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Simultaneous optimization of orientation and constituent volume in piezoelectric composites

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1. Introduction

Being brittle and hard, ceramics are difficult to assemble directly into a device. Hence flexible composites could be an alternative useful in practical purposes. A variety of piezoelectric composites can be manufactured by combining a piezoelectric ceramic

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material and a polymer [1]. Piezoelectric (PE) composites constitute an important class of materials in engineering technology [2]. For instance, a composite based PE actuator, which could act as a sensor or receiver, would integrate well with smart structures. The piezoelectrics obtained from this combination greatly extend the range of material properties offered by the conventional piezoelectric ceramics and polymers [3]. There are several practical limitations to implementing monolithic wafers of delicate PE material in all these applications. First, the brittle nature of ceramics makes them vulnerable to accidental breakage during handling and bonding procedures. Another drawback is their extremely limited ability to conform to curved surfaces. As most of the other ceramics, piezoelectric ceramics (PEC) are brittle and usually fractures at strains less than 1% [4]. Thus, they can only be subjected to small strain deformations and be integrated only with a narrow set of substrate materials. Also, there is a large add-on mass associated with using a typically lead-based PEC. The idea of a composite material consisting of an active PEC phase embedded in a polymeric matrix phase remedies many of the aforementioned limitations and offers additional benefits [5, 6]. The flexible nature of the polymer matrix allows the material (composite) to more easily conform to the curved surfaces found in tangible industrial and aerospace applications while retaining piezoelectric properties [7, 8]. For instance, with an appropriate polymer the composite can be easily formed into curved shapes for steering and focussing the acoustic beam in ultrasonic transducers [9]. These types of devices are also capable of being added to a lay-up as active layers along with conventional fiber-reinforced laminae.

The anisotropy of the composite materials as well as the numerous material choices, if utilized judiciously, would enhance the performance characteristics of the corresponding devices. Realizing a piezocomposite (of a polymer and a PE) with improved mechanical reliability against loads and enhanced piezoelectric sensitivity are fraught with the following impediments; determination of the optimal volume fraction of the PE/polymer, determining the optimal orientation of the PE/polymer matrix and determining the optimal orientation distribution of the piezoelectric phase. The efforts, so far, in this direction were limited to exploring any one of the above instances and were treated independent of each other [10–15]. Nevertheless, to maximize the piezoelectric response, one has to simultaneously obtain the volume fraction of the PE/polymer material phase in the composite and their crystal orientation/grain orientation distribution. Crystal orientation is applicable if either of the phase in the composite is single crystalline and grain orientation distribution is attached to polycrystalline PE material used. A simulation methodology which can combine the above aspects simultaneously in one platform is thus necessary to identify optimal solutions of volume fractions and orientations/orientation distribution corresponding to technologically important objectives in a piezocomposite.

Stochastic optimization has been applied to single phase ferroelectric materials in an effort to fulfilling the above objective of extracting the maximum possible piezoelectric strain. Moreover, it has been demonstrated that it is possible to enhance the piezoelectric properties by tailoring the microstructure [16, 17]. In this paper, we extend this previous work to composites wherein the design space is expanded to include the proportion and orientation of the constituents and would search for an optimal PE-polymer composite by a simulation interfacing homogenization with optimization. This model is presumably valid when the lateral spatial scale of the composite is sufficiently fine (for the excitation frequencies of interest) that the composite can be treated as an effective homogeneous medium with a new set of equivalent material properties.

2. Optimization procedure

2.1. Homogenization of PE composite

As PE ceramic is an aggregate of randomly oriented ferroelectric crystallites/domains, developments in the direction of controlled manipulation of domains could open opportunities for novel device architectures. The orientation misalignment of the constituent grains would impact the overall piezoelectric performance of the PE material [11, 18]. A two-scale homogenization method treats this problem of finding the equivalent properties of PEC from the knowledge of the local field solutions has already been applied to single phase materials [18, 19]. This procedure is eventually being used in this paper for the calculation of the effective electromechanical coefficients of a PE-polymer composite. The homogenization, mathematically applicable to heterogeneous media with reasonable contrasts in physical properties, replaces the heterogeneity by an equivalent effective medium with uniform physical characteristics [20]. The constitutive laws [21] connecting stress σ_{ij}, strain ϵ_{ij}, electric field E_j and electric displacement D_i, therefore, can be rewritten with the effective properties and average fields as,

$$\langle\sigma_{ij}\rangle = \widetilde{C}^E_{ijkl}\langle\epsilon_{kl}\rangle - \widetilde{e}_{kij}\langle E_k\rangle,\ \langle D_i\rangle = \widetilde{e}_{ijk}\langle\epsilon_{jk}\rangle + \widetilde{\kappa}^{\epsilon}_{ij}\langle E_j\rangle \tag{1}$$

where $\langle\cdot\rangle$ denotes volume averages *viz.*, $(\frac{1}{|V|}\int_V \cdot dV)$ and the coefficients with tilde, viz., $\widetilde{C}^E_{ijkl}, \widetilde{e}_{ijk}$ and $\widetilde{\kappa}^{\epsilon}_{ij}$ refers to the homogenized elastic, piezoelectric and dielectric coefficient tensors of the composite. These tensors satisfy the usual symmetry and positivity properties [22]. Throughout this paper, we have assumed Einstein summation convention that repeated indices are implicitly summed over and is of course applied to equation 1. We would use the contracted matrix notation for electromechanical property tensors in the sense that Greek indices would represent the contracted matrix notation and the Latin indices would indicate the tensor notation. Thus, for instance $\widetilde{C}^E_{ijkl}$ in the tensor form would be represented as $\widetilde{C}^E_{\mu\nu}$ in matrix form and accordingly the tensor indices would be transformed into matrix indices as $11 \to 1$, $22 \to 2$, $33 \to 3$, $23 \to 4$, $13 \to 5$ and $12 \to 6$.

A three-dimensional (3D) model is developed to compute the homogenized electric and mechanical properties of PE composites possessing the lowest crystallographic symmetry (i.e., triclinic). Such a modeling framework would be generic and thus could be useful for treating PE materials belonging to any crystallographic symmetry. For instance, the ferroelectric $BaTiO_3$ has tetragonal *P4mm* symmetry and hence possess 6 independent (non-vanishing) elastic stiffness, 3 piezoelectric and 2 dielectric constants from among the full electromechanical property matrix [23]. The asymptotic analysis of the piezoelectric medium would result in the homogenization of the piezoelectric, dielectric and elastic coefficients (in tensor form) as (Refs. [18, 19] ,

$$\widetilde{e}_{prs}(\boldsymbol{x}) = \frac{1}{|Y|}\int_Y \Big[e_{kij}(\boldsymbol{x},\boldsymbol{y})\Big(\delta_{kp} + \frac{\partial R^p}{\partial y_k}\Big)\Big(\delta_{ir}\delta_{js} + \frac{\partial \chi_i^{rs}}{\partial y_j}\Big) - e_{kij}(\boldsymbol{x},\boldsymbol{y})\frac{\partial \Phi_i^p}{\partial y_j}\frac{\partial \Psi^{rs}}{\partial y_k}\Big]dY \tag{2}$$

$$\widetilde{\kappa}^{\varepsilon}_{pq}(\boldsymbol{x}) = \frac{1}{|Y|}\int_Y \Big[\kappa^{\varepsilon}_{ij}(\boldsymbol{x},\boldsymbol{y})\Big(\delta_{ip} + \frac{\partial R^p}{\partial y_i}\Big)\Big(\delta_{jq} + \frac{\partial R^q}{\partial y_j}\Big) - e_{kij}(\boldsymbol{x},\boldsymbol{y})\Big(\delta_{kp} + \frac{\partial R^p}{\partial y_k}\Big)\frac{\partial \Phi_i^p}{\partial y_i}\Big]dY \tag{3}$$

$$\widetilde{C}^E_{rspq}(\boldsymbol{x}) = \frac{1}{|Y|}\int_Y \Big[C^E_{ijkl}(\boldsymbol{x},\boldsymbol{y})\Big(\delta_{ip}\delta_{jq} + \frac{\partial \chi_i^{pq}}{\partial y_j}\Big) \times\Big(\delta_{kr}\delta_{ls} + \frac{\partial \chi_k^{rs}}{\partial y_l}\Big) + e_{kij}(\boldsymbol{x},\boldsymbol{y})\Big(\delta_{ip}\delta_{jq} + \frac{\partial \chi_i^{pq}}{\partial y_j}\Big)\frac{\partial \psi^{rs}}{\partial y_k}\Big]dY. \tag{4}$$

where e_{ijk}, $\kappa^{\varepsilon}_{ij}$ and C^E_{ijkl} are the piezoelectric, dielectric and elastic coefficients of the constituent materials of PE composites in general. The piezoelectric d coefficients are related to the e coefficients through $\widetilde{d}_{ijk} = \widetilde{e}_{ilm}\widetilde{s}_{jklm}$, where $\widetilde{s}_{jklm}$ are the effective compliance. Also, $\chi_i^{rs}(\boldsymbol{x},\boldsymbol{y})$, $R(\boldsymbol{x},\boldsymbol{y})$, $\Phi_i^p(\boldsymbol{x},\boldsymbol{y})$ and $\Psi^{rs}(\boldsymbol{x},\boldsymbol{y})$ are characteristic functions of the composite microstructure of size Y, satisfying a set of microscopic equations [24]. δ is the Kronecker delta symbol. Here the microstructure refers to the representative volume element of the piezocomposite. The numerical solution of the coupled piezoelectric problem is sought using the finite element method (FEM) and would be used in the evaluation of homogenization [18]. The homogenization applied to monolithic piezoelectric material yielded very good results and compares very well with the experiments as shown in table 1. However, in the case of composites, where we can discern the constituent phases either as polycrystalline or single crystalline, the role of these coefficients would assume either the properties of crystallographic grains or single crystals [16]. In that case the anisotropy of the PE material is to account for by incorporating modifications in properties due to grain/crystal orientation. i.e., for instance, if one phase of the composite is a polycrystal, the above coefficients e_{ijk}, $\kappa^{\varepsilon}_{ij}$ and C^E_{ijkl} represent that of a grain. (Here as well as in further sections we assume that the piezoelectric polycrystal is an aggregate of *single crystalline* grains). On the other hand, if a phase is single crystalline, these coefficients would represent the single crystal properties.

The piezoelectric response is determined along an arbitrary crystallographic direction determined by the Euler angles (ϕ, θ, ψ) measured with respect to the microstructure coordinates $\mathbf{y}$. While this is the picture in single crystals, we can assign orientations to polycrystalline ceramics PEs by picking up individual crystallites (grains) in it and assign the Euler angles. This would be implemented as follows. For instance,

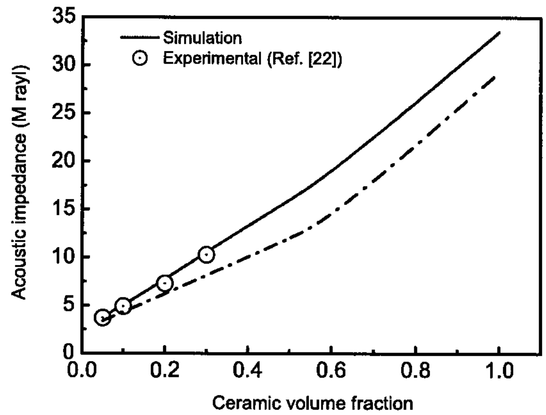

Figure 1. Acoustic impedance $\widetilde{Z}$ results of PZT (piezoceramic) - Spurr epoxy (polymer) fiber reinforced 1–3 type composite along with experimental (from Ref. [26]) and analytical results (from Ref. [6]).

if we have a ceramic composed of say n grains, one can generate n set of Euler angles (ϕ, θ, ψ) from a random generator if the grain configuration in the ceramic is random. However, if the ceramic is aligned in a particular direction (textured) as in the case of a poled PE ceramic, one could assume that the grain orientations fall in certain orientation distribution function, say a normal distribution, and prompt the random generator to generate n Euler angles accordingly. Here it must be noticed that many domains/grains cannot be reoriented due to a complex set of internal stresses and electric fields in grains and because some domains will switch back after the poling field is removed [25]

2.2. Choice of microstructure or RVE

The composite microstructure or representative volume element (RVE) is composed of piezoelectric material and the bulk polymeric material phases. These phases can be either polycrystalline (or PEC) or single crystalline in nature according to the configuration chosen for the composite material (different possible configurations of the composite would be discussed in section 2.4.). The most comprehensive case would be the one with both the phases being polycrystalline with a grain structure and we perform optimization employing such an RVE in the present study. In such an instance, the microstructure is an aggregate of randomly oriented single crystal grains. Firstly, the conflicting situation with regard to the choice of a meaningful microstructure or representative volume element (RVE) to be used for the optimization is to be addressed. The RVE should be a meaningful representative volume of the actual ferroelectric polycrystal so that it could be able to reasonably capture the inhomogeneities of the material. While its size should be small enough to be considered as a volume element in the continuum model, it should be sufficiently large to be statistically representative of the PEC. The latter requirement will ensure the robustness of the finite element solution as well as the randomness of the grain distribution but fails to uphold the compactness of the RVE. Moreover, the microstructure should be big enough to encompass sufficient number of grains in order to surpass the statistical fluctuations of the effective piezoelectric constants. Thus, the microstructure should be a typical sample of the real macroscopic material [27]. We have performed a numerical homogenization simulation varying the number of finite elements in the microstructure for accomplishing this goal of finding out a meaningful RVE. Since one finite element in the present model surrogates a crystallographic grain, this would invariably mean varying the number of grains in the microstructure.

We have started this experiment with a microstructure discretized by 125 (= $5 \times\ 5 \times\ 5$ mesh) finite elements which corresponds to as much number of grains. 125 random numbers corresponding to the grain orientations are (generated from *Matlab*) picked up randomly from a normal distribution to assign orientations to the grains in the RVE. The normal distribution used for this purpose has standard deviation $\sigma = 0.7$ and mean $\mu = 0$. The homogenized piezoelectric coefficients corresponding to this RVE are calculated for $BaTiO_3$ using the numerical homogenization model implemented in *Fortran*. Computations are repeated with the addition of more number of grains to the microstructure. The set of orientation angles characterized by the Euler angle θ are generated randomly from the random generator and it will be different each time the generator is invoked. We have used four sets of θ at $\sigma = 0.7$ and mean $\mu = 0$ and the corresponding $\widetilde{d}_{j\nu}$ values are evaluated. The scatter of values (due to the four diffrent sets of θ) of $\widetilde{d}_{j\nu}$ are found to be decreasing with increasing number of grains. Here we have to make a trade-off between the computational cost and the accuracy of the homogenization results. At a 14^3 (used in the present optimization studies) mesh we found that the statistical fluctuations on $d_{i\mu}$ are less than 4%. Since the bounds are found to be apparently narrow at this juncture, we could rely on the asymptotic homogenization method for the evaluation of effective properties compared to more rigorous averaging methods [28].

After using the usual approximations of FEM, the set of linear equations for each load case is obtained where each global stiffness, piezoelectric and dielectric matrix is the assembly of each element's individual matrix, and the global force and charge vectors are the assembly of individual force vectors for all the elements. Two-point Gaussian integration rule in each direction is used for the evaluation of the stiffness, piezoelectric and dielectric matrices as well as for the homogenization. As the RVE is expected to capture the response of the entire piezoelectric system, particular care is taken to ensure that the deformation across the boundaries of the cell is compatible with the deformation of adjacent cells. Thus all the load cases are solved by enforcing periodic boundary conditions in the unit-cell for the displacements and electrical potentials. The input parameters, i.e., the single crystal data for carrying out the numerical homogenization of ceramic $BaTiO_3$ is taken from Ref. [29].

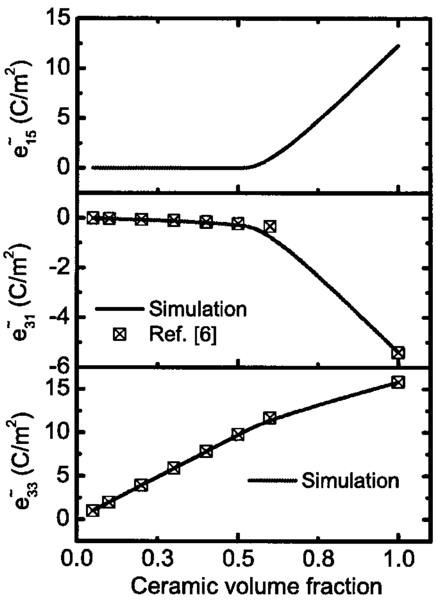

Figure 2. Piezoelectric coefficient $\widetilde{e}_{j\nu}$ results of PZT (piezoceramic) – Spurr epoxy (polymer) fiber reinforced 1–3 type composite along with analytical results (from Ref. [6]).

Table 1. Values of the homogenized piezoelectric strain coefficients $d_{j\nu}$(in pC/N), piezoelectric stress coefficients $e_{j\nu}$ (in C/m^2) and free dielectric permittivity κ^T_{ij} (in κ_0) of single crystal BaTiO$_3$. (κ_0 is the permittivity of free space).

Method	d_{15}	d_{31}	d_{33}	e_{15}	e_{31}	e_{33}	κ^T_{11}	κ^T_{33}
Simulation	560.7	-33.7	94.0	34.2	-0.7	6.7	4366	132
Experiment [29]	564.0	-33.4	90.0	34.2	-0.7	6.7	4380	129

2.3. Validation of homogenization model

A parametric study on a PZT–Spurr epoxy piezoelectric composite is performed in order to validate the homogenization model. The homogenization results agree well with the experiments reported in Ref. [26] and with analytical results from Ref. [6]. The connectivity chosen for this study is 1–3 fibre (PZT) reinforced polymer (Spurr epoxy) matrix suitable for transducer applications. The effective characteristic acoustic impedance, $\widetilde{Z} = (\widetilde{C}^D_{33}\widetilde{\rho})^{1/2}$ which determines the effectiveness of the coupling of ultrasonic energy is plotted in Fig. 1 along with resonance technique measurements made using low frequency acoustic waves ($\approx$ 0.4 MHz) by Gururaja et al., [26]. Here $\widetilde{C}^D_{33} = \widetilde{C}^E_{33} + (\widetilde{e}^2_{33}/\widetilde{\kappa}^\epsilon_{33})$ and $\widetilde{\rho}$ is the effective density of the composite. The simulation results show good agreement with the experimental data (available only up to the volume

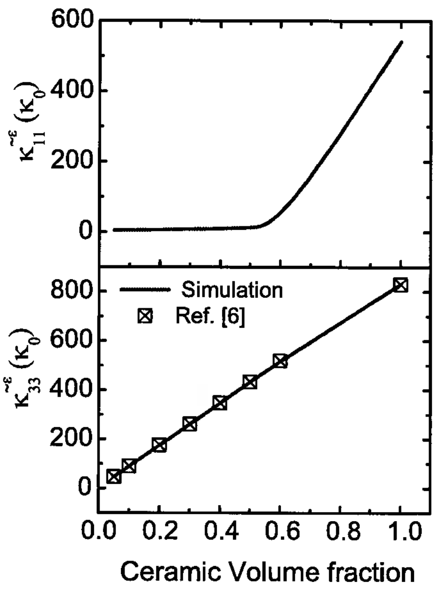

Figure 3. Dielectric permittivity $\widetilde{\kappa}^{\epsilon}_{ij}$ results of PZT (piezoceramic) – Spurr epoxy (polymer) fiber reinforced 1–3 type composite along with analytical results (from Ref. [6]). Here $\widetilde{\kappa}^{\epsilon}_{ij}$ is expressed in units of κ_0, the permittivity of free space.

fraction of 30% in [26]) of the piezoelectric ceramic PZT [26]. The data plotted in dotted line in figure 1 is analytical results computed using the formula given in Smith and Auld [6]. The deviation of analytical results of Smith and Auld [6] from the present simulation and the experiments are expected as the simplifying assumptions used by them, viz., the independence of strain throughout the xy-plane of the individual phases are not obviously valid in detail. This discrepancy is especially prominent in acoustic impedance which is a property derived significantly from stiffness (see the above equation for $\widetilde{Z}$). figures. 2 and 3 presents the results of the homogenized piezoelectric coefficients obtained in our study along with the available analytical results of from Ref. [6]. The present results and analytical results are in very good agreement. In summary, the robustness of the homogenization method is proved by comparing the electromechanical properties with experimental results and with other theoretical models.

2.4. Optimization

2.4.1. Piezoelectric 2–2 laminate composite In this paper, we optimize the microstructure of PE-polymer composite material aiming to maximize the overall piezoelectricity. One can conceive four possible combinations if the PE material and the polymer. The first being the PE material as well as the polymer be crystalline (see Fig. 4(a)), second being the PE material still be crystalline while the polymer being not subjected to rotation (noncrystalline) (see figure 4(b)). The other two combinations has one layer of polycrystalline PE material with polymer being either

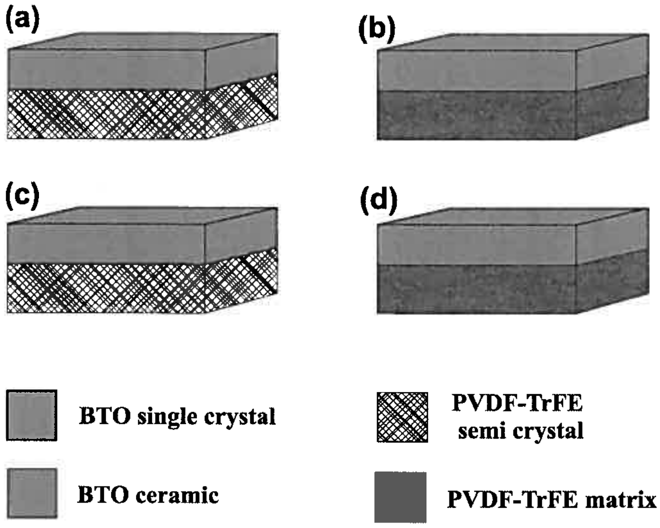

Figure 4. Schematic diagram of the four configurations [viz., (**a**), (**b**), (**c**) and (**d**)] of a composite two-phase piezoelectric (BTO) – polymer (PVDF–TrFE) laminate.

crystalline or noncrystalline (figures 4(c) and (d)). The primary configuration mentioned above has PE phase single-crystalline where the piezoelectricity is a function of discrete orientations defined by Euler angles (ϕ, θ, ψ).

However in the latter set of composites involving PE ceramics, the orientations of grains that constitute the polycrystalline PE are not uniform but falls in certain distribution. There exists a number of possible grain configurations available for potential manufacture. The grain distribution is modeled using a Gaussian distribution of Euler angles in polycrystals. Hence, we must optimize the grain orientation distribution as well as the volume fraction of the PE phase simultaneously to arrive at the best composite material configuration. In a piezocomposite, the PE material connects to a flexible polymer in various patterns to form a piezoelectric composite [1]. Nevertheless, many applications of ferroelectric ceramics, ranging from components for sensors, memory devices, microelectromechanical systems (MEMS), and energy convertors, all involve planar and rigid layouts [30]. Moreover, layering would be preferred considering the heat dissipation through the area of the layers when composites are used in actuator layouts[2, 31].

Here we optimize a laminate 2–2 piezocomposite (i.e., 2–2 connectivity where sheets of PE material is juxtaposed in a layered layout with a polymer as shown in figure 4) with the objective to use it for piezoelectric applications such as energy harvesting. The flexible component in the present composite is a piezoelectric polymer. Due to its light weight and flexibility, polyvinylidene fluoride (PVDF) based polymers are useful for many applications where flexibility deemed critical [32]. We treat four possible instances of the 2–2 lamination of semicrystalline PVDF–trifluoroethylene (PVDF–TrFe) and the piezoelectric $BaTiO_3$ (BTO) as detailed in Fig. 4, viz., case (**a**) where both BTO and PVDF–TrFe are crystalline, case (**b**) where BTO is still single crystalline and PVDF–

TrFe is a polymer matrix (non-crystalline) not subjecting to rotation, case (**c**) where BTO is polycrystalline ceramic and PVDF-TrFE is semi crystalline with orientational properties and case (**d**) where BTO is ceramic and PVDF-TrFE is polymer (not subjecting to rotation). Here in configuration **a**), (**c** we took advantage of the polymer's poling direction along with that of BTO. (Hereafter we refer these configurations by (**a**), (**b**), (**c**) and (**d**)).

2.4.2. Simulated Annealing An approach combining a stochastic optimization technique (of simulated annealing) with a generalised Monte Carlo method would be employed for optimization [34]. Since, we couldn't explicitly express $\widetilde{e_{i\nu}}$ and for that matter $\widetilde{d_{i\nu}}$ as functions of orientation distribution parameters μ and σ (the *design variables* of the optimization problem), it would not be possible to express derivatives of $\widetilde{d_{i\nu}}$ (the *objective function*) and then to have sensitivities computed. Thus it is not possible to rely on derivative based optimization techniques in this study. Moreover, since the design variables are random, stochastic optimization is more suitable for this problem. The simulated annealing method transposes the process of the annealing to the solution of an optimization problem: the objective function of the problem, similar to the energy of a material, is then minimized, with the help of the introduction of a fictitious *temperature*, which is, in this case, a simple controllable parameter of the algorithm [35]. A work flow of the algorithm is shown in Table 2. In practice, the technique exploits the Metropolis algorithm, which enables us to describe the behavior of a thermodynamic system in *equilibrium* at a certain temperature [33]. In the case of laminate composites involving single crystals, viz., (**a**) and (**b**), PE material is allowed rotations specified by the Euler angles (ϕ, θ, ψ) and the polymer too is subjected to rotation in (**a**). Thus the PE phase has a specific orientation say $(\phi, \theta, \psi)_{\mathrm{E}}$ and the polymer phase is oriented by $(\phi, \theta, \psi)_{\mathrm{P}}$ at a particular iteration of optimization.

The infinite fold rotation axes (∞) in the macroscopic ensemble of crystallites(grains) in a PE polycrystal forbids the global piezoelectricity, no matter what crystallographic symmetry the constitutive crystallites belongs to. This is because the crystallites/grains are randomly oriented in an as-grown polycrystalline pre–poled PE material. Post poling, the aggregate texture (orientation distribution) for polycrystalline PEs follows a normal distribution, the probability distribution function (*pdf*) being defined by, $f(\alpha \mid \mu, \sigma) = (1/\sigma\sqrt{2\pi}) \exp -[(\alpha - \mu)/\sqrt{2}\sigma]^2$ about the direction of the electric field. μ, the mean value of angles and σ, the standard deviation are the parameters of the distribution. α stands for Euler angles (ϕ, θ, ψ). The *pdf* described could be able to encompass the various grain configurations in between a random (pre–poled) polycrystal and a textured (fully poled) PE material. This is accomplished by treating the limiting cases of the standard deviation $\sigma \to \infty$ while modeling the random polycrystal and $\sigma \to 0$ for fully textured polycrystal PE. The normal distribution (of grain orientation) would get flatter as $\sigma \to \infty$ and approaches the shape of a uniform distribution while it becomes narrower and approaches crystalline texture as $\sigma \to 0$. In general, a poled PE polycrystal would assume standard deviation of orientation $0 < \sigma < \infty$. However,

Table 2. Work flow of the optimization algorithm for maximization

N = number of moves to attempt, T = current temperature
k_B = the Boltzmann constant, v_f = PE volume fraction
$(\phi, \theta, \psi)_E$, $(\phi, \theta, \psi)_P$ = Euler angles for crystalline PE and polymer
$(\mu_\theta, \sigma_\theta, \mu_\phi, \sigma_\phi, \mu_\psi, \sigma_\psi)_E$ = Distribution parameters of PE ceramic.

|| *Initial configuration* $(=\gamma_s)$ ||;
    if (material type == laminate **a**) [refer Fig. 4(a)]
        $\gamma_s = [(\phi, \theta, \psi)_E, (\phi, \theta, \psi)_P, v_f]$
    else if (material type == laminate **b**) [refer Fig. 4(b)]
        $\gamma_s = [(\phi, \theta, \psi)_E, v_f]$
    else if (material type == laminate **c**) [refer Fig. 4(c)]
        $\gamma_s = [(\mu_\theta, \sigma_\theta, \mu_\phi, \sigma_\phi, \mu_\psi, \sigma_\psi)_E, (\phi, \theta, \psi)_P, v_f]$
    else if (material type == laminate **d**) [refer Fig. 4(d)]
        $\gamma_s = [(\mu_\theta, \sigma_\theta, \mu_\phi, \sigma_\phi, \mu_\psi, \sigma_\psi)_E, v_f]$
    end
    Invoke homogenization
    || *Compute the objective function* $f_s(\gamma_s)$ ||
Invoke Optimization
for m= 1 to N {
    Generate a random move t;
    New configuration γ_t
    Invoke homogenization
    || *Compute new objective function* $f_t(\gamma_t)$ ||
    Evaluate the change in energy, $\Delta E (\equiv f_t - f_s)$;
    if $(\Delta E > 0)${
        || *downhill move; accept it* ||
        accept this move and update configuration
    }
        Metropolis step [33]
    else {
        || *uphill move; may be accepted* ||
        accept with probability $P = e^{\Delta E / k_B T}$
        update configuration if accepted;
    }
} || *end for loop* ||

a standard deviation of $\sigma = 5$ would render the PE ceramic sufficiently random to have a near zero, if not null, piezoelectricity [16].

Our objective is to search for the optimum configuration of PE ceramic or single crystal and for the optimum volume fraction in a composite with a compliant polymer. The optimization would identify the ideal configuration that would enhance the effective piezoelectric coefficient $\widetilde{d}_{33}$ used as the figure of merit for applications such as actuators [36]. First we would calculate the homogenized piezoelectric stress coefficients $\widetilde{e}_{i\nu}$ and then with the aid of effective compliance $\widetilde{s}_{\mu\nu}$, we would calculate the $\widetilde{d}_{j\nu}$. In order to be consistent with our definition of design variables, $E(R_i) \equiv \widetilde{d}_{j\nu}(\gamma)$, be the surrogate of *system energy* E of a particular configuration R_i. γ in this equation stands for the design variables. Here we are optimising two possibilities, viz., the single crystal PE-polymer laminate and PEC-polymer laminate. In the first instance, the design variables are the Euler angles (ϕ, θ, ψ) and the volume fraction v_f of the PE single crystal. In the second configuration, the pair of mean and standard deviation μ and σ decide the scatter of orientations (of the crystallites/domains) together with volume fraction v_f would assume the role of design variables. A control parameter similar to the *temperature* in physical annealing is introduced in optimization which will dictate the number of states to be accessed in going through the successive steps of the optimization algorithm before being settled in the the optimum configuration.

2.4.3. Problem formulation Based on the above discussion, the optimization problem for various configurations **a**, **b**, **c**, and **d** of the laminate composite (as depicted in figure 4) can be summarised as to find (γ) that (see Table 2 as well);

$$\left.\begin{array}{ll}\text{Maximize}: & f(\gamma) \equiv \widetilde{d}_{33}(\gamma) \\ \quad\gamma & \\ \text{subject to}: & 0 < v_f < 1\end{array}\right\} \qquad (5a)$$

$$\left.\begin{array}{l}\text{where,} \quad \gamma = [(\phi,\theta,\psi)_E, (\phi,\theta,\psi)_P, v_f] \\ \text{subject to}: \\ : -\pi \le (\phi,\theta,\psi)_E, (\phi,\theta,\psi)_P \le \pi\end{array}\right\} \text{ for the laminate } \mathbf{a} \qquad (5b)$$

$$\left.\begin{array}{l}\gamma = [(\phi,\theta,\psi)_E, v_f] \\ \text{subject to}: \\ : -\pi \le (\phi,\theta,\psi)_E \le \pi\end{array}\right\} \text{ for the laminate } \mathbf{b} \qquad (5c)$$

$$\left.\begin{array}{l}\gamma = [(\mu_\theta,\sigma_\theta,\mu_\phi,\sigma_\phi,\mu_\psi,\sigma_\psi)_E, (\phi,\theta,\psi)_P, v_f] \\ \text{subject to}: \\ : 0 \le (\mu_\theta,\mu_\phi,\mu_\psi)_E \le \pi/2 \\ : 0 \le (\sigma_\theta,\sigma_\phi,\sigma_\psi)_E \le 5 \\ : -\pi \le (\phi,\theta,\psi)_P \le \pi\end{array}\right\} \text{ for the laminate } \mathbf{c} \qquad (5d)$$

Table 3. The results of optimization, viz., the optimal value of effective $\widetilde{d}_{33}$ (pC/N) of the composite laminate $BaTiO_3$-(PVDF-TrFE) and the corresponding solutions (θ, ϕ, ψ) (in degrees), $(\mu_\theta, \sigma_\theta, \mu_\phi, \sigma_\phi, \mu_\psi, \sigma_\psi)$ (in radians) and v_f the volume fraction of the piezoelectric component. Refer figure 4 and related text for 2-2 laminate configurations mentioned in cases (**a**), (**b**), (**c**) and (**d**).

laminate		Solution	v_f	$\widetilde{d}_{33}$
(a)	$BaTiO_3$	$\phi = -140$, $\theta = -50$, $\psi = 180$	0.64	222.2
	PVDF-TrFE	$\phi = 20$, $\theta = 35$, $\psi = -60$		
(b)	$BaTiO_3$	$\phi = -145$, $\theta = 50$, $\psi = -180$	0.14	218.7
(c)	$BaTiO_3$	$(\mu_\theta,\ \sigma_\theta,\ \mu_\phi,\ \sigma_\phi,\ \mu_\psi,\ \sigma_\psi) = (0.7, 0.1, 0.61, 2.6, 0.09, 0.2)$	0.21	201.9
	PVDF-TrFE	$\phi = 40$, $\theta = 175$, $\psi = -175$		
(d)	$BaTiO_3$	$(\mu_\theta,\ \sigma_\theta,\ \mu_\phi,\ \sigma_\phi,\ \mu_\psi,\ \sigma_\psi) = (1.05, 0, 1.31, 2.2, 0.09, 0)$	0.36	204.3

$$\left.\begin{array}{l} \gamma = [(\mu_\theta, \sigma_\theta, \mu_\phi, \sigma_\phi, \mu_\psi, \sigma_\psi)_E, v_f] \\ \text{subject to :} \\ : 0 \leq (\mu_\theta, \mu_\phi, \mu_\psi)_E \leq \pi/2 \\ : 0 \leq (\sigma_\theta, \sigma_\phi, \sigma_\psi)_E \leq 5 \end{array}\right\} \quad \text{for the laminate } \mathbf{d} \qquad (5e)$$

The constraint corresponding to the volume fraction of PE component of the laminate composite viz., $0 < v_f < 1$ is common to all the instances of the laminate configurations studied in this paper. Hence, $0 < v_f < 1$ is applicable to all the above equations $(5a)$.

2.4.4. Numerical evaluation Substituting the finite element solutions of the local problems (Refs. [18, 19]) into equations. (2), and subsequently using $\widetilde{d}_{33} = \widetilde{e}_{3\nu}\widetilde{s}_{33\nu}$, (see section 2.1 above) one arrives at the homogenized piezoelectric coefficient $\widetilde{d}_{33}$, which is our objective function. For convenience, the symmetry properties of the PVDF-TrFE are considered to belong to the point group $6mm$ as in Ref. [10] and the property values are taken from Ref. [37] and that of single crystal $BaTiO_3$ (belonging to the $P4mm$ tetragonal symmetry) from Ref. [29] for the evaluation of the homogenized property tensor of the piezocomposite. An interface is developed in *Matlab* to connect the homogenization program written in *Fortran* with the stochastic optimization program written in *Matlab.*

3. Results and discussion

The piezoelectric coefficient $\widetilde{d}_{33}$ in tensor form is expressed as $\widetilde{d}_{33} = \widetilde{d}_{333}E_3$, where $\widetilde{d}_{33}$ is the piezoelectric strain along the electric field E_3. Since $\widetilde{d}_{33}$ better quantifies the strain level of a piezoelectric material against applied electric field, we designate it as the objective function for our optimization problem. The optimization results obtained for various configurations are shown in figures 5 and 6 respectively. The overall piezoelectric coefficient $\widetilde{d}_{33}$ of the composite converges to the maximum value after the initial *uphill*

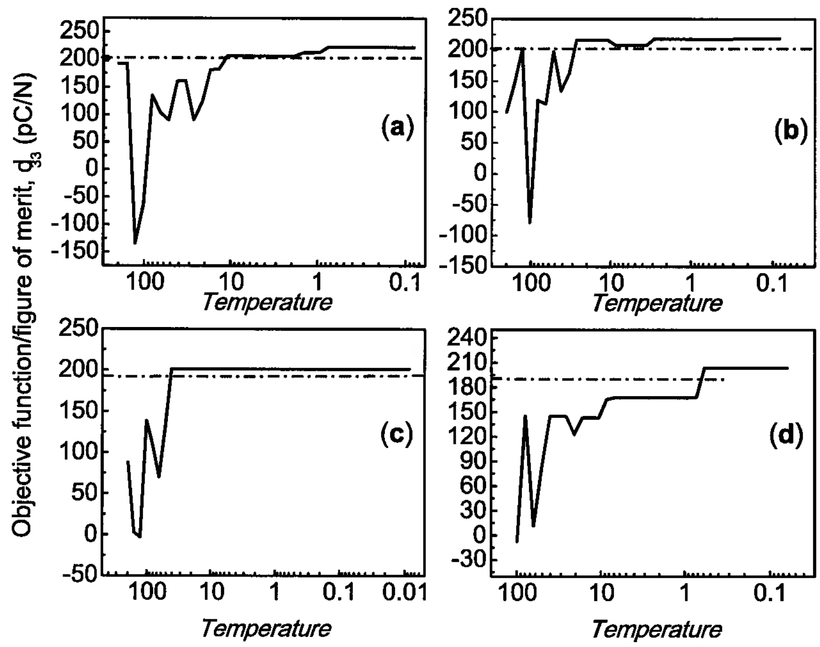

Figure 5. Result of the optimization of a composite two-phase piezoelectric ($BaTiO_3$)-polymer(PVDF-TrFE) laminate with objective to maximize the effective piezoelectric coefficient $\widetilde{d}_{33}$. In (**a**) and (**b**) the PE phase is single crystalline and in (**c**) and (**d**) it is ceramic (refer also figure 4 and related text). The dotted lines represent experimental values for d_{33} of $BaTiO_3$ (value of [111]-oriented single crystal from Ref. [38] in (a) and (**b**) and that of poled ceramic from Ref. [39] in (**c**) and (**d**)).

moves allowed by the simulated annealing algorithm. The constituents of the patterns mentioned in cases (**a**), (**b**), (**c**) and (**d**) are detailed in figure 4 and related text. The objective function (piezoelectric coefficient $\widetilde{d}_{33}$) of the PE single crystal composite configuration exhibits values ($\widetilde{d}_{33} = 222.2$ and 218.7 pC/N respectively for cases (**a**) and (**b**)) better than experimental value of $d_{33} = 203$ pC/N [38] of [111] rotated single crystal BTO (figures 5(a) and (b) and Table 3). Moreover, piezocomposite exhibits better piezoelectric response ($\widetilde{d}_{33} = 222.2$ pC/N) when the polymer would also be oriented. A remarkable point here is that polarization vector, of BTO and PVDF-TrFE makes an angle $\approx 90°$ between them. i.e., the optimal polar angles θ (in the case (**a**) in Table 3), which essentially quantifies the orientation of the polarization vectors of both BTO and PVDF-TrFE differs by 85°. $\widetilde{d}_{33}$ of the ceramic BTO-PVDF-TrFE (see figure 5(c) and (d) and Table 3) converges in the range ≈ 202 to 204 pC/N which is comparable to the experimental value ($d_{33} = 203$ pC/N) of the rotated single crystal [38] and is well above the poled ceramic value ($d_{33} = 191$ pC/N) obtained experimentally [39]. This result shows that for maximum piezoelectricity one should keep the polarization vectors of the individual domains in the piezoceramic oriented to some extent (given by the optimal

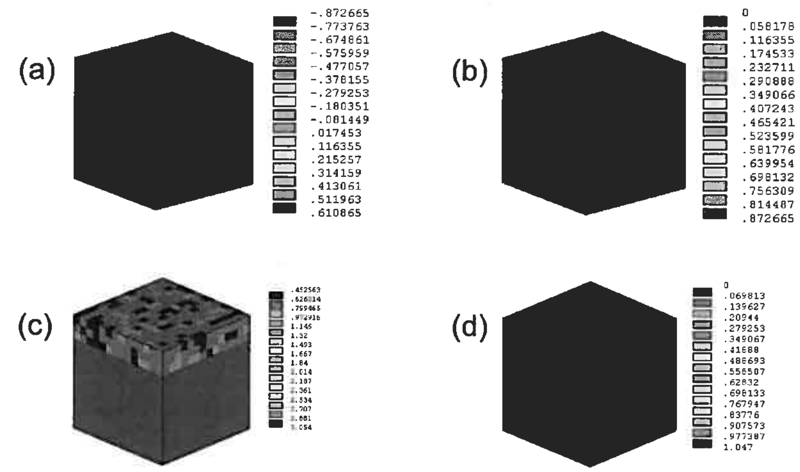

Figure 6. The optimal orientation/distribution of the Euler angle θ, mapped in color, obtained in cases (**a**), (**b**), (**c**) and (**d**). The bottom layer depicts polymer while the top layer represents the PE. (**a**), (**b**), (**c**) and (**d**) pertains to the composite laminate configurations described in figure. 4 and the related text.

μ_θ) but with minimal scatter (as shown by the optimal results of the standard deviation of θ, i.e., σ_θ). The misalignment of the PE/polymer with the external loading axis may impart more piezoelectric strain at the interphase, which could plausibly enhance the overall piezoelectricity of the composite. The volume fraction v_f of the PE phase is below 40% except in case (**a**). Especially in configurations (**b**) and (**c**) the volume fraction of piezoelectric phase is $< 25\%$. Optimization thus demonstrates that one can achieve better piezoelectricity with minimum amount of the piezoelectric material if we consider the orientation too as a design variable.

Figure 6 depicts the optimal orientation distribution of the microstructure obtained in respect of the four instances of optimization problems mentioned above viz., the composite configurations in cases (**a**), (**b**), (**c**) and (**d**). These distributions are generated using the optimal Euler angles (θ) derived from the solution given in Table 3. For instance the optimal θ for $BaTiO_3$ layer in case (**a**) is $\theta = -50°$ which in radians is ≈ -0.872665 and for PVDF-TrFE the optimal $\theta = 35° \approx 0.610865$ radians. The orientation distribution of the microstructure pertaining to polycrystalline $BaTiO_3$, for instance the case (**c**), is drawn as follows. Generate a set of Euler angles θ according to the optimal standard deviation $\sigma_\theta = 0.1$ and mean $\mu_\theta = 0.7$ (refer Table 3) using a random generator (here we used the one from *Matlab* for the piezoelectric $BaTiO_3$ layer. Here the polymer layer has a uniform orientation with $\theta = 175° \approx 3.054$ radians. The optimal Gaussian distribution for the piezoelectric layer is narrow in cases (**c**) and (**d**) where the PE phase is polycrystalline (refer Table 3). Poling treatment of ceramics post synthesis is a common method to achieve preferential orientation. Combining a suitable processing method such as templated grain growth which ensures a high degree of texturing in ceramics with suitable electrical poling would be a preferable approach to synthesise a ceramic layer with certain narrow orientation distribution [40]. The Lotgering factor f used by crystallographers to characterise the orientation distribution can be related to the distribution parameters μ_θ and σ_θ treated in this paper [41, 42]. The Lotgering factor f is 1 for a fully textured ceramic and is 0 for fully random material. Hence we could suggest an inverse proportionality between f and σ such that $\sigma \propto (1-f)/f$ to guide an experimental realization of the ceramic laminar phase [43, 44].

In summary, a novel computational framework for the microstructure design of piezoelectric composites to explore simultaneous optimization of volume fraction and orientation distribution of the constituent phases is implemented and validated against experiments. This methodology brings forth a set of design variables which would maximize the piezoelectric strain level of the composite superior to the constituent piezoelectric material. We have validated the homogenization procedure by applying the model to a fiber reinforced 1–3 piezoelectric composite. With the very good agreement of the present simulation with experiments and an analytical model, we go on to apply the model to a planar configuration of a piezoelectric-polymer laminate. Combining a piezoelectric ceramic and a polymer to form a piezocomposite help design new piezoelectrics that offer substantial advantages over the conventional piezoelectric ceramics and polymers. A range of optimal grain orientation/distribution of the PE/polymer phase were identified and presented which would eventually equip the manufacturers with more degrees of freedom. A minimum fraction of PE material in a composite is found to be sufficient to achieve better piezoelectricity than a monolithic piezoelectric material. The optimal PEC–polymer composite which exhibits better piezoelectricity than oriented single crystals bears much import, given the ease and economy in manufacturing ceramics. Moreover, extension of this method to other connectivity patterns and materials would certainly unfold quality piezoelectric composites surpassing the existing ones.

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