO_3/CoFe_2O_4$/PVDF particulate composite, and showed a maximum ME voltage around 26mV/cmOe. Jadhav et al. (2009) prepared a $Ni_{0.5}Cu_{0.2}Zn_{0.3}Fe_2O_4/BaTiO_3$/PZT combination and measured a maximum ME coeffcient of 975 μV/cmOe. For theoretical investigations, Kuo (2010) and Kuo and Pan (2011) estimate the overall behavior of multiferroic composites with coated ciruclar/elliptic fibrous under generalized anti-plane deformation. Dinzart and Sabar (2011) employed Green's functions techniques, interfacial operators, and Mori-Tanaka's model for solving the magnet-electro-elastic coated inclusion problem.

In the work of Friebel et al. (2006), to estimate the overall property of viscoelastic composites with coated inclusions, they proposed a two-level recursive scheme and two-step method together with Mori-Tanaka or double-inclusion mean-field models as the homogenization method. Later, Kuo and Wu (2012) applied the two-level recursive scheme in conjunction with the Mori-Tanaka's model to a core-shell-matrix particulate multiferroic composite. They showed that the solutions are in good agree-

ment with the prediction by the finite element anaylsis. In this paper, we adopt the similar method to investigate the effective property of the coated fibrous composites made of piezoelectric and piezomagnetic phases.

This article is organized as follows: In Section 2, we formulate the basic equations for a piezoelectric-piezomagnetic composite and define the effective properties of the composite. In Section 3 we propose a micromechanical method to estimate the overall behavior of core-shell-matrix, three-phase multiferroic composites. We introduce the finite element analysis in Section 4. Both methodologies are illustrated in Section 5. We study how the magnetoelectric voltage coefficent depends on the radious ratio of the core and shell, volume fractions of the fiber phase, and material properties of constituent phases. Furthermore, we improve the ME coupling effect by tuning the material parameters, and summarize a few useful design principles.

2 Problem statement

2.1 Basic equations

Let us consider a three-phase, coated fibrous composite made of piezoelectric and piezomagnetic materials as shown in Figure 1. The cylinders are infinitely long with fibers aligned in x_3-direction. The composite is consisting of a continuous matrix phase, m, in which there are embedded inhomogeneities of a circular shell phase, c, and a shell phase, s, which represents a layer of cpating that encapsulates each particle of the core phase. The radii of the core and coating are a and b, respectively, and the ratio between them is definsed as $\gamma \equiv a/b$. The general constitutive laws for

the rth phase are given by (see Alshits et al., 1992, for example)

$$\begin{aligned} \sigma_{ij}^{(r)} &= C_{ijkl}^{(r)}\varepsilon_{kl}^{(r)} - e_{lij}^{(r)}E_l^{(r)} - q_{lij}^{(r)}H_l^{(r)}, \\ D_i^{(r)} &= e_{ikl}^{(r)}\varepsilon_{kl}^{(r)} + \kappa_{il}^{(r)}E_l^{(r)} + \lambda_{li}^{(r)}H_l^{(r)}, \\ B_i^{(r)} &= q_{ikl}^{(r)}\varepsilon_{kl}^{(r)} + \lambda_{il}^{(r)}E_l^{(r)} + \mu_{il}^{(r)}H_l^{(r)}, \end{aligned} \tag{2.1}$$

where σ_{ij}, D_i, B_i, ε_{ij}, E_i and H_i are the stress, electric displacement, magnetic flux, strain, electric field and the magnetic field, respectively. C_{ijkl} is the elastic moduli; e_{ikl} and q_{ikl} are the piezoelectric and piezomagnetic constants; κ_{il}, μ_{il} and λ_{il} are the dielectric permittivity, magnetic permeability and magnetoelectric coefficient. The symmetry conditions satisfied by the moduli are given by Nye (1985).

The strain ε_{ij}, electric field E_i, and magnetic field H_i are respectively defined by the displacement u_i, electric potential φ, and magnetic potential ψ via

$$\varepsilon_{ij} = \frac{1}{2}\left(u_{i,j} + u_{j,i}\right), \ E_i = -\varphi_{,i}, \ H_i = -\psi_{,i}. \tag{2.2}$$

On the other hand, the balance of linear momentum, Gauss's law, and the condition of no magnetic poles give that the stress, electric displacement, and magnetic intensity satisfy the following equilibrium equations

$$\sigma_{ij,j} = 0, \ D_{i,i} = 0, \ B_{i,i} = 0. \tag{2.3}$$

These differential equations can be solved, subject to suitable interface and boundary conditions. We assume that the interfaces are perfectly bonded, and therefore the

field quantities satisfy

$$\begin{aligned} [[\sigma_{ij}n_j]] &= 0, \ [[D_i n_i]] = 0, \ [[B_i n_i]] = 0, \\ [[u_i]] &= 0, \ [[\varphi]] = 0, \ [[\psi]] = 0, \end{aligned} \tag{2.4}$$

where $[[\cdot]]$ denotes the jump in some quantity across the interface, and n_i is the unit outward normal to the interface.

For simplicity, we write the above constitutive laws (2.1), strain-displacement (2.2) and equilibrium equations (2.3) can be rewritten in more compact form as (Alshits et al., 1992)

$$\Sigma_{iJ} = L_{iJMn} Z_{Mn}, \ Z_{Mn} = U_{M,n}, \ \Sigma_{iJ,i} = 0, \tag{2.5}$$

where

$$\Sigma_{iJ} = \begin{cases} \sigma_{ij}, & J = 1,2,3, \\ D_i, & J = 4, \\ B_i, & J = 5, \end{cases} \quad Z_{Mn} = \begin{cases} \varepsilon_{mn}, & M = 1,2,3, \\ -E_n, & M = 4, \\ -H_n, & M = 5, \end{cases} \quad U_M = \begin{cases} u_m, & M = 1,2,3, \\ \varphi, & M = 4, \\ \psi, & M = 5. \end{cases} \tag{2.6}$$

The magnetoelectroelastic moduli are expressed as

$$L_{iJMn} = \begin{cases} C_{ijmn}, & J,M = 1,2,3, \\ e_{ijn}, & M = 4,\ J = 1,2,3, \\ q_{ijn}, & M = 5,\ J = 1,2,3, \\ e_{imn}, & J = 4,\ M = 1,2,3, \\ -\kappa_{in}, & J = 4,\ M = 4, \\ -\lambda_{in}, & J = 4,\ M = 5, \\ q_{imn}, & J = 5,\ M = 1,2,3, \\ -\lambda_{in}, & J = 5,\ M = 4, \\ -\mu_{in}, & J = 5,\ M = 5, \end{cases} \tag{2.7}$$

where the upper case subscript ranges from 1 to 5 and the lower case subscript ranges from 1 to 3. Repeated upper case subscripts are summed from 1 to 5.

2.2 Effective moduli

In this study, we are interested in determining the overall properties of the multiferroic composites in terms of their microstructure. The macroscopic properties are defined in terms of average fields,

$$\langle \Sigma_{iJ} \rangle = L^*_{iJMn} \langle Z_{Mn} \rangle , \tag{2.8}$$

where $\mathbf{L}^*$ denotes the macroscopic magnetoelectroelastic coefficients of the hetergeneous material, and the angular brackets denote the average over the representative volume element (RVE; unit cell in the case of periodic composites),

$$\langle \Sigma_{iJ} \rangle = \frac{1}{V} \int_V \Sigma_{iJ} dx_i, \ \ \langle Z_{Mn} \rangle = \frac{1}{V} \int_V Z_{Mn} dx_i.$$

Here, V is the area of RVE. Note that, although in each component, the magneto-electric coefficient is zero, i.e., $\boldsymbol{\lambda} = \mathbf{0}$,the coupling effect $\boldsymbol{\lambda}^*$ may be non-zero.

Due to the linearity, the generalized strain in the r-th phase for a matrix-based multiphase multiferroic composite is given by (Srinivas et al., 2006)

$$Z_{Mn}^{(r)} = A_{MnAb}^{(r)} \langle Z_{Ab} \rangle , \tag{2.9}$$

where $A_{MnAb}^{(r)}$ is the generalized strain concentration tensor of the r-th phase, satisfying

$$\sum_{r=1}^{N} A_{MnAb}^{(r)} = I_{JiAb}, \tag{2.10}$$

where I_{JiAb} is the fourth-order identity tensor. As a result, from the average generalized stress and strain theorems, the effective moduli can be determined for a $(N+1)$-phase composite as

$$L_{iJAb}^{*} = L_{iJAb}^{(m)} + \sum_{r=1}^{N} f_r \left(L_{iJMn}^{(r)} - L_{iJMn}^{(m)} \right) A_{MnAb}^{(r)}. \tag{2.11}$$

Here f is the volume fraction of the inclusion, and the superscripts m and r denote the matrix and the r-th phase, respectively. The concentration tensor can be determined by various micromechanical models.

3 Micromechanical approach

To estimate the effectifve moduli of multiferroic composites, we first turn to the direct Mori-Tanaka method, which approximates the coated particle problem using a composite with distinct particles representing the core and shell phases. The key assumption of the Mori-Tanaka method, which is essentially a mean-field method, is

that the average field in the rth inclusion of the heterogeneous material is equivalent to the field in a single partivle embedded in an infinite mideium, with the unknown average field in the matrix applied at the boundary. This gives the effective properties of the core-shell-matrix mutliferroic as Eq. (2.11). Here, the concentration tensor for the core ($j = 1$) or shell ($j = 2$) is

$$A^{(j)}_{MnAb} = A^{dil\ (j)}_{MnJi} \left(f^{(m)} I_{JiAb} + f^{(1)} A^{dil\ (1)}_{JiAb} + f^{(2)} A^{dil\ (2)}_{JiAb} \right)^{-1}, \ j = 1, 2, \tag{3.1}$$

where

$$A^{dil\ (j)}_{MnJi} = \left[I_{MnAb} + S^{(j)}_{MnLk} (L^{(m)}_{LkiJ})^{-1} \left(L^{(j)}_{iJAb} - L^{(m)}_{iJAb} \right) \right]^{-1}. \tag{3.2}$$

Here S_{MnAb} is the magnetoelectroelastic Eshelby tensor, which is a function of the magnetoelectroelastic moduli of matrix, the shape and orientation of the inclusion, and is described by (Li and Dunn, 1998b)

$$S_{MnAb} = \frac{1}{8\pi} L_{iJAb} \begin{cases} \int_{-1}^{1} \int_{0}^{2\pi} \left[G_{mJin}(z_i) + G_{nJim}(z_i) \right] d\theta d\xi_3, & M = 1, 2, 3, \\ 2 \int_{-1}^{1} \int_{0}^{2\pi} G_{4Jin}(z_i) d\theta d\xi_3, & M = 4, \\ 2 \int_{-1}^{1} \int_{0}^{2\pi} G_{5Jin}(z_i) d\theta d\xi_3, & M = 5. \end{cases} \tag{3.3}$$

In the above equation, $z_i = \xi_i / a_i$ (no summation on i), a_i is the semi-axis of size and ξ_1 and ξ_2 can be expressed in terms of ξ_3 and θ by $\xi_1 = \sqrt{1 - \xi_3^2} \cos\theta$ and $\xi_2 = \sqrt{1 - \xi_3^2} \sin\theta$. In addition $G_{MJin} = z_i z_n K^{-1}_{MJ}(z)$, where K^{-1}_{MJ} is the inverse of $K_{JR} = z_i z_n L_{iJRn}$. Li and Dunn (1998a) have obtained the closed-form expressions of magnetoelectroelastic Eshelby's tensors for the aligned elliptic cylinder inclusion in a transversely isotropic medium. For the coated fibrous composites with arbitrary crystal symmetry, we resort to Gauss quadrature numerical method to calculate S_{MnAb}. The integral (3.3) then is approximated by the weighted sum of function values at

certain integration points (Li, 2000a).

However, we will show later that this prediction deviates largely from those determined by the finite element analysis. Therefore, the direct Mori-Tanaka method is not good in estimating the coupling constants. We now turn to another appraoch, the two-level recursive scheme in conjunction with the Mori-Tanaka technique. The two-level recursive scheme is based on the idea that the matrix sees coated particles that are tmeselves composite. This procedure was first used to predict the behavior of viscoelastic composites containing multiple phases of coated inclusions. As illustrated in Fig. 2, each coated particle inclusion is seen (deepest level) as a two-phase composite, which, once, homogenized, plays the role of a homogeneous inclusion for the matrix material (highest level).

Further, at each levle, we employ the Mori-Tanaka appraoch in predictin the effective moduli of te the corresponding two-phase composites. Using this model, at the deepest level, the coated inlcusions are seen as a two-phase composite with effective moduli

$$L^{*(sc)}_{iJAb} = L^{(s)}_{iJAb} + \frac{f^{(c)}}{f^{(i)}} \left(L^{(c)}_{iJMn} - L^{(s)}_{iJMn} \right) A^{(c)}_{MnAb}. \tag{3.4}$$

Here, the superscripts c, s, and i represent core, shell and inclusion (core plus shell), respectively. The concentration tensor $A^{(c)}_{MnAb}$ can be determined as

$$A^{(c)}_{MnAb} = f^{(c)} A^{dil\ (c)}_{MnJi} \left(f^{(s)} I_{JiAb} + f^{(c)} A^{dil\ (c)}_{JiAb} \right)^{-1}, \tag{3.5}$$

with the dilute concentration tensor $A^{dil\ (c)}_{MnJi}$ given by

$$A^{dil\ (c)}_{MnJi} = \left[I_{MnAb} + S^{(c)}_{MnLk} (L^{(s)}_{LkiJ})^{-1} \left(L^{(c)}_{iJAb} - L^{(s)}_{iJAb} \right) \right]^{-1}. \tag{3.6}$$

At the highest level, the effective coated fibers plya the role of reinfocements and, similarly, we have the effective behavior

$$L^*_{iJAb} = L^{(m)}_{iJAb} + f^{(i)} \left(L^{(sc)}_{iJMn} - L^{(m)}_{iJMn} \right) A^{(sc)}_{MnAb}. \tag{3.7}$$

Again the concentration tensor can be dtermined as

$$A^{(sc)}_{MnAb} = A^{dil\ (sc)}_{MnJi} \left(f^{(m)} I_{JiAb} + f^{(c)} A^{dil\ (sc)}_{JiAb} \right)^{-1}, \tag{3.8}$$

with the dilute concentration tensor

$$A^{dil\ (sc)}_{MnJi} = \left[I_{MnAb} + S^{(sc)}_{MnLk} (L^{(m)}_{LkiJ})^{-1} \left(L^{*(sc)}_{iJAb} - L^{(m)}_{iJAb} \right) \right]^{-1}. \tag{3.9}$$

Here, $S^{(sc)}_{MnLk}$, is the generalized Eshelby tensor for effecitve coated particles, which is a function of the moduli of the matrix and the shape and orientation of the coated fibers (coreplus shell).

4 Finite element method

In this section, we introduce the finite element method which is used for comparison with the above micromechanical solutions. We first choose an appropriate representative volume element (RVE), a periodic unit cell, which captures the major features of the underlying microstructure. There are five possible ways of packing cylinders in regular arrays in two dimensions (See Kittel, 2005, for instance). Here we concentrate on the two lattices, square and hexagonal arrangements (Fig. 2). A square packing is more frequently employed than a hexagonal packing in the literature, and in the case of conduction, square symmetry and transverse isotropy become identical (Perrins

et al., 1979.). However, in our case of magnetoelectroelasticity, it lacks the transverse isotropy in that most unidirectional composites possess owing to the random distribution of fibers in the matrix over the cross-section perpendicular to fibers (Li, 2000).???(material symmetry 3mm)

Further, due to the periodicity in the composite structure, the displacement u_i, the electric potential φ and the magnetic potential ψ in any point of the unit cell can be expressed in terms of those at an equivalent point in another RVE such that the periodic boundary conditions

$$\begin{aligned} U_M(d, x_2, x_3) &= U_M(-d, x_2, x_3) + \langle U_{M,1} \rangle 2d, \\ U_M(x_1, d, x_3) &= U_M(x_1, -d, x_3) + \langle U_{M,2} \rangle 2d, \\ U_M(x_1, x_2, d) &= U_M(x_1, x_2, -d) + \langle U_{M,3} \rangle 2d, \end{aligned} \tag{4.1}$$

are satisfied for the square lattice. Here U_M is defined in (2.6) and $2d$ is the length of the unit cell. The comma in the subscript denotes the partial derivative. Similarly, the periodic boundary conditions for a hexagonal lattice are

$$\begin{aligned} U_M(d, x_2, x_3) &= U_M(-d, x_2, x_3) + \langle U_{M,1} \rangle 2d, \\ U_M\left(x_1, \sqrt{3}d, x_3\right) &= U_M\left(x_1, -\sqrt{3}d, x_3\right) + \langle U_{M,2} \rangle 2\sqrt{3}d, \\ U_M(x_1, x_2, d) &= U_M(x_1, x_2, -d) + \langle U_{M,3} \rangle 2d. \end{aligned} \tag{4.2}$$

In order to evaluate the effective coefficients of the above periodic multiferroic composite, the strain ε_{ij}, electric field E_i, and magnetic field states H_i are applied individually to the unit cell. The periodic boundary conditions have to be applied to the unit cell in such a way that, apart from one component of the strain, electric field, or magnetic field $\langle U_{M,i} \rangle$ in Eq. (4.1), all other components are made equal to zero.

Then each effective constant be determined by (2.8). We perform the finite element analysis using the software COMSOL Multiphysics.

5 Results and discussion

As a numerical example, we take a composite made of PE cores coated PM shell in a PM matrix. For the piezoelectric material, we first choose the widely used $BaTiO_3$ (BTO) ceramic as the core phase. For the piezomagnetic material we choose $CoFe_2O_4$ (CFO) as the shell phase while Terfenol-D (TD) as the matrix phase. They are all transversily isotropic, i.e., with 6mm symmetry. For convenience, we denote the composite as BTO/CFO/TD. The independent material constants of these constituents are given in Table 1 in Voigt notation, where the x_1x_2 plane is isotropic and the poling direction/magnetic axis is along the x_3-direction. Note that in all materials, the ME coefficients are zero, i.e. $\lambda_{ij} = 0$.

In our study, we are particularly interested in the effective magnetoelectric (ME) response. The induced voltage is proportional to the applied magnetic field and the constant of proportionality is the effective ME voltage coefficient. It combines the coupling and dielectric coefficients, and is defined by

$$\alpha^*_{E,ij} = \lambda^*_{ij}/\kappa^*_{ij}, \text{ no summation.} \tag{5.1}$$

Figure 3 shows how the ME voltage coefficients depend on both the inclusion volume fraciotn, f_i, and the ratio of radii, γ, for the BTO/CFO/TD three-phase multiferroic composite. for this composite. In the micromechanical approach, there is no upper limit on the volume fractions, since Mori-Tanaka's model is a mean-field theory. On the other hand, the finite element analysis is estimated for discrete volume

fractions and stops around $f = \pi/4$ and $f = \pi/2\sqrt{3}$ for the square and hexagonal arrays, respectively, when the inclusions touch. The ratio of the radius between the circular fibr and the coating shell is defined as $\gamma \equiv a/b$. It is obvious that if $\gamma = 0$, then $a = 0$. In other words, there is no fiber phase. On the other hand, if $\gamma = 1$, it means that there is no coating shell. The prediction of the Mori-Tanaka's approach is in good agreement with the result of the finite element analysis. The maximum ME voltage coefficient $\alpha^*_{E,11}$ is $xxxx$V/cmOe at volume fraction $f = 0.xx$, while the maximum $\alpha^*_{E,33} = xxxx$V/cmOe at volume fraction $f = 0.xx$. Note that the results of the hexagonal array are closer to the Mori-Tanaka's estimation than those of the square array. This is because a hexagonal array is a closed packing structure, and the Mori-Tanaka's model allows the inclusion to fulfill the matrix. In addition a square array lacks the transversely isotropy that this composite possesses (Li, 2000b).

Further, Fig. 3 compares the overall moduli with those predicted by the direct Mori-Tanaka method for the case $\gamma = 0.8$. It is observed that the prediction deviates largely from those determined by the finite element analysis. Therefore, the direct Mori-Tanak method is not good in estimating the coupling constants, although calculations show that they evaluate elastic stiffness well.

Finally, Fig. 3(a) also compares the effective moduli with the prediction by Kuo and Pan (2011). Kuo and Pan considered multiferroic composites with coated circular fibers under anti-plane shera with in-plane electric-magnetic fields.

We now turn to study how the effective ME voltage coefficient depends on the elastic moduli, C_{PE} and C_{PM}, dielectric permittivities, κ_{PE} and κ_{PM}, and magnetic permeabilites, μ_{PE} and μ_{PM}, of the PE and PM materials, piezoelectric constant, e_{PE}, of the PE material, and piezomagnetic coefficent, q_{PM}, of the PM material. For ease of comparison, we choose the material properties of BTO and CFO as the

reference and define hte normalized materials properties of the PE and PM phases as

$$C_{r,Core}\mathbf{I} = \mathbf{C}_{PE}(\mathbf{C}_{BTO})^{-1},\ C_{r,Shell}\mathbf{I} = \mathbf{C}_{PM}(\mathbf{C}_{CFO})^{-1},\ C_{r,Matrix}\mathbf{I} = \mathbf{C}_{PM}(\mathbf{C}_{CFO})^{-1},$$

and, likewise, are $e_{r,Core}$, $q_{r,Shell}$, $q_{r,Matrix}$, $\kappa_{r,Core}$, $\kappa_{r,Shell}$, $\kappa_{r,Matrix}$, $\mu_{r,Core}$, $\mu_{r,Shell}$, $\mu_{r,Matrix}$. Note that all the compnents of the material constant are magnifuied simultanesouly for simplicity. Belowm we numerically compute the ME voltage coefficients $\alpha^*_{E,11}$ and $\alpha^*_{E,33}$ and their dependence on the normalized material properties of core (PE), shell (PM), and materix (PM) phases.

Figure 4 shows the ME voltage coefficient $\alpha^*_{E,11}$ with respect to the crystallographic orientation of CFO and BTO. It happens be optimal when the poling direction of piezoelectric phase coincides with the magnetic axis of the piezomagnetic phase. We observe that the maximum of -2.4823V/cmOe occurs at Euler angles $(\alpha, \beta, \gamma) = (\alpha, 90°, 90°)$, where α is arbitrary. This degeneracy of optimal orientation reflects the $6mm$ symmetry. Further, If $\alpha = 0$, it is equivalent to the poling direction/magnetic axis along [010]. Significantly, the optimized value of -2.4823V/cmOe is almost *one hundred and one* times higher than -0.0244V/cmOe, which is the value of the normal cut where the c axis of the CFO and BTO is along the fiber axis.

Figure 5

Motivated by the above study, we do a similar calculation for $LiNbO_3$ (LNO), $CoFe_2O_4$, and Terfenol-D as the core, shell, and matrix phases, since LNO has lower dielectric permittivity and the matrix TD has lower elastic stiffness and magnetic permeability. The material constants of LNO are listed in Table I. Figure 6 shows the ME voltage coeffcients, volume fraction, and ratio of radii dependence of LNO/CFO/TD. Significantly, the maximum values are enhanced to xxx V/cmOe and xx V/cmOe for $\alpha^*_{E,11}$ and $\alpha^*_{E,33}$, respectively.

6 Concluding remarks

We have proposed a micromechanical model, the two-level recursive scheme in conjunction with the Mori-Tanaka' model, to compute the effective magnetoelectric response of a core-shell-matrix, three-phase, fibrous composites made of piezoelectric and pizomagnetic phases. The results are compared wiht finite element analysis and the semi-analytical method proposed by Kuo (2010) and Kuo and Pan (2011). The magnitudes and trends among them are in good agreement. We have used it to show that, for the

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References

[1] Aboudi, J., 2001. Micromechanical analysis of fully coupled electro-magneto-thermo-elastic multiphase composites. Smart Mater. Struct. **10**, 867-877.

[2] Alshits, V. I., Darinskii A. N., Lothe, J. 1992. On the existence of surface waves in half-infnite anisotropic elastic media with piezoelectric and piezomagnetic properties. Wave Motions **16**, 265-284.

[3] Arfken, G. B., Weber, H. J., 2001. Mathematical Methods for Physicists. Academic Press, San Diago, pp.199.

[4] Astrov, D. N., 1960. The magnetoelectric effect in antiferromagnetics. Sov. Phys. JETP 11, 708-709.

[5] Benveniste, Y., 1995. Magnetoelectric effect in fibrous composites with piezoelectric and piezomagnetic phases. Phys. Rev. B **51**, 16424-16427.

[6] Bichurin, M. I., Petrov, V. M., Srinivasan, G., 2003. Theory of low-frequency magnetoelectric coupling in magnetostrictive-piezoelectric bilayers. Phys. Rev. B **68**, 054402.

[7] Camacho-Montes, H., Sabina, F. J., Bravo-Castillero, J., Guinovart-Díaz, R., Rodríguez-Ramos R., 2009. Magnetoelectric coupling and cross-property connections in a square array of a binary composite. Int. J. Eng. Sci. 47, 294-312.

[8] Dinzart, D., Sabar, H., 2011. Magneto-electro-elastic coated inclusion problem and its application to magnetic-piezoelectric composite materials. Int. J. Solids Struct. **48**, 2393-2401.

[9] Eerenstein W., Mathur, N. D., Scott, J. F., 2006. Multiferroic and magnetoelectric materials. Nature **442**, 759-765.

[10] Fiebig, M., 2005. Revival of the magnetoelectric effect. J. Phys. D: Appl. Phys. **38**, R123-R152.

[11] Huang, J. H., 1998. Analytical predictions for the magnetoelectric coupling in piezomagnetic materials reinforced by piezoelectric ellipsoidal inclusions. Phys. Rev. B **58**, 12-15.

[12] Huang, J. H., Kuo, W. -S., 1997. The analysis of piezoelectric/piezomagnetic composite materials containing ellipsoidal inclusions. J. Appl. Phys. **81**, 1378-1386.

[13] Huang, H. T., Zhou, L. M., 2004. Micromechanics approach to the magnetoelectric properties of laminate and fibrous piezoelectric/magnetostrictive composites. J. Phys. D: Appl. Phys. **37**, 3361-3366.

[14] Kittel, C., 2005. Introduction to Solid State Physics. John Wiley & Sons, New Jersey. pp.8.

[15] Kuo, H.-Y., 2011. Multicoated elliptic fibrous composites of piezoelectric and piezomagnetic phases. Int. J. Eng. Sci. **49**, 561-575.

[16] Kuo, H.-Y., Pan, E., 2011. Effective magnetoelectric effect in multicoated circular fibrous multiferroic composites. J. Appl. Phys. **109**, 104901.

[17] Kuo, H.-Y., Wu, T.-S., 2012. Magnetoelectric effect of three-phase core-shell-matrix particulate multiferroic composites. J. Appl. Phys. Accepted.

[18] Kuo, H.-Y., Slinger, A., Bhattacharya, K., 2010. Optimization of magnetoelectricity in piezoelectric-magnetostrictive bilayers. Smart Mater. Struct. **19**, 125010.

[19] Lee, J., Boyd IV, J. G., Lagoudas, D. C., 2005. Effective properties of three-phase electro-magneto-elastic composites. Int. J. Eng. Sci. **43**, 790-825.

[20] Li, J. Y., 2000a. Magnetoelectroelastic multi-inclusion and inhomogeneity problems and their applications in composite materials. Int. J. Eng. Sci. **38**, 1993-2001.

[21] Li, S., 2000b. General unit cells for micromechanical analyses of unidirectional composites. Composites: Part A **32**, 815-826.

[22] Li, J. Y., Dunn, M. L., 1998a. Micromechanics of magnetoelectroelastic composite materials: average fields and effective behaviour. J. Intel. Mat. Syst. Struct. **9**, 404-416.

[23] Li, J. Y., Dunn, M. L., 1998b. Anisotropic coupled-field inclusion and inhomogeneity problems. Philos. Mag. A **77**, 1341-1350.

[24] Liu, G., Nan, C.-W., Cai, N., Lin, Y., 2004. Calculations of giant magnetoelectric effect in multiferroic composites of rare-earth-iron alloys and PZT by finite element method. Int. J. Solids Struct. **41**, 4423-4434.

[25] Nan, C. -W., 1994. Magnetoelectric effect in composites of piezoelectric and piezomagnetic phases. Phys. Rev. B **50**, 6082-6088

[26] Nan, C.-W., Bichurin, M. I., Dong, S, Viehland, D., Srinivasan, G., 2008. Multiferroic magnetoelectric composites: Historical perspective, status, and future directions. J. Appl. Phys. **103**, 031101.

[27] Nye, J. F., 1985. Physical Properties of Crystals. Oxford University Press, Oxford.

[28] Rado, G. T., Folen, V. J., 1961. Observation of the magnetically induced magnetoelectric effect and evidence for antiferromagnetic domains. Phys. Rev. Lett. **7**, 310-311.

[29] Spaldin, N. A., Fiebig, M., 2005. The renaissance of magnetoelecitrc multiferroics. Science **309**, 391-392.

[30] Srinivas, G., Rasmussen, E. T., Galleogos, J., Srinivasan, R., Bokhan, Y. I., Laletin, V. M., 2001. Magnetoelectric bilayer and multilayer structures of magnetostrictive and piezoelectric oxides. Phys. Rev. B **64**, 214408.

[31] Srinivas, S., Li, J. Y., Zhou, Y. C., Soh, A. K., 2006. The effective magneto-electroelastic moduli of matrix-based multiferroic composites. J. Appl. Phys. **99**, 043905.

[32] Srinivasan, G., 2010. Magnetoelectric composites. Annual review of naterials research **40**, 153-178.

[33] Wang, Y., Or, S. W., Chan, H. L. W. Zhao, X., Luo H., 2008. Enhanced magnetoelectric effect in longitudinal-transverse mode Terfenol-D/$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ laminate composites with optimal crystal cut. J. Appl. Phys. **103**, 124511.

[34] Wu, T. -L., Huang, J. -H., 2000. Closed-form solutions for the magnetoelectric coupling coefficients in fibrous composites with piezoelectric and piezomagnetic phases. Int. J. Solids Struct. **37**, 2981-3009.

[35] Yang P., Zhao K., Yin Y., Wan H. G., Shu, J. S., 2006. Magnetoelectric effect in magnetostrictive/piezoelectric laminate composite Terfenol-D/ LiNbO3[(zxtw)129°/30°]. Appl. Phys. Lett. **88**, 172903.

[36] Zheng, H., Wang, J., Lofland, S. E., Ma, Z., Mohaddes-Ardabili, L., Zhao, T., Salamanca-Riba, L., Shinde, S. R., Ogale, S. B., Bai, F., Viehland, D., Jia, Y., Schlom, D. G., Wuttig, M., Roytburd, A., Ramesh, R., 2004. Multiferroic $BaTiO_3$-$CoFe_2O_4$ nanostructures. Science **303**, 661-663.

Table 1: Material parameters of $BaTiO_3$ and $CoFe_2O_4$ (Li and Dunn, 1998a)

Figure 1: The fibrous composite configurations.

Figure 2: A schematic representation of a unit cell. (a) A square array. (b) A hexagonal array.

Figure 3: The ME voltage coefficients of the CFO fibers in a BTO matrix at the normal direction versus the fiber volume fraction. (a) In-plane ME voltage coefficient $\alpha^*_{E,11}$. (b) Out-of-plane ME voltage coefficient $\alpha^*_{E,33}$.

Figure 4: The in-plane ME voltage coefficient of the CFO fibers in a BTO matrix for various orientations of CFO and BTO. The subscripts i and m denote the inclusion and matrix, respectively. Note that this coefficient depends only on the Euler angles β and γ and is independent of α. The optimized constant occurs at both phases poled along the same direction.

Figure 5: The out-of-plane ME voltage coefficient of the CFO fibers in a BTO matrix for various orientations of CFO and BTO. The subscripts i and m denote the inclusion and matrix, respectively. Note that this coefficient depends only on the Euler angles β and γ and is independent of α. The optimized constant occurs at both phases poled along the same direction.

Figure 6: The optimal ME voltage coefficients of the CFO fibers in a BTO matrix for various fiber volume fraction. (a) In-plane ME voltage coefficient $\alpha^*_{E,11}$. (b) Out-of-plane ME voltage coefficient $\alpha^*_{E,33}$.

Figure 7: The ME voltage coefficients of the BTO fibers in a CFO matrix at the normal direction versus the fiber volume fraction. (a) In-plane ME voltage coefficient $\alpha^*_{E,11}$. (b) Out-of-plane ME voltage coefficient $\alpha^*_{E,33}$.

Figure 8: The in-plane ME voltage coefficient of the BTO fibers in a CFO matrix for various orientations of BTO and CFO. The optimized constant occurs at both phases poled along the same direction.

Figure 9: The out-of-plane ME voltage coefficient of the BTO fibers in a CFO matrix for various orientations of BTO and CFO. The optimized constant occurs at both phases poled along the same direction.

Figure 10: The optimal ME voltage coefficients of the BTO fibers in a CFO matrix for various fiber volume fraction. (a) In-plane ME voltage coefficient $\alpha^*_{E,11}$. (b) Out-of-plane ME voltage coefficient $\alpha^*_{E,33}$.