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Stoichiometry and particle morphology effects on the aptitude to compaction of apatitic structure powders

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A B S T R A C T

Apatitic calcium phosphates powders with Ca/P molar ratio of 1.5 to 1.8 were synthesized at 25 °C using the neutralization method. These powders, differing by stoichiometry and particle morphology, were compacted in similar conditions. For a similar morphology of particles, compacts of the non-stoichiometric powders have better cohesion than those of the stoichiometric hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$: Ca/P = 1.67). The lacunar structure, with deficiency of calcium ($Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$: $1.5 < Ca/P < 1.67$), seems to favour the densification process and cohesion between particles during the compaction. The better tensile strength (0.79 MPa) was obtained for the powder with the lowest atomic ratio (Ca/P = 1.5, $x = 1$). The apatite powder (Ca/P = 1.78), which has a smooth and porous structure, presented the best transmission load ratio (95.5%), the lowest die-wall friction ($\mu = 0.1$) and the highest strength (3.12 MPa). These results show the importance of chemical composition and morphological properties of synthesized particles in the development of better hydroxyapatite powders for the compaction process.

Keywords:
Hydroxyapatite powders
Die-compaction
Mechanical properties

1. Introduction

Biomaterials synthesized from calcium phosphates such as hydroxyapatite (HAP) $Ca_{10}(PO_4)_6(OH)_2$, are frequently used as substitutes for the treatment of pathologies in dental surgery. These biomaterials present a good biocompatibility and an excellent bioactivity [1,2]. Calcium phosphates are prepared in different forms: powder, granule or block. For implants with a shape adapted to the bone defect, the powders are compacted in shaped die. To increase the density of the piece, a sintering operation follows the cold compaction. However, the inherent problems of the calcium phosphate, especially hydroxyapaptite, are the poor mechanical properties of the resulting compact [3]. The mechanical properties of this material are largely dependent on their micro-structural features, such as micro-structural defects [4,5] and sintered density. The first important step in producing dense materials is the preparation of a fine powder with particle properties favourable to the compaction. Recently, various studies on the preparation of apatites with different stoichiometry and morphology have been carried out. The aim of this study is to bring a better understanding of the relation between the microstructure and the aptitude of powders to cold compaction. For this purpose, apatitic calcium phosphate powders with different particles properties, were synthesized by the neutralization method (1).

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \quad (1)$$

The reactants do not contain counter ions that could replace the apatitic sites and influence the aptitude to compression of the powders. As raw material we used ortho-phosphoric acid (produced in Morocco by EMAPHOS — Euro-Maroc-PHOSphore) with controlled chemical composition, and calcium carbonate used in the production of pharmaceutical drugs. We examined the influencing parameters such as stoichiometry, granule morphology and surface properties on the aptitude of apatitic structure powders to compaction.

2. Materials and methods

2.1. Powder synthesis

The synthesis was carried out by reaction between the calcium hydroxide and the ortho-phosphoric acid. In the first stage, calcium oxide is dispersed under agitation in double distilled water. The calcium oxide is prepared by calcination of $CaCO_3$ (Merck 99%) at 900 °C for a period of 24 h. The acid solution is made from ortho-phosphoric acid (EMAPHOS 85%) and added to the suspension under mechanical agitation. The reaction is carried out at 25 °C and pH = 5.5 to 9. The precipitate obtained is filtered and dried at 105 °C for 24 h. Five apatitic powders were prepared with atomic ratio Ca/P between

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Table 1
Characteristics of synthesis materials

Materials	Ca/P molar ratio (±0.005)	Mean particle size (μm)	True density g /cm^3	Bulk density g /cm^3
HAP 1	1.512	91.2±0.1	2.6806±0.020	0.403
HAP 2	1.622	81.9±1.0	2.9234±0.019	0.412
HAP 3	1.630	89.4±0.8	2.9794±0.003	0.403
HAP4	1.676	90±1.0	–	–
HAP 5	1.720	76.4±1.2	2.9103±0.022	0.411
HAP 6	1.781	15.2±0.5	3.0014±0.018	0.202

1.5 and 1.8. The sample was referred as HAP1, HAP2, HAP3, HAP4 and HAP5. Also, Carbonate-apatitic powder was synthesized in the same condition at pH=8, in presence of ions carbonates. The sample was referred as HAP6.

2.2. Characterization of powders

The physical and chemical analyses were carried out on the dried precipitate and the powder calcined at 900 °C for 24 h. The phases formed were identified by the atomic ratios Ca/P, determined by infrared spectroscopy (Perkin-Elmer FTIR 1600), and by X-ray diffraction (Counter D500, λ_{Cu}=1.5408 Å). The software used for data processing of X-ray diffraction was DIFFRACT/AT. The ratio of calcium and phosphorus was determined by an atomic emission spectrophotometer with argon plasma and inductive coupling (ICP-AES) using the wavelengths characteristic of calcium λ=317.933 nm and of phosphorus λ=213.618 nm. Laser diffraction was used to analyse particle size on the Mastersizer 2000 (from Malvern Instruments Ltd.). The true density ((ρ_{true} g/cm^3) was determined using a helium pycnometer (Accupyc 1330, Micrometrics Instruments). Morphologies of granules were observed using a Scanning Electron Microscope.

2.3. Powder compaction

The synthesised materials (HAP sample 1 to 5) were ground in a mortar. The powder obtained was sieved to obtain a particle size ranging from 40 to 125 μm. The HAP6 sample was not ground as its particle size was lower than 40 μm. Tablets of 0.4±0.01 g of powder were prepared by compaction using a reciprocating press (Frogerais OA). The upper and lower punchs were instrumented with load and displacement sensors. The cylindrical die of 11.28 mm in diameter was instrumented with a gauge measuring the radial stress during the compaction cycle. The gauge was positioned at 1.5 mm from the position of the lower punch. Thus, at the end of the compaction, the tablet height was between 3 and 3.5 mm and thus, the gauge measures the radial stress at the middle of the tablet. As the radial stress depends on the tablet height, the measured value will be considered as the mean along the height. The powder was poured into the die and compacted at different pressures. To define the range of admissible pressures where the samples could be compacted (and compared), two pressures were characterized for each sample: the lowest pressure needed to form a tablet easy to handle and the highest pressure after which systematic capping happened. The lower pressures were estimated in the range 30–40 MPa and the maximum pressures were in the range 90–110 MPa. Once the tablet ejected, its mass was measured with an electronic balance (CP 224S — Sartorius Germany) and its dimensions were measured with digital micrometer (Mitutoyo). The apparent and relative densities were recorded. The diametrical crushing load was also measured with the Erweka TBH 30 apparatus.

2.4. Characterization of the compaction

In the compaction process, two ratios are classically used to compare and analyze the behavior of powders. The transmission ratio (2), defined as the ratio of the transmitted pressure σ_b to the bottom punch over the applied pressure σ_u on the upper punch. This ratio measures the capacity of powder to transmit the load from the top to the bottom of the powder bed. The transfer ratio (3) represents the ratio of the radial pressure σ_r over the applied pressure σ_u [6].

$$tr = \sigma_b/\sigma_u \tag{2}$$

$$\alpha = \sigma_r/\sigma_u \tag{3}$$

Due to the load transfer to the radial direction, a part of the energy of the compaction is stored as elastic energy in the die. During the unloading, a part of this elastic energy is restored to the tablet and contributes to the tension of the tablet. During the compaction, the die wall friction is the dominant property that controls the density

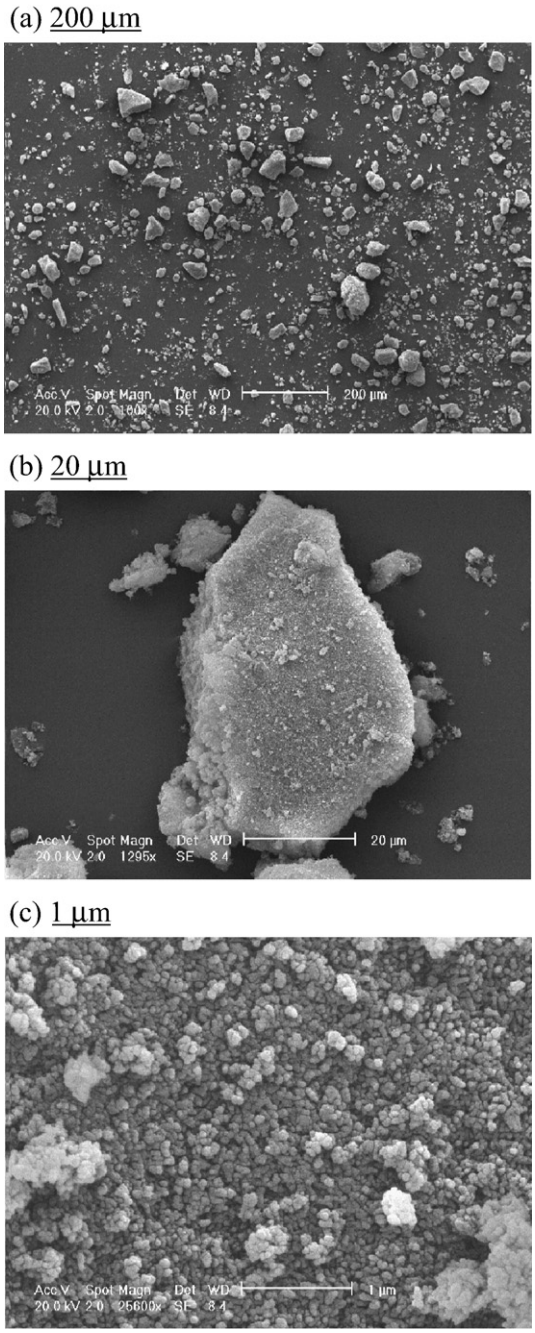

Fig. 1. SEM micrographs of the synthesised powder HAP1 (Ca/P=1.512). (a) Polydispersed population, (b) granule of the powder, (c) typically surface morphology.

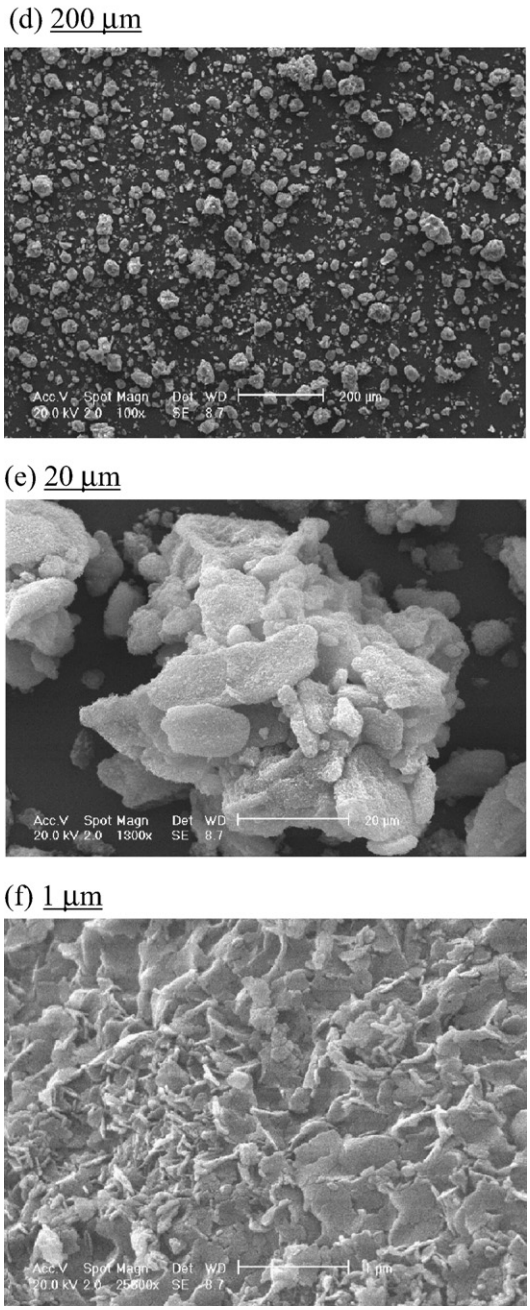

Fig. 2. SEM micrographs of the synthesised powder HAP6 Ca/P = 1.781. (d) Poly-dispersed population, (e) granule of the powder, (f) typically surface morphology.

distribution and the load transmission over the powder bed. Assuming the Coulomb friction and adopting the 'method of differential slices' [7], the die-wall friction may be obtained:

$$\mu = \ln(\sigma_b/\sigma_u)/(-4\alpha H/D) \quad (4)$$

where H/D named the aspect ratio, is the ratio of the height over the diameter of the tablet at the end of the compaction. The tensile strength (σ_t) of the tablet was calculated from the diametrical crushing load F as:

$$\sigma_t = 2F/(\pi DH) \quad (5)$$

To analyze the aptitude of powders to compaction and to establish correlations with stoichiometric ratio and particles morphologies, a pressure of 70 MPa (value in the admissible pressures range of all the samples) was used.

3. Results

3.1. Population, morphology, composition of granules

Chemical analyses of the calcium and phosphorus elements, carried out by ICP, enabled us to calculate the atomic molar ratio Ca/P of all the samples. The results are given in Table 1.

Scanning Electron Microscopy images of the samples showed two structure groups (Figs. 1 and 2). Micrographs of the powder HAP1 (HAP2, HAP3, HAP4 and HAP5 were similar to HAP1) showed poly-dispersed population (a), irregular granule shape, composed of small spherical particle agglomerates (b), and a rough surface (c). The typical agglomerate size of these powders was 91.2 ± 1.0 µm (for the other powders, values are given in the Table 1). Indeed, micrographs of the powder HAP6 (Fig. 2) showed a mono-dispersed population (d), spherical particles in an assembly of agglomerate layers (e) and presented a smooth surface (f). The means agglomerates size was 15.2 ± 0.5 µm. Furthermore, there is a more important intra-granular porosity comparative to powders HAP1… HAP5.

Characterization the synthesised powders by infrared spectroscopy (Fig. 3) showed for all the samples the characteristic bands of phosphate groups at 470, 560–600, 960, 1030–1120 cm^{-1}. The bands at 630 and 3560 cm^{-1} were characteristic of groups OH. A band at 875 cm^{-1} could be attributed to HPO_4 which is characteristic of calcium deficient hydroxyapatite (samples HAP1, 2 and 3). The bands at 1640 cm^{-1} and the bands at 875.4, 1420 and 1450 cm^{-1} indicate respectively the presence of traces of water and carbonate groups. The sample 6 clearly showed some CO^{3-}derived bands observed at 870 cm^{-1} and around 1420–1480 cm^{-1} characteristic of carbonate apatite.

The XRD patterns of the precipitated powders are shown in Fig. 4. All powders dried at 105 °C had the same apatitic structure as hydroxyapatite and no other crystalline phase was detected (Fig. 4b). During the calcination at 900 °C of the samples 1 to 5 (Fig. 4a), a calcium excess (Ca/P > 1.67 for sample 5) resulted in the presence of

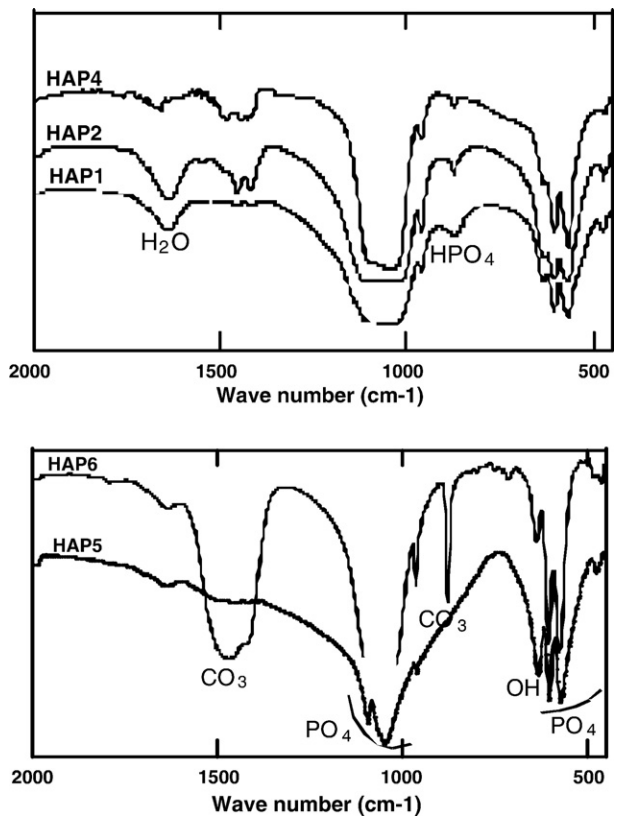

Fig. 3. IR spectrum of synthesised powders (HAP1, HAP2, HAP4, HAP5 and HAP6).

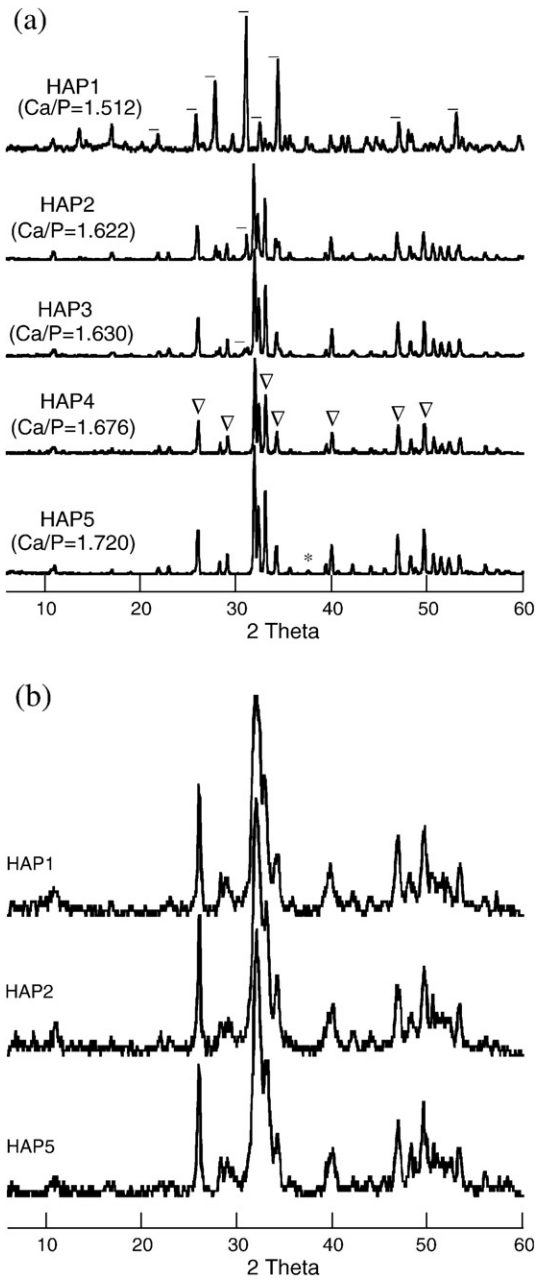

Fig. 4. XRD pattern of calcined powder (a) and synthesized powder (b). −β−$Ca_3(PO_4)_2$, Δ $Ca_{10}(PO_4)_6(OH)_2$, ∗$Ca(OH)_2$

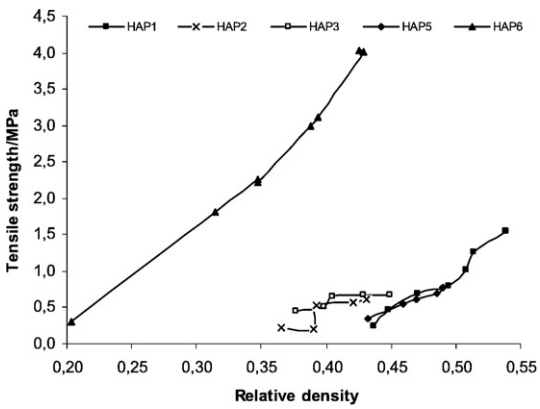

Fig. 5. Tensile strength versus relative density of tablets prepared from HAP powders.

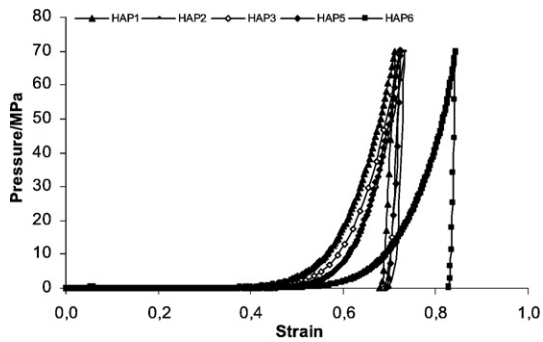

Fig. 6. Axial pressure versus axial strain during die-compaction of HAP powders.

calcium oxide as the secondary phase, whereas a phosphorus excess (Ca/P < 1.67 for samples 1, 2, and 3) results in the presence of tri-calcium phosphate type (β-TCP) [8]. The initial apatite dissociated into a mixture of HAP and β-TCP according to the overall reaction:

$$Ca_{10-x}(HPO_4)_x(PO4)_{6-x}(OH)_{2-x} \rightarrow (1-x)Ca_{10}(PO_4)_6(OH)_2 + 3xCa_3(PO_4)_2 + xH_2O, \text{ With } 0 \le x \le 1$$

The XRD patterns of the sample HAP1 with $x \approx 1$ highlights the structure of pure tricalcic phosphate β-$Ca_3(PO_4)_2$. This indicates that the initial powder has the formula: $Ca_9(HPO_4)(PO_4)_5OH$.

The XRD patterns of the sample 4 with $x = 0$ (Fig. 4) highlights the structure of the stoichiometric hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$.

3.2. Aptitude of powders to the die-compaction

The compressive behaviour of the powders of apatitic structure with different molar fractions and two different morphologies were analysed prior to the aptitude to compression. The admissible pressures of the studied powders were estimated between 30 and 110 MPa. The tensile strength versus relative density of powders in this pressure range, is plotted in Fig. 5. The results concerning stoichiometric apatite (HAP4) are not presented because of the low cohesivity of the powder. For samples HAP1 (Ca/P = 1.512) and HAP6 (Ca/P = 1.781), the tensile strength increases with pressure. However, strength of powder HAP3 (Ca/P = 1.630) and HAP5 (Ca/P = 1.720) underwent little changes and remains weak.

The axial stress versus the axial strain of the compaction at 70 MPa, is plotted in Fig. 6. Curves showed the better compressibility for the powder HAP6 (the axial strain of the bed at 70 MPa was higher 84%) whereas the bed of powders HAP1, 2, 3 and 5 was deformed up to 70%. The aptitude of the powders to compaction was characterised by the transmission ratio (Eq. (1)), the transfer ratio (Eq. (2)) and the die-wall friction (Eq. (3)) calculated from measurements at the end of the compaction. Values of these ratios are reported in the Table 2. The transmission ratio was found to be in the range 71–95.5%, the powder HAP6 gave the highest value (95.5%), followed by the powders HAP1, HAP2 and HAP3 (90%; 90%; 88%). The lowest value of the transmission was obtained with the powder HAP5 (71%). The transfer ratio was between 41.8 and 45.8. The powders HAP1, 5 and 6 show similar

Table 2
Mechanical properties of compact

Material	Relative density	Transmission ratio	Transfer ratio	Die-wall friction	Tensile strength (MPa)
HAP 1	0.4905	90	41.8	0.22	0.79 ± 0.02
HAP 2	0.4307	90	45.3	0.20	0.61 ± 0.03
HAP 3	0.4489	88	45.8	0.24	0.67 ± 0.08
HAP 5	0.4599	71	43	0.69	0.55 ± 0.03
HAP 6	0.3936	95.5	42	0.1	3.12 ± 0.08

values 41.8, 43 and 42, indeed, the transfer ratio of the powders HAP2 and HAP3 takes 45.3 and 45.8. The ratio characterizing the die-wall friction gave complementary information on the behaviour of the powders. This ratio is 0.1 for the powder HAP6, and 0.2 to 0.24 for the powders HAP1, HAP2 and HAP3 and 0.69 for the powder HAP5.

In the last column of the Table 2, the tensile strength of the powders compacted at 70 MPa are given and the values showed the highest value for the powders HAP6 (3.12 MPa) and the lowest value for the powder HAP 5 (0.55 MPa).

4. Discussion

4.1. Stoichiometry and morphology of apatitic granules

Various physicochemical analyses give the compositions and the morphologies of all the powders prepared. All the powders have a badly crystallized apatitic structure. The sample HAP4 of atomic ratio Ca/P = 1.676 corresponds to a stoichiometric hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$).

The samples HAP1, 2 and 3 are Ca-deficient apatites with substitutions of grouping PO_4 by HPO_4 according to the formula: $(Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x})$ x takes the values 0.268 and 0.220 successively for the powders HAP2 and HAP3. The powder 1 of atomic ratio Ca/P = 1.512 ($x \approx 1$) corresponds to tricalcium phosphate of apatitic structure ($Ca_9(HPO_4)(PO_4)_5OH$). Sample 5 of atomic ratio Ca/P = 1.720 is a hydroxyapatite with a slight excess in calcium. The simples (1 to 5) showed similar shape and particle size. It appears to have a non regular shape and a poly dispersed paricle size. Also, low intra-granular porosities may be noted. The effect of stoichiometry on the morphology of these powders was negligible. Measurements of the specific surface and true density show little differences between the powders.

The sample HAP6 is an apatite carbonate where ions PO_4 are substituted by carbonate ions. This powder shows a rounded shape and near regular size. Moreover, observation of granule shows a smooth surface of the layers and an important intra-granular porosity due to the geometrical structure of the granule. The bulk density of the powder HAP6 was twice the bulk density of the powders HAP1 to 5. This was mainly due to the porous structure of the granules of the powder HAP6.

4.2. Effect of stoichiometry and morphology on the aptitude to the compaction

For the powders HAP1, 2 and 3, the transmission ratio and the die-wall friction were similar for the compaction up to 70 MPa. The resulting tensile strength (0.61–0.79 MPa) shows the best tensile value for the powder HAP1 (0.79 MPa). The lowest value of the transfer ratio for this powder (α = 41.8) means that the elastic energy stored in the die during the compaction was lower than the case of compaction of the powders 2 and 3 (α = 45.3–45.8). During the decompression step, the elastic energy restored to the tablet was thus lower for the powder 1. This favours tension in the tablet and may reduce the tensile strength. The lower value of the tensile strength of the powder HAP5 could be explained by the high value of the die-wall friction (μ = 0.69) and the bad transmission ratio (tr = 71%). In these conditions, the top of the tablet was quite compacted, whereas, the bottom was poorly compressed. These results indicate that stoichiometry and non-stoichiometry plays an important role for the aptitude to the compaction. The substitution of ions PO_4 by ions hydrogeno-phosphate (HPO_4) in the network leads to an apatite that lacks calcium. Electric neutrality is then ensured by reduction in the cation load, by substitution of Ca, and then by the creation of vacancy according to the formula ($Ca_{10-x}\square_x(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ where $\square$ represents ionic vacancies) $0 \leq x \leq 1$. The amount of hydrogeno-phosphate ions and the vacant sites increase with the reduction in the Ca/P ratio. Comparatively to the powders 2, 3, 4 and 5, the better tensile strength of the powder HAP1 (Ca/P = 1.521) was probably due to the chemical composition where the presence of voids and molecular groups HPO_4 were important. This structure seems to support the connection between particles during the compaction. The sample 5 with excess in Ca presented the highest value of die-wall friction and the sample 4 with Ca/P = 1.676 presents a bad cohesion between the particles. The overall results indicate that the good aptitude with the compaction decreases, following the sequence of Ca/P: 1.512 > 1.622 > 1.630 > 1.720 > 1.676.

The low value of the die-wall friction (μ = 0.1) of the powder HAP6 (Ca/P = 1.781) may be attributed to the smooth porous structure of the granules surface. The brittle and porous structures of the granules act in favour of the compressibility. In fact, the better transmission ratio (95.5%) and the low die-wall friction favours the homogeneous density and hence the highest tensile strength. It could be concluded, that the morphology in its smoothness and the porous structures of the granule surface were the most important factor for the aptitude to the compaction than the non stoichiometry.

The overall results show the importance of chemical composition and morphological properties of synthesized particles in the development of better hydroxyapatite powders for the compaction process.

5. Conclusion

In this study, we have examined parameters such as stoichiometry, granule morphology and surface properties which influence the aptitude to compaction of apatitic structure powders. The samples were synthesized at low temperature using the neutralization method and compacted in similar conditions. The results indicate that stoichiometry plays an important role for the aptitude to the compaction. During compression, the lacunar structure of Ca-deficient apatites seems to support the cohesion between particles. But the morphology in its smoothness and the porous structures of the granule surface were the most important factors for the aptitude to the compaction that leads to the homogeneous density and hence the highest tensile strength.

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