Mechano-optical analysis of piezoelectric hydroxyapatite composites

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Abstract. The piezoelectric behavior of Hydroxyapatite (HAp) composites by the mechanical action of high optical irradiances was studied. The piezoelectric and optical properties of HAp composites were considered based on previous researches. Using a finite method element and computational software, an approximation of mechanical deformation by using a direct current voltage as input. It was considered a mechano-optical model to reproduce a normal force acting on the surface of the HAp composites provided by a nanosecond pulsed laser irradiation. The generated voltage was estimated under high optical irradiance using a proposed mathematical approach. This study can assist in the characterization of piezoelectric crystals by noninvasive disturbances. These results exposed the possibility of developing novel measurement procedures that involve nonlinear optical processes.

1. Introduction

Hydroxyapatite (HAp) has gained a great interest in different branches of science since it can be used to replace inorganic matter of bone tissue due to the similarity of its composition. The existence of pathological problems, in which some tissue component does not perform its proper function, drives to search an engineering solution. In this case, the biomaterials that produce and transmit the necessary bioelectric signals are the piezoelectric [1]. Particularly the HAp that is formulated of calcium phosphate is synthesized in crystal form and exhibits piezoelectricity [2]. It is of great importance to study this phenomenon because there is a relationship with bone growth and acceleration of fracture joints; this is described by Wolff’s law [3]. Moreover, when collagen or HAp are deformed, it results in a change of...
electrical dipoles that can be related to negative polarity on the compressed surface and positive polarity in the stressed area. This effect causes the electric dipoles to have a reorganization in the material, increasing negative charges in the compression area in order to attract calcium ions and, therefore, the phosphate ion [4]. Moreover, the physicochemical, piezoelectric, and dielectric properties of a sample composed of collagen-HAp help in cell growth and bone regeneration. Properties such as the elastic constant 2.93×10^6 m^2/N, the tensioning element of the piezoelectric stress (0.041 pC·N⁻¹), and dielectric permittivity (2.509) were measured from characterization by thermal analysis, x-ray diffraction, and impedance spectrum [5].

The importance of measuring piezoelectric effects in HAp is crucial to evaluate their performance in bioengineering systems. For that purpose, it must be tested an efficient physical mechanism of propagation through the crystal lattice of HAp. For instance, some authors reported an optical method to examine mechanical properties in nanostructures. This method senses the influence of interferometric optical signals using a nanosecond pulse irradiation to induce mechano-optical deformations in liquid samples [6]. The high-speed propagation and spatial accuracy of laser beams open the possibility to induce similar mechano-optical perturbation in synthetic HAp crystals, which have high biocompatibility with bone tissue. Furthermore, this compound can establish a connection and exchange chemicals in order to form interfacial bonds with living tissue to achieve a bone growth process [7]. Based on the evidence, this work performs a numerical study of piezoelectricity in HAp and HAp-collagen bio-crystal systems considering electrical inputs and mechano-optical deformations.

2. Methodology

A piezoelectric analysis in two synthetics, HAp, and HAp-collagen samples, was conducted by numerical calculations considering parameters that have been reported elsewhere [5]. The finite element method using a computational software assisted in the approximation of the piezoelectric characteristics. By combining the electrical, mechanical, and optical characteristics of HAp, the mechano-optical strains can be estimated. In ref. [5], the collagen was prepared by solubilization of collagen from bovine serosa with a homogenization process in acetic acid at pH 3.5. Furthermore, they obtained powder of HAp by precipitation between Ca(OH)₂ and H₃PO₄, with heat treatment of 1100°C for 1 hr. The composites were deposited in film forms with a thickness between 134 to 417 μm. The geometry of both samples was chosen as cylindrical solids similar to the commercial ones. On the other hand, the structural displacements were studied by static analysis using an electric field. It is necessary to specify the isotropic properties such as the Poisson’s ratio (0.27), bulk modulus (4.45×10¹¹ Pa), shear modulus (8.9×10¹¹ Pa), and Young’s modulus (11.4×10¹¹ Pa) [8]. The equations that combine the properties of the electric with the mechanical fields are [5]:

\[
S = s^T + dE \tag{1}
\]

\[
D = dT + \sigma E \tag{2}
\]

where \(S\) is the strain, \(T\) is the stress applied to the material, \(E\) is the electric field, \(D\) is the electrical displacement, \(s^T\) is the compliance for the constant electric field, \(\varepsilon\) is the dielectric permittivity and \(d\) is the piezoelectric strain element. The equation (1) exhibits inverse piezoelectricity, while the equation (2) depicts direct piezoelectricity. From the above relationships and for oriented textures of biopolymers, it can be determinate the matrix of following tensors of dielectric and elastic constants. Matrix of 3×3 and 3×6 where all elements are zero except \(\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}\) and \(\varepsilon_{41}, \varepsilon_{52}\) respectively. Also, the constants fulfil \(\varepsilon_{22} = \varepsilon_{11}, \varepsilon_{44} = \varepsilon_{14}\) and \(\varepsilon_{52} = -\varepsilon_{14}\) [5].

Additionally, the boundary conditions were defined, as shown in figure 1. These architectures were selected since the type of physics involved was electromechanical. In figure 1(a) is observed the support point on the lower face. Moreover, figure 1(b) delimits the electrical conditions: the lower face of each sample as positive and the upper face as negative biased. In order to optimize the computational tool, the geometries have meshed into 635 elements with 1459 nodes. Finally, a direct bias voltage from 0 to 10 V was applied to compute the piezoelectricity.
Figure 1. Boundary conditions of HAp compound wafers. (a) Clamping, (b) electrical bias.

3. Results

Table 1 shows the compendium of properties necessary to study the static piezoelectric behavior of the HAp composites samples. The capacitances were computed by $C = \varepsilon A/t$, where $A$ is the sample’s transverse area, $\varepsilon$ is dielectric permittivity, and $t$ is thickness.

| Parameters                  | Unit  | HAp    | HAp-collagen |
|-----------------------------|-------|--------|--------------|
| Diameter                    | Ø [m] | 0.0338 | 0.0121       |
| Capacitance                 | C[pF] | 9.5800 | 0.5700       |
| Thickness                   | $t$ [µm] | 417.00 | 417.00       |
| Density                     | $\rho$ [kg/m$^3$] | 3040.0 | 903.88       |
| Dielectric permittivity     | $\varepsilon_{11}/\varepsilon_0$ | 12.220 | 2.5909       |
| Piezoelectric strain tensor | $d_{14}$ [pC/N] | 14.000 | 0.0410       |
| Piezoelectric stress constant | $\sigma_{14}$ [C/m$^2$] | 0.6060 | 0.00170      |

The mechanical strain was numerically obtained as a function of the applied voltage in the samples using the matrix of dielectric and elastic tensors and the values in Table 1. These parameters were collected from the references [5,9]. Figure 2(a) presents the field deformation of the samples with respect to its original geometry using a fixed bias voltage (5 V). The maximum deformations are $6.75 \times 10^{-12}$ m and $1.97 \times 10^{-14}$ m for HAp and HAp-collagen, respectively. The diameter does not affect the deformation index for this measurement. Based on the previous calculations, it is interesting to evaluate the deformation of the biomaterials by modulating the electric field. In figure 2(b) is shown the results as a function of the applied voltage to the transverse faces in a range of 0 to 10 V. It is observed that the behavior is linear for both samples; however, a nonlinear effect when a high magnitude voltage is applied can be expected. At this limit value, there should be saturation in the deformation, causing a fracture in the crystalline matrix.
Figure 2. Piezoelectric deformation of HAp and HAp-collagen composites wafers. (a) deformation with respect to its original geometry at constant voltage (5V). (b) Graphic of results as a function of the applied voltage to the transverse faces in a range of 0 to 10 V. Left axis HAp and right axis HAp-collagen.

Since the typical piezoelectric response of HAp is well reported, it is interesting to estimate the voltage of the studied samples at high optical irradiance in the visible range, particularly at 532 nm wavelength. It was considered this perturbation as the mechanical load on the surface of the wafers. In order to achieve the mechano-optical input, the energy that absorbs the sample is $E_{HAp}=\alpha_{abs}E_l$ where $\alpha_{abs}$ is the absorbance of HAp ($\alpha_{abs}=0.1$) [10], $E_l$ is the energy per pulse of the laser that is considered from 0 to 30 $\mu$J, and $E_{HAp}$ is the mechanical work that performs the electromagnetic wave when passing through the sample. For this reason, and with an analogy to mechanical work, the strength is given by the following equation $F=\alpha_{abs}E_l/t$ [11]. Additionally, the estimation of the generated voltage for the HAp and HAp-collagen samples by considering a force disturbance is given by [9]:

$$U = \frac{d_{44}\Theta F}{Ct} = \frac{d_{44}\Theta \alpha_{abs}E_l}{Ct^2}$$ (3)

In equation (3), the voltage is described as a function of the optical properties of the samples and the energy source. Furthermore, figure 3(a) depicts a linear behavior in the application of the high-intensity optical disturbance from 0 to 30 $\mu$J, obtaining a voltage of 0.9 mV and 15 $\mu$V for HAp and HAp-collagen composites, respectively.

Furthermore, the high susceptibility of the HAp sample opens the possibility of studying the piezoelectricity in a scalable and handle systems. Due to its thermal, mechanical, and optical properties, HAp in thin film form can be very useful for biological coatings and active elements in the prosthesis. It is not feasible to subject thin films to classical mechanical deformations to examine their piezoelectric properties because it would cause an easy rupture due to the thickness dimensions. Therefore, mechano-optical force must be proposed using a rapidly propagated and spatially accurate system such as a focused beam of light. Remarkable nonlinear optical effects have been reported experimentally in HAp for high irradiance in the visible range. In order to approach a model that linked the piezoelectric phenomena with the nonlinear optical field, is used the absorption given by $\alpha(I_0)=\alpha_0+\beta I_0$ [13], where $\alpha_0$ is the linear absorptivity, $\beta$ is the nonlinear absorptivity coefficient, and $I_0$ is the input irradiance. Moreover, nonlinear absorbance of the material will be calculated by the next equation [12], considering a neglected reflectance.

$$\alpha_{abs} = 1 - \frac{\exp[-(\alpha_0 + I_0)t]}{1 + I_0t}$$ (4)
Furthermore, combining equations (3) and (4), and using the general formula of capacitance, the expression to obtain the voltage of piezoelectric material by considering as nonlinear optical medium is

\[ U = 4d_{14}E_{\infty} \alpha_{\infty} / \sigma v \phi t \].

The optical properties of HAp thin films were measured with an irradiance close to 7.47 kW/cm² [13]. In order to estimate the piezoelectric effect, a maximum irradiance of 18 kW/cm² was proposed by the same previous energy laser conditions, 4 ns pulse duration, and 0.3 cm beam radius. The optical properties to compute the electric function are linear absorption (\( \alpha = 3591.22 \text{ cm}^{-1} \)), dielectric properties (\( \varepsilon_r \varepsilon_0 = 3.67 \times 10^{-10} \text{ F/m} \)), and nonlinear absorbptivity coefficient (\( \beta \)) of HAp thin film with 400 nm thickness. The studied samples were considered as function of nonlinear absorbptivity: 0 cm/W, 0.2 cm/W and 0.4 cm/W. These values are close to those reported [14]. The structural properties \( d_{14} \) and \( \phi \) was chosen as 14 pC/N and 0.0388 m, respectively. Figure 3(b) shows the behavior of voltage at high optical irradiances for different nonlinear absorbptivity coefficients of HAp crystals. For this graphic, it is concluded that the increase of the generated voltage increases proportionally along with the energy of the laser, congruent with the previous results in wafer form. Furthermore, when the nonlinear absorbptivity increases; this domain the piezoelectric activity at low irradiance before it reaches saturation. However, the energy of the laser continues to grow, and consequently, the system behaves linearly. Due to the low dimension on the film thickness, scattering effects tend to disappear, and discrete wave propagation is exposed; thus, nonlinear optical absorbance highly affects the piezoelectricity. Therefore, it is expected to exist an ablation at a certain energy threshold.

**Figure 3.** (a) Voltage generated in the samples by mechano-optical perturbance. Left axis HAp and right axis HAp-collagen. (b) Voltage behavior of HAp thin film by optical irradiance at different \( \beta \).

### 4. Discussions

Two remarkable systems based on HAp crystals in such a way that a high-power optical source acted as a mechanical perturbation are reported. The effective propagation of photons through the crystalline lattice of the biomaterial has been used to characterize the piezoelectricity of thin films. The HAp has the characteristic of being a transparent crystal; hence, Michelson interferometer to measure the mechanical and electrical properties and to determine its piezoelectricity is proposed [14,15]. Mechano-optical effects can assist in measuring the stress limit of nanostructures with a noninvasive procedure [16]. Couple with this, electrostriction can superpose to the piezoelectric effect by considering high irradiance. When a material is subjected to an electric field, it suffers a deformation, and its density increases as a linear rate concerning the irradiance [17]. From the results of figure 2(b), the slope of the piezoelectricity (\( d_{14}E_{\infty} \)) is proportional to the piezoelectric strain tensor element (\( d_{14} \)), and this value changes as the inverse of the square root of the density [5], hence it is expected a nonlinear behavior at combining these models. Moreover, to achieve a considerable change in density, more significant
irradiation is required; thus, it is considered the results presented in this work as a good approximation. Additionally, it can be considered low-dimensional systems with autotuning optical properties via the piezoelectricity by light-light interaction [18]. This principle can be achieved in a two-wave mixing experiment by analyzing the properties of the reflected probe beam.

5. Conclusions
The piezoelectric effect of biocrystals of HAp was studied numerically in different architectures. With properties reported in the literature, HAp and its compounds are shown to exhibit piezoelectricity. With the finite element method, the piezoelectric response was simulated, achieving a deformation by applying a voltage through the HAp and HAp-collagen samples. The piezoelectric properties of a crystal can change by modifying the organization in the lattice structure; thus, it is obtained that HAp deformed more than HAp-collagen. The resulting deformation in both samples by modulating the electric field was a linear dependence. Besides, a linear behavior was achieved by evaluating the voltage after applying an optical disturbance. A mathematical approximation was obtained through nonlinear optics and considering the piezoelectric properties, which includes those specific properties that serve to create a new method to characterize piezoelectric materials. From the above, nonlinear interaction between the irradiance and the voltage was analyzed by changing the nonlinear absorptivity coefficient of the HAp thin film. However, it has expected a different mechanism related to electrostriction when increasing the input irradiance.

Acknowledgements
The authors acknowledge the financial support for the realization of this work provided to the Government of Mexico by the National Council of Science and Technology (CONACYT) and the Instituto Politécnico Nacional, also to the Government of Chile by FONDECYT postdoctoral grant 3190552. The authors acknowledge partial support from projects 20201964 and 20200930, as well as an EDI grant, all provided by SIP/IPN.

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