Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 25 (2005) 375–383

www.elsevier.com/locate/jeurceramsoc

Processing and mechanical properties of hydroxyapatite pieces obtained by the gelcasting method

S. Padilla[a], M. Vallet-Regí[a,*], M. P. Ginebra[b], F. J. Gil[b]

[a] *Departamento de Química Inorgánica y Bioinorgánica, Facultad de Farmacia, Universidad Complutense de Madrid,*
Pza Ramon y Cajal s/n, 28040 Madrid, Spain
[b] *Departament de Ciència dels Materials i Enginyeria Metal-lúrgica, Universitat Politècnica de Catalunya,*
Av. Diagonal 647, 08028 Barcelona, Spain

Received 16 October 2003; received in revised form 18 February 2004; accepted 25 February 2004
Available online 21 July 2004

Abstract

The aim of this work was to prepare hydroxyapatite (HA) pieces, by the gelcasting method, with appropriate mechanical properties for using as bone implants. The mechanical properties of the obtained pieces were evaluated. The influence of the solid content on the rheological behaviour of the slurries and, in turn, on the mechanical properties, was investigated. Pieces were prepared by using slurries containing 55 and 60 vol.% of an HA calcined at 1200 °C and 47 vol.% of HA calcined at 1100 °C. HA powders calcined at lower temperature than 1100 °C were not suitable for producing concentrated slurries. The raw and calcined HA were characterised by XRD, FTIR, X-ray fluorescence and elemental analysis. The pieces sintered at different temperatures and times were characterised by XRD, and the sintering treatment applied to the specimens for mechanical testing (1300 °C for 24 h) was selected taking into account the phases present after sintering.

The mechanical properties of the green bodies were higher than obtained by other methods and the ones of the final pieces were comparable to those obtained by other techniques. The results indicated that slurries with a solid content higher than a limit value (for which limited contraction occurs) must be used and that the rheological properties of the slurries play an important role in the mechanical properties of the resulting pieces.

Keywords: Gelcasting; Apatite; Suspensions; Sintering; Mechanical properties

1. Introduction

Hydroxyapatite (HA) is the main inorganic component of the hard tissues (bone and teeth) of vertebrate animals and humans. For this reason HA has received considerable attention over the past three decades as an implant material showing excellent biocompatibility.[1,2] Many efforts have been made in order to improve the mechanical properties of HA and several forming techniques have been used. In addition to common pressing method (uniaxial,[3] hot pressing,[4] hot isostatic pressing[5]), other methods have been proposed, such as slip-casting,[6,7] tape-casting,[8,9] injection moulding[10] and viscous plastic processing.[11]

Colloidal processing offers the potential to produce reliably ceramic films and bulk forms through careful control of the initial suspension “structure” and its evolution during fabrication.[12] Among these methods, the gelcasting has significant advantages over the other processes, in terms of dimensional accuracy and complex shaping capabilities, the uniform structure and high strength of the green bodies, simplicity, as well reduced manufacturing cost. Therefore, the gelcasting method would be very useful to obtain pieces of HA with complex shapes, as it is required for clinical applications.

The gelcasting process is based on the gelling, by in situ polymerisation, of a concentrated ceramic slurry suspended in a monomeric solution. The as-formed organic network encapsulates the ceramic particles, producing very uniform green bodies with high strength. This method differs from slip-casting, which has been used for complex forming of HA, in the solidification step. In the former, the solidification occurs via gelification and in the latter it is induced by fluid removal: the fluid flows into a porous gypsum mould via capillary-driven transport. Therefore, slip-casting requires rather long process times and the strength of the green bodies

---

[*] Corresponding author. Tel.: +34-91-3941861; fax: +34-91-3941786.
E-mail address: vallet@farm.ucm.es (M. Vallet-Regí).

0955-2219/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2004.02.017

is weak. In addition, the density gradient in thick green bodies become significant. The notable merit of gelcasting, compared to slip-casting, is that the green bodies are uniform and strong.

Gelcasting has rapidly developed in the past decade as a promising colloidal in situ forming technique. It has been utilised in the forming of many sorts of ceramic material systems.[13–24] However, few reports about the use of this method for HA shaping are found in the literature.[25] In that work[25] a 38 vol.% suspension was prepared and by using a foaming agent porous ceramics were obtained. One of the reasons why this method has not been used to prepare HA ceramics seems to be the difficulty of preparing HA slurries with a high solid content (>50 vol.%), which is one of the requirements. In most of the works dealing with the preparation of HA suspensions, only solid contents equal[29] or lower[7,26–28] than 50 vol.% have been achieved.

In order to prepare HA suspensions with a solid content higher than 50 vol.%, different factors affecting the colloidal stability of HA slurries were studied in a previous work.[30] The parameters studied were the calcination temperature of the HA powder, its particle size and distribution, the type and concentration of dispersant, the pH of the dispersing medium, the mixing time and solid concentration. Slurries with a concentration of solids as high as 60 vol.% were obtained by using an HA calcined at 1200 °C, dry milled for 20 h and using Darvan 811 as dispersant. The decrease of the surface area and porosity of the HA powders with the calcination temperature reduced significantly the viscosity of the slurries and, therefore, suspensions with a solid content higher than 50 vol.% could only be obtained with HA calcined at 1200 °C.

The aim of this work was to evaluate the mechanical properties of the pieces obtained by the gelcasting method and to study the influence of the solid content on the rheological behaviour of the slurries and, in turn, on the mechanical properties. Pieces were obtained from slurries containing 55 and 60 vol.% of an HA calcined at 1200 °C. On the other hand, considering that the sintering process could not be effective enough when this HA was used, pieces from a slurry containing HA calcined at 1100 °C were also prepared, but in this case the maximum solid content that could be reached was lower.

2. Materials and methods

2.1. HA preparation and characterisation

The synthesis of HA was carried out by the precipitation method by reaction of an aqueous slurry of $Ca(OH)_2$ (Riedel-DeHäen) with a solution of H_3PO_4 (Merck) as previously described.[30] The obtained powder was ground in a vibrating mill and then calcined at 1100 °C (HA-1100) or at 1200 °C (HA-1200) for 1 h. The calcined powders were dry milled for 20 h.

The initial and calcined HA were characterised by XRD, FTIR, elemental analysis and X-ray fluorescence. Phase composition was determined by XRD in a Philips X'Pert MPD diffractometer (Cu Kα radiation) in the range of 5–120° 2θ with step size of 0.02° and a time per step of 10 s. Quantitative analysis of Ca and P were performed by X-ray fluorescence on a S4 EXPLORER, Brucker AXS equipped with an Rh X-ray tube (1000 W, 50 mA). The elemental analysis was carried out in a Leco CNS-200 carbon, nitrogen and sulphur analyser. FTIR analyses were made on a Nicolet Nexus spectrometer.

2.2. Rheological measurements

Rheological measurements were carried out at 20 °C in a Haake ReoStress RS75 rheometer with a cone-plaque system, in the shear rate range of 1–700 s^{-1}.

The surface area (BET-N_2 adsorption method, Micromeritics AutoPore III) of HA powder calcined at 1100 °C milled for 20 h was equal to 8.3 m^2/g and the average particle size (Sedigraph Micromeritics 5100) was 0.7 μm whereas the surface area of HA-1200 powder after milling for 20 h was 3.5 m^2/g and the average particle size was 3 μm.

2.3. Suspensions and pieces preparation

The suspension vehicle was an aqueous solution containing 15 wt.% of methacrylamide (Aldrich) and *N*,*N*′-methylenebisacrylamide (Aldrich) monomers in a 6/1 ratio.

The conditions to prepare slurries with HA calcined at 1200 °C were established in a previous work.[30] The HA was dry milled for 20 h, Darvan 811 (R.T. Vanderbilt Company, Inc.) was used as dispersant (concentration, 5 mg/m^2) and the components of slurries were mixed for 30 min. To prepare slurries with HA-1100 the same conditions were used except for the concentration of dispersant, since it had been previously established that the amount of dispersant for obtaining the lowest viscosity in slurries of HA calcined at 900 and 1200 °C was different.[30] To determine the best dispersant concentration for dispersing HA-1100 slurries, the variation of viscosity of slurries containing 40 vol.% as a function of D811 concentration was studied.

In order to study the maximum content of solid for which the slurries are fluid enough for casting and degassing, slurries with different content of solid were prepared.

The HA suspensions were prepared by mixing the suspension vehicle, the dispersant and the HA powder in a planetary ball mill for 30 min. After this time, appropriate amounts of a 10 wt.% solution of ammonium persulphate (Aldrich) and a 99 wt.% solution of *N*,*N*,*N*′,*N*′-tetramethylene diamine (Aldrich) were added as initiator and catalyst, respectively and mixed for 3 min.

The as obtained suspension was cast into moulds (55-mm length, 8-mm width and 5-mm height) put on a vibrating surface. After that, the moulds were placed in a cham-

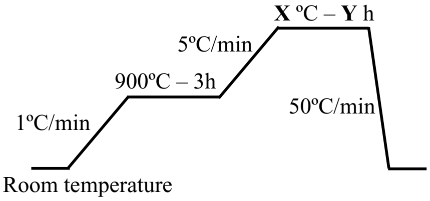

Fig. 1. Scheme of the thermal treatment applied to the pieces. **X**: 1300 or 1400 °C, **Y**: 1, 6, 12 or 24 h.

ber and vacuum was applied in order to eliminate the air bubbles trapped inside the suspension, after a N_2 was applied for 15 min. Then, the closed chamber was heated up to 50 °C for 2.5 h in order to gel the system. The gelled pieces were carefully dried in four steps to avoid cracking. They were kept first for 4 h at 92% relative humidity (RH), then at 72% RH for 15 h, and dried 8 h under normal atmosphere at room temperature. Finally, they were dried at 50 °C for 12 h.

Different thermal treatments were applied at 1300 and 1400 °C for 1, 6, 12 and 24 h in order to select the sintering temperature taking into account the phase composition after sintering. The thermal treatment applied was 900 °C for 3 h using a heating rate of 1 °C/min and, finally, at 5 °C/min until reaching the sintering temperature (Fig. 1).

2.4. Piece characterisation

The phase composition of sintered pieces was determined by XRD as described above. First, the surface was analysed by glancing angle XRD and after that, the pieces were ground and the powder analysed. The phase quantification was made by the Rietveld method[31] using the X'Pert Plus software (Philips).

The SEM study of the as find surface and of the fracture surface was made in a JEOL 6400 Microscope-Oxford Pentafet super ATW system; the samples were gold plated. The density and porosity of pieces (two specimens) were determined by Hg intrusion porosimetry in a Micromeritics ASAP2010 porosimeter. The contraction (eight specimens) was determined by geometrical measurements before and after sintering.

Flexural strength was measured using the four-point configuration in a MTS Bionix 858 equipped with a load cell of 2.5 kN and following the standard MIL-STD-1942.[32] The crosshead speed was 0.5 mm/min. Outer and inner spans were 40 and 20 mm, respectively. The strength values reported are the average of at least eight measurements. The indentation test was performed in a Matzuzawa microhardness tester, with a Vickers indenter, applying a load of 0.5 kg for 15 s. Interference lenses were used in the optic microscope to determine clearly the indentation. The mechanical properties were measured after surface polishing. The statistical analyses were carried out using the ANOVA test ($P < 0.05$).

3. Results

3.1. HA characterisation

X-ray fluorescence was carried out on the raw powder finding the following elemental composition: 40.15 wt.% Ca, 18.47 wt.% P, which leads to a molar ratio $Ca/P = 1.68 \pm 0.04$. The XRD patterns of the initial and calcined HA at 1100 and 1200 °C are shown in Fig. 2a. Raw HA and calcined powders at 1100 °C only showed maxima corresponding to HA[33] while the pattern of HA calcined at 1200 °C showed in addition two maxima corresponding to CaO.[34] The content of CaO as determined by the Rietveld method was 1.3 wt.%.

The IR spectrum of raw HA shows (Fig. 2b) the bands corresponding to PO_4^{3-} group at 1092 (ν_3) and 1040 cm^{-1} (ν_3), 962 (ν_1), 603 (ν_4) and 567 cm^{-1} (ν_4), together with the bands at 3569 (ν) and 631 cm^{-1} (librational mode) assigned

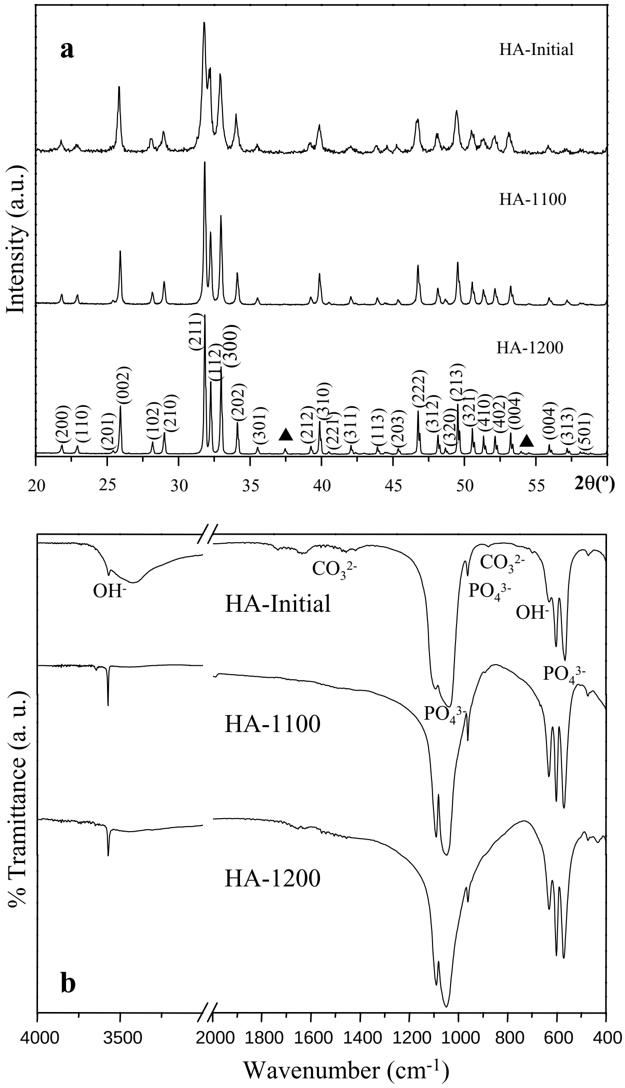

Fig. 2. (a) XRD patterns and (b) FTIR spectra of HA powders calcined at different temperatures. The symbol (▲) corresponds to CaO.

to OH group. In addition, bands at 1472, 1417 and 877 cm^{-1} can be observed, corresponding to vibration modes ν_3, ν_3 and ν_2, respectively, of carbonate group. The positions of the carbonate bands indicate that the CO_3^{2-} groups are substituting the PO_4^{3-} positions.[35] The amount of carbonate was obtained by elemental analysis, which showed a 0.123 wt.% of C (0.74 wt.% of carbonate). In the FTIR spectra of powder calcined at 1100 and 1200 °C the bands assigned to carbonate was not observed and the bands corresponding to OH and PO_4 groups appeared with higher resolution.

The results of HA characterisation show that raw HA is a type B carbonatehydroxyapatite, which decomposes with temperature producing hydroxyapatite and CaO.

3.2. Slurries preparation and characterisation

Fig. 3 shows the variation of viscosity of slurries containing 40 vol.% of HA-1100 as a function of D811 concentration. The lowest viscosity was achieved with 1.5 wt.% of dispersant that corresponds to a concentration of 1.8 mg/m^2, whereas in slurries containing HA-1200 the optimum concentration of dispersant was 5 mg/m^2.

Fig. 4 shows the rheological curves of slurries containing 40 and 47 vol.% of HA-1100 as well as the curves of slurries containing 40, 55 and 60 vol.% of HA-1200. Higher content of solid in the slurries provoked a considerable increase of viscosity, not suitable for casting.

The curves of the slurries containing 40 and 55 vol.% of HA-1200 showed a Newtonian behaviour, whereas the slurry containing 60 vol.% showed a shear thinning behaviour at low shear rate and at higher shear rate the viscosity was constant.

The slurry containing 40 vol.% of HA-1100 had a similar viscosity (a little higher) than those with HA calcined at 1200 °C, however it showed a shear thinning behaviour at low shear rate. The viscosity of the slurry with 47 vol.% of HA-1100 was higher than the slurry containing 55 vol.% of HA-1200 and showed a shear thinning behaviour at low shear rate.

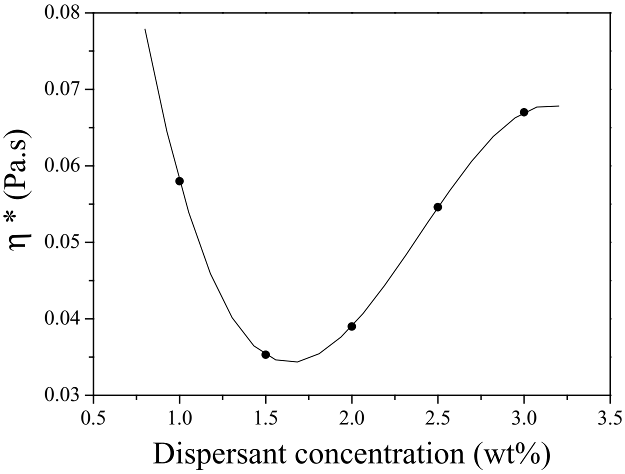

Fig. 3. Influence of dispersant concentration on the viscosity of slurries containing 40 vol.% of HA-1100.

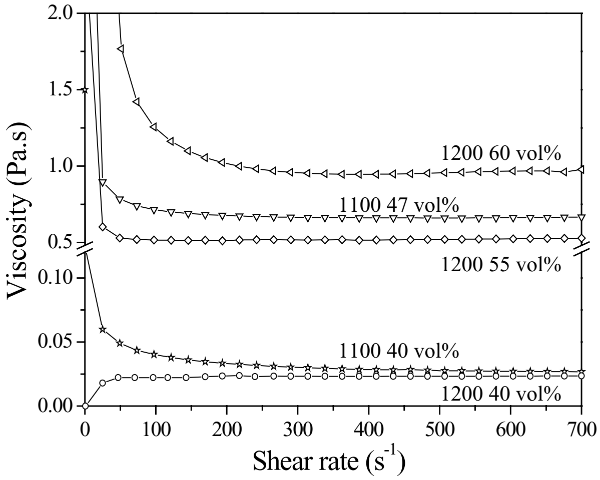

Fig. 4. Curves of viscosity vs. shear rate for slurries containing different concentration of HA-1100 and HA-1200.

3.3. Piece characterisation

Suspensions containing 55 and 60 vol.% of HA-1200 and 47 vol.% of HA-1100 were used to prepare ceramic bodies. These slurries were fluid enough for casting. In Table 1 the nomenclature and composition of the studied pieces are shown.

The pieces were well polymerised; they could be easily demoulded obtaining well-shaped pieces. In pieces S-1, S-2 and S-3 no cracks were formed during drying and the green pieces could be handled. However, the lower content of solid used in S-4 samples lead to a contraction during drying and in some samples cracks were observed.

The green pieces prepared with HA-1100 and from 60 vol.% slurry of HA-1200 were sintered at 1300 and 1400 °C for different times in order to select the temperature for sintering according to the phase transformations during sintering. The XRD patterns of sintered pieces after milling (bulk) are shown in Fig. 5 and Table 2 shows the results of the phase quantification. In samples sintered at 1300 °C for 1 h small maxima corresponding to $Ca_4(PO_4)_2O$ (TTCP)[36] were observed and the intensity of CaO maxima decreased with respect to HA powder calcined at 1200 °C. After treatment for 6 h the TTCP amount become higher and no CaO was detected, as was the case for samples treated at 1300 °C for 12

Table 1
Nomenclature, composition and solid content of studied pieces

Series	HA	Solid concentration of slurries (vol.%)	Thermal treatment
S-1	1200	55	No
S-2	1200	55	Yes
S-3	1200	60	Yes
S-4	1100	47	Yes

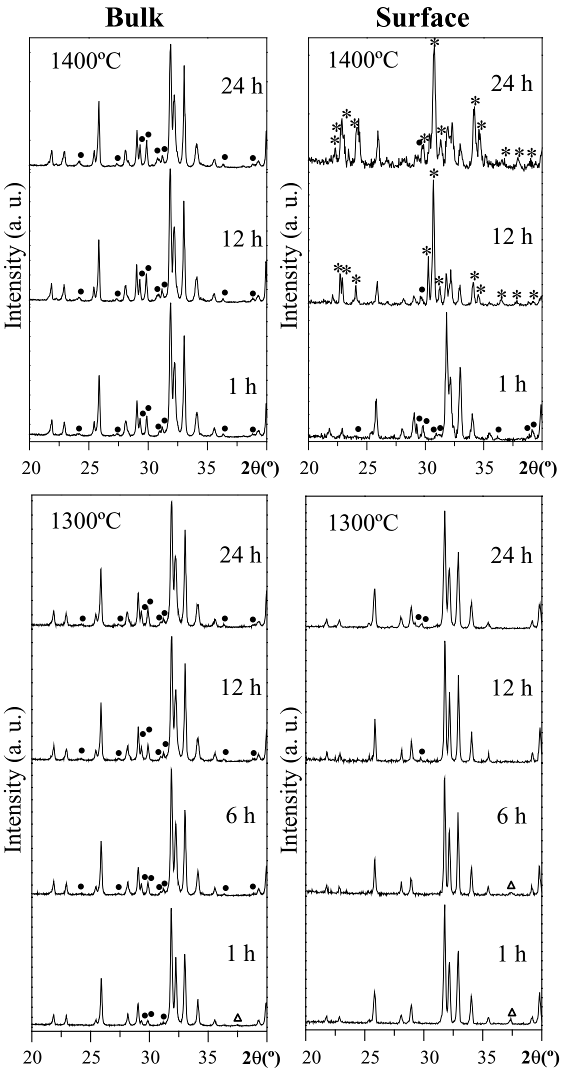

Fig. 5. XRD patterns of the bulk and surface of the pieces sintered at different temperatures and times. (△) CaO, (●) TTCP, (*) α-TCP, not indexed maxima correspond to HA.

and 24 h and at 1400 °C for 1 h. When samples were sintered at 1400 °C for 12 h an increment of the content of TTCP took place, being similar for sample sintered during 24 h.

However, the XRD patterns of the as find surface of the pieces (Fig. 5) showed a different phase composition from that of the bulk material. In samples sintered at 1300 °C for 1 and 6 h maxima corresponding to CaO were observed and TTCP was not present; whereas the XRD patterns of samples treated for 12 and 24 h at 1300 and 1400 °C for 1 h did not show CaO maxima and TTCP was observed. After the thermal treatment at 1400 °C for 12 and 24 h the XRD patterns were very different; decomposition of the HA took place and the main phase was α-$Ca_3(PO_4)_2$ (α-TCP)[37] instead of HA.

Table 2
Phase composition of HA pieces after different thermal treatment (wt.%)

Thermal treatment		HA	TTCP	CaO
1300 °C	1 h	94.0 (3)	5.7 (2)	0.3 (2)
	6 h	87.1 (6)	12.9 (4)	
	12 h	84.5 (6)	15.5 (5)	
	24 h	84.2 (7)	15.8 (5)	
1400 °C	1 h	82.6 (3)	17.4 (2)	
	12 h	77.3 (7)	22.7 (6)	
	24 h	77.4 (8)	22.6 (7)	

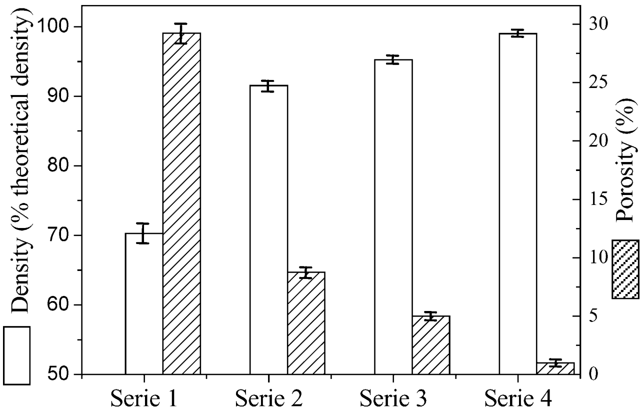

Fig. 6. Density and porosity of the obtained pieces.

These results show that the decomposition of HA starts at the surfaces of the bodies, the amount of α-TCP formed was low since that this phase was not detected when the samples were milled and all the sample analysed. However, this little decomposition of HA could affect the mechanical properties of the pieces. Taking into account these results the thermal treatment applied to the specimens for mechanical testing was sintering at 1300 °C for 24 h.

Bending of some pieces of S-4 series was observed after sintering at 1300 °C for 24 h and in this series the contraction was considerable, while it was not observed in samples S-2 or S-3. These differences in the contractions are reflected in the density and porosity results (Fig. 6). For the sintered specimens the highest density was observed in S-4 pieces (99%) and the lowest for S-2 (92%). The differences between series were statistically significant. The porosity decreased from a 30% in the green bodies to a 9% after sintering (S-2). The porosity of samples S-3 and S-4 was 5 and 1%, respectively.

The contraction in samples S-2 and S-3 was around 10.5% (Fig. 7a) and there were not statistically significant differences between these samples, whereas the contraction for sample S-4 was higher (18%) being statistically higher than in S-2 and S-3.

The surface morphology of the specimens and their fracture surface are shown in Fig. 8. The samples prepared with 55 vol.% before sintering (S-1) are constituted by particles of different size, homogenously distributed in the specimens. After sintering (S-2), the morphology was very different and corresponds to a sintered material with pores. The morphology of the specimens prepared from slurries with 60 vol.% (S-3) was similar to the S-2 series but a lower number of

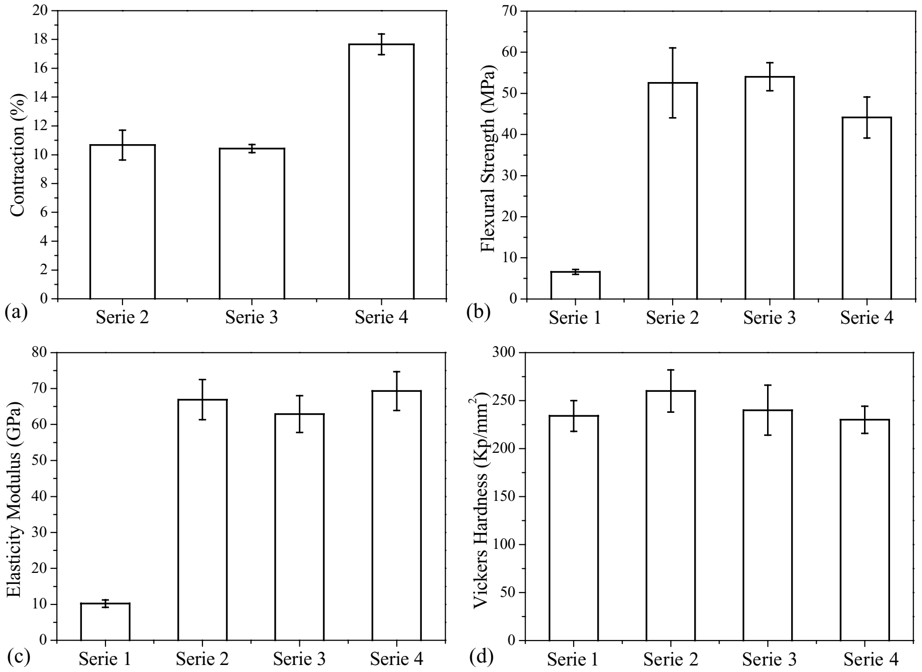

Fig. 7. (a) Pieces contraction (%) after sintering and mechanical properties of obtained pieces, (b) flexural strength, (c) elasticity modulus and (d) Vickers hardness.

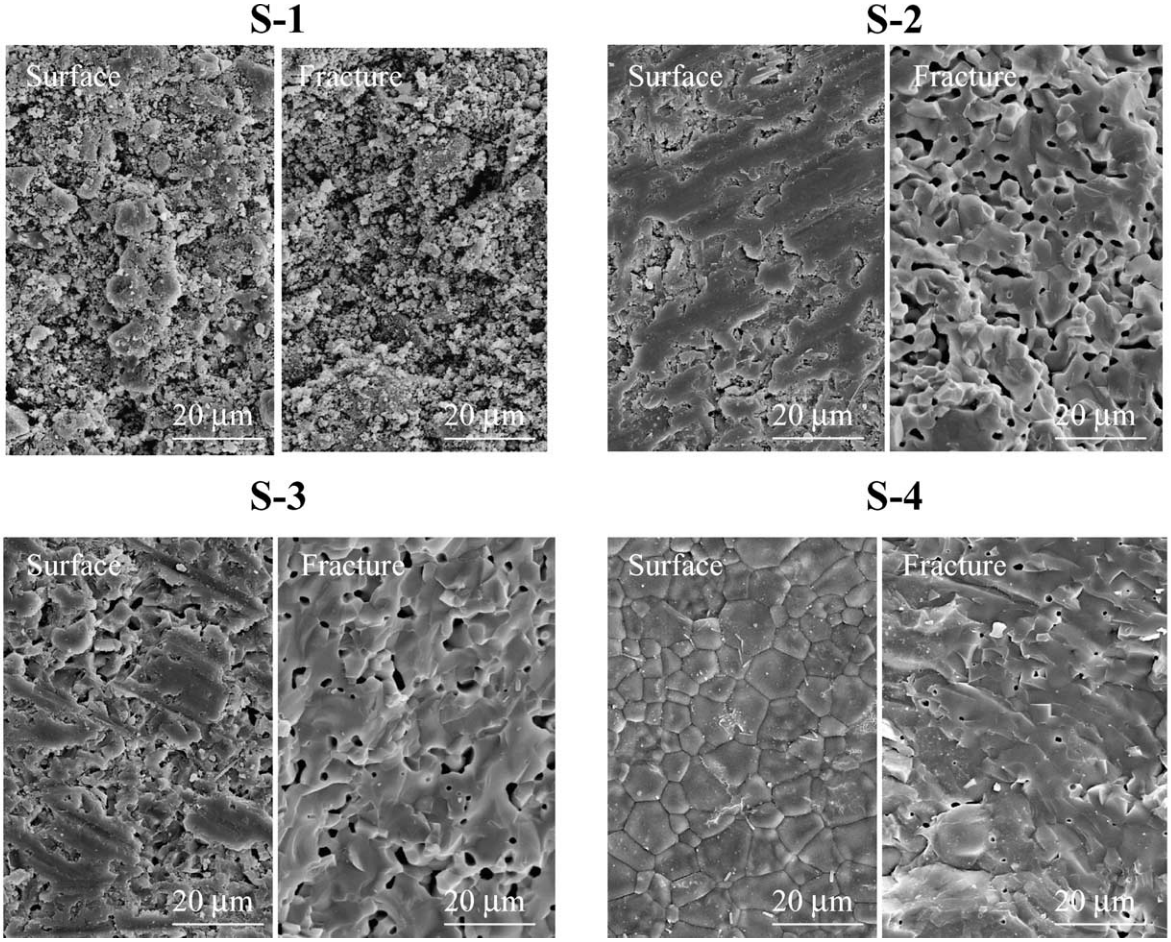

Fig. 8. Surface and fracture microstructure of HA pieces.

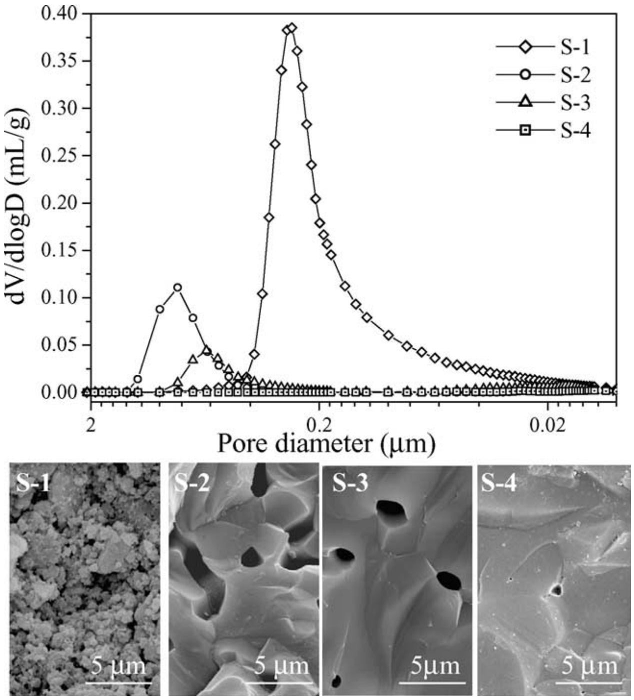

Fig. 9. Pore size distribution and fracture micrographs of HA pieces.

pores were observed. However, in pieces S-4 a higher sintering was observed as well as a higher density and a lower number and pore size.

In curves of pore diameter distribution (Fig. 9), obtained by Hg porosimetry, a monomodal distribution of pores around 0.3 μm was observed for samples before sintering (S-1). After sintering (S-2) these pores were not observed and pores with a higher size (≈0.9 μm) appeared. The pore size was lower for S-3 (≈0.6 μm). The curve corresponding to S-4 specimens did not show pores. The differences observed, in the pore size of sintered samples by SEM and Hg porosimetry, indicate that the pores inside the pieces could be isolated or only accessible through mouths that are smaller than the principal cavity of the pores.

3.4. Mechanical properties

Fig. 7b shows the flexural strength of the samples before (S-1) and after sintering (S-2, S-3, S-4). The green bodies present the lowest flexural strength, as expected, but the dispersion is much lower than in the sintered pieces. These results indicate that homogeneous green bodies were obtained by using a slurry with 55 vol.% and that during sintering the formation of defects took place. It is remarkable the fact that the flexural strength of green bodies was higher than those reported when other methods were used. The values of flexural strength for sintered pieces are in the range reported for HA.[7,38,39] The samples S-2 and S-3 have values of flexural strength similar; the difference is not statistically significant. The flexural strength of S-4 is significantly lower than S-2 and S-3.

The decrease in the porosity provoked an increase in the elasticity modulus, the specimens before sintering (S-1) having lower values (Fig. 7c). Not statistically significant differences were observed in the elasticity modulus of the sintered samples (S-2, S-3 and S-4).

The values of Vickers hardness are shown in Fig. 7d, the differences between the studied series were not statistically significant.

4. Discussion

The HA used as raw material is a carbonatehydroxyapatite type B, where the CO_3 groups are substituting the PO_4 groups. The carbonate incorporation seems to be due to the carbonatation of raw $Ca(OH)_2$ or during the ageing of the HA slurry. By thermal treatment the decomposition takes place, with the formation of CaO and CO_2 (Eq. (1)), being the CaO observed (by DRX) at 1200 °C.[35]

$$\begin{aligned}&Ca_{10-x+y}(PO_4)_{6-x}(CO_3)_x(OH)_{2-x+2y(s)}\\&\quad\rightarrow (1-x/6)Ca_{10}(PO_4)6(OH)_{2(s)} + (y+2/3x)CaO_{(s)}\\&\qquad + xCO_{2(g)},\quad 0\le x\le 2 \text{ and } 2y\le x \end{aligned}\tag{1}$$

At higher temperature (from 1300 °C, 6 h) the CaO disappear and TTCP is formed suggesting that a reaction between HA and CaO occurs, with the formation of TTCP, as represented in Eq. (2).

$$2Ca_5(PO_4)_3OH_{(s)} + 2CaO_{(s)} \rightarrow 3Ca_4P_2O_{9(s)} + H_2O_{(g)}\tag{2}$$

On the other hand, at the surface of the pieces the decomposition of HA takes place with the formation of α-TCP, being this phase majority from treatment at 1400 °C during 12 and 24 h. However, the formation of α-TCP occurs very superficially considering that in the sample bulk, this phase is not detected. The superficial decomposition of HA occurs according to the following reaction (Eq. (3)):

$$2Ca_5(PO_4)_3OH_{(s)} \rightarrow 2Ca_3(PO_4)_{2(s)} + Ca_4P_2O_{9(s)} + H_2O_{(g)}\tag{3}$$

Series S-2 and S-3, were prepared from slurries containing HA powders calcined at the same temperature (1200 °C) but with a different solid content. The samples with a higher content of solid had a higher density and lower porosity but the contraction during sintering was similar, because the HA used had been calcined at same temperature. However, when an HA calcined at lower temperature (1100 °C) was used (S-4), the contraction was significantly higher than in series S-2 and S-3 and therefore the density of the obtained pieces was also higher. According to this result it should be expected that the mechanical properties for samples S-4 were higher than for samples S-2 and S-3 and that those prepared from slurries with 60 vol.% (S-3) were higher than those containing 55 vol.% (S-2). However, this behaviour was not observed and the mechanical properties of S-2 and S-3 were statistically similar and the flexural strength of S-4 was statistically lower than S-2 and S-3.

This could be attributed to the fact that, although the sintering was higher when HA calcined at 1100 °C (S-4) was used, only a solid concentration of 47 vol.% could be achieved. This provoked a higher contraction during drying, that produced pieces with fissures and internal flaws and some specimens even broke during drying and after sintering some bended samples were obtained. The formation of defects during drying and sintering seems to have more significant influence in the mechanical properties than the higher densification and lower porosity and pore size as occur in specimens S-4.

By using an HA calcined at 1200 °C slurries with higher content of solid could be prepared and, although the sintering efficiency was lower, the mechanical properties were higher than those prepared with HA-1100. However, the specimens prepared from slurries with a solid content equal to 60 vol.% did not show better mechanical properties than those prepared from slurries containing 55 vol.% of solid. This fact could be due to the lower viscosity and better rheological behaviour of the slurries containing a 55 vol.% than slurries with a 60 vol.%. Consequently, the introduction of defects such as particles flocks, air bubbles, etc., would be smaller in slurries with lower content of solid. In addition, in slurries with lower viscosity the elimination of air bubbles by degassing process is most effective and, therefore, the defects in the final pieces would be lower. This aspect seems to be more important than the higher density and lower porosity reached by using slurries containing a higher content of solids.

This phenomenon have been reported by Wasche and Steinborn,[40] they investigated the influence of slip viscosity on the mechanical properties of high purity alumina obtained by gelcasting. They suggested that the interaction of rheological behaviour of the suspension and the generation of flaws in the green body are of crucial importance in view of an optimised microstructure for the gelcasting process. Liu et al.[21] studied the effects of the rheological behaviour of suspensions on the mechanical properties of Al_2O_3–ZrO_2 composites. The results suggested that the rheological behaviour of the suspensions might have a critical influence on the mechanical properties of the sintered samples prepared by the in situ gelcasting process.

The results obtained in this work indicate that slurries with a solid concentration higher than a limit value (50 vol.%) for which a non-excessive contraction occurs must be used. In slurries with a higher solid content the viscosity and rheological properties are more important than the higher density and lower pore size reached when a high content of solids is used. Therefore, a higher content of solid do not necessary imply an improvement in the mechanical properties. For these reasons, a compromise between viscosity/rheological properties and solid concentration must be reached.

The mechanical properties of the obtained pieces are good, in spite of the HA used was carbonated and previously calcined at 1200 °C, fact that negatively affects the sintering process. Therefore, in the most unfavourable case the mechanical properties are sufficiently acceptable for clinical applications, in addition to this, these results are similar to those previously reported for stoichiometric HA. Consequently, by using a non-carbonated HA and lower calcination temperature, it would be possible to improve the mechanical properties described at present.

5. Conclusions

1. The gelcasting resulting a simple, reproducible and non-expensive method to prepare HA pieces with the complex shapes that are required in clinical applications.
2. It was possible to prepare slurries with a high solid content (60 vol.% using HA-1200 and 47 vol.% using HA-1100).
3. The mechanical properties of the green bodies were higher than those obtained by other methods and the ones of the ceramic pieces were comparable to those obtained by other techniques.
4. Pieces containing 47 vol.% of HA-1100 showed an excessive contraction during drying and therefore lowest mechanical properties, in spite of highest density after sintering.
5. The mechanical properties of pieces prepared from slurries with high solid content (55 and 60 vol.%) were influenced by the rheological properties of the slurries.
6. Pieces with the best properties were prepared with slurries containing 55 vol.% of HA calcined at 1200 °C.

Acknowledgements

Financial support of CICYT, Spain, through research projects MAT02-0025 and ICI-MEC/PR264/97 are acknowledged. Authors also thank C.A.I. electron microscopy and C.A.I. X-ray diffraction, UCM, for valuable technical and professional assistance, and to Ricardo Molina S.A. for kindly supply the dispersant employed in this work.

References

1. Jarcho, M., Calcium phosphate ceramics as hard tissue prosthetics. *Clin. Orthop. Rel. Res.* 1981, **157**, 259–269.
2. Aoki, H., *Science and Medical Applications of Hydroxyapatite*. Takayama Press, Tokyo, 1991, p. 1.
3. Rodríguez-Lorenzo, L.M., Vallet-Regí, M. and Ferreira, J. M. F., Fabrication of hydroxyapatite bodies by uniaxial pressing from a precipitated powder. *Biomaterials* 2001, **22**, 583–588.

4. Levitt, S. R., Crayton, P. H., Monroe, E. A. and Condrate, R. A., Forming methods for apatite prosthesis. *J. Biomed. Mater Res.* 1969, **3**, 683–685.
5. Uematsu, K., Takagi, M., Honda, T., Uchida, N. and Saito, K., Transparent HA prepared by HIP of filter cake. *J. Am. Ceram. Soc.* 1989, **72**, 1476–1478.
6. Liu, D. M., Preparation and characterization of porous hydroxyapatite bioceramic via a slip-casting route. *Ceram. Int.* 1998, **24**, 441–446.
7. Rao, R. and Kannan, S. K., Dispersion and slip-casting of hydroxyapatite. *J. Am. Ceram. Soc.* 2001, **84**, 1710–1717.
8. Krajewski, A., Ravaglioli, A., Fiori, C. and Dalla Casa, R., The processing of hydroxyapatite-based rolled sections. *Biomaterials* 1982, **3**, 117–120.
9. Arita, I. H., Wilkinson, D. S. and Castazo, V. M., Synthesis and processing of hydroxyapatite ceramic tape casting with controlled porosity. *J. Mater. Sci.: Mater. Med.* 1995, **6**, 19–23.
10. Reis, R. L., Cunha, A. M., Oliveira, M. J., Campos, A. R. and Bevis, M. J., Relation between processing and mechanical properties of injection molded high molecular mass polyetilene + hydroxyapatite composites. *Mat. Res. Innovat.* 2001, **4**, 263–272.
11. Shaw, J. H., Best, S. M., Bonfield, W., Marsh, A. and Cotton, J., Study of the application of viscous plastic processing to hydroxyapatite. *J. Mater. Sci. Lett.* 1995, **14**, 1055–1458.
12. Lewis, J. A., Colloidal processing of ceramics. *J. Am. Ceram. Soc.* 2000, **83**, 2341–2359.
13. Janney, M. A., *Method for Forming Ceramic Powders into Complex Shapes*. U.S. Patent 4894194, 1990.
14. Omatete, O. O., Janney, M. A. and Strehlow, R. A., Gelcasting—a new ceramic forming process. *Am. Ceram. Soc. Bull.* 1991, **70**, 1641–1649.
15. Young, A. C., Omatete, O. O., Janney, M. A. and Menchhofer, P. A., Gelcasting of alumina. *J. Am. Ceram. Soc.* 1991, **74**, 612–618.
16. Omatete, O. O., Blair, A., Westmoreland, C. G. and Young, A. C., Gelcast zirconia–alumina composites. *Ceram. Eng. Sci. Proc.* 1991, **12**, 2084–2094.
17. Omatete, O. O., Pollinger, J. P. and O'Young, K., Optimization of the gelcasting of a silicon nitride formulation. *Ceram. Trans.* 1995, **56**, 337–343.
18. Waesche, B. and Steinborn, G., Influence of slip viscosity on the mechanical properties of high purity alumina made by gelcasting. *Key Eng. Mater.* 1997, **132–136**, 374–377.
19. Sepulveda, P. and Binner, J. G. P., Processing of cellular ceramics by foaming and in situ polymerisation of organic monomers. *J. Eur. Ceram. Soc.* 1999, **19**, 2059–2066.
20. Ma, L. G., Huang, Y., Yang, J. L., Xie, Z. P., Xu, X. L. and Zhao, J. S., Improving the breakdown strength of rutile capacitor by gelcasting. *J. Mater. Sci. Lett.* 2001, **20**, 1285–1288.
21. Liu, X., Huang, Y. and Yang, J., Effect of rheological properties of the suspension on the mechanical strength of Al_2O_3–ZrO_2 composites prepared by gelcasting. *Ceram. Int.* 2002, **28**, 159–164.
22. Vlajic, M. D. and Krstic, V. D., Strength and machining of gelcast SiC ceramics. *J. Mat. Sci.* 2002, **37**, 2943–2947.
23. Yi, Z. Z., Xie, Z. P., Huang, Y., Ma, J. T. and Cheng, Y. B., Study on gelcasting and properties of recrystallized silicon carbide. *Ceram. Int.* 2002, **28**, 369–376.
24. Guo, D., Cai, K., Li, L. T. and Gui, Z. L., Application of gelcasting to the fabrication of piezolelectric ceramic parts. *J. Eur. Ceram. Soc.* 2003, **23**, 1131–1137.
25. Sepulveda, P., Binner, J. G. P., Rogero, S. O., Higa, O. Z. and Brsessiani, J. C., Production of porous hydroxyapatite by the gel-casting of foams and cytotoxic evaluation. *J. Biomed. Mater. Res.* 2000, **50**, 27–34.
26. Lelievre, F., Bernache-Assollant, D. and Chartier, T., Influence of powder characteristics on the rheological behaviour of hydroxyapatite slurries. *J. Mater. Sci.: Mater. Med.* 1996, **7**, 489–494.
27. Toriyama, M., Ravaglioli, A., Krajewski, A., Galassi, C., Roncari, E. and Piancastelli, A., Slip casting of mechanochemically synthesized hydroxyapatite. *J. Mater. Sci.* 1995, **30**, 3216–3221.
28. Yasuda, H. Y., Mahora, S., Umakoshi, Y., Imazato, S. and Ebisu, S., Microstructure and mechanical property of synthesized hydroxyapatite prepared by colloidal process. *Biomaterials* 2000, **21**, 2045–2049.
29. Rodríguez-Lorenzo, L.M., Vallet-Regí, M. and Ferreira, J. M. F., Colloidal processing of hydroxyapatite. *Biomaterials* 2001, **22**, 1847–1852.
30. Padilla, S., García-Carrodeguas, R. and Vallet-Regí, M., HA suspensions as precursors of pieces obtained by gelcasting method. *J. Eur. Ceram. Soc.* 2004, **24**, 2223–2232.
31. Hill, R. J., Data collection strategies: fitting the experiments to the need. In *The Rietveld Method IUCT*, ed. R. A. Young. Oxford University Press, New York, 1998, p. 95.
32. MIL-SRD-1942(MR). Flexural strength of high performance ceramics at ambient temperature. U.S. Department of Defense, 1983.
33. Powder Diffraction File, No. 9-432. Data base sets 1–49 plus 70–86. International Centre for Diffraction Data, 1999.
34. Powder Diffraction File, No. 43-1001. Data base sets 1–49 plus 70–86. International Centre for Diffraction Data, 1999.
35. Elliot, J. C., *Structure and Chemistry of the Apatite and other Calcium Orthophosphates in Inorganic Chemistry, No. 18*. Elsevier, Amsterdam, 1994, pp. 213–229, 234.
36. Powder Diffraction File, No. 25-1137. Data base sets 1–49 plus 70–86. International Centre for Diffraction Data, 1999.
37. Powder Diffraction File, No. 29-0359. Data base sets 1–49 plus 70–86. International Centre for Diffraction Data, 1999.
38. Suchanek, W. and Yoshimura, M., Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants. *J. Mater. Res.* 1998, **13**, 94–117.
39. Rodriguez-Lorenzo, L. M., Vallet-Regí, M., Ferreira, J. M. F., Ginebra, M. P., Aparicio, C. and Planell, J. A., Hydroxyapatite ceramic bodies with tailored mechanical properties for different applications. *J. Biomed. Mater. Res.* 2002, **60**, 159–166.
40. Wasche, R. and Steinborn, G., Influence of slip viscosity on the mechanical properties of high purity alumina made by gelcasting. *Key Eng. Mater.* 1997, **132–136**, 374–377.