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New brushite cements analysis

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Some brushite cements were developed using β-tricalcium phosphate (β-TCP) and monocalcium phosphate monohydrate (MCPM) as precursors and acidic solutions of chitosan lactate as setting solutions. The influence of the chitosan lactate concentration and of liquid to powder ratio (L/P) on setting times and compressive strength were analyzed. Cement samples were characterized by XRD, and SEM. Increasing L/P ratio results in an increase of initial and final setting times. On the other hand, increase of the chitosan lactate concentration leads both to a decrease of setting time and an increase of compressive strength. When very acidic setting solutions are used a mixture of brushite and monetite are obtained. The better cement was obtained using as setting liquid a solution of 5% chitosan lactate in 1.4 M lactic acid.

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1. Introduction

A series of cements, based principally on different calcium orthophosphate compounds, are suitable for repair, augmentation and regeneration of bones. Currently these materials are known as calcium phosphate cements (CPC). Such cement is a mixture of calcium phosphates powders which, upon mixing with an aqueous solution, forms a moldable paste that sets to a firm mass, especially by precipitation processes. Final product is also an orthophosphate. About 15 different binary combinations of calcium phosphates can gave pastes which set at room or body temperature into solid cement [1-4].

According to orthophosphate solubility data, depending on pH value of the cement paste, only two major end products are obtained: hydroxyapatite (crystalline HA or calcium deficient hydroxyapatite (CDHA)) - at pH higher than 4.2 and brushite (dicalcium phosphate dihydrate – DCPD) – at pH lower than 4.2, but, in practice, this pH limit is displaced to a value comprised between 6 and 7.

The most studies have been devoted to apatite cements, HA and CDHA, because they are usually set at a pH value close to the physiological environment pH, and are analogous to human bone. Although HA is mechanically more favorable, this have the lowest solubility among the all the calcium phosphate phases and cements based on HA have a low *in vivo* resorbability.

Contrary to hydroxyapatite, in physiological conditions brushite is a metastable calcium phosphate phase, being much faster resorbable after implantation [5,6]. Consequently, despite to HA advantages, brushite calcium phosphate cements have raised a large interest in the last years. Because under acidic conditions, at pH≤4.2, DCPD (brushite) and dicalcium phosphate (DCP - monetite) are the least soluble calcium phosphate phases. Almost all brushite cements have been set by acid-base reaction, the more basic component being β-tricalcium phosphate (β-TCP) or tetra calcium phosphate (TTCP), while the acidic component is monocalcium phosphate monohydrate (MCPM) [7] or ortho-phosphoric acid (H_3PO_4) [8, 9]. In very acid conditions, when the initial pH of the cement paste is lower than 2.0, the most stable is MCPM [3] and monetite. During setting reaction the paste pH varies from very acidic value to almost neutral pH value.

Between the disadvantages of the brushite forming cements is very short setting times, accompanied by inferior mechanical properties, especially low compressive strengths. Setting times can be increased by the use of either a low powder/liquid ratio or a high setting retardant concentration in the cement paste [9-11]. As setting retardants for brushite base cements were used: sulphuric acid, sodium pyrophosphate sodium citrate, citric acid [11]. Increasing the retardant composition led to an increased setting time and improves the compressive strength.

However, at very high retardant concentrations can take place a decrease of mechanical strength [10]. The liquid composition and powder-to-liquid ratio are very important characteristics because these determine both setting times and bioresorbability. A better modeling of the calcium phosphate properties have been made by means of various additives. In particular polymeric additives are used, both to increase the mechanical properties and to reproduce the hard tissue characteristic.

Several studies [12-14] have been reported the ability of chitosan and chitosan derivatives as a good substrate for osteo-blasts and other cells related with bone regeneration. On this basis the chitosan was used either as additive for setting time and mechanical properties control or as component in the calcium phosphate composite.

In this study the chitosan was used as additive in the setting liquid composition, analyzing their influence on the setting time, compressive strength and phase composition of brushite cement obtained on the basis of b-TCP and MCPM.

2. Experimental

The reactants for the cement powder mixture were $Ca_3(PO_4)_2$ (an old product of Riedel de Haen A.G. Hannover) and $Ca(H_2PO_4)_2.H_2O$ (Fluka Analytical). As the tricalcium phosphate was an older product, an additional characterization was necessary, analyzing the structure (by X-ray measurements), compozition (by FT-IR), thermal behaviour (thermogravimetry) and granulometric distribution (laser difraction analyse). These studies indicate that the used product is very well crystallized, but one can identify two crystalline phases: β-TCP and α-TCP; the β phase is prevalent, being in a proportion of more than 90 %. The FT-IR spectra indicates almost exactly the presence of a quantity of calcium carbonate and a very small quantity of $Ca(OH)_2$. The thermogravimetric measurements attest the presence in the sample of the calcium carbonate (about 7%) and of the $Ca(OH)_2$ traces (about 2%). These traces cannot influence considerably the behaviour of β-$Ca_3(PO_4)_2$ in cements and composites. The median value of the particle diameter in the volume distribution is 63 nm, and differential volumetric distribution curve present a quite sharp peak.

The cement powder was obtained by mixing, in a vibrating unit, equimolar amounts of the two starting components. As setting liquids, acidic solutions of chitosan lactate were used. These solutions were prepared dissolving a medium molecular weight chitosan sample (Vanson Chemicals Redmond WA, USA) in lactic acid solution: solution A: 1.5 % chitosan lactate in 0.5 M lactic acid, pH=1.25; solution B: 3.0 % chitosan lactate in 1M lactic acid, pH=2.19; solution C: 5.0 % chitosan lactate in 1.5M lactic acid, pH= 2.85. (This is in fact a consistent gel)

A control cement sample was realized using as setting liquid a 0.5 M citric acid, with pH=1.82. All cement samples were prepared by mixing in an agate mortar the cement powder with the appropriate amount of liquid. The cement pastes were cast into a teflon mould to make cylindrical sample, of 6 mm diameter and 12 mm height, for compressive strength measurements. The mould with cement cylinders was stored for 24 h, at a temperature of 37 ^oC in a sealed container saturated with water vapor. The samples were withdrawn from mould and left to dry in air before compressive strength measurements. The compressive strength was measured with an Electronic universal testing machine type WDW-50E (Beijing TIME High Technology Ltd, China), at a crosshead speed of 1mm min^{-1}. A part of the cement paste was used to assess the setting times (three determinations), using a **Vicat** type apparatus. The device consists in a stand for a mobile rod with a weight of 150 g to which we can add an additional weight up to 300 g. The plunger's rod is 10 mm in diameter and to the lower end is attached a steel needle of 1 mm in diameter. In the present study we identified two phases in the process of hardening the cements: ***the initial setting time*** –determined as the time after which the rod weighing 150 g fails to make a perceptible circular identation on the cement surface and ***the final setting time (hardening time)*** **–**determined as the time after which the movable system weighing 300 g does not enter in the cement, namely the steel pin does not leave a circular trace which can be perceived on the surface of the hardened mass.

After hardening and drying, some of the cement samples were characterized by X-ray diffraction (DRON 2.0 diffractometer (Russian), and Scanning electron microscopy (VEGA-TESCAN).

3. Results and discussions

The chitosan lactate concentration in the hardening liquid influences both the setting time and mechanical properties. Fig. 1 presents the dependence of initial and final setting times on chitosan lactate concentration, while Fig. 2 shows the influence of the chitosan concentration on the compressive strength. All cement samples were prepared taking into account a liquid/ powder ratio of 0.45 mL/g.

Increasing the concentration of the chitosan lactate in the liquid phase results in a decrease of both initial and final setting times, but produce a significant increase of the compressive strength of the hardened cement.

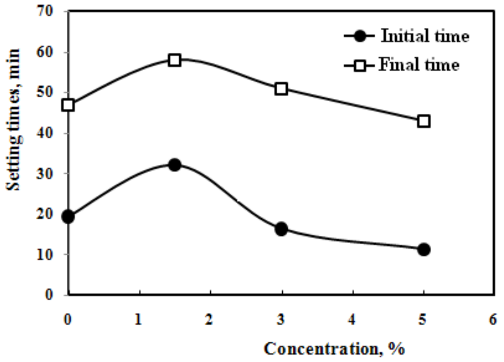

Fig. 1. Setting times versus chitosan lactate concentration in hardening liquid.

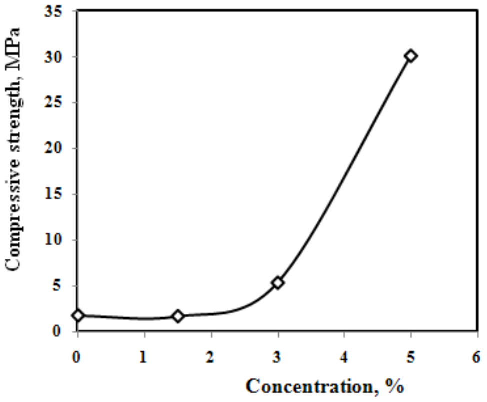

Fig. 2. Compressive strength of the hardened cement as a function of chitosan lactate concentration in the hardening liquid.

Using a hardening liquid with 5% chitosan lactate one obtain a compsite brushite/chitosan lactate with a good mechanical resistance (a compressive strength of 30 mPa) at a reasonable setting time (about 10 – 12 min).

Phase composition of the hardened samples may be analyzed on the basis o the XRD patterns presented in Fig. 3. Approval test, the cement set with citric acid, appears as an commixture of brushite and monetite in comparable quantities. This is right by of the very high acidity of the setting liquid (pH=1.82): before pH=2 the predominant product is monetite. As the setting reactrion get forward, the pH increase and, after pH=2, the brushite is predominant product. The cement sample set with 1.5 % chitosan lactate (pH=1.25) contain principally monetite, with trace of brushite and unreactioned β-tricalcium phosphate.

The utilization of a setting liquid with 5% chitosan lactate, having a pH= 2.85, conduct to a cement constituted principally from brushite. Trace of MCPM are still present (the peak appeared at 2θ value of 7.94). This behaviour is due to the fact that the pH of the setting liquid is in the stability domain of brushite. The highest value of the compressive strength is assured by the increased percent of chitosan lactate which constitute a matrix for the precipitated brushite. The microstructure of the cement formed in this case is illustrated in Fig. 4, where is presented a photomicrograph of the fractured surface at a manification of 5000x.

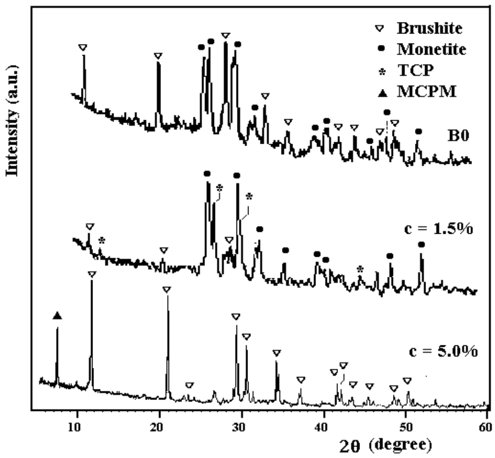

Fig. 3. X-ray diffraction patterns for Control sample (B0), sample set with 1.5% chitosan lactate and sample set with 5% chitosan lactate.

The influence of the liquid to powder ratio (L/P) on both setting time (initial time) and hardening time (final time) is presented in Fig. 5 for cements set with two different setting liquids.

These data point out that in the case of liquid with 3% chitosan lactate the convenient setting times are obtained when the L/P ratio is situated between 0.4 and 0.45, while when a 5% chitosan lactate is used the advantageous ratio is situated in the range 0.5 – 0.6.

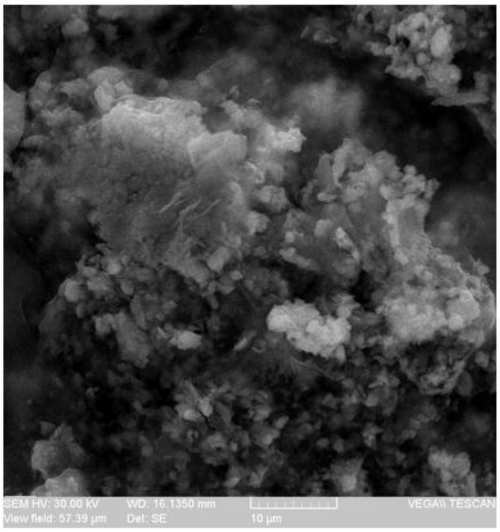

Fig. 4. SEM image of the fracture surface of the cement sample set with 5% citosan lactate.

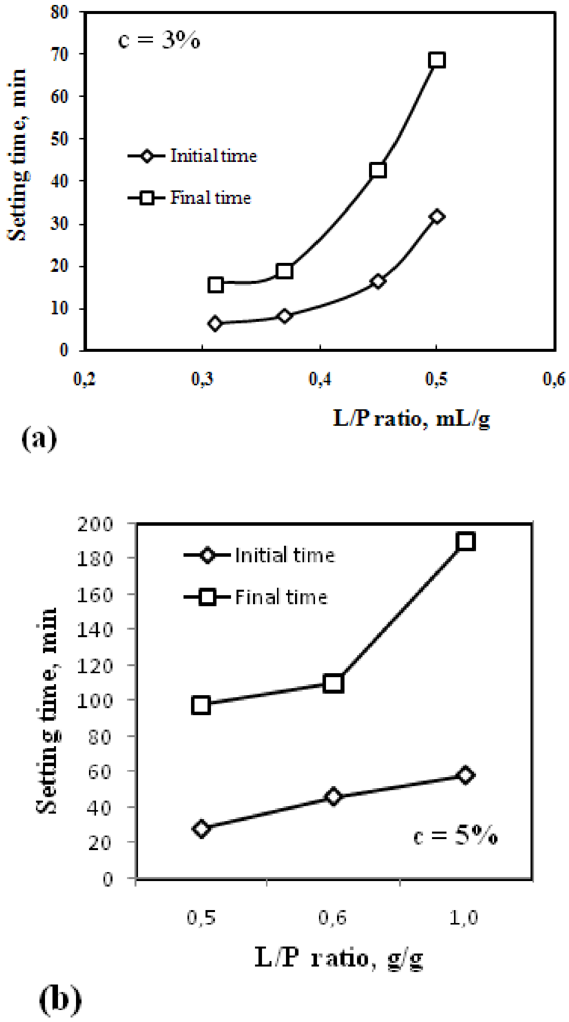

Fig. 5. Initial and final setting times vs. Liquid to powder ratio; (a)Setting liquid :3% chitosan lactate, (b) Setting liquid: 5% chitosan lactate.

4. Conclusions

In this study it was shown that it was possible to produce advanced brushite cements on the basis of β-TCP/MCPM precursors using chitosan lactater solutions assetting liquids. The concentration of chitosan lactate was changed between 1.5 – 5.0 percent in the setting liquid, the increase of concentration having as effect a pronounced increase of compressive strength and and a decrease of the setting time and a decrease of setting and hardening times. The XRD patterns point out that with very acidic setting solutions monetite or a mixture of monetite and brushite are obtained, while when a 5% chitosan lactate with a pH>2.5 is used the final product is only brushite.

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