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Physico-chemical properties and ultrasonic characterization of calcium phosphate ceramics

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Calcium phosphate compounds have been studied for biomedical applications due to their chemical and structural similarity to the mineral phase of bone and tooth. The composition, physical and chemical properties, crystal size and morphology of synthetic apatite are extremely sensitive to preparation conditions and sometimes it resulted into non- stoichiometric calcium deficient hydroxyapathite (Hap) powders. The present paper refers to calcinations of calcium phosphate ceramics at 800 and 10000C. The effect of heat treatment were previously investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR), differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). FTIR spectra showed the presence of various PO3_4 and OH- groups present in the powders. Powders compacted and sintered at 800 and 10000C showed an increasing density. The main objective of the paper is a comparison of results obtained by the previous methods to those obtained using the ultrasonic air-coupling technique. Modulated ultrasonic signals of 450 kHz central frequency have been transmitted through the calcium phosphate ceramics specimens. Correlation between signals allowed some conclusions concerning density, attenuation and preparation temperature influence on these specimens. These comparisons and correlation of methods, allow a better characterization of such important materials

1 Introduction

Acoustic properties of porous materials represent an important research objective during the last decades. From the pioneer works of Biot [1, 2] which are dedicated mainly to porous materials saturated with fluids of comparable densities, many other specialists were involved in such researches, with two main directions: audible frequency-range with obvious technical and architectural applications and high frequency range, have various applications among which the biomedical ones. From the first category, the study [3] has applications in sea-bed characterization.

A new macroscopic theory of acoustic wave propagation through porous media, valid at high frequencies, is presented in [4], which explains the occurrence of a slow compressional wave. The theory is experimentally verified for an artificial rock saturated with water [5]. A plane-wave analysis derives expressions for the slowness, attenuation, and energy velocity vectors, and quality factor for homogeneous viscoelastic waves. The slow wave is proven to have an anomalous polarization behavior [6]. The method of acoustical holography is used in [7] to measure the reflection coefficient of a porous layer at oblique incidence.

Ultrasonic attenuation measurements are used in [8] to determine the viscous characteristic length of an air-filled material. A model based on the systems theory is used in [9] to estimate propagation characteristics of sound in porous media. Nonlinear dynamic equations introduced by Biot to model porous media are revised and a mathematical model of the physical nonlinearity is established in [10]. Expressions for the viscosity correction function, density, compressibility, and propagation constant, are obtained in [11] for a rigid frame porous medium whose pores are prismatic with fixed cross-sectional shape having variable pore size distribution. Surface waves above porous layers between 1.8 and 6 mm of plastic foams, saturated by air, at ultrasonic frequencies are investigated in [12]. Acoustical characterization of absorbing porous materials through transmission measurements in a free field, is presented in [13]. A theory of compressional and shear wave propagation in consolidated porous rocks is developed in [14] by extending ideas already introduced in connection with unconsolidated marine sediments. For thin bead layers saturated by air, a pole of the reflection coefficient related to a trapped mode inside the layer and a surface wave in air is predicted in [15]. Acoustic wave propagation in porous medium, which is assumed in [16] to have a rigid frame, so that the propagation takes place in the air which fills the material. In [17] is presented the application of a simple model for the prediction of the acoustic properties of porous granular media with some assumed pore geometry and pore size distribution close to log-normal. One of the first biomedical studies of the bone as a porous medium is presented in [18] with the objective of proving if scattering alone may cause such a high attenuation as that observed in calcaneus. A water-saturated porous cylinder is tested in a shock tube. Agreement was found between the experimental data and the two-dimensional modeling of the shock tube which was based on Biot's theory in [19]. A temporal model of the direct and inverse scattering problem for the propagation of transient ultrasonic waves in a homogeneous isotropic slab of porous material having a rigid frame is investigated in [20]. The porous medium is modeled via Biot's theory and the scattering by a single pore is characterized from the definition of a scattering matrix. A general set of time-domain equations describing linear sound propagation in a rigid-frame gas-saturated porous medium is derived in [21].

2 Experimental study

Hydroxyapathite is used in bio-medical applications due to its bio-compatibility with bone structure. Used as coating for some protease, it improves the healing duration and the quality of the body acceptance. It is useful to determine as many as possible from its mechanical, bio-compatibility, chemical and physical properties. In the present experimental study, some mechanical properties a sintered powder of Hydroxyapathite are correlated using ultrasonic techniques.

Three discs of Hydroxyapathite were produced by high pressure and various temperatures in special moulds of the same diameter. The heat produced a reduction in diameter and thickness, for the same initial quantity used in the process. The ultrasonic technique is used as possible method of porosity measurement of the sintered powder.

2.1 Experiment layout

The experimental layout consists of two air-coupled ultrasonic transducers mounted coaxially and face to face (Fig. 1..4). The distance between the two transducers has been selected such that diffraction of ultrasonic waves around the samples is minimised, yet allowing all signals to be determined in the same time interval, so 60 mm have been selected (Fig. 2).

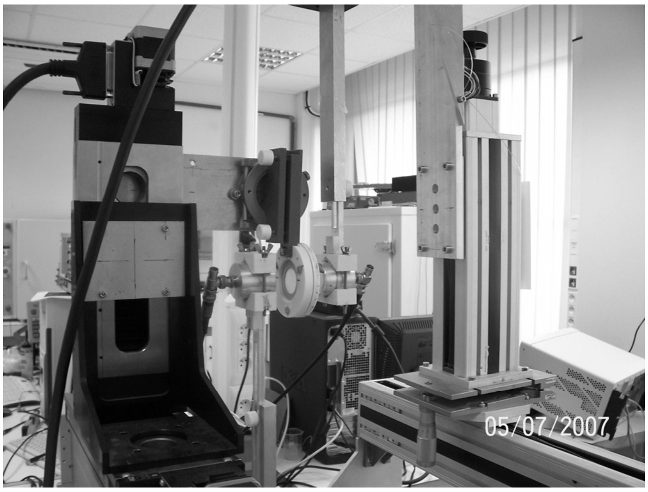

Fig. 1 General view of the experimental setup

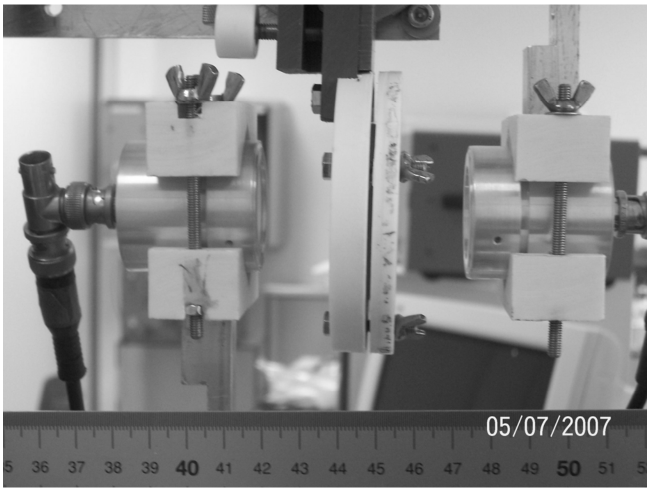

Fig. 2 Side-view of the specimen inserted between the two air-coupled transducers

The samples have been slightly pressed between two hard paper diaphragms mounted in two Teflon discs which are kept parallel by two screws (Fig. 3 and Fig. 4).

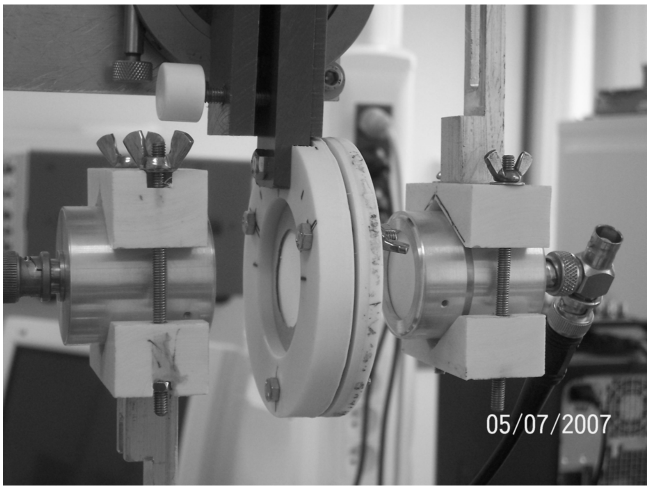

Fig. 3 View of the transmission side of the propagation path

Expecting a high attenuation of the ultrasonic signals in air, a relatively low frequency burst signal has been selected.

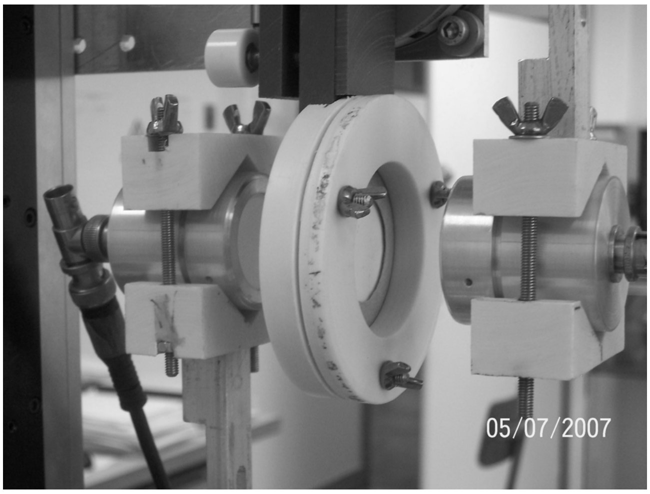

Fig. 4 View of the incident and reflection side of the propagation path

The reference signal sent as a burst, is received as indicated in Fig. 5. It is a relatively long burst because it was intended to keep a narrow frequency bandwidth, around 450 kHz (Fig. 6).

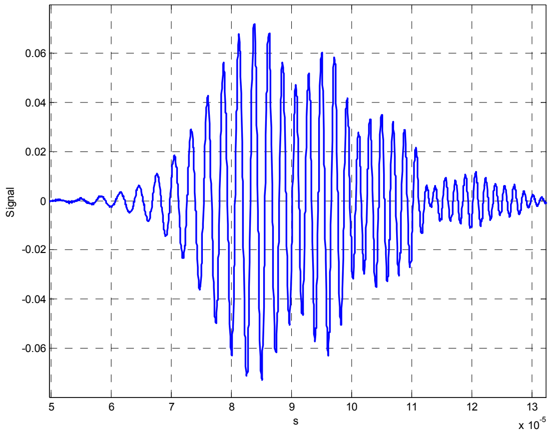

Fig. 5 Reference signal in direct propagation

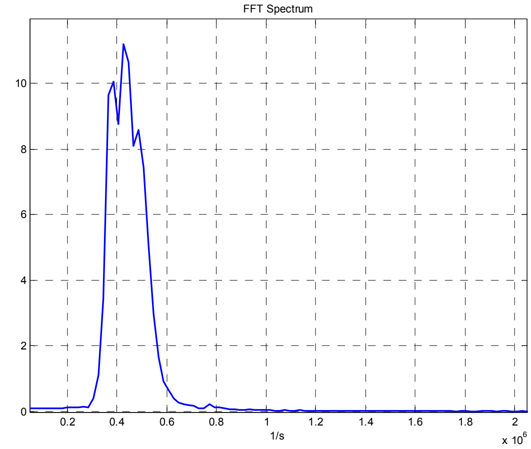

Fig. 6 Frequency spectrum of the incident signal

The hydroxyapathite samples which were tested were 40mm in diameter, thickness 4, 3.2 and 2.7 mm respectively. Their sintering temperatures are indicated in Table 1.

The received signals at the same scale and same time origin are presented in Fig. 7.

Sample	Sintering temperature (ºC)	Mass density (g/cm^3)	C_{11} (GPa)
TCPRT	15	0.4795	2.3
TCP800	800	0.5505	1.8
TCP1000	1000	0.6472	1.5

Table 1 Sample properties

Using these time signals and samples data, the following velocities in the three samples have been determined: c_1=2200 m/s, c_2=1800 m/s, c_1=1500 m/s, respectively. These values correspond to the elastic coefficients of the equivalent homogeneous material indicated in the last row of Table 1.

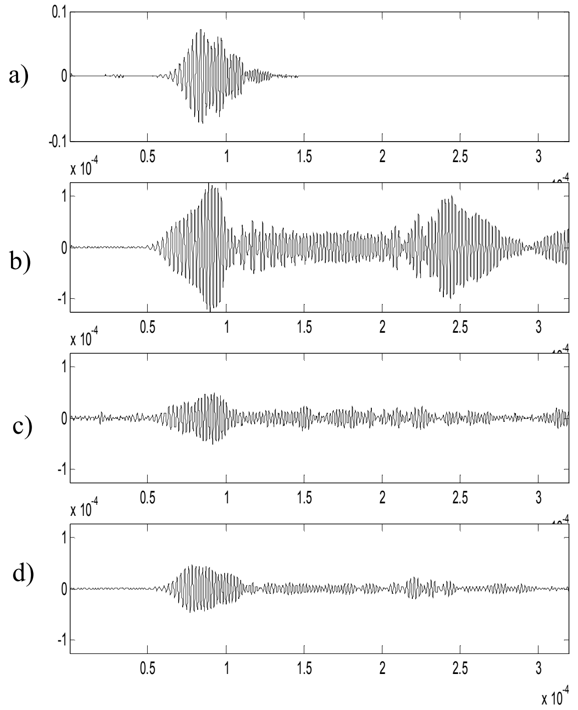

Fig. 7 Time history of the reference signal (a) and of the three samples (b,c,d). (Abscissa in s)

The maximum levels of signals after transmission, relative to the maximum incident amplitude are 1.5e-3 (a), 6.25e-4 (b) and 5.75e-4 (c) respectively.

The long trailing signals bear information about internal reflections in the samples, which are influenced by the porosity. The first sample (TCPRT) has a peculiar behavior in the transmitted signal. After a trail lasting more than 0.12 ms, a large amplitude signal appears with opposite gradient compared to the first transmitted burst. It can be attributed to the specular reflection of the transmitted signal back and forth between the sample and the receiver transducer, but this phenomenon is not repeated for the next two samples.

3 Conclusions

The experimental measurements of ultrasonic bursts transmitted through three sintered discs of hydroxyapathite are presented. The time history of the signals allowed estimation of one elastic constant and signal attenuation as function of preparation conditions. More detailed experiments are however required to predict with some degree of confidence, the porosity of the material and this is the object of ongoing researches.

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