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Synthesis and characterization of hydroxyapatite obtained from different organic precursors by sol–gel method

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Abstract The synthesis of four types of hydroxyapatite synthesized from calcium chloride and four different organic phosphites is presented. The method of synthesis chosen is the sol–gel route, which has a number of advantages compared to other methods, like the intimate contact between reactants and the milder synthesis conditions. The samples were thermally treated, the TG/DTG/DTA curves being obtained at four heating rates, namely: 7, 10, 12 and 15 °C $\min^{-1}$. The samples were characterized before and after the thermal treatment using FT-IR analysis. The FT-IR spectra certified that the formed compounds represent hydroxyapatite. Based on the information from the TG curves and IR spectra interpretation, a reaction mechanism was proposed.

Keywords FT-IR · Hydroxyapatite · Sol–gel · Thermal analysis

Introduction

Bioactive ceramic materials have been largely used as bone substitutes for many decades. Among these bioceramics, a particular degree of attention has been attributed to hydroxyapatite due to the fact that it represents a natural component of the human bone, and due to its high biocompatibility [1].

A number of methods have been applied in the production of synthetic hydroxyapatites. Among these methods, an increasing attention has been given to the sol–gel method, due to advantages such as: the possibility of mixing the calcium and phosphorus precursors at a molecular level and that it requires incomparably milder conditions for the synthesis process, compared with the conventional methods, etc.

In the majority of cases, the phosphorus precursor—oxide, triethylphosphite or triethylphosphate—is introduced by a solvent, which can be either an aqueous or an organic phase. In the solution phase the reaction between the calcium precursor and the phosphorus precursor occurs slowly (depending on the nature of the reagents), that is why a quite long period of time called “ageing period” is required, minimum 24 h, for the desired compound to form.

The scope of the present research was the synthesis of hydroxyapatite (HA) using the sol–gel method, and the characterization of the formed compounds. The precursors were different from the ones found in the literature [2–4], and we used four different phosphorus precursors in order to perform a comparative study of the resulting compounds.

Materials and methods

The precursors used for the sol–gel synthesis of hydroxyapatites are presented in Table 1.

The Ca/P ratio in the compounds that fulfill the role of substituents of the natural bony tissue must be equal to 1.67, identical to the one in the bony mineral and in

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Table 1 Precursors used for the sol-gel synthesis of hydroxyapatite

Calcium precursor	Phosphorus precursor	Compound symbol
Calcium chloride	Diethylphosphyte	HA1
$CaCl_2 \cdot 2H_2O$	$(CH_3CH_2O)_2POH$	
Calcium chloride	Dibutylphosphyte	HA2
$CaCl_2 \cdot 2H_2O$	$(CH_3(CH_2)_3O)_2POH$	
Calcium chloride	Tris-(2-chloroethyl)phosphite	HA3
$CaCl_2 \cdot 2H_2O$	$(ClCH_2\text{-}CH_2O)_2PO(CH_2CH_2Cl)$	
Calcium chloride	Di-isopropylphosphite	HA4
$CaCl_2 \cdot 2H_2O$	$((CH_3)_2CHO)_2POH$	

hydroxyapatite, which is why the reactants were used in the same proportion, of 10/6.

The syntheses were performed according to the algorithm presented in Fig. 1.

The calcium chloride was introduced as an aqueous solution, just like the phosphorus precursor that was added under vigorous stirring for 30 min. The solutions were then aged for 96 h at room temperature. Then the pH was measured, the registered values being presented in Table 2.

After the pH was measured, the samples were dried for 24 h in the water bath at 60 °C, obtaining transparent hygroscopic gels of hydroxyapatite (HA2 and HA3 are highly hygroscopic), that changed into white, opaque gels after drying in the oven for 3 h at 95 °C.

The next stage consisted in the thermal treatment of the samples using the Diamond Perkin Elmer thermoanalyzer in order to transform the acid gel into a solid product with biocompatibility and osteoconductivity properties.

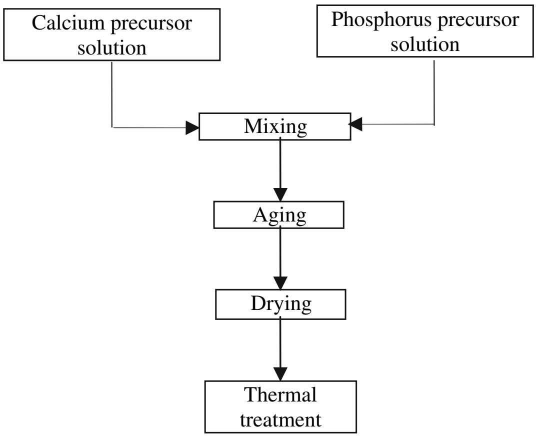


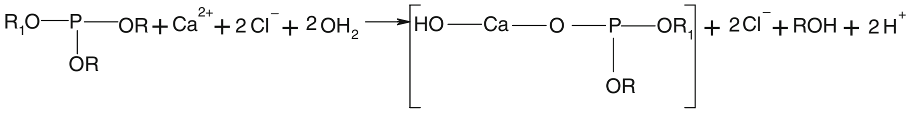
Fig. 1 The algorithm used for the hydroxyapatite synthesis

Table 2 The pH values for the aged solutions, before drying

Sample	HA1	HA2	HA3	HA4
pH	1.1	2.5	1.2	2

Results and discussions

The ageing stage is expected to produce pH modifications, due to the fact that the hydrolysis of the phosphatic precursor takes place, the hydrolysis products form a complex with the calcium ions in solution. After aging, the phosphorus hydrolyzed sol probably interacted with the calcium sol, forming derivatives that contain, as a base group, the Ca–O–P bond. For such a process, based on the mass loss results and our previous experience [5], it is considered that a reaction of the presented type can take place (Eq. 1). The mechanism we propose here is different from the one found in the literature [4]:



$$R_1O-\underset{\displaystyle OR}{\underset{|}{P}}-OR + Ca^{2+} + 2Cl^- + 2OH_2 \longrightarrow \left[HO-Ca-O-\underset{\displaystyle OR}{\underset{|}{P}}-OR_1\right] + 2Cl^- + ROH + 2H^+ \quad (1)$$

The samples were heated in aluminium crucibles under dynamic air atmosphere (100 mL/min), with four different heating rates: 7, 10, 12 and 15 °C min^{-1}, in order to perform a kinetic analysis of the thermal treatment stage of the samples. Such an experimental strategy was used in our previous studies [5].

In order to identify the formed compounds, the IR spectroscopy was used, on samples before and after the described thermal treatment. The IR spectra were recorded using a Perkin Elmer Spectrum 100 Device, using the U-ATR technique.

In Eq. 1, R_1 represents the hydrogen atom, for the case of HA1, HA2, and HA4 samples, and is identical to the R radical in the formulation, for tris-(2-chloroethyl)phosphite (sample HA3). For the samples HA1, HA2, and HA4, the radical R represents the organic radical in the phosphite precursor.

Drying the product causes the removal of the solvent, together with internal dehydration and polymerization/polycondensation reactions, having as a result the formation of a big number of Ca–O–P bonds in the dried gels. The slow evaporation provides not only the conditions of an intimate interaction, but also the thermal energy required for the achievement of the process.

Thermal treatment

The samples in state of gels were thermally treated in order to obtain crystalline materials. In order to perform a correct study upon the thermal behavior of the materials, according to our previous experience [5, 6], the samples were heated up to 550 °C with four different heating rates: 7, 10, 12 and 15 °C min^{-1}. The use of the four heating rates was necessary in order to perform a kinetic analysis of the thermal treatment stage.

Presented here are the thermal curves for the HA1 sample, at four heating rates (Fig. 2).

All the curves obtained present superposed or incomplete processes, which raise difficulties regarding the interpretation and kinetic studies. All the processes present endothermal effects, as can be seen in the DTA curves (the Perkin Elmer device identifies the DTA curve as Heat Flow), although in certain cases, towards the high temperatures region, some exothermic effects peaks appear, but with small appearance.

In Table 3, the main data regarding the thermal behavior of the samples heated with 15 °C min^{-1} is presented.

The correspondence of the maximum DTG and the maximum DTA can be observed; this correspondence is observed in all the other cases, meaning that each mass loss is doubled by a thermal event and they represent chemical processes.

There are three major decomposition processes observed on the TG curve for the HA1 sample. It was noticed that for the second process, the area of the peak from the DTG curve increases with the increase of the heating rate, and also an increase of the thermal effect was observed. The same thing was noticed for the process number 4 from the thermal curve, which can be better differentiated for higher heating rates, signifying the existence of some complex reactions.

For the HA2 sample, the high number and small amplitude processes observed for small heating rates decrease by number and unify in larger peaks, for higher heating rates. The endothermal effects observed for smaller heating rates in the range <200 °C also separate, and the effect of the first decomposition step increases.

For the HA3 sample, phenomena take place the opposite way compared to the HA2 sample case; towards higher heating rates the curves appear more complicated, although certain ranges of the curves get precise shapes. The second decomposition step is considered to be formed, for the 10 °C min^{-1} decomposition curve, of three stages, phenomenon not observed in the other cases; therefore, not all the mentioned stages were taken into consideration in the calculus of the mass loss.

In the HA4 case, once with the shift to the right of the peaks with the increasing heating rate, the tendency to unify of some of them can be noticed, so as at the heating rate of 15 °C min^{-1} there only exists one decomposition step instead of two or three. It is also noticed that the tendencies of the thermal effects modify with the heating rate, the processes from the small temperatures range having the tendency to give more and more endothermal effects, while the processes in the field of medium temperatures give smaller and smaller thermal effects.

The general observed tendency consists in significant differences between the decompositions of the same sample at different heating rates, the decomposition stages on one curve do not appear or they are shifted on another curve. This can be easily ascribed to unstable products of sol–gel synthesis, and possibly due to the fact that the reactions that took place in solution were incomplete. The sol–gel reactions take place very slowly, requiring large aging periods. In the present case, it can be presumed that the reactions did not end with the end of the aging period allocated during the synthesis, continuing and being probably activated or accelerated by the thermal treatment. Also, a possible cause for the observed irregularities may be the fact that the samples were heat-treated only up to 550 °C because of the Al crucibles.

IR spectra

Presented here are the spectra before and after the thermal treatment of HA1 sample (Fig. 3).

The spectra of the four analyzed substances are quite similar, that is the reason why only the spectra for one sample were presented here. Even if some small differences appear between the values of the peaks, fundamentally they represent the same types of vibrations, the basic characteristics being the same, namely: the presence of the OH groups, crystallization water, respectively, in plane or out of plane vibration of the OH bond, valence vibration of the PO bond, symmetrical or asymmetrical vibration of the O–P–O bonds (with conjugation between the two oxygen atoms) and the same types of symmetrical or asymmetrical vibrations for the phosphate group. Isolated, the presence of a P–O–R aliphatic or CH bond can be noticed, which may symbolize the fact that the reaction whose product is crystalline hydroxyapatite is still on the course to be achieved, but it is not complete, according to the synthesis procedure described.

A detail that deserves all the attention is the peak around the value of 1,050 cm^{-1}, considered in the specialty literature as one of the main clues of hydroxyapatite formation in the system, also observed in the present case [8].

The wide and intense peak from the region 3,200–3,400 cm^{-1} represents the alcohol OH vibration, due to

Fig. 2 The curves of the four samples heated with the rate of 7 °C min^{-1} in dynamic air atmosphere

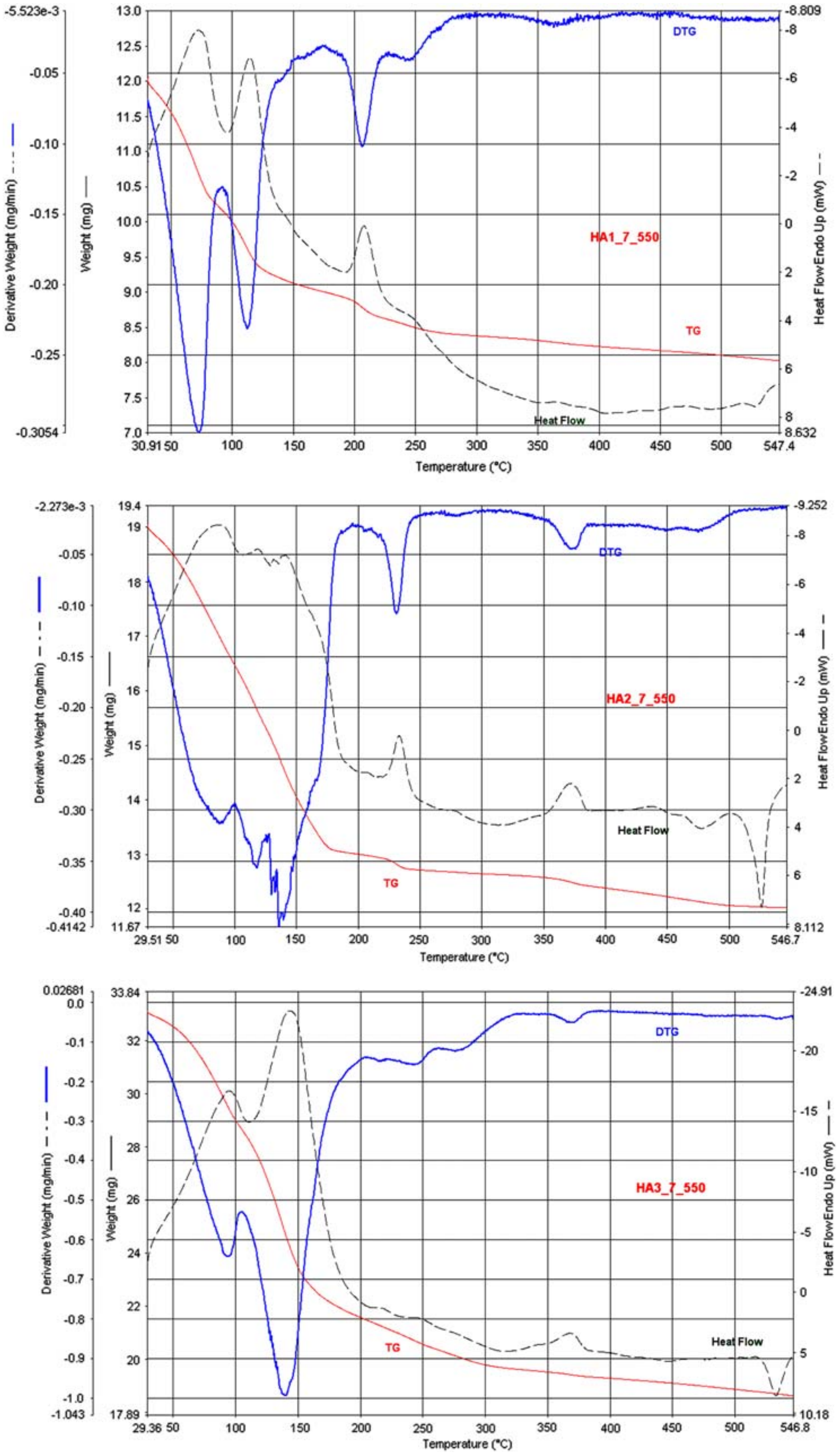


Fig. 2 continued

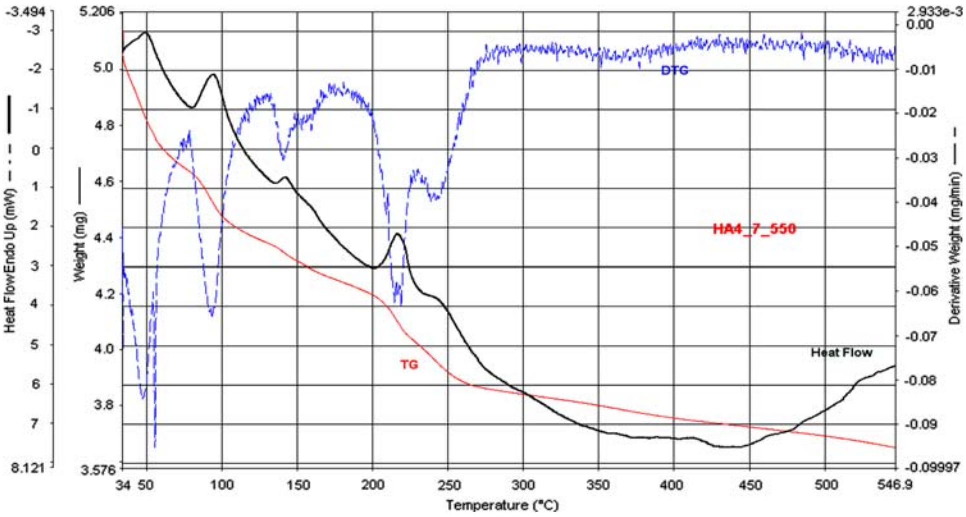


Table 3 Parameters of the thermal decomposition of the HA1–HA4 samples heated with 15 °C $\min^{-1}$

Sample	Process/step	T_i	T_f	DTG_{max}	DTA_{max}
HA1	1	40	101	82	82
	2	101	180	124	124
	3	200	241	219	219
	4	245	285	256	256
HA2	1	60	110	86	87
	2	135	143	138	138
	3	148	212	150	150
	4	228	266	241	241
	5	366	390	377	377
HA3	1	65	112	88	88
	2	108	225	153	153
	3	230	270	250	250
	4	355	385	375	375
HA4	1	96	180	167	167
	2	180	205	183	183
	3	252	293	260	260

intermolecular associations between the OH groups by hydrogen bonds [7, 9].

The differences observed between the substances obtained from different precursors can be ascribed to the nature of the precursors and their influence on the chemical reaction. The organic radical brings into the reaction a quite important contribution, even if the final product should be practically the same. The presence of the Ca–O bond cannot be evidenced because its characteristic vibration is situated below the detection limit of the equipment, around the value of 400 cm^{-1}.

Following the thermal treatment of the samples, the number of peaks on the FT-IR spectra decreases, as a proof for the removal of the impurities or solvents tracks, due to the chemical reactions taking place during the heating of the substances. For the samples heated at 500 °C, the peaks assigned to the organic functions disappeared.

The same differences are observed between the values under which a certain group or chemical bond appears in the spectra, but this is probably due to the nature of the reactants and the way they influence the reaction itself.

The basic characteristics of the hydroxyapatite are evidenced by the presence of the P–O vibration, phosphate group, the phosphorus atom bonded by two oxygen atoms (symmetrical or asymmetrical vibration) with conjugation effects, valence and both in-plane and out-of-plane deformations of the hydroxyl group and also the presence of water.

The peaks in the range 700–600 cm^{-1} can be ascribed to the valence vibration of the P–C or P–C–Cl bond, signifying the presence of some impurities in the HA1 and HA4 samples, or the formation of chloroapatite (side effect of the synthesis process), which is not necessarily a negative phenomenon, considering the fact that the chloride ions reach a concentration of 0.23% mass in the human bone during a 20–30 years period [8].

An important mention is that the wide peak observed before the thermal treatment around the value 1,050 cm^{-1} has shifted towards the value 1,025 cm^{-1}, but represents the same basic indication of hydroxyapatite formation.

The reference literature [4] confirms the present result, namely, the formation of hydroxyapatite can be observed (thermal treatment and FT-IR spectra) around a relatively low temperature, 500 °C, although in order to obtain crystalline hydroxyapatite higher temperatures, over 800 °C, are required.

The hygroscopic nature of the synthesis products is confirmed by the broad peaks present in the range 3,364–3,368 cm^{-1} for HA1–HA3 and 3,193 cm^{-1} (reduced) for HA4.

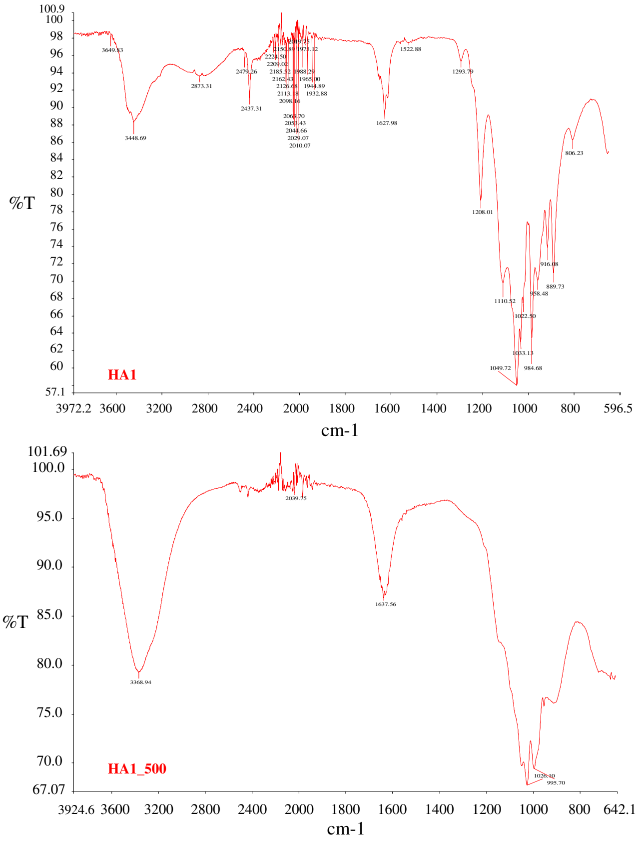


Fig. 3 HA1 IR spectra, before and after the thermal treatment at 550 °C

For a future research, important information, such as: the reaction media is very acidic, and in acidic catalysis the break of the C–O bond is predominant, comparing to the break of the P–O bond that takes place mostly in alkaline catalysis, is to be considered.

We presume that intramolecular condensation reactions take place, either by water loss or alcohol loss. The correlations with IR spectroscopy data seem to confirm this hypothesis, the formation of condensed compounds with a large number of Ca–O–P groups.

The first process of the thermal decomposition of HA1 sample presents a mass loss of 12.88%, close to the value theoretically calculated for the mechanism of condensation with loss of alcohol, of value 13.85%, this similarity constituting a good proof for the correctness of the working hypothesis.

Conclusions

The synthesis of hydroxyapatite was achieved, from calcium chloride and four organic phosphorus precursors, by sol-gel method. It was presumed that dehydration and polycondensation phenomena take place during the process, with formation of a large number of Ca–O–P groups. A reaction mechanism was proposed based on the gathered information, mechanism that is different from the mechanism found in the literature.

The obtained substances were thermally treated up to 550 °C with four different heating rates. The curves present complex phenomena, reason why a kinetic analysis of the thermal decomposition processes was not possible, despite the fact that data at four different heating rates were available. There exist major differences between the decompositions of the same sample with different heating rates, all processes being accompanied by endothermal effects. The calculated mass loss (based on the proposed mechanism) was compared with the experimental mass loss (from curves) and a good correlation between the sets of values was achieved, leading to the conclusion that the proposed mechanism is correct.

The FT-IR spectra were recorded for each sample before and after the thermal treatment. The spectra confirmed the formation of hydroxyapatite in all cases, even if some differences were noticed between the values under which a certain vibration appears in the spectra. The basic indication of hydroxyapatite formation is the peak presented at around 1,050 cm^{-1} in the spectra before the thermal treatment and 1,025 cm^{-1} in the spectra after the thermal treatment. Also, the IR spectra confirm the proposed reaction mechanism and provide information useful in further research.

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