# Environmentally-friendly piezoelectric composites for additive manufacturing: nonlocal and nolinear effects

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# ENVIRONMENTALLY-FRIENDLY PIEZOELECTRIC COMPOSITES FOR ADDITIVE MANUFACTURING: NONLOCAL AND NONLINEAR EFFECTS

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**Abstract.** Lead-free piezocomposites represent an environmentally friendly route for sensing mechanical stimuli and for interconversion of electrical and mechanical energy. Current lead-free composites lag state-of-the-art lead-based composites in terms of performance. A major approach to bridge this gap is to devise design strategies to enhance the piezo-response of lead-free composites. Fundamental to this is the understanding of the roles of various physical processes which are conventionally overlooked. From a modelling perspective, it is necessary to develop refined models which account for non-local and non-linear effects, which could have significant roles in deciding the response of the composite. This paper develops such refined electro-elastic models considering the flexoelectric and electrostrictive contributions to the piezo-response in addition to the linear piezoelectric response. The roles of these non-local and non-linear contributions are studied on a simple architecture consisting of a $BaTiO_3$ inclusion within a polymer matrix. Insights obtained through this model will be further used to develop efficient piezoelectric composites.

## 1 INTRODUCTION

Piezoelectric composites generally consist of piezoelectric crystalline inclusions embedded in a polymer matrix. This enables the optimal combination of electrical and elastic properties of both the matrix and the filler, resulting in a composite material that can be designed to suit specific application needs. For example, by embedding highly rigid piezoelectric crystalline inclusions, such as $BaTiO_3$, PZT and so on, with polymer matrices, it is possible to make piezoelectric composites which are flexible [1]. The recent interest in such composite materials stems from the fact that there is a need to develop lead-free materials which can perform at par with the state-of-the-art lead-based composites [1]. The development of such materials is important from the point of view of sustainable green technology, with current materials posing long-term ecological threats [1, 2]. A second motivation to study such materials is the ease with which the associated devices can be fabricated using the emerging scalable methods such as 3D printing which offer detailed resolutions down to the micrometer scale in the material distribution [3]. The gap in the performance between these two classes of materials is due to the intrinsic properties of the piezoelectric inclusions and therefore most design strategies involve tuning the electro-elastic properties of the surrounding matrix to enhance the piezoelectric response. These approaches involve either hardening the matrix [4] to improve the coupling of mechanical stimuli to the embedded inclusions or improving the permittivity of the matrix [5] to allow easy flow of the generated electric flux to the electrodes enclosing the composite. Recent efforts in material design and modelling have explored these avenues to tune these electro-elastic properties of the matrix to improve the piezo-response. However, these models overlook some physical processes which could significantly control the piezoelectric response. Some of these processes include (a) flexoelectricity – non-local generation of electric flux by strain-gradients as opposed to linear piezoelectricity where a homogeneous strain generates electric flux and (b) electrostriction – non-linear coupling between the strain and the electric field. Flexoelectricity can occur even in non-centrosymmetric materials [6] and electrostriction is a common process in most dielectrics [7]. Alhough such effects might often be negligible at the macroscopic level, they can influence the overall design principles of composite materials, created on the basis of hierarchically architectured microstructures, for 3D printing and subsequent applications. Moreover, possible defects and agglomerations of added nanoparticles in such composite materials under certain conditions may create an environment for flexoelectricity to play a more pronounced role. Both these aspects hint the possibility of even the matrix materials contributing to the piezoelectric response. Further, lead-free materials such as $BaTiO_3$ have flexoelectric coefficients which are relatively larger compared to other piezoelectric materials [8], thus offering a possible route to enhancing the performance of the composite. Therefore, our focus in this contribution is on the design and modelling issues of lead-free piezoelectric composites, amenable to 3D printing, in order to achieve their higher performance. Although the developed modelling framework is quite general and can be applied to other materials, as an example, our results are discussed in the context of barium titanate piezoelectric inclusions embedded into a polymeric matrix. In what follows, we will first provide the details of the electro-elastic model which includes these non-local and non-linear effects. Following this, we will discuss some preliminary results which can provide important insights relating to the contributions of these effects to the overall material performance.

## 2 ELECTRO-ELASTIC MODEL

In this section, we will provide the details of the mathematical framework that describes the electroelastic behavior of piezoelectric composites, accounting for flexoelectric (strain-gradient) and electrostrictive contributions. The constitutive relations are obtained from the electrical Gibbs free energy density defined as follows [6, 9, 10]:

$$G = \frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} - \frac{1}{2}\epsilon_{ij}E_iE_j - e_{kij}E_k\varepsilon_{ij} - \frac{1}{2}B_{klij}E_kE_l\varepsilon_{ij} - \mu_{ijkl}E_i\varepsilon_{j,kl} \tag{1}$$

The terms on the right-hand side of (1) are contributions to the free energy density from the elastic, electric, linear piezoelectric, electrostrictive, and flexoelectric processes, respectively. Here, $c_{ijkl}$, $\epsilon_{ij}$, $e_{ijk}$, $B_{ijkl}$, and $\mu_{ijkl}$ are the elastic, permittivity, piezoelectric, electrostrictive, and flexoelectric coefficients. Additionally, the field variables include the strain tensor components $\varepsilon_{ij}$, the electric field components $E_i$ and the strain-gradient components $\varepsilon_{i,jk}$.
The constitutive relations describing electro-elastic behavior are obtained as follows:

$$\begin{gathered}\sigma_{ij} = \frac{\partial G}{\partial \varepsilon_{ij}} = c_{ijkl}\varepsilon_{kl} - e_{kij}E_k - \frac{1}{2}B_{klij}E_kE_l,\\ \hat{\sigma}_{ijk} = \frac{\partial G}{\partial \varepsilon_{ij,k}} = \mu_{lijk}E_l,\\ D_i = -\frac{\partial G}{\partial E_i} = \epsilon_{ij}E_j + e_{ijk}\varepsilon_{jk} + B_{ijkl}E_j\varepsilon_{kl} + \mu_{ijkl}\varepsilon_{jk,l}.\end{gathered} \tag{2}$$

In (2), $\hat{\sigma}_{ijk}$ and $D_i$ are the higher order stress components and electric flux density components, respectively. These constitutive relations are further subjected to the governing balance laws given by:

$$\begin{gathered}\left(\sigma_{ij} - \hat{\sigma}_{ijk,k}\right)_{,j} + F_i = 0,\\ D_{i,i} = 0,\end{gathered} \tag{3}$$

where $F_i$ represent the components of the body forces, which are assumed to vanish in our model. This model is applied to a simple architecture consisting of a $BaTiO_3$ inclusion within a PDMS polymeric flexible matrix, illustrated in Figure 1. The boundary conditions applied to the composite architecture are also schematically illustrated in the Figure 1. The model is reduced to two dimensions in the $x_1$-$x_3$ plane [5, 11].

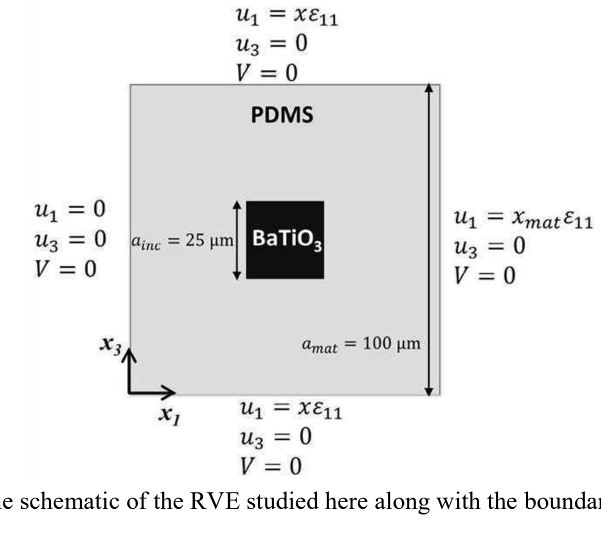


**Figure 1** – The schematic of the RVE studied here along with the boundary conditions used.

The material properties adopted for this study are summarized in Table 1. It is to be noted that the electrostrictive coefficients entered in the table need to be transformed into a different form before using them in the constitutive equations. This transformation is given by $[\mathrm{B}] = [\mathrm{C}][\mathrm{M}]$, where the matrix [M] has the electric field-related electrostrictive coefficients [12]. Typically, experimental values of these coefficients are in terms of the polarization density, the conversion into the electric-field-related version of which requires the following transformation [13]:

$$M_{ijkl} = Q_{opkl}\eta_{oi}\eta_{pj}, \tag{4}$$

where $Q_{opkl}$ represent the polarization-related electrostriction coefficients in the units of $\mathrm{m^2C^{-4}}$, $M_{ijkl}$ represent the electric-field-related electrostriction coefficients in the units of $\mathrm{m^2V^{-2}}$, and the $\eta_{oi}$ are the components of the dielectric susceptibility tensor of the material.

**Table 1** – Electro-elastic material properties used in the simulations. Typical values of electrostrictive coefficients are considered for the polymer matrix ($M_{33} \approx 1 \times 10^{-17}\mathrm{m^2V^{-2}}$ in conjunction with equation 4)

| Material property | Values for $BaTiO_3$ | Values for PDMS matrix |
|---|---|---|
| **Elastic coefficients (Moduli in Pa)** | | |
| $c_{11}$ | $275.1 \times 10^9$ [14] | $\lambda_m + 2\mu_m$ |
| $c_{13}$ | $151.55 \times 10^9$ | $\lambda_m$ |
| $c_{33}$ | $164.8 \times 10^9$ | $\lambda_m + 2\mu_m$ |
| $c_{44}$ | $54.3 \times 10^9$ | $\mu_m$ |
| Young's modulus, $E_m$ | N.A. | $2 \times 10^6$ [15] |
| Poisson's ratio, $\nu_m$ | N.A. | 0.499 [15] |
| **Relative permittivity** | | |
| $\epsilon_{11}/\epsilon_0$ | 1970 [14] | 2.72 [15] |
| $\epsilon_{33}/\epsilon_0$ | 109 | 2.72 |
| **Piezoelectric coefficients ($\mathrm{Cm^{-2}}$)** | | |
| $e_{15}$ | 21.3 [14] | |
| $e_{31}$ | $-2.69$ | Matrix is non-piezoelectric |
| $e_{33}$ | 3.65 | |
| **Flexoelectric coefficients ($\mathrm{Cm^{-1}}$)** | | |
| Longitudinal, $\mu_{11}$ | $10 \times 10^{-6}$ [8] | $1 \times 10^{-10}$ [6] |
| Transverse, $\mu_{12}$ | $10 \times 10^{-6}$ | $1 \times 10^{-10}$ |
| Shear, $\mu_{44}$ | 0 | 0 |
| **Electrostrictive coefficients, $b_{ijkl}$ ($\mathrm{m^4C^{-2}}$)** | | |
| Longitudinal, $b_{11}$ | 0.1 [16] | $1.7242e+08$ [7] |
| Transverse, $b_{12}$ | $-0.034$ | 0 |
| Shear, $b_{44}$ | 0.029 | 0 |

## 3 RESULTS AND DISCUSSION

The current analysis in this paper centers around miscroscale inclusions in a polymer matrix. Under such conditions, the flexoelectric effect has negligible effect. The plots of the volume averaged electric flux density in the $x_3$ direction, shown in Figure 2(a), demonstrate this with the two curves obtained from the linear piezoelectric model alone and the model with flexoelectric contributions almost coinciding. However, the contributions due to the non-linear effects are non-trivial. Although non-linear effects due to electrostriction have contributions to the generated electric flux which are negligible at small strains ($\varepsilon_{app} \approx 10^{-6}$) but show considerable increases at larger strains (for example at $\varepsilon_{app} = 10^{-2}$). This is illustrated in the volume averaged electric flux density plotted in the Figure 2(a), with and without the electrostrictive contributions. This shows that as the applied strain increases, while the linear piezoelectric model predicts a constant response, the presence of non-linear effects shows an increased volume averaged flux generation. This increase stems from the electrostrictive contributions in both the matrix and the inclusion, as seen from the increased flux density $D_3$ both in the inclusion and in the matrix (Figure 2(b) and (c)). These initial results clearly demonstrate the role of non-linear and non-local effects in deciding the electro-elastic response of lead-free piezoelectric composites.

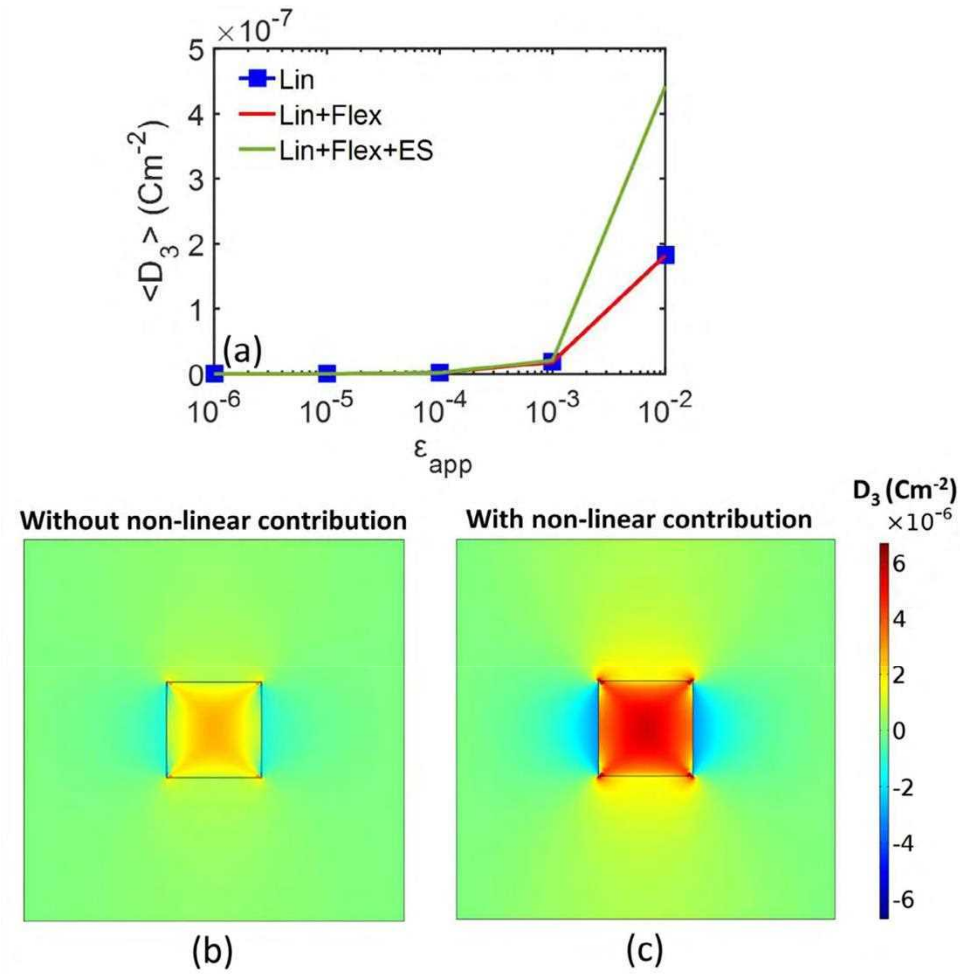


**Figure 2** – (a) The volume averaged $x_3$-component of the generated electric flux density with (i) linear piezoelectric model (Lin), (ii) linear model with flexoelectric contributions (Lin+Flex), (iii) Linear model with flexoelectric model and non-linear electrostrictive contributions (Lin+Flex+ES), (b) and (c) show the distribution of the $D_3$ flux density component with and without non-linear contributions, respectively.

## 4 CONCLUSIONS

We have developed a modeling framework for piezo-composites which accounts for the non-local flexoelectric effects and non-linear electrostrictive effects, with specific focus on lead-free $BaTiO_3$ based piezocomposites with polymer matrices, which are amenable to scalable 3D printing and additive manufacturing. On studying the implication of these effects in lead-free piezocomposites, we see that with microscale inclusions, while the flexoelectric effect has only negligible contributions, the non-linear electrostriction has considerable contributions which are more pronounced at higher operational strains. These findings clearly emphasize the need to consider these physical effects in the modelling-based design of high-performance environmentally friendly piezoelectric composite materials.

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