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Mechanical properties of calcium phosphate biomaterials

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ABSTRACT
Calcium phosphate biomaterials were used to repair bone defects as prosthetic coatings. Powders and bioceramics from hydroxyapatite and β-tricalcium phosphate were fabricated using a low-cost process and characterized with different techniques. Their thermal stability and mechanical properties were investigated under water environment. This study was to investigate the effect of water moieties to cause permanent damage to calcium phosphate bioceramics by determining their mechanical properties changes.

KEYWORDS
Calcium phosphate; Microstructure; degradation; humidity effect; Mechanical properties

Introduction

The development of advanced biomaterials is among the most important advantages to repair lost or damaged bony tissues [1–3]. Materials based on calcium phosphates developing high bonding with bone tissue exhibit a good osteo-conductive and bio-resorption behaviours [4–5], show the greatest potential for bone substitution. Various types of calcium phosphate materials can be elaborated such as dicalcium phosphate dehydrate (Brushite, $CaHPO_4.H_2O$), dicalcium phosphate anhydrous (Monetite, $CaHPO_4$), β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$), tetracalcium phosphate ($Ca_4P_2O_9$), octacalcium phosphate ($Ca_8H_2(PO_4)_6.5H_2O$), calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and calcium fluorapatite ($Ca_{10}(PO_4)_6F_2$). They are available in various physical forms: particles or blocks; dense or porous [6]. These materials differ in their solubility and physico-chemical reactions with bone tissues [7]. The most used in surgery and the most studied are hydroxyapatite (HAP) and β-tricalcium phosphate (β-TCP) related to their low solubility at a neutral pH when compared to other calcium phosphate phases having a higher Ca/P ratio [8]. Solubility of HAP and β-TCP varies with different factors: porosity, grain size, crystallinity, sintering temperature [9–11]. Porous biomaterial dissolves more rapidly than dense biomaterial and its crystals size increases with the sintering temperature in reducing the number of lattice defects [12–13]. In the addition, when HAP or β-TCP bioceramics are in contact with living system, they undergo a good biodegradation/biodissolution [14]. This process results in physico-chemical changes like breaking into smaller particles, loss of mechanical strength, modification of micro-and macroporosities, modification of the implant size. Dense hydroxyapatite shows mechanical and surface-related characteristics very different from those of porous ceramics

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[15–16]. Many critical and complex reactions take place during the preparation and fabrication of bioceramics where the structural and chemical evaluation is primordial to determine the success of HAP and β-TCP bioceramics, in which the elemental chemical composition and surface properties play a very important role in mechanic properties. Knowledge of the mechanisms and change phases of bioceramic is important to understand the physicochemical mechanisms involved during the densification process in varying the method and conditions of HAp and β-TCP formation. Furthermore, the mechanical properties of the last bioceramics are strongly influenced by humidity or water environment such as described for other materials [17–20]. Together with the development of bioceramics, several efforts have been pursued in order to explain the mechanisms responsible for the change of mechanic properties with ceramic process and densification behaviour of ceramic placed at various environments. Mechanic degradation of calcium phosphate ceramics is caused by :(i) physiochemical dissolution, which depends on the solubility product of the material and local pH of its environment; (ii) Physical disintegration into small particles due to preferential chemical attack of grain boundaries and (iii) dissolution process, which caused by a decrease in local pH. Many biomaterials such as calcium phosphate, when placed in an aqueous environment, absorb water by a diffusion process. Nevertheless, this water exerts significant effect on the mechanical and dimensional properties of bioceramics. Thus, the aim of this study is to follow the changes of mechanical properties of HAp and β-TCP bioceramics in the wet condition.

2. Materials and methods

2.1. Materials

The synthesis of the hydroxyapatite powder used to obtain monophase was carried out by the wet method with $Ca(OH)_2$ (Aldrich, Germany) and H_3PO_4 as the reagents with Ca/P molar ratio equals to 1.67 [21]. The β-tricalcium phosphate powder (β-TCP) has been elaborated by chemical wet method using $(NH_4)_2HPO_4$ and $Ca(NO_3)_2{,}4H_2O$ precursors in appropriate stoichiometric molar ratio Ca/P = 1.5 such as reported elsewhere [21]. The both obtained gelatinous precipitates were aged, rinsed with distilled water, dried and heated at 900°C for 3 h. White powders were collected and the phase purity was confirmed by X-ray diffraction (XRD) for as-precipitated and calcined samples. The HAP and β-TCP pellets have been obtained according to the protocol used in our previous studies [20–21]. They have been subsequently ground on 800, 1200 and 2400 grit SiC paper before polishing with a 1 mm diamond suspension as the final polishing step. This operation removed 1 mm layer from the 4 mm thick pellet and thus avoided any surface features that may have formed on the outside of the sample during the sintering operation. The highly polished surface provided a suitable surface reproducible for the indentation. After drying and sieving, parallelepipedic bars with the dimensions of $40\times20\times3$ mm^3 are produced by pressing uniaxially at 60 MPa and isostatic pressing at 300 MPa. For dilatometer measurements, the thermal cycles applied in the dilatometer consists in heating from 25°C to 1400°C by holding and cooling with same heating rate of 5°C.min^{-1}. The sintering process is performed at various temperatures from 1050 to 1300°C for 3 h in air (5°C min^{-1} as heating rate). To study the water exposure effect on mechanic properties of ceramics, HAP and β-TCP bioceramics were placed in water at neutral pH and at physiological temperature 37°C during six weeks.

2.2. Techniques

The crystalline phases have been characterized using X-ray diffraction (X'Pert Pro MPD Panalytical diffractometer operating at Cu Kα radiation) and infrared spectroscopy (Perkin-Elmer FT-IR1600 spectrophotometer). Nitrogen adsorption-desorption isotherms have been recorded at 77 K using a Micromeretics ASAP 2010 instrument. The specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method using adsorption data in the relative pressure range from 0.05 to 0.25. The sample powder was chemically analyzed by inductively coupled plasma (ICP) emission spectroscopy. The bulk density of HAP and β-TCP samples has been determined by hydrostatic weighing and the relative density has been calculated by taking their theoretical densities. Vickers indentation method has been used to determine both microhardess (H_v) and fracture toughness (K_{1c}) of the samples, using Vickers hardness tester (microindenter WOLPERT). The indentation load (< 200 g) has been applied and held in place for 10 s. Ten (10) indentations have been made for each sample and the average value has been taken. The indentation K_{1c} has been determined from the equation proposed by Niihara [23]. The strength measurements have been recorded using INSTRON 8512.

3. Results and discussions

3.1. Structural and textural characterization

X-ray diffraction patterns of as-received powders exhibit a poorly crystalline apatite phase biomaterials. However, the calcined powders at various temperatures beyond 900°C have a single phase attributed to apatite and β-$Ca_3(PO_4)_2$ structures such as reported in our previous work [21]. From chemical analysis, it is worth noting that the molar ratio Ca/P of the dried or calcined HAP powders equals to 1.66, larger than that of β-$Ca_3(PO_4$ (Ca/P = 1.5), suggesting that the prepared calcium phosphate biomaterials are extremely stoichiometric. The porous characteristics of the as-prepared biomaterials are determined, indicating similar surface area HAP (90 $m^2.g^{-1}$) and TCP (86 $m^2.g^{-1}$), though when materials are calcined at 900°C, the specific surface area is dramatically reduced in the case of the β-TCP (8 $m^2.g^{-1}$) compared to the HAP case (25 $m^2.g^{-1}$). The dilatometric analysis was used to study the shrinkage mechanism during sintering. As a rule, the dilatometer curves of the complete cycles give a general idea on the behaviour of the both biomaterials during the whole thermal cycle putting in evidence any dilatometric anomaly or defect. Fig. 1 shows the dilatometric curves for HAP and β-TCP compacts recorded during a complete sintering cycle. It can be observed that the β-TCP and HAP compact starts to sinter at critical temperature T_c of 1160°C and 1200°C, respectively. The small deviation of 40°C can be due to the full-size grains of the β-TCP and consequently to its higher packing density. Beyond 1300°C, the same shrinkage rate is reached for both samples. At the critical temperature, the optimum time is 3 hours sufficiently large to obtain a good densification.

The sintering temperature and the particle size influence strongly the densification, which subsequently affects the resulting mechanical properties. From SEM analysis reported elsewhere [21–22], the mean size of individual particles increases from 3 μm to 12 μm. Therefore, the densities of the sintered bodies clearly depend on the crystalline growth of HAP and β-TCP particles and the removal of the most specimen porosity. Nevertheless, the irregularity of the high-temperature density is due only to the pores generation after the heat

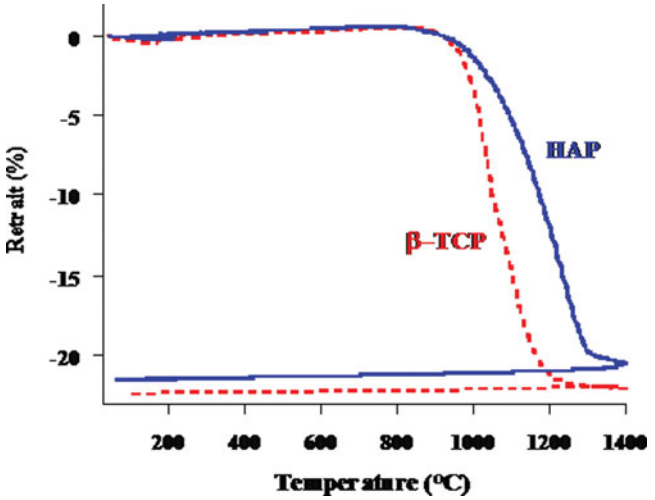

Figure 1. Dilatometric curves from HAP and β-TCP recorded using the thermal cycle employed to sinter the multilayered biomaterials.

treatment. The mechanical properties of the HAP and β-TCP bioceramics in dry environment were firstly investigated and related results are reported elsewhere [21–22]. Results of tests (flexural strength, Young modulus, Vickers hardness and Toughness) performed on the un-exposed samples versus sintering temperature are gathered in Table 1. Data reveal a significant loss in mechanical properties for sintering temperatures up to critical T_c (1160°C for β-TCP and 1200°C for HAP), induced by an apparent density change. The decrease in density up T_c attributed to the presence of micro-cracks and pore generation such as showed by SEM images [21–22). The maximum K_{1c} and flexion toughness values obtained in this study are close to those reported for other biomaterials [19–20]. The advantages of current HAP and β-TCP materials are low-cost of synthesis route as well as their high densities. Above T_c taken as critical sintering temperature, mechanical characteristics declined due to both the pore generation and the presence of micro-cracks even if no major structure change is stated from XRD and SEM analyses [21–22].

However, the exposure to water environment at neutral pH and physiological temperature of 37°C, the flexion strength and fracture toughness-indentation (K_{1c}) of HAP and β-TCP bioceramics are degraded (Figs. 2 and 3). Such deterioration is ascribed to the sorption of water molecules at ceramics surfaces affecting further the relative density which fell from 98% to 91% and 81% for HAP and β-TCP bioceramics, respectively. Precisely, fracture toughness of water-exposed sample is reduced by 35% compared to same bioceramics in dry condition

Table 1. Mechanical data for HAP and β-TCP bioceramics.

Sintering temperature (°C)		1100	1160	1200	1250
Density (%)	HAP	90.02	93.13	97.87	98.66
	β-TCP	97.04	98.3	97.25	95.00
Young's modulus (GPa)	HAP	97	99	108	100
	β-TCP	95	97.5	94	89
Flexion strength (MPa)	HAP	16	28	35	45
	β-TCP	33	46	50	48
Indentation (K_{1c}) ($MPa.m^{1/2}$)	HAP	0.51	0.7	0.96	0.92
	β-TCP	1.34	1.62	1.48	1.27

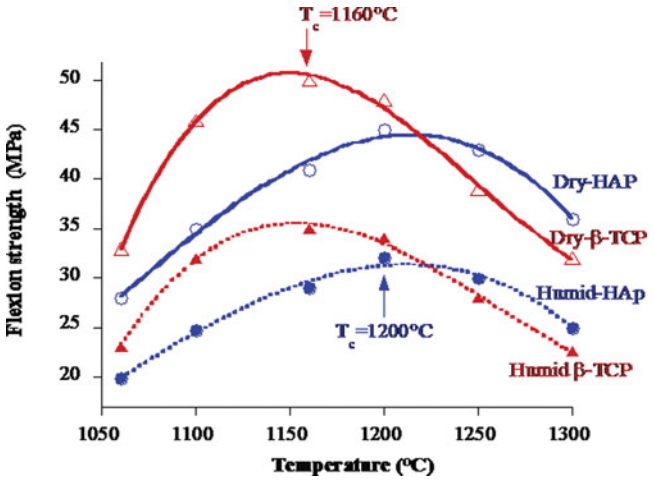

Figure 2. The evolution of the flexion strength versus sintering temperature for un-exposed, exposed HAP and β-TCP bioceramics to water.

(Fig. 3), but β-TCP exhibits farther reduction compared to HAP ceramic. In the presence of water, the interference between water and HAP ceramic surface reduces the intermolecular forces. As result, higher proton mobility and increase of free volume affect density and the strength.

As consequence, flexion strength as well as indentation K_{1c} characteristics are much decreased. The hydration of calcium phosphate ceramic makes into double nature: (i) water bound by high-energy sorption centres stabilizating through intramolecular hydrogen bond; (ii) structural water bounded to the hydrophilic phosphate groups (PO_4^{3-}) to form P-OH responsible in fixing the biological species at implant/bone [24]. Moreover, it is widely believed that water is the first molecule to contact biomaterials in any clinical application.

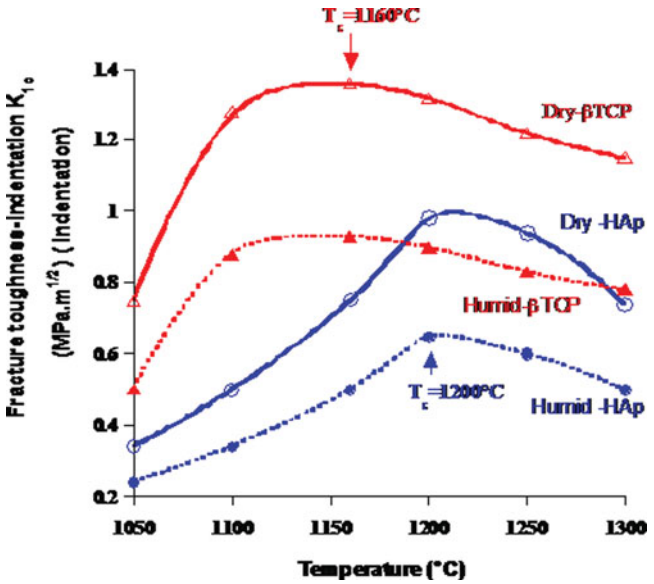

Figure 3. Variation of fracture toughness-indentation (K1c) versus sintering temperature for un-exposed, exposed HAP and β-TCP bioceramics to water.

Another feature of ion solvation important in biomaterials is that Ca^{2+} ions are more hydrated than PO_4^{3-} affecting the porosity and density of ceramics. Regardless of sintering process in dry and wet conditions, there is a definite correlation between mechanical greatnesses and grain size in HAP and β-TCP materials. Consequently, the physico-chemical and mechanical properties of calcium phosphate ceramics and the environment, in which they are placed, are an interesting study because many materials, when placed in an aqueous environment, absorb water by a diffusion process and afterward their mechanical characteristics are affected.

Conclusion

This study was to determine the mechanical properties of hydroxyapatite and β-tricalcium phosphate ceramics in water environment, which they are very sensitive to the grains size and densification process. The flexion strength and fracture toughness of water-exposed bioceramics are degraded. The occurrence of this phenomenon seems to be related to the hydradation process via the water diffusion into HAP and β-TCP structures affecting the granular growth, which subsequently influences the relative density.

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