

Piezoelectric Activity and Sensitivity of Novel Composites Based on Barium Titanate-Hydroxyapatite Composite Ceramics

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Abstract. This paper describes the effective electromechanical properties of hydroxyapatite-BaTiO₃ 0-3 composites as a potential bone substitute material. The permittivity, d_{3j} and g_{3j} piezoelectric coefficients are calculated for composites at a range of compositions and connectivities to understand the relationships between composite composition and piezoelectric and dielectric properties. The properties of the composites can be tailored by adjusting the volume fraction and aspect ratio of the BaTiO₃ particles and the shape and level of porosity in the hydroxyapatite matrix.

Introduction

Recent work has observed enhanced bone osteobonding and new bone growth on polarised hydroxyapatite due to the generation of a permanent surface charge [1-4]. Bone growth is accelerated on the negatively charged surface of polarised hydroxyapatite and decelerated on the positively charged surface. The overall mechanism is unclear, but rapid bone formation on the negative surface is possibly due to adsorption of Ca²⁺ ions which act as nuclei for calcium phosphate formation. Piezoelectric materials have also attracted interest as a potential biomaterial, since natural bone is piezoelectric [5] and develops a charge under the application of a mechanical stress. Park et al. [6] and Hwang et al. [7] considered crystal growth formation on piezoelectric BaTiO₃ *in vitro*. Calcium phosphate crystals rapidly grew on the negatively charged surface, but not on the positive surface, indicating that polarised BaTiO₃ can improve bioactivity. Limited research has attempted to combine the bioactive properties of hydroxyapatite (HA) with a piezoelectric and high permittivity ferroelectric ceramic, such as BaTiO₃. Feng et al. [8] prepared HA – BaTiO₃ composites with a d_{33} piezoelectric charge coefficient of 6 pC/N, which promoted osteogenesis in the jawbones of dogs. Almeida et al. [9] reported on the optical and electrical properties of screen-printed HA – BaTiO₃ thick films, but no piezoelectric properties. In the present work HA – BaTiO₃ composites are studied to understand the relationship between composite composition and the dielectric and piezoelectric properties of the materials.

Modelling methodology

The model considers a 0–3-type composite consisting of isolated spheroidal ferroelectric ceramic (FC) inclusions in a continuous hydroxyapatite (HA) matrix, see Fig. 1. The shape of the FC inclusions is described by the equation $(x_1 / a_1)^2 + (x_2 / a_1)^2 + (x_3 / a_3)^2 = 1$ relative to the axes of the rectangular co-ordinate system (X₁X₂X₃), with the semi-axes of the spheroid $a_1 = a_2$ and a_3 and the aspect ratio $\rho = a_1 / a_3$. The inclusions are uniformly aligned in the matrix, and the remanent polarisation vector of each inclusion is oriented along the OX₃ coordinate axis, which is the poling axis for the sample. In the limiting case with $a_3 \rightarrow \infty$ and $\rho \rightarrow 0$ the composite can be considered as a 1–3-type with rods of FC in a continuous hydroxyapatite matrix. The matrix was considered as either

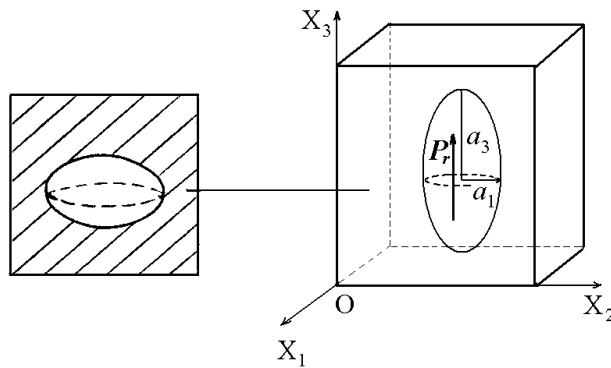


Fig. 1. Schematic of the composite studied. The spontaneous polarisation vector \mathbf{P}_r of the FC BaTiO_3 inclusion is denoted by an arrow. $X_1X_2X_3$ is the rectangular coordinate system. A spheroidal air pore in the HA matrix is shown in the left inset.

monolithic HA or containing regularly distributed spheroidal pores (Fig. 1, left part) that occupy the sites of a simple tetragonal lattice. The radius or the largest semiaxis of the pore is considerably less than a_1 and a_3 .

The effective electromechanical properties of the 0–3 composite were determined as a function of the volume fraction, m , and the aspect ratio, ρ , of the FC inclusions by an effective field method, i.e. the Mori-Tanaka method [10] generalised for heterogeneous piezoelectric media [11]. The effective field method, based on Eshelby's concept of spheroidal inclusions [12], is a variant of the self-consistent scheme for the determination of effective properties of the piezo-active composites. The matrix of the effective constants of the 0–3 composite was determined using formulas [13] as,

$$\|C^*\| = \begin{pmatrix} \|c^{*E}\| & \|e^*\|^t \\ \|e^*\| & -\|\varepsilon^{*\zeta}\| \end{pmatrix},$$

where the superscript “ t ” denotes the transposition and the matrices of elastic moduli $\|c^{*E}\|$, piezoelectric coefficients $\|e^*\|$ and dielectric permittivity $\|\varepsilon^{*\zeta}\|$ correspond to ∞mm symmetry of the whole composite. The effect of matrix porosity (i.e., pore aspect ratio ρ_p , analogous to ρ , and the volume fraction of pores m_p within the matrix) was taken into account using formulas [11, 13].

Based on elements of $\|C^*\|$, the effective piezoelectric coefficients $\|d^*\| = \|e^*\| \cdot \|c^{*E}\|^{-1}$ and $\|g^*\| = \|d^*\| \cdot \|\varepsilon^{*\sigma}\|^{-1}$ were determined as functions of FC volume fraction (m), FC aspect ratio (ρ), porosity volume fraction (m_p), and porosity aspect ratio (ρ_p). The volume fraction of BaTiO_3 ranged from 0 to 50 %. Modelling was carried out using the complete sets of the electromechanical constants of the BaTiO_3 FC [14] and HA [15] at room temperature. The following section is concerned with a series of fraction dependences calculated for the BaTiO_3 -HA composites (Fig. 2) with both dense (monolithic) and porous HA matrices.

Results and discussion

Fig. 2a shows the BaTiO_3 -HA composite permittivity as a function of m , with the BaTiO_3 aspect ratio ranging from equi-axed spheres ($\rho = 1$) to rods aligned in the poling direction ($\rho = 0$). In all cases the permittivity increases as the volume fraction of ferroelectric BaTiO_3 increases. When fabricating BaTiO_3 -HA composites by co-sintering of HA and BaTiO_3 powders [8] the ferroelectric phase is likely to be equi-axed and when $\rho = 1$ the increase in permittivity from m of 0 to 0.5 is relatively small; since the overall permittivity is dominated by the continuous hydroxyapatite matrix. Fig. 2b shows the variation of the piezoelectric charge coefficients (d_{3j}^*) with m at a range of FC aspect ratios. Since HA is non-ferroelectric the magnitude of both d_{33}^* and $|d_{31}^*|$ increases as the BaTiO_3 volume fraction increases. Low piezoelectric coefficients (< 6 pC/N [8]) are observed for the condition $\rho = 1$, but an elongation of the FC phase in the through-thickness/poling direction ($\rho \rightarrow 0$)

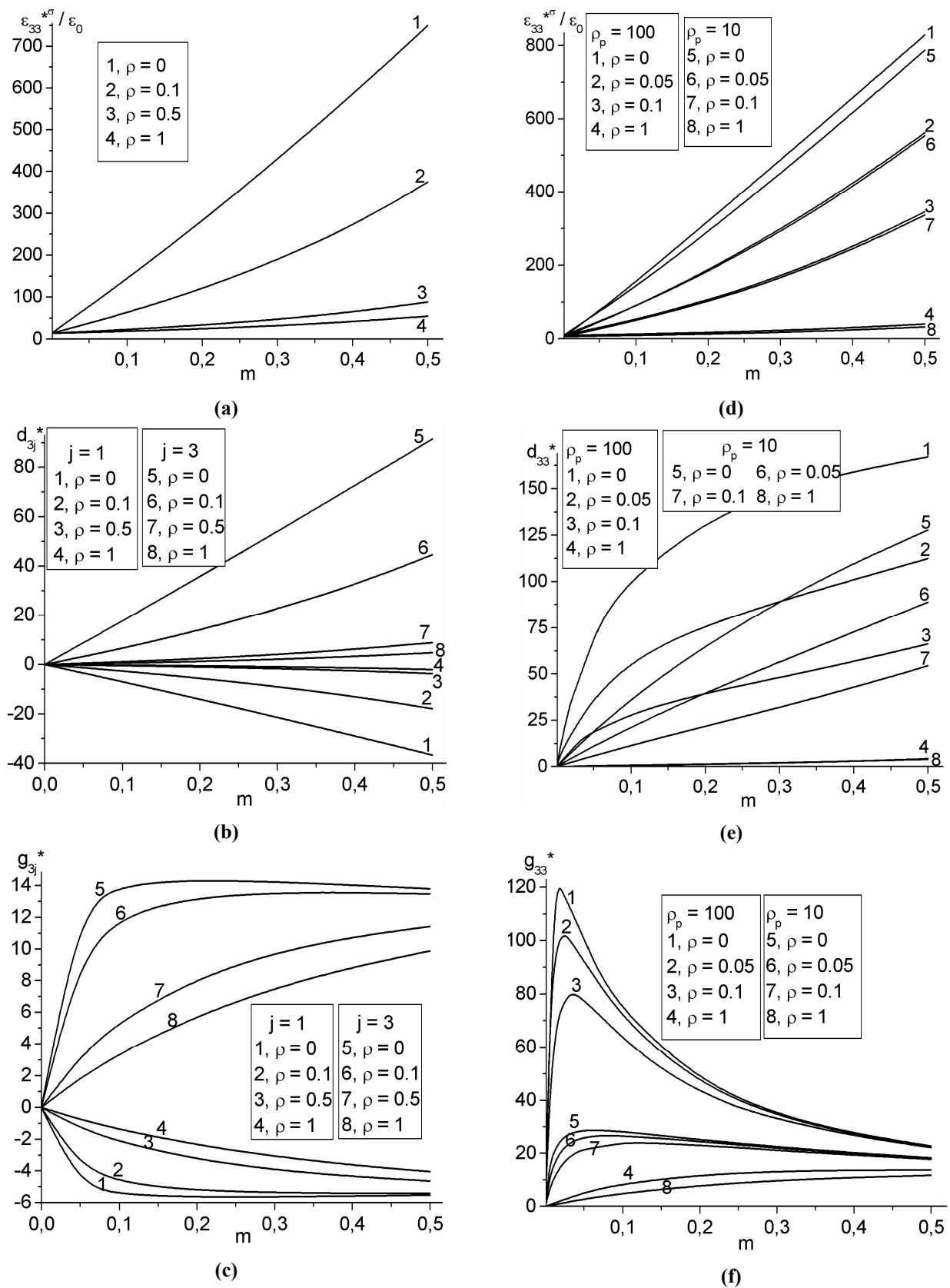


Fig. 2. Fraction dependences of the effective parameters calculated for the BaTiO₃ FC / HA composite (a, b and c) and the BaTiO₃ FC / porous HA composite (d, e and f). FC inclusions are characterised by the aspect ratio $\rho = 0$ to 1. The porous HA matrix contains oblate spheroidal air pores with the volume fraction $m_p = 0.1$ and the aspect ratio $\rho_p = 10$ or 100. Units are: $[d^*] = \text{pC/N}$ and $[g^*] = \text{mV m/N}$.

leads to an increase in the magnitude of the piezoelectric charge coefficients. For an implant application it is necessary to consider the electric field generated as a result of an applied stress, determined from the piezoelectric voltage coefficient (g_{3j}^*). Fig. 2c shows the $g_{33}^*(= d_{33}^* / \epsilon_{33}^{*\sigma})$ and $g_{31}^*(= d_{31}^* / \epsilon_{33}^{*\sigma})$ coefficients for the composites. For the condition $\rho = 1$, both g_{33}^* and $|g_{31}^*|$ gradually increases as the fraction of BaTiO₃ increases, primarily due to d_{33}^* and d_{31}^* from a zero value at $m=0$. As observed with d_{3j}^* , an elongation of the ferroelectric in the poling direction leads to improved g_{3j}^* values.

An additional method of tailoring the properties of the composite is to reduce the permittivity and stiffness and of the HA matrix by the addition of porosity. For a porosity level of 10 % (i.e. $m_p = 0.1$), this leads to relatively small changes in permittivity (Fig. 2d) compared to the dense matrix (Fig. 2a). However, more significant changes are observed for d_{33}^* (Fig. 2e). The porosity leads to a decrease in the stiffness of the HA matrix and increases the load transfer into ferroelectric phase, resulting in high d_{33}^* values compared to the dense HA matrix (Fig. 2b); although the composites with spherical FC particles are not greatly affected. The increases in d_{33}^* also results in high g_{33}^* values, with distinct maxima in the volume fraction dependence of g_{33}^* for pores of $\rho_p = 100$ and $\rho < 0.1$, see Fig. 2f.

Conclusions

The electromechanical properties of the BaTiO₃–HA composites have been studied to understand the property-composition relationships for novel bone substitute ceramics. For equi-axed BaTiO₃ FC particles ($\rho = 1$) in a dense HA matrix, the d_{3j}^* piezoelectric charge coefficients are predicted to be small (< 6 pC/N) for the range of compositions studied. The d_{33}^* and g_{33}^* coefficients of the composites can be increased by a reduction in the stiffness of the matrix (by addition of porosity) or elongation of BaTiO₃ particles in the through-thickness/poling direction. The use of HA particles in a continuous BaTiO₃ matrix or a interpenetrating HA and BaTiO₃ phases (3–3 connectivity) will also be evaluated in future investigations.

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