COMUNICACIÓN CORTA

Dual setting α-tricalcium phosphate composite cement obtained by 3d printing

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INTRODUCCIÓN

Calcium phosphate cements (CPCs) could be employed as synthetic bone graft substitutes or scaffolds for tissue engineering allowing the fabrication of more complex geometries and the customization of the implants mainly due to the possibility to be molded.[1] Moreover, the use of additive manufacturing technologies at low temperatures such as 3D printing allows the fabrication of pieces with enhanced performance over traditional techniques.[2,3] Usually, the obtained pieces have low mechanical strength; however, the use of polymeric additives such as acrylamide (AA) and ammonium polyacrylate (PA), could reinforce the system through *in situ* polymerization and increase the mechanical properties of the final piece.[4]

Some studies reports the use of calcium phosphate powders such as α-tricalcium phosphate [β-$Ca_3(PO_4)_2$; β-TCP], tetracalcium phosphate [$Ca_4(PO_4)_2$], and α-tricalcium phosphate [α-$Ca_3(PO_4)_2$; α-TCP] as row material in the manufacture of scaffolds by means of 3D printing technology.[5,8] However, none reported studies refer the use of dual setting α-TCP-based cement hydraulic system as proposed by the authors. Thus, the aim of this work was the fabrication and characterization of a dual setting composite cement based on α-tricalcium phosphate (α-TCP)/AA/PA by 3D printing technology.

A Z310 Plus Printer Prototyper was used to print the pieces. Previously synthetized αp-TCP powder,[9] was mixed with ammonium persulfate [$(NH_4)_2S_2O_8$] and printed using a binder composed by a solution of 5 wt % Na_2HPO_4, 10 wt% acrylamide, 1 wt % N,N methylenebisacrylamide and 0.5 wt % N,N,N,N- tetramethylethylenediamide.[4] All chemical reagents were analytical grade and purchased from Dyneα. The binder liquid/powder ratio was 0.31 mL/g and the layer thickness was set to 0.0875 mm. Phase composition of the samples was determined by X-Ray Diffraction (XRD) in a PHILLIPS-X´Pert MPD diffractometer; morphological differences were observed by Scanning Electron Microscopy (SEM) using a JEOL microscope (JSM-6060); while compressive strength (CS) and flexure stress (FS) were measured in a servohydraulic Universal Testing Machine (Instron 3369) [10,11]. Water absorption, apparent porosity, and apparent specific gravity were calculated according to the Standart C373-88.[12] The number of replicas for the characterization was n=10 and a two-sample t-test was used to compare mean values ($t_{0.05}$).(Fig. 1).

Fig. 1. *3D printed pieces.*

shows the XRD patterns of α-TCP powder and prototyped cement after 7 days in water at 37.5 °C (Fig. 2). After setting and aging, some α-TCP peaks (JCPDS 09-0348), indicating the incomplete transformation of this phase during hydrolysis, could be identified in addition to the characteristic peaks of calcium deficient hydroxyapatite (CDHA) (JCPDS 46-0905).

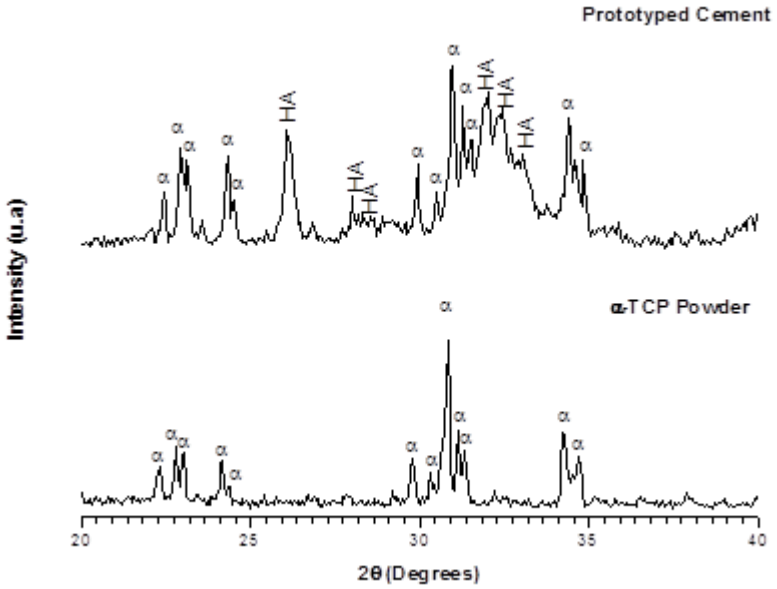

Fig. 2. *XRD of □-TCP row material and prototyped cement.*

Microstructural features of the prototyped material are shown in Fig. 3. Typical petal-like plates distinctive of setting and hardening α-TCP-based cements can be detected both on the surface and the fracture surface; however, the crystals in the inside of the material are higher than those found in the surface. Also a greater homogeneity is observed. In addition, some unreacted α-TCP grains and macropores from about 5 μm of diameter can be noticed, mainly in outward of materials. They were found no evidence of the presence of the hydrogel formed during polymerization of the acrylamide.

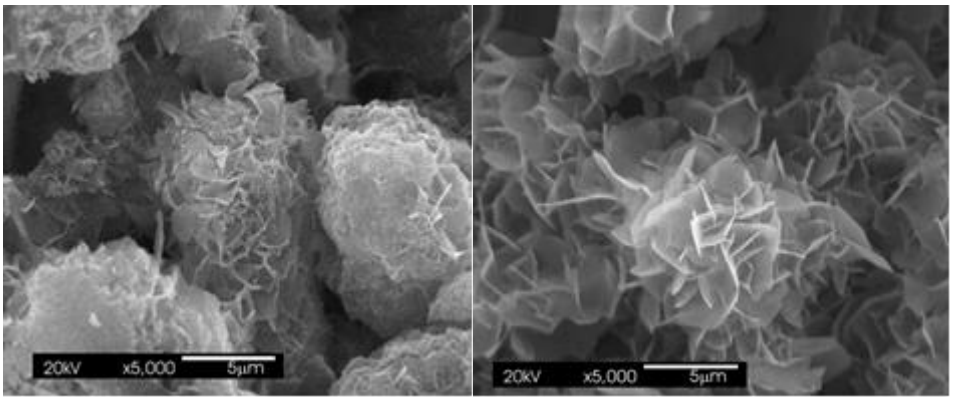

Fig. 3. *SEM micrographs of surface (A) and fracture surface (B) of prototyped materials*

Mechanical properties, water absorption, apparent porosity and density values are displayed in Table 1. Values of both compressive strength, and flexure stress were very low. No significant differences were found for the apparent porosity of pieces; however, the values of apparent porosity and water absorption were dependent on the design of prototyped piece.

Table 1: Mechanical properties, water absorption, apparent porosity and density of prototyped cement.

Mechanical Strength (MPa)	Format Piece	
	Bars	Cylinders
Compressive strength (MPa)	--	1.3 ± 0.1
Flexure stress (MPa)	3.3 ± 0.2	--
Apparent Porosity (%)	57 ± 1	61 ± 1
Water absorption (%)	54 ± 2	62 ± 2
Apparent Density (g/cm^3)	2.49 ± 0.07	2.54 ± 0.03

The precipitation of CDHA is responsible for the adherence and interlocking of the crystalline grains, which results in hardening; so, the fall in mechanical strength can be attributed to the low transformation of α-TCP into CDHA (Eq 1) according to XRD. The value of the apparent density was closer to the theoretical value of α-TCP (2.86 g/cm^3) than CDHA (2.97 g/cm^3); suggesting the incomplete transformation into this phase.

$$3\alpha - Ca_3(PO_4)_{2(s)} + H_2O = Ca_9(HPO_4)(PO_4)_5OH_{(s)} \qquad \text{Eq 1}$$

According to previous results, when polymerization is conducted in aqueous slurry of ceramic powder, the obtained cross-linked polyacrylamide hydrogel is able to bind the ceramic particles and provide strength to the resulting system.[13] But, in this case, the presence of the polymeric additives hinder the solubility of the α-TCP particles and therefore inhibits the precipitation of the CDHA; so the strength of materials decreases. Water absorption values were not significantly different from those found for samples of cement without hydrogel additions,[14] which reinforces the idea that the *in situ* polymerization of the acrylamide have not occurred in large extension. It is possible that the amount of hydrogel formed at this point of reaction was not enough to provide strength to the prototyped materials, probably do to the low liquid-to-powder ratio. Moreover, if the liquid was not able to complete wet and penetrate the top layer of powder, the adhesion between layers and consequently, the final mechanical properties could be compromised[15]. On the other hand, the high porosity of the prototyped materials also negatively influence the mechanical strength obtained.

Differences in crystal size in SEM micrographics are due to the mechanism of hydrolysis which is dependent on the diffusion of fluid through the layer formed and occurs from the inside to the outside of the material. However, even though the presence of this entanglement of CDHA could provide mechanical strength, the existence of unreacted α-tricalcium phosphate and the high porosity of the prototyped materials are critical factors in the final properties of the cement.

In conclusion, it is possible to obtain scaffolds based on α-tricalcium phosphate (α-TCP)/AA/PA by 3D printing. The mechanical properties thereof are low for applications where high mechanical stresses were required. Nevertheless, the obtained pieces were high porosity and could be used as scaffolds for cellular growth and cancellous bone replacement.

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