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Multiple-scattering approach to effective properties of piezoelectric composites

Ce-Wen Nan
Research Institute for Advanced Materials, Wuhan University of Technology, Wuhan, Hubei 430070, China

Fu-Sheng Jin
Department of Mechanics, Wuhan Institute of Technology, Wuhan, Hubei 430070, China
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We develop a general theoretical framework for predicting the effective properties of piezoelectric composites in terms of multiple-scattering theory. For transversely isotropic piezoelectric composites of aligned cylindrical fibers exhibiting transversely isotropic piezoelectricity embedded in an isotropic matrix, we give the first-order approximation of the theory and present a numerical study of the effective piezoelectric coefficients. It predicts the enhanced hydrostatic and voltage piezoelectric coefficients for the two-phase fiber-reinforced piezoelectric composites. The theoretical predictions also compare reasonably well with the experimental results.

I. INTRODUCTION

Recently, the determination of the effective properties of composites with coupled or cross linear-response coefficients, such as the piezoelectric effect, the magnetoelectric effect, and the thermoelectric effect, have received attention in the literature. An effective-medium approach for the thermoelectric effect was provided by Webman, Jortner, and Cohen.[1] Milgrom and Shtrikman[2] have recently given compatibility conditions between the effective constants for coupled problems where each driving force induces not only its conjugate flux but also other fluxes, and where each driving force is derivable from a potential function and each flux is divergenceless. Their technique is not suitable for the piezoelectric problem since the mechanical aspect of the problem involves tensors rather than vectors.

The piezoelectric effect is one of the most complex coupled linear-response problems. The approaches generally used are to choose a relatively simple geometrical model for which the boundary value problem involved is tractable,[3] or else to assume that elementary series-parallel models will reasonably describe bulk behavior.[4–6] Recently, Schulgasser[7] has generalized the relations found by Hill[8] for the purely elastic case to the piezoelectric case and given the relationships between some of the effective properties of transversely isotropic piezoelectric composites. But there is little work that attempts to go beyond these simple averaging-type schemes for the complex piezoelectric problem of composites.

In this work, following a similar but somewhat different approach to multiple-scattering theory which has been widely employed to treat the general linear-response properties and some nonlinear-response problems of inhomogeneous media (see, for example, the recent review[9]), we propose to develop a suitable theoretical framework to treat the complex effective properties of the piezoelectric composites. Section II contains the theoretical framework derived by the Green's-function method and the general solution to the effective properties of the piezoelectric composites. As a practical example, we consider specifically the case of aligned cylindrical fibers exhibiting transversely isotropic piezoelectricity embedded in an isotropic matrix, which are the technologically important composites which have been introduced in recent years to obtain enhanced performance in transducers.[10–12] An approximate solution to the effective properties of the piezoelectric composites of this type is given and the results of the application are discussed in Sec. III. The conclusions are summarized in Sec. IV.

II. GENERAL FRAMEWORK

The piezoelectric effect can be expressed by

$$\begin{aligned} \boldsymbol{\sigma} &= C\mathbf{S} - e\mathbf{E} \,, \\ \mathbf{D} &= e^T\mathbf{S} + \varepsilon\mathbf{E} \,, \end{aligned} \tag{1}$$

where $\boldsymbol{\sigma}$ and $\mathbf{S}$ are the stress and strain tensors, respectively; $\mathbf{D}$ and $\mathbf{E}$ are the electric displacement and field; C, ε, and e are the elastic stiffness, permittivity, and piezoelectric constant, respectively; and e^T is the transpose of e. For simplicity of notation, we have used the direct notation of tensors, and dropped the often used superscript $\mathbf{E}$ on the elastic stiffness which denotes the constancy of the electric field and the superscript $\mathbf{S}$ on the permittivity which is used to denote the constant-strain conditions. This should cause no confusion since no other form of constitutive equations will be used. For further simplicity, we can rewrite Eq. (1) as the matrix form

$$\begin{bmatrix} \boldsymbol{\sigma} \\ \mathbf{D} \end{bmatrix} = \begin{bmatrix} C & -e \\ e^T & \varepsilon \end{bmatrix} \begin{bmatrix} \mathbf{S} \\ \mathbf{E} \end{bmatrix} . \tag{2}$$

The matrix of these constitutive constants is a 9×9 matrix. For a piezoelectric composite, these quantities are local values depending on the spatial position. The effective constitutive constants of the piezoelectric composite are defined in terms of averaged stress $\langle\sigma\rangle$, electric displacement $\langle\mathbf{D}\rangle$, strain $\langle\mathbf{S}\rangle$, and electric field $\langle\mathbf{E}\rangle$, namely,

$$\begin{bmatrix} \langle \sigma \rangle \\ \langle \mathbf{D} \rangle \end{bmatrix} = \begin{bmatrix} C^* & -e^* \\ e^{T*} & \varepsilon^* \end{bmatrix} \begin{bmatrix} \langle \mathbf{S} \rangle \\ \langle \mathbf{E} \rangle \end{bmatrix} . \tag{3}$$

The local constitutive constants can be written as

$$\begin{bmatrix} C & -e \\ e^T & \varepsilon \end{bmatrix} = \begin{bmatrix} C^0 & -e^0 \\ e^{T^0} & \varepsilon^0 \end{bmatrix} + \begin{bmatrix} C' & -e' \\ e^{T'} & \varepsilon' \end{bmatrix} , \tag{4}$$

where the first term is the constitutive constants of a homogeneous comparison medium and the second term is the fluctuation on the first. In the equilibrium case the local fields within the piezoelectric composite can be obtained in terms of the Green's-function method as

$$\begin{bmatrix} \mathbf{S} \\ \mathbf{E} \end{bmatrix} = \begin{bmatrix} \mathbf{S}^0 \\ \mathbf{E}^0 \end{bmatrix} + \begin{bmatrix} G^u & 0 \\ 0 & G^\phi \end{bmatrix} \begin{bmatrix} C' & -e \\ e^T & \varepsilon' \end{bmatrix} \begin{bmatrix} \mathbf{S} \\ \mathbf{E} \end{bmatrix} , \tag{5}$$

where G^u and G^ϕ are the familiar purely elastic displacement and electric potential Green's function for the homogeneous medium (C^0, ε^0), respectively, and $(\mathbf{S}^0, \mathbf{E}^0)$ are the homogeneous fields in the homogeneous medium.

We iterate Eq. (5) and obtain an explicit solution for the local fields as

$$\begin{bmatrix} \mathbf{S} \\ \mathbf{E} \end{bmatrix} = \begin{bmatrix} T^{66} & -T^{63} \\ T^{36} & T^{33} \end{bmatrix} \begin{bmatrix} \mathbf{S}^0 \\ \mathbf{E}^0 \end{bmatrix} \tag{6}$$

with

$$\begin{aligned} T^{66} &= [I - G^u C' + G^u e(I - G^\phi \varepsilon')^{-1} G^\phi e^T]^{-1} , \\ T^{63} &= T^{66} G^u e(I - G^\phi \varepsilon')^{-1} , \\ T^{33} &= [I - G^\phi \varepsilon' + G^\phi e^T (I - G^u C')^{-1} G^u e]^{-1} , \\ T^{36} &= T^{33} G^\phi e^T (I - G^u C')^{-1} , \end{aligned} \tag{7}$$

where I is the unit tensor. Obviously, this T matrix is much more complicated than that for the general linear-response problems. With the equations above, we get the general solution to the effective properties of the piezoelectric composite

$$C^* = \langle C T^{66} - e T^{36} \rangle A + \langle C T^{63} + e T^{33} \rangle B , \tag{8}$$

$$e^* = \langle (C - C^*) T^{63} + e T^{33} \rangle \langle T^{33} \rangle^{-1} , \tag{9}$$

$$e^{T*} = \langle e^T T^{66} + \varepsilon T^{36} \rangle A - \langle \varepsilon T^{33} - e^T T^{63} \rangle B , \tag{10}$$

$$\varepsilon^* = \langle \varepsilon T^{33} + (e^{T*} - e^T) T^{63} \rangle \langle T^{33} \rangle^{-1} , \tag{11}$$

where

$$\begin{aligned} A &= [\langle T^{66} \rangle - \langle T^{63} \rangle \langle T^{33} \rangle^{-1} \langle T^{36} \rangle]^{-1} , \\ B &= \langle T^{33} \rangle^{-1} \langle T^{36} \rangle A . \end{aligned} \tag{12}$$

These results are exact and independent of the models assumed for the piezoelectric composites, and also constitute the relationships between these effective constants. Obviously, the results, Eqs. (8) and (11), for the effective elastic C^* and permittivity ε^* of the piezoelectric composites are different from those for general linear-response problems.[9] Equations (8) and (11) contain the cross or coupled effects. After ignoring these coupled terms, we get

$$C^* = \langle C T^{66} \rangle \langle T^{66} \rangle^{-1} , \tag{13}$$

$$\varepsilon^* = \langle \varepsilon T^{33} \rangle \langle T^{33} \rangle^{-1} , \tag{14}$$

$$e^* = \langle (C - C^*) T^{63} + e T^{33} \rangle \langle T^{33} \rangle^{-1} , \tag{15}$$

where the T tensors are simplified as

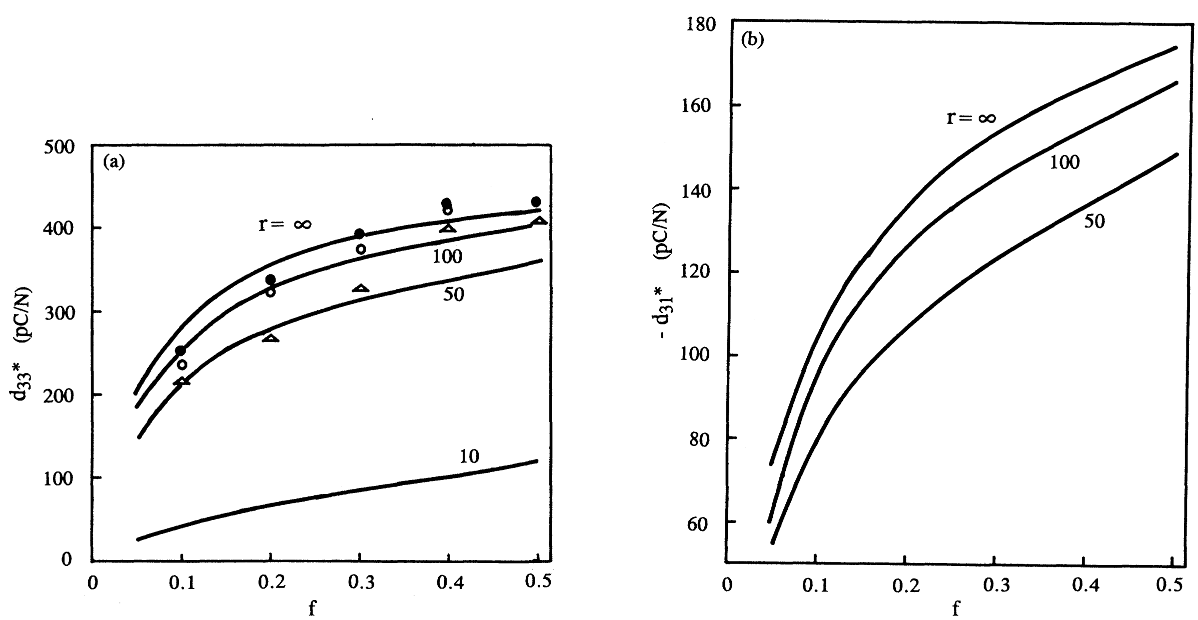

FIG. 1. Variations of (a) d_{33}^* and (b) d_{31}^* with the volume fraction f of PZT particles for the different aspect ratio r. The experimental results (Ref. 10) in (a) are for rod diameters of (●) 400 μm, (○) 600 μm, and (△) 840 μm.

$$T^{66}=(I-G^{u}C')^{-1}\ ,$$
$$T^{63}=(I-G^{u}C')^{-1}G^{u}e(I-G^{\phi}\varepsilon')^{-1}\ , \qquad (16)$$
$$T^{33}=(I-G^{\phi}\varepsilon')^{-1}\ .$$

Equations (13) and (14) are the same as the results for the general linear-response problems.

III. ANALYSIS AND DISCUSSIONS

In order to better understand the above results, we consider a technologically important case of aligned fibers exhibiting transversely isotropic piezoelectricity [such as lead zirconate titanate (PZT) ceramics] embedded in an isotropically nonpiezoelectric continuous matrix such as epoxy. Piezoelectric composites of this type (sometimes referred to as 3-1 composites) have been introduced in recent years to obtain enhanced performance in transducers. The 3 direction of the composite is along the direction in which the fibers are aligned and poled. Such a piezoelectric composite is described by a total of ten overall effective constants. These are the following: five stiffnesses ($k^*=C^*_{11}+C^*_{12}$, $m^*=C^*_{11}-C^*_{12}$, C^*_{13}, C^*_{33}, C^*_{55}); three piezoelectric constants (e^*_{31}, e^*_{33}, e^*_{15}); and two permittivity constants (ε^*_{11}, ε^*_{33}).

Let f denote the volume fraction of the inclusion fibers. The material properties will be superscripted by "f" or "m" as the property applies to the fibrous phase or the matrix phase. For the piezoelectric composites of this type, we can reasonably take $C^0=C^m$ and $\varepsilon^0=\varepsilon^m$. After ignoring the f^2 terms in C^*, we can get these following ten effective constants from Eqs. (8)–(12):

$$\begin{aligned}
k^*&=\frac{k^m(k^f+m^m)+fm^m(k^f-k^m)}{k^f+m^m-f(k^f-k^m)}\ ,\\
m^*&=m^m\frac{k^m(m^m+m^f)+2m^m m^f+fk^m(m^f-m^m)}{k^m(m^m+m^f)+2m^m m^f-f(m^f-m^m)(k^m+2m^m)}\ ,\\
C^*_{13}&=\frac{C^m_{12}(k^f-k^*)+C^f_{13}(k^*-k^m)}{k^f-k^m}\ ,\\
C^*_{33}&=C^m_{11}+f(C^f_{33}-C^m_{11})-2f\frac{(C^f_{13}-C^m_{12})^2(k^f-k^*)}{(k^f+m^m)(k^f-k^m)}\ ,\\
C^*_{55}&=\frac{m^m(m^m+2C^f_{55})+fm^m(2C^f_{55}-m^m)}{2(m^m+2C^f_{55})+2f(m^m-2C^f_{55})}\ ,\\
e^*_{31}&=fe^f_{31}(k^*+m^m)/(k^f+m^m)\ ,\\
e^*_{33}&=fe^f_{33}-2fe^f_{31}(C^f_{13}-C^*_{13})/(k^f+m^m)\ ,\\
e^*_{15}&=\frac{fe^f_{15}\varepsilon^m(m^m+2C^*_{55})}{[(1+f)\varepsilon^m+(1-f)\varepsilon^f_{11}](m^m+2C^f_{55})}\ ,\\
\varepsilon^*_{11}&=\varepsilon^m\frac{(1-f)\varepsilon^m+(1+f)\varepsilon^f_{11}-2f(e^*_{15}-e^f_{15})e^f_{15}/(m^m+2C^f_{55})}{(1+f)\varepsilon^m+(1-f)\varepsilon^f_{11}}\ .\\
\varepsilon^*_{33}&=\varepsilon^m+f(\varepsilon^f_{33}-\varepsilon^m)-2fe^f_{31}(e^*_{31}-e^f_{31})/(k^f+m^m)\ .
\end{aligned} \qquad (17)$$

The relations for the effective elastic moduli and e^*_{31}, are identical to those found by Hill,[8] and Schulgasser,[7] respectively. These equations cannot only give the results of the ten effective constants from the volume fraction of the fibrous phase and the constitutive constants for each of the two phases, but they also constitute the relationships between these ten effective constants for transversely isotropic piezoelectric composites. The piezoelectric constants of interest, d^*_{31} and d^*_{33}, are derived from the interrelationships between the various sets of constants, and furthermore, two important piezoelectric coefficients, hydrostatic piezoelectric (d^*_h) and voltage coefficient (g^*_h), can be obtained by

$$d^*_h=d^*_{33}+2d^*_{31},\quad g^*_h=d^*_h/\varepsilon^*_{33}\ . \qquad (18)$$

Some theoretical predictions of the effective piezoelectric properties for PZT-epoxy composites are shown in Figs. 1–4. The properties of both phases are taken as $C^m_{11}=6.5$ GPa, $C^m_{12}=3.5$ GPa, and $\varepsilon^m=7$ for the epoxy matrix $C^f_{11}=118.4$ GPa, $C^f_{12}=58.5$ GPa, $C^f_{13}=59.6$ GPa, $C^f_{33}=102.8$ GPa, $\varepsilon^f_{33}=1600$, $d_{31}=-205$ and $d_{33}=450$ pC/N for PZT particles. For the sake of comparison with experiment, the experimental results[10] for the composites with embedding extruded PZT rods in an epoxy matrix are also shown in these figures. These PZT rods-epoxy composites have special 3-1 connectivity[10] where the length of the aligned PZT rods with larger diameter (400, 600, and 840 μm) is equal to the thickness of the composite samples. In this case, the aspect ratio r of the PZT rods may be considered to be larger than their real aspect ratio, and the PZT particles are continuous along the direction of their length. In spite of the speciality of these composite samples, it can be seen from these figures

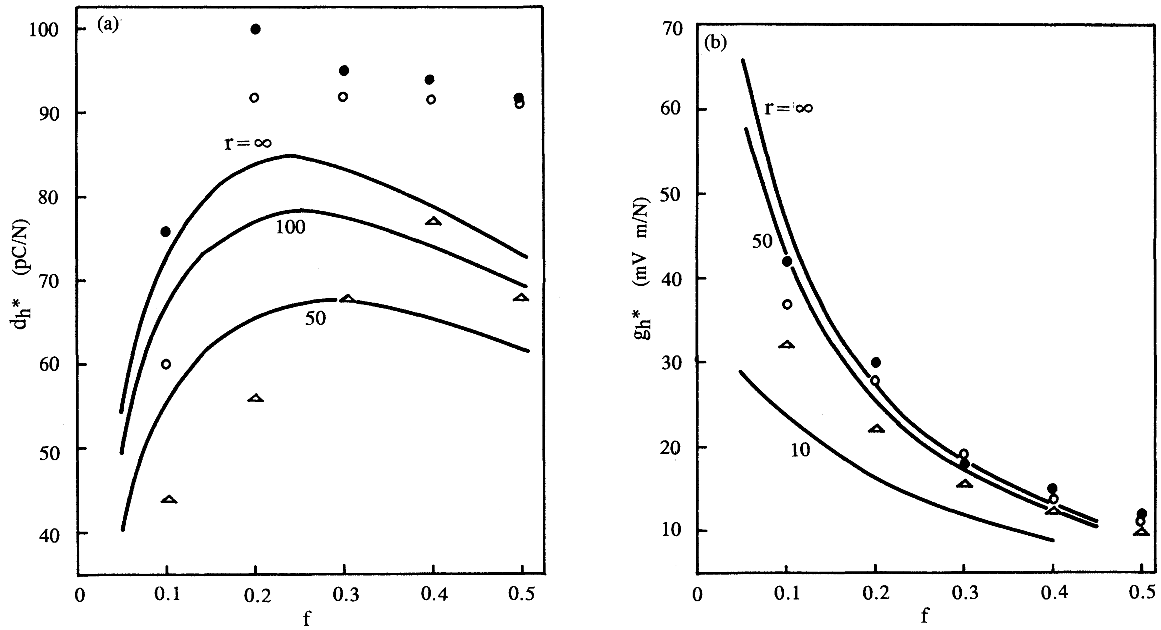

FIG. 2. Variations of (a) d_h^* and (b) g_h^* with the volume fraction f of PZT particles for the different aspect ratio r. The experimental results (Ref. 10) in (a) are for rod diameters of (●) 400 μm, (○) 600 μm, and (△) 840 μm.

that the theoretical trends are consistent with experiment. The piezoelectric constants (d_{33}^*, $|d_{31}^*|$, and d_h^*) increase, and g_h^* decreases, with the increase in the volume fraction of PZT particles, respectively. The composites with a larger aspect ratio of PZT rods have enhanced d_h^* and g_h^*. The discrepancy between theoretical predictions and experiments in the range of the higher volume fraction of PZT can result from the original shortcoming of the first-order approximation. As the volume fraction of PZT particles increases, the anisotropy of the composites increases. In this case, that the isotropic epoxy phase is taken as the homogeneous comparison medium will re-

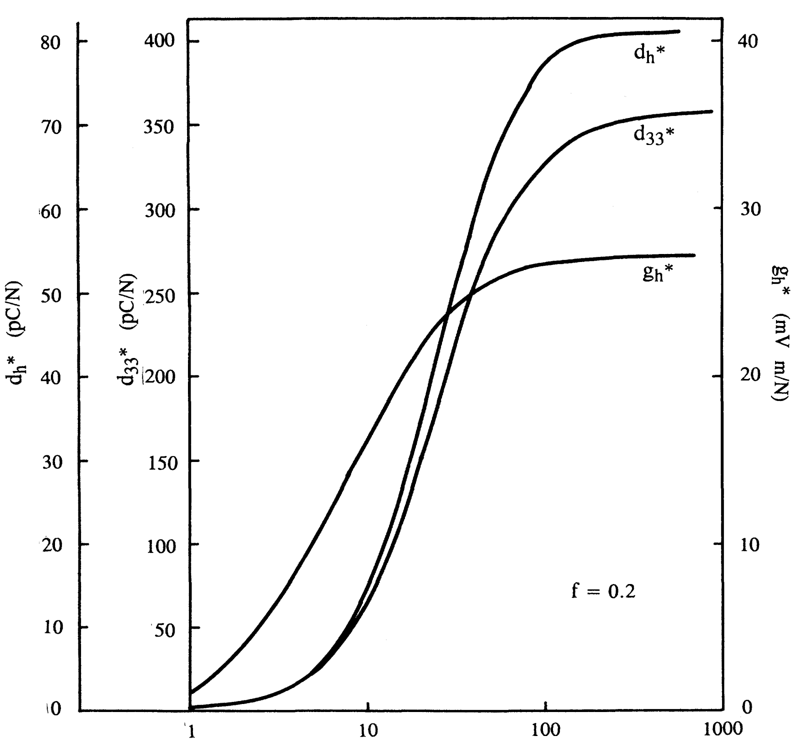

FIG. 3. The effect of the aspect ratio r of PZT particles on the piezoelectric constants.

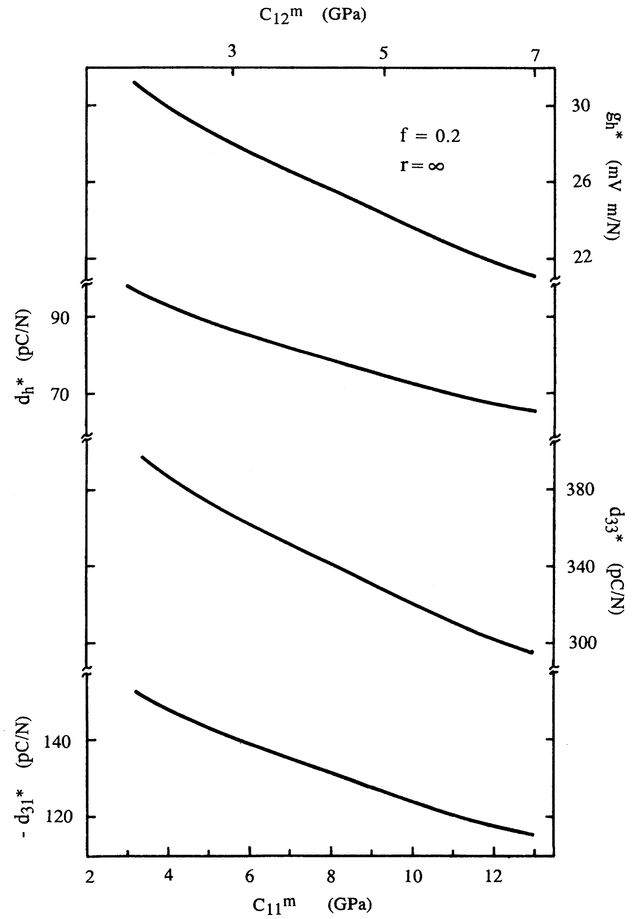

FIG. 4. The effect of the elastic moduli of polymer matrices on the piezoelectric constants.

sult in the deviation of theoretical results from experiment. In the meantime, the interaction between PZT particles needs to be considered at high concentrations. On the other hand, in these 3-1 composites,[10] a larger amount of stress is borne by the PZT rods. Consequently, a greater piezoelectric response than the theoretical predictions is induced at high concentrations.

An interesting consequence of the theoretical predictions is that there is also a maximum in the relations of d_h^* vs f, as in the experimental results (Fig. 2). The first-order approximation theoretically predicts the enhanced hydrostatic and voltage piezoelectric coefficients in the piezoelectric composites. The characteristic volume fraction corresponding to the maximum enhancement in d_h^* decreases with the increase in the aspect ratio of prolate PZT particles. At a larger aspect ratio, this characteristic volume fraction is almost constant.

The aspect ratio r of PZT particles has a pronounced effect on the effective piezoelectric properties (Fig. 3). As the aspect ratio is less than 10, the effective piezoelectric coefficients of the composites are lower and slowly change with f and r. In the intermediate range of $10 < r < 100$, the effective piezoelectric coefficients rapidly increase with the increase in r. As $r > 100$, the effective piezoelectric coefficients slightly change with r, and approach the values in the limit case of aligned fibers ($1/r = 0$). The effective piezoelectric properties are also strongly influenced by the elastic stiffness of the epoxy matrix, as shown in Fig. 4. The effective piezoelectric properties of composites can increase through the use of softer polymer matrices. This is directly attributed to the improved stress transfer capability of the more flexible polymers.

IV. CONCLUSIONS

In this paper we have developed the multiple-scattering theory for the piezoelectric response of piezoelectric composites which cannot only give the results of the effective moduli, but also constitute the interrelationships between these effective moduli. For the transversely isotropic composites in the system of PZT-epoxy, explicit numerical calculations have been done following the first-order approximation of the theory. The composites with fibrous PZT particles have a greatly enhanced hydrostatic coefficient and voltage piezoelectric coefficient. The effective piezoelectric properties of composites can be strongly influenced by the volume fraction and the aspect ratio of the PZT particles and the elastic moduli of the polymer matrix. The present theoretical framework can be generalized to the composites with other coupled or cross moduli. Finally, it may be mentioned that the present first-order approximation is a most reasonable one in the low concentration range. At high concentrations, more reasonable approximations of the theory need to be considered.

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