

SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE FOR ANTI-CORROSION PURPOSES

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Abstract

The goals of this work are to determine the effect of precipitation conditions (pH, precipitation rate, Ca/P ratio) on the synthesis of hydroxyapatite and characterization of its properties for anticorrosion intention. This work is especially focused on the possibility of synthesis of hydroxyapatite by the wet precipitation method. Synthesized pigments were assessed for crystallite size and morphology, particle size distribution and phase composition. For their possible anticorrosion application, preliminary corrosion tests were performed, which include: determination of pH and resistivity of aqueous suspensions of pigments (10%), gravimetric determination of weight loss of steel plates and determination of corrosion indicators. Subsequently, accelerated corrosion tests were performed.

Introduction

In recent years, considerable attention has been paid to the use of hydroxyapatite (calcium hydroxyphosphate) in the field of orthopedics, where these phosphates have to replace either partially or completely bone tissue^{1, 2}. The cause of the extension of phosphate pigments nowadays is more stringent environmental and hygienic limits, which require for the replacement of toxic lead and chromate pigments with nontoxic but very effective pigments³. The main applications of hydroxyapatite are its use as a coating of metallic prostheses, which has two important functions: to protect the implant against corrosion and to improve implant's biocompatibility with the human body⁴. Since hydroxyapatite is very suitable and useful for the protection of implants against corrosion it can be very functional even for steel protection like do other phosphate pigments⁵. Since this consideration has not been previously studied, it has become the main theme of this work.

Experimental part

In order to select suitable synthesis conditions for the formation of a pure hydroxyapatite phase, the thermodynamic stability of the hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ in aqueous solution was analyzed and approved in laboratory conditions. The selected suitable precipitation conditions (Ca/P=1, 1.67, 3; pH=7, 12) were adjusted to synthesize pure hydroxyapatite to form $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. For the synthesis of powders, 1M solutions of starting compounds ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)\text{H}_2\text{PO}_4$) were prepared. The precise concentrations of these solutions were determined using analytical methods (titration, gravimetric and photometric analyses). Altogether, 12 samples were synthesized at different synthesis conditions (Table 1, precipitation rate 2 ml/min). The prepared powders were aged during 24 hours, filtered and washed with distilled water to neutral pH, then dried at 80 °C for 6 h. The prepared samples were studied before and after aging in terms of particle size distribution (Mastersizer 2000 MU, Mie approach). Crystallinity and morphology were performed by an optical microscope (MP - 1326 and Dino-Lite Rack - MS 34 B) directly after precipitation and in 2 and 24 hours of aging. The phase composition of the prepared powders was analyzed by the X-ray diffraction instrument (Rigaku MiniFlex 600). For their possible application, preliminary corrosion tests were implemented, including determination of pH and resistivity of aqueous suspensions of pigments (10%), gravimetric determination of weight loss of steel plates, determination of corrosion indicators and determination of corrosion indicators for the steel plates after being dived into pigment extracts for 2 months and the change of pH and resistivity during this process. The formed corrosion products were analyzed using optical microscope and their phase composition was determined by XRD analysis. Next, for accelerated corrosion tests, pigments were distracted in water-based primer paint and applied on steel plates and tested in corrosion testing chambers (Hydrotherm 519, Erichsen) during 3 weeks. The assessment of the degradation of the coatings was made with respect to the degree of rusting, cracking, blistering, flaking, and delamination according to ISO standards. Corrosion defects were also analyzed using an optical microscope. The commercial pigments ZP-10 (mixture $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$; Heubach, Germany) and Zp-Bs-M (mixture $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and ZnO; France) were tested in parallel with the synthesized samples.

Table I

Overview of the obtained samples and the synthesis conditions

Sample	Ca/P ratio	Precipitation rate [ml·min ⁻¹]	pH
1	1	5	7
2	1.67	5	7
3	3	5	7
4	1	5	12
5	1.67	5	12
6	3	5	12
7	1	0.5	7
8	1.67	0.5	7
9	3	0.5	7
10	1	0.5	12
11	1.67	0.5	12
12	3	0.5	12

Result and discussion

Effect of synthesis conditions on pure hydroxyapatite formation

All prepared samples were studied by optical microscope after 2 hours and 24 hours maturation. In both cases, agglomerates of small crystals of different sizes and shapes were visible. According to a result of the SEM analysis of synthesized samples, hydroxyapatite phase was formed as nanocrystalline whose the size and shape of crystals depend on the Ca/P ratio (Ca/P = 1 needle-shaped shapes are identified, Ca/P = 1.67 – tabular plates, Ca/P = 3 - different needle-like shapes, tabular plates, and bulky formations) and pH (pH = 7 - larger and thinner particles, pH = 12 - larger and smaller particles) and does not depend on the precipitation rate.

The particle size distribution of the samples was measured after 24 hours aging by the device Mastersizer 2000 MU. The signal evaluation was made using Mie scattering and the distribution curves and d_{10} , d_{50} , d_{90} , and distribution spans were obtained. Particle size measurements of all samples showed the values of d_{50} in range from 1.8 to 16.4 μm . The results provide information on the size of the agglomerates, not the real size of the crystals. Some dependence between the Ca/P ratio and the mean d_{50} and span was demonstrated. At the Ca/P = 1 ratio, agglomerates with the highest span, distribution width and d_{50} (7.2-19.5 μm) were almost always obtained. Conversely, at a Ca/P ratio of 1.67, lower d_{50} values (1.8-7.7 μm) were always obtained.

The phase composition of the samples was determined by XRD analysis. Two distinct structures of hydroxyapatite have been identified: monoclinic and hexagonal. Figure 1 shows the diffractogram of sample 1 containing the hydroxyapatite diffraction line $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ with the following parameters: hexagonal crystalline system; space group P63/m. Figure 1 also shows a diffractogram of sample 2 containing the hydroxyapatite diffraction line $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ with the following parameters: monoclinic crystalline system; space group P21/b. These structural types of hydroxyapatite were selected based on the lowest value of FOM (figure of merit), i.e., based on the best match. The crystal size was calculated from the diffractogram based on the diffraction line width using the Scherrer equation, Williamson-Hall (WH)⁶ and the Halder-Wagner (HW) method⁷. Comparison of the crystal size results obtained from SEM and XRD analysis revealed that the minimum dimensions of SEM analysis were comparable to the maximum dimensions of XRD analysis. In general, SEM analysis shows a larger crystal size. This phenomenon can be explained by the fact that for the maximum crystal size analysis the largest particles that are visible in the SEM images are selected. The contributions of these largest particles to the average crystal size are small. Further, this phenomenon can be explained by the fact that the largest crystals visible in the SEM figures are made up of smaller crystals.

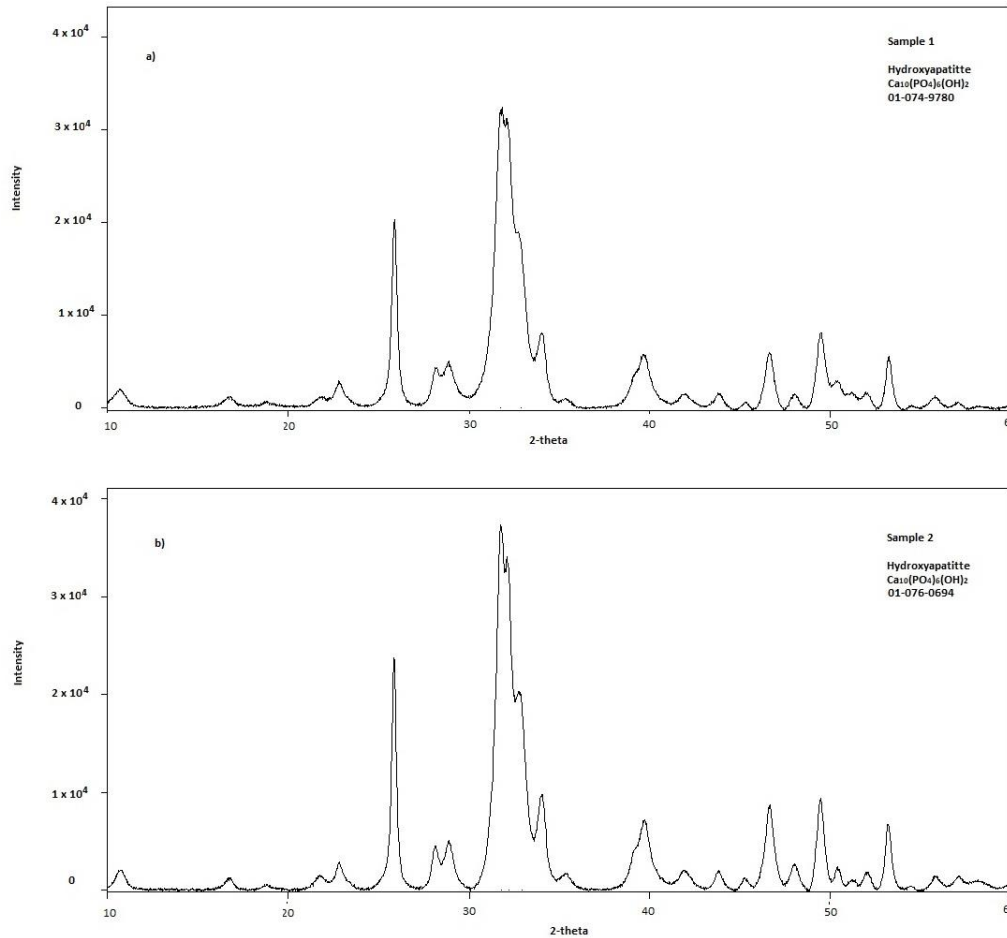


Figure 1. Diffractogram of sample 1 (hexagonal HAP); b) diffractogram of sample 2 (monoclinic HAP).

Effect of pure hydroxyapatite on corrosion efficiency

Measurement of pH and resistivity of aqueous suspensions of pigments is designed to stimulate the working conditions of pigments. Figure 2 shows the change in pH and conductivity of the pigment suspension during 28 days. From the measured values, hydrolysis of pigment ions prefers the formation of acid species, leading to a reduction of pH. The conductivity of the samples was very different, but in general, it increased indicating that the concentration of dissociated ions has increased over time.

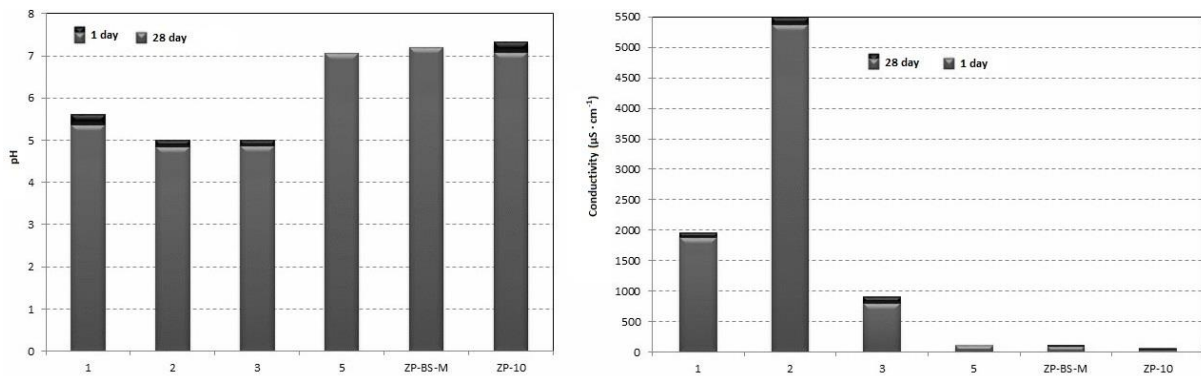


Figure 2. Results of preliminary corrosion tests: change of the pH and conductivity of the pigment suspensions during 28 days of aging.

The aqueous suspensions of the pigments were filtered and the pigments extracts were used for the evaluation of weight loss of steel plates, which were submerged in it during 2 months. During the test, significant color change of the extracts due to release of corrosion products was observed. At the same time, the district increase pH also indicated intense corrosive processes. However, for all samples, the conductivity value decreased. This

means that the dissociated ions from the pigment extract have been involved in the formation of a protective layer on the steel surface.

Next, corrosion indicators were calculated on basis of corrosion losses of steel plates. On basis of the corrosion indicators, the samples can be divided into 3 groups according to their anticorrosion efficiency. The first group includes samples with high corrosion efficiency that prevent corrosion processes. The concentration of phosphates in these extracts is sufficient to inhibit corrosion and phosphate protective coating, which is related to the average range of conductivity and Vivianite formation. The second group includes samples that did not show anticorrosive properties. The concentration of phosphates in these extracts is insufficient for corrosion efficiency, which is related to the low conductivity value and the formation of FeO(OH) as the major corrosion product. The third group includes samples that promote corrosion. In these samples, the corrosion processes were very intensive, which may be explained by the intensive reaction between the leachate and the steel substrate. Conductivity values were very high, causing expressive surface damage and FeO(OH) formation. For the accelerated corrosion tests, samples of 1, 2, 3, 5 and ZP-10 were selected. Examples of coating degradation for the selected samples are shown in Figure 3. The evaluation of the degradation of the coatings after the accelerated corrosion test showed that the best corrosion properties exhibit sample 5 and the worst is sample 3. The least damaged sample is the sample ZP-10 (commercial pigment). For all tested HAP samples, the formation of small crystals on the coating surface was observed (Fig. 3). XRD analysis of these crystals identified only organic compounds in their phase composition, which indicate destruction of the coating in testing corrosion chamber. Consequently, HAP samples showed poor corrosion properties for coating applications in comparison to standard pigment (ZP-10). The poor corrosion properties of sample 3 in the accelerated corrosion tests agree with the results of preliminary corrosion tests.

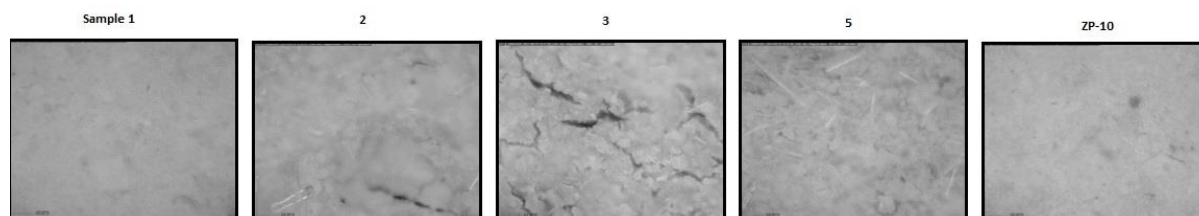


Figure 3. Appearance of coatings after accelerated corrosion test.

Conclusion

The selected synthesis conditions are suitable for the formation of crystalline hydroxyapatite phase.

On basis of preliminary corrosion tests, pigments were divided into 3 groups according to their anticorrosion effectivity: pigments with high anticorrosion efficiency; pigments without anticorrosion properties; pigments that promote corrosion. The samples of needle-like crystallites of smallest size show the best anticorrosion efficiency (sample 1). Preliminary corrosion tests show that some samples of HAP have higher anticorrosive effectivity than the commercial pigments (ZP-10).

From the accelerated corrosion tests, it is obvious, that HAP samples have deficient corrosion inhibition properties for coating applications compared with the commercial pigment. The poor corrosion properties of the pigments in the coating may be related to their low compatibility with the coating, which could be solved by surface modification of the pigment.

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