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Biphasic Calcium Phosphates Prepared via Heat Treatment of Powders Synthesized by Wet Precipitation Using Phosphoric Acid and Calcium Hydroxide

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The aim of the present paper is to investigate biphasic calcium phosphates prepared via heat treatment of precipitated powders. The precursors are prepared by wet precipitation using phosphoric acid and calcium hydroxide. The as-synthesized powders are subjected to heat treatment varying with temperature and time. The degree of crystallinity as well as qualitative and quantitative analyses of the phase composition in the crystalline part of the investigated powders are done by SEM, XRD and FTIR. New data about the changes in the quantity of the crystalline and amorphous phases of the investigated powders are found depending on the heat treatment parameters. Increasing the calcination temperature leads to linear increase/decrease of the crystalline/amorphous phases, respectively. The crystalline phase of the as-synthesized precursor consists only of hydroxyapatite (HA). Phase transformation takes place at 700 °C calcination, resulting in the formation of a biphasic structure, consisting of HA and a low amount of β-tricalcium phosphate (TCP). Heat treatment in the temperature range 900 – 1300 °C leads to formation of biphasic HA/β-TCP structure with HA as the predominant phase. Clear correlation between the heat treatment parameters and the HA/β-TCP ratio is not observed. The highest β-TCP amount (39.2 %) is found at 1000 °C, while at high temperatures (1100 – 1300 °C) it is about 30.6 – 32.6 %. Increasing the duration from 1 h to 4 h leads to an increase of β-TCP up to 50.9 %. The new data on the crystallinity and HA/β-TCP ratio, obtained in the present study, will be used for optimization of the process parameters in the design of BCPs with definite composition, optimized resorbability, and mechanical properties.

Keywords: biphasic calcium phosphates, wet precipitation, heat treatment parameters, hydroxyapatite, β-tricalcium phosphate.

1. INTRODUCTION

The calcium phosphates are inorganic compounds, discovered in the distant 1769, and the presence of calcium orthophosphates in bones was found in the 1770s [1, 2]. Chronologically, monocalcium phosphate monohydrate (MCPM) and monocalcium phosphate anhydrous (MCPA) were the first prepared during the 19th century. The calcium deficient hydroxyapatite (CDHA) was developed in 1807 and its properties were described in 1819. During the same year, the MCPM was differentiated from the dicalcium phosphate dihydrate (DCPD). Thus, the investigations of the composition and properties of the calcium orthophosphates continues intensively till now. The information about the first attempts for treatment of different diseases by calcium orthophosphates was dated to the last decade of 18th century [1].

At present, the calcium phosphate ceramics (CPCs) are a group of biomaterials that have been widely used in bone reconstruction surgery due to their excellent biological properties and tissue behaviour. The CPCs are characterized by biocompatibility, cost-effectiveness, and predictable results. They are preferred grafting materials in orthopaedic, maxillofacial, and oral surgery as well as implant dentistry, neurosurgery, etc. [3 – 8].

The hydroxyapatite (HA) and tricalcium phosphate (TCP) are the most frequently used CPCs as they resemble the inorganic constituent of the bone [3 – 5, 9 – 11]. The HA is a stable, biocompatible mineral that can serve as an excellent scaffold for bone regeneration. The TCP ceramics are biocompatible, bioactive, and osteoconductive and do not cause toxic reactions and immunologic responses. They can be found in three polymorphic modifications: β-TCP with rhombohedral crystal lattice and high-temperature α- and α′-TCP with monoclinic and hexagonal crystalline structures, respectively [2, 3, 12]. Different structure defines differences in the chemical and biological properties of the β- and α-TCP. The relatively rapid bioresorbability (lower than α-TCP and higher than HA) and biodegradability of β-TCP allow for its absorption and replacement by new bone [13].

According to the review of the existing calcium orthophosphates and their properties, the solubility of the CPCs decreases with increasing the Ca/P ratio in the interval 1.0 – 1.67 [2, 3, 5, 9]. The HA is relatively stable in living organisms and comprises half of the bone weight. The Ca/P ratio in HA is 1.67. Numerous studies have demonstrated that the HA biodegradability is too low to allow bone replacement but can serve as a scaffold for more rapidly dissolving materials. In addition, the HA has mechanical properties similar to those of the cancellous bone. On the

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other hand, the Ca/P ratio in α-TCP and β-TCP is 1.5. They have poorer mechanical properties than HA and greater solubility (α-TCP > β-TCP > HA) and degradation, which does not allow for sufficient bone adhesion [14, 15].

The biphasic calcium phosphates (BCPs) were created in the mid of 1980s [5]. They were composed mainly of HA and β-TCP thus improving the resorbability and mechanical properties of the grafting material [5, 6]. The degradability of the final product can be adjusted by altering the Ca/P ratio during the synthesis. The BCPs have been used to ensure controlled bioactivity and solubility and, thus, overcome the limitations of the single-phase bioceramics [16]. Adjusting the CPC combinations can obtain gradual material resorption and its subsequent replacement with new bone. BCPs have various medical and dental applications. They can be used as bone substitutes, cements, scaffolds, implant coatings, and systems for controlled drug release [3 – 6]. It has been suggested that the amount of material resorption and bone deposition is inversely proportional to the HA/β-TCP ratio [17, 18].

Various methods for TCP synthesis have been developed, such as wet-chemical precipitation [19 – 22], solid-state synthesis [23 – 25], thermal conversion [26], sol-gel method [10, 27, 28], and solution combustion synthesis [29]. Regardless of the different technological processes, it is very difficult to prepare pure substances on the basis of calcium orthophosphates [5]. Actually, each of the synthesized CPC powders consists of a mixture of one or two main phases and several phases in minimal quantity.

Wet precipitation is one of the most preferred methods for TCP synthesis due to its simplicity, low working temperatures, high percentage of pure products and cost-effectiveness [10, 30 – 32]. The parameters of the wet precipitation method include starting materials and Ca/P ratio, reaction temperature, aging time, pH of the solution, addition rate of the ingredients, reactant concentration, and stirring speed [12, 20, 26]. It is very important to know that a slight variation in the parameters could lead to quite different composition of the as-synthesized powder, which can affect the final product. The composition of the precursor, temperature, holding time at the highest temperature and cooling rate are the most important parameters of the following heat treatment [23, 26, 33 – 35].

The most common materials used in the wet precipitation synthesis are phosphoric acid and calcium hydroxide. When using these materials, Othman R. et al. [20, 21] have found that HA can be obtained if the Ca/P ratio is 1.67. For preparation of β-TCP, the Ca/P ratio should be 1.5. If the Ca/P ratio is between these two values, biphasic structures are formed. Kwon S. et al. [19] have revealed that the Ca/P ratio is influenced on the pH of the solution. In pH = 7.4, the Ca/P ratio is about 1.5, increasing the pH up to 8.0 leads to increase of the Ca/P ratio until 1.6. According to them the proper pH value for obtaining biphasic HA/TCP is 8.0. Gibson I. et al. [30] have synthesized Ca-deficient apatite with Ca/P ratio 1.5, which was then calcined for 2 hours at temperatures 500 – 1100 °C. Natasha A. et al. [10] have obtained biphasic HA/β-TCP mixtures after heat treatment at 800 – 900 °C temperatures.

The BCPs are mainly prepared by thermal methods: sintering of non-stoichiometric types of CPCs, such as amorphous calcium phosphates (ACP) and CDHA at temperatures in the range 1000 – 1300 °C for obtaining different composition (HA/β-TCP or HA/α-TCP); solid-state reactions among the solid reagents performed at elevated temperatures; flame spray pyrolysis and combustion synthesis [5, 36, 37]. There are attempts to prepare BCPs in a liquid mix or by sol-gel technique; however, each of these processes should be followed by sintering [27, 38, 39]. The BCPs, produced by different methods, are characterized by different compositions and properties which could influence their biomedical applications.

As it is shown above, the slight variation in the parameters of the wet precipitation synthesis could lead to obtaining of powder with quite a different composition. That is why, it is preferred to prepare BCPs by thermal methods, in which precursors with definite composition and properties are used, and the only variables are the parameters of the heat treatment process. Researchers, who prepare BCPs by wet-chemical precipitation of the precursors followed by calcination at high temperature, often obtain different results due to the influence of multiple parameters [15, 19, 31, 33]. Therefore, more investigations are needed for optimization the parameters of both wet-precipitation and heat treatment processes in order to obtain BCPs with definite composition and properties.

The aim of the present paper is to investigate the biphasic calcium phosphates prepared via heat treatment of powder synthesised by wet precipitation method using phosphoric acid and calcium hydroxide. The as-synthesized precursor is subjected to calcination with variation of the temperature and time. The degree of crystallinity as well as qualitative and quantitative analyses of the phase composition of the obtained BCPs, are performed. The obtained data will be used for optimization of processes parameters in the design of BCPs with a definite composition.

2. EXPERIMENTAL DETAILS

2.1. Wet precipitation synthesis

For precursor's preparation, phosphoric acid and calcium hydroxide, ensuring an initial Ca/P ratio of 1.5, were used. At first, 100 ml of 0.30 mol phosphoric acid (85 % H_3PO_4, Chempur, Piekary Slas-kie, Poland) were added slowly (2 ml/min) dropwise to 300 ml of 0.45 mol suspension of calcium hydroxide ($Ca(OH)_2$, Chempur, Piekary Slaskie, Poland). The pH of the as-prepared suspension was 10 and it was stirred at 600 rpm speed by a magnetic stirrer (MS10-H500-Pro, DLAB Scientific Co., Ltd. Beijing, China) at a temperature of 70 °C for 24 hours. After completion of the reaction, the mixture was filtered and washed twice with distilled water and absolute ethyl alcohol. The resulting precipitate was dried 24 h at 120 °C temperature in a laboratory dryer (DZ-2BL, Faithful Instrument Co., Huanghua, China). The dried precipitate was ground in a mortar and divided into portions of two grams each, which were subjected to heat treatment.

2.2. Heat treatment

The as synthesized powders are subjected to heat treatment (calcination) in a furnace LH 30/14 (Nabertherm

GmbH, Bahnhofstr, Germany). At first, initial experiments were performed by heating the powders up to 700 °C temperature and 1 – 4 hours holding time. It was found that incomplete phase transformations took place at this temperature, leading to biphasic composition with minimal β-TCP amount. That is why, the experiments continued with heat treatment of the samples at higher temperatures 900 – 1300 °C and holding time of 1 – 4 hours. The heat treated powders were ground in a mortar.

The designation of the samples and the calcination parameters are given in Table 1.

Table 1. Samples designation and calcination parameters

№	Samples designation	Calcination parameters	
		Temperature, °C	Time, h
1	M1-0-0	0	0
2	M1-700-1	700	1
3	M1-700-4	700	4
4	M1-900-2	900	2
5	M1-1000-1	1000	1
6	M1-1000-2	1000	2
7	M1-1000-4	1000	4
8	M1-1100-2	1100	2
9	M1-1200-2	1200	2
10	M1-1300-2	1300	2

2.3. Samples characterization

The morphology and composition of the precipitated and calcined powders were studied by scanning electron microscopy (SEM, Zeiss Evo 10, Jena, Germany) equiped with EDX detector.

The chemical and phase composition of the as-synthesized and heat treated powders were investigated by XRD and FTIR analysis. The XRD analysis was performed in Cu Kα irradiation in the range of 2Θ = 9 – 54° with step of 0.02° using Bruker D8 Advance diffractometer (Billerica, MA, USA). A specialized software DIFFRAC.Eva, developed by Bruker, was used for the identification of the individual phases and their relative ratio. To determine the phase distribution and degree of crystallinity the following Crystallography Open Database (COD) records were used: 1) record code 9010052 for HA ($Ca_5(PO_4)_3(OH)$); 2) record code 1517238 for β-TCP ($Ca_3(PO_4)_2$). For identification and calculation of the phases, the specialized software DIFFRAC.Eva was used, which allowed fitting the peaks (via PseudoVoigt peak profile) of the phases from XRD data. Next, the peaks of the phases were fitted and the ratio between the phases was determined.

The calculation of the degree of crystallinity is based on a semi-quantitative analysis, using the following hypothesis: all the phases are crystalline and detected, which means that the software assumes that their sum is 100%. The concentration of the phases is set in the pattern from the COD database. The analysis is performed based on the pattern's relative heights and measured intensities of the crystalline peaks. This procedure is implemented in the used software. The calculation of the crystallinity is based on the following Eq. 1:

$$Crystallinity = \frac{Area\ of\ Crystalline\ peaks}{Area\ of\ all\ peaks} \qquad (1)$$

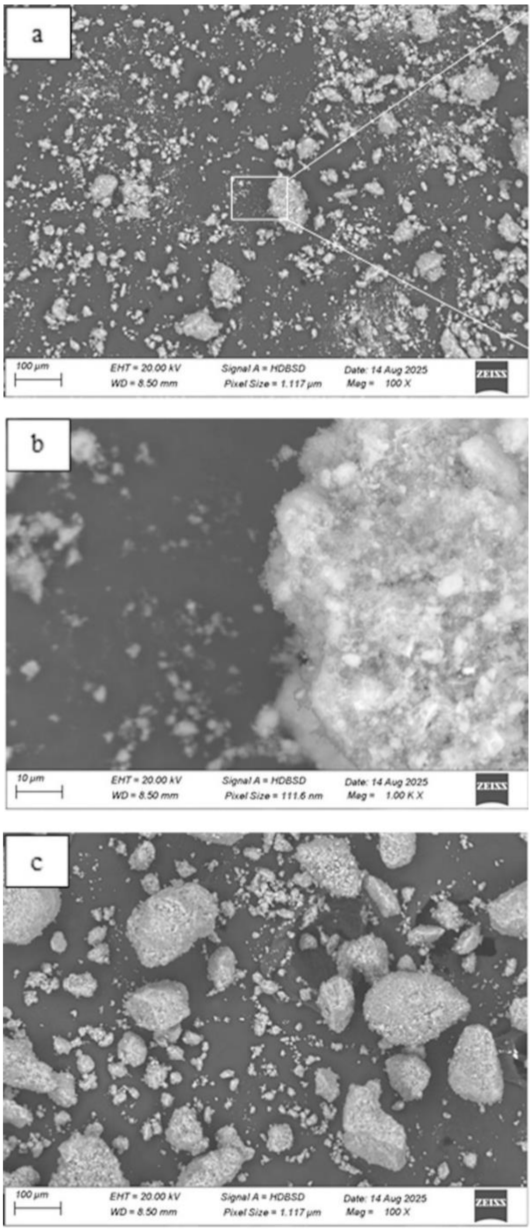
For this procedure, the used software can calculate the areas of the crystalline peaks based on the widths of the peaks and baseline of the diffractogram. Based on the diffractogram baseline, the area of all peaks on the diffractogram can also be calculated. After that the crystallinity is calculated using Eq. 1.

The bonding architecture and type of the functional groups in the samples were investigated by FTIR analysis in the range of 4000 – 500 cm^{-1} using Shimadzu BX II (Perkin Elmer, USA).

3. RESULTS AND DISCUSSION

3.1. Powder morphology and composition

The morphology and grains sizes of the as-synthesized and heat treated powders are shown in Fig. 1 and Fig. 2.



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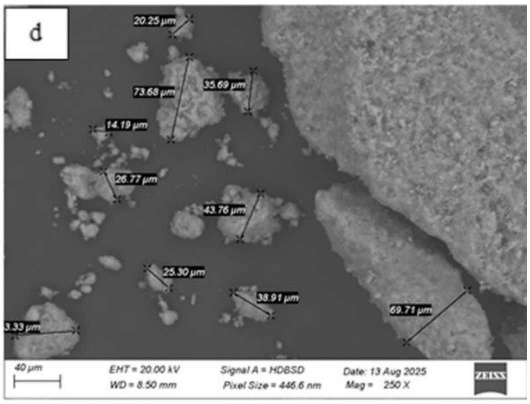


Fig. 1. a, b – morphology of the as-synthesized powder; c, d – after 2 h calcination at 1000 °C

The precipitated powder (Fig. 1 a, b) consists of aglomerates with different shape and sizes that vary in the range of 3 – 83 µm (Fig. 2 a). The powder particles after heat treatment (Fig. 1 c, d) are characterized with an irregular shape, smooth walls and larger sizes varying in wide interval of 10 – 570 µm (Fig. 2 b). It is very difficult to distinguish the individual particles in both samples. The pictures at high magnification in Fig. 1 b and Fig. 1 d have shown that the precipitated agglomerates and calcined powder particles are built of tiny, less than 1 µm, particles.

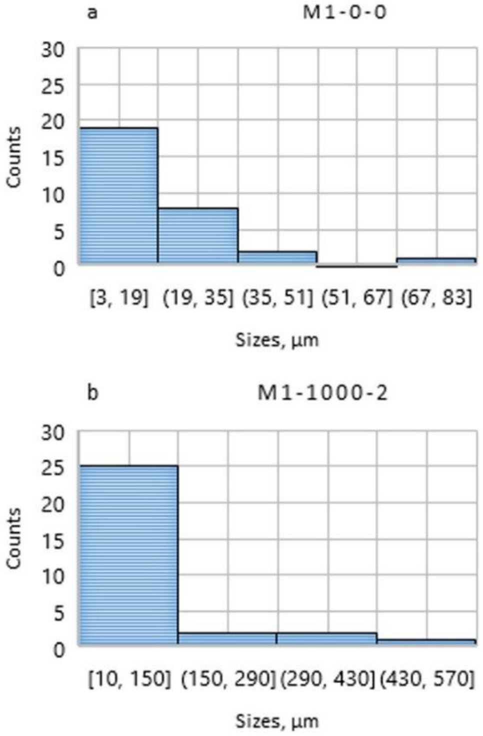
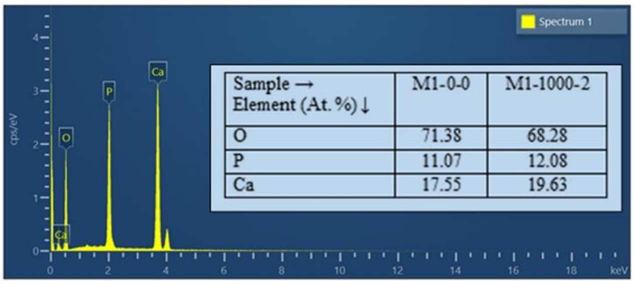


Fig. 2. a – grains sizes of the as-synthesized powder (M1-0-0); b – grain sizes of powder heat treated 2 h at 1000 °C (M1-1000-2)

Fig. 3 shows the chemical composition of the as-synthesized and heat treated powders. Only oxygen, phosphorus and calcium are detected. The calculated Ca/P ratio of the precipitated powder is 1.59 and that of the calcined powder is 1.62. According to Othman R. et al. [20, 21] biphasic structures are formed if the Ca/P ratio is in the range 1.5 – 1.67, which is proved by our experiment and the following investigation of the phase composition.



Sample → Element (At. %) ↓	M1-0-0	M1-1000-2
O	71.38	68.28
P	11.07	12.08
Ca	17.55	19.63

Fig. 3. Chemical composition of the as-synthesized powder (M1-0-0) and powder heat treated 2 h at 1000 °C (M1-1000-2)

3.2. Phase analysis

The results of the present study have shown that the phase composition of the powders consists of crystalline and amorphous phases at different ratios depending on the heat treatment parameters (Fig. 4).

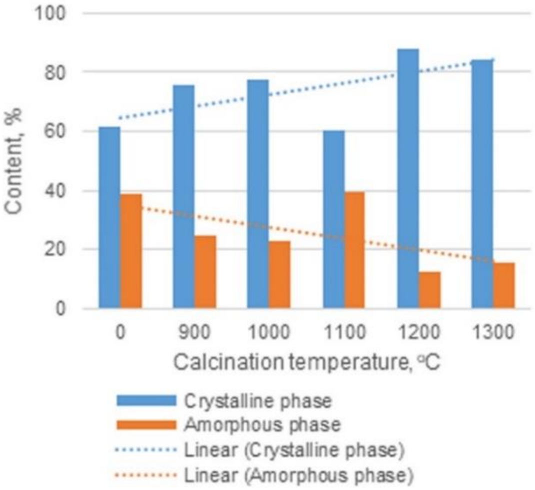


Fig. 4. Quantity of the crystalline and amorphous phases of as-synthesized powder (0 °C) and after 2 hours calcination at different temperature.

The crystalline/amorphous phase ratio of the as-synthesized samples is 61.4/38.6 %. The increase of the calcination temperature in the range 900 – 1300 °C leads to increase of the crystalline phase amount, as the maximum (87.9 %) is at 1200 °C. The graph in Fig. 4 shows nearly linear tendency of the crystalline phase increase and the amorphous phase decrease with increasing the calcination temperature. These findings are comparable with the results of Massit A. et al. [12] who have obtained crystallinity in the range of 72 – 86.

Since only crystalline phases can be identified by XRD analysis, in this study, our talk will be only about the crystalline part of the investigated powders.

The XRD analysis of the as-synthesized powder shows that the crystalline phase consists only of HA (Fig. 5 a). The HA peaks are wide and diffuse which is an evidence of poor crystallinity. According to Dorozhkin S.V. [2 – 4] Ca-deficient hydroxyapatite (CDHA) can be found in pH 6.5-9.5 and Ca/P ratio between 1.5 – 1.67. Gibson et al. [30] have revealed that as a result of the chemical reaction of the same initial substances, Ca-deficient apatite is formed with structure and diffraction peak positions matching closely to that of the stoichiometric HA. In our case, the solution pH is 10, which leads to increase of the Ca/P ratio, resulting in formation of CDHA with 1.59 Ca/P ratio.

After 1-hour calcination at 700 °C (Fig. 5 b), the HA peaks become sharper and well distinguished and small peaks of β-TCP appear as well. Increasing the calcination time until 4 hours leads to decrease of the HA peaks and increase of the β-TCP peaks intensities (Fig. 5 c). Therefore, raising the calcination time leads to higher β-TCP amount. Fig. 6 shows diffractograms of the samples heat-treated 2 hours in the temperature range 900 – 1300 °C. Sharp peaks of the two phases HA and β-TCP, showing good crystallinity, can be clearly seen. At high temperatures (1200 and 1300 °C), peaks of α-TCP are not observed.

Therefore, the heat treatment leads to a change of the phase composition of the crystalline part of the investigated powders from monophasic HA of the as-synthesized sample to biphasic HA/β-TCP of the heat treated ones. The highest peak (largest amount) of β-TCP is formed after calcination at 1000 °C, that is why this temperature is chosen to study the influence of the calcination duration.

When investigating the phase composition after heat treatment at 1000 °C for different holding times of 1, 2 and 4 hours, the same products are obtained (Fig. 7). Clear sharp peaks of HA and β-TCP are observed. The intensity of β-TCP peaks increases and that of HA peaks decreases at 4 h holding time. These results indicate an increase in the β-TCP and decrease of the HA amount.

Our findings are in agreement with the results obtained by Gibson et al. [30], Natasha A. et al. [10], and Othman R. et al. [20, 21]. Gibson et al. [30] have revealed that the Ca-deficient apatite transforms into β-TCP in the temperature range 710 – 740 °C. Depending on the Ca/P ratio of the precipitate, the Ca-deficient apatite can be transformed to HA or β-TCP/HA. Natasha A. et al. [10] have confirmed that the decomposition of deficient apatite into HA/β-TCP biphasic mixtures took place in the temperature interval 800 – 900 °C. As the Ca/P ratio of the precipitated powder in our study is 1.59, biphasic HA/β-TCP powder is obtained after heat treatment with different parameters.

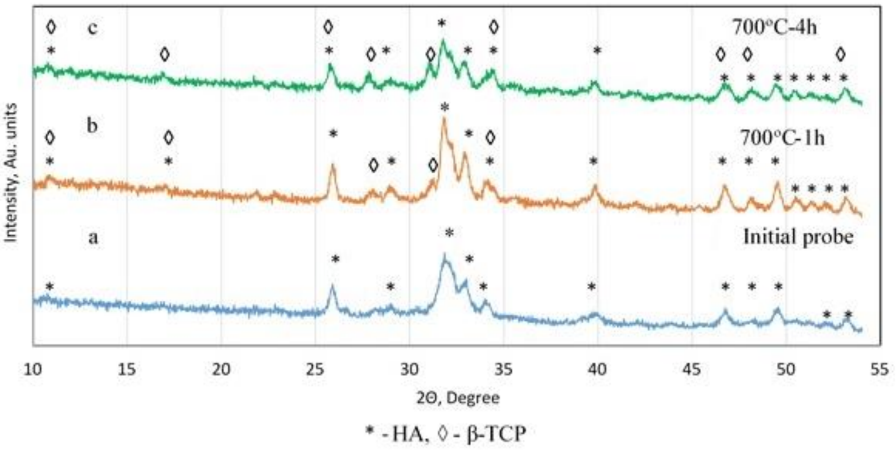


Fig. 5. Phase composition of as-synthesized powder and after calcination at 700 °C

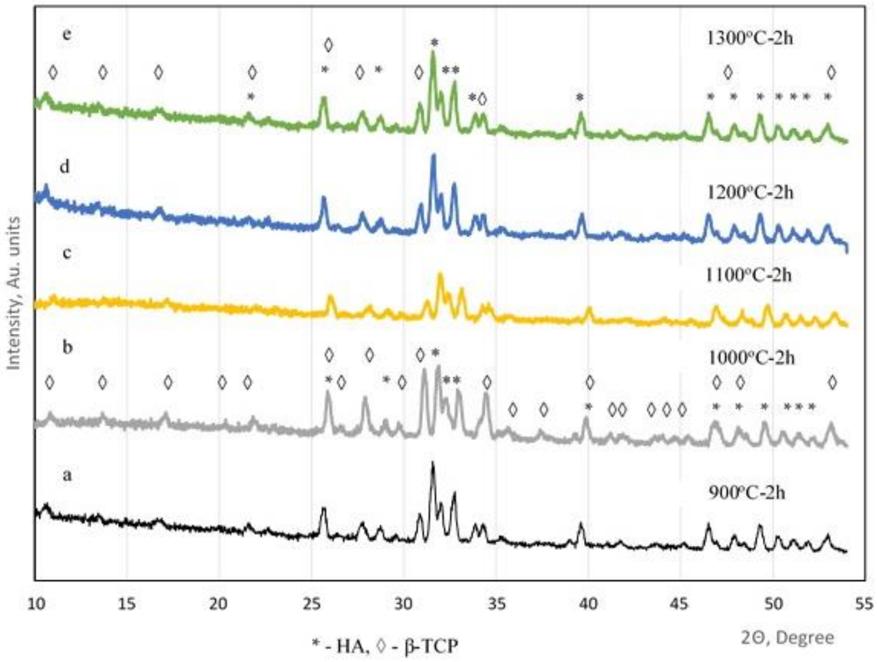


Fig. 6. Phase composition of powder after 2 h calcination at different temperature

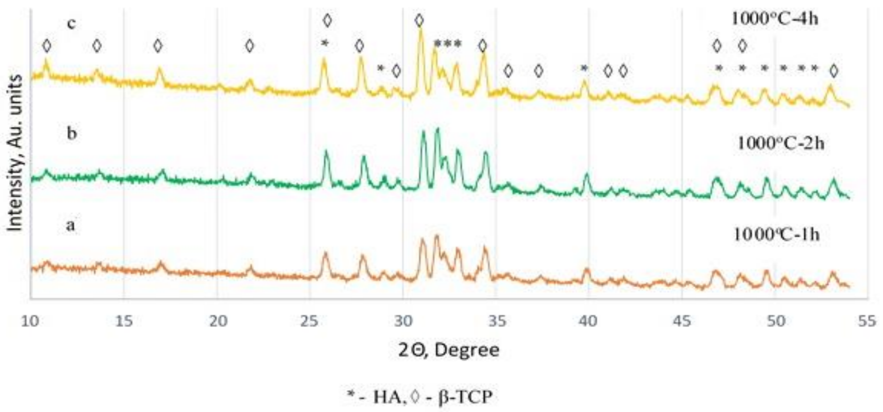


Fig. 7. Phase composition of powder after calcination at 1000 °C and different duration

3.3. FTIR analysis

The results of FTIR investigation (Fig. 8 and Table 2) have shown peaks of the phosphate (PO_4^{3-}) group at 547, 609, 987, 1041, and 1111 cm^{-1}, which can be attributed to the Ca-deficient apatite in the as synthesized samples. The peaks at 655 and 3580 cm^{-1} are typical for the hydroxyl group (OH^-).

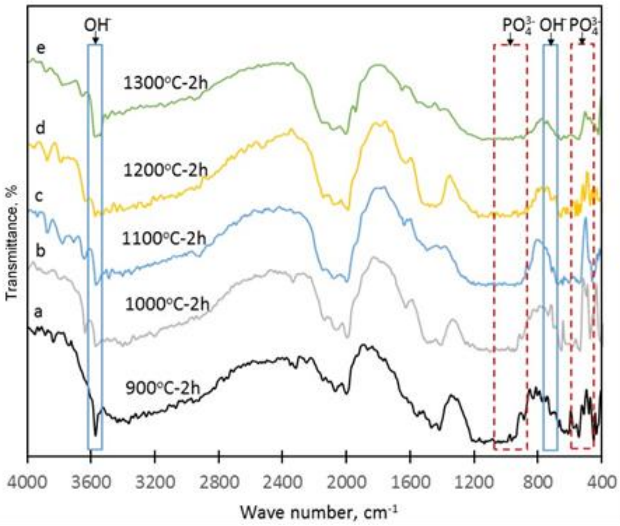


Fig. 8. FTIR spectra of powder after 2 h calcination at different temperatures

Table 2. Characteristic FTIR peaks (wavenumber, cm^{-1}) and corresponding functional groups presented in the samples

№	Sample	PO_4^{3-}	OH^-
	Initial sample	HA	HA
1	M1-0-0	547, 609, 987, 1041, 1111	655, 3580
	Heat treated	β-TCP and HA	HA
2	M1-700-1	578, 594, 956, 1033, 1087	640, 3556
3	M1-700-4	555, 586, 972, 1003, 1095	678, 3572
4	M1-900-2	540, 594, 964, 1064, 1118	632, 3572
5	M1-1000-1	578, 609, 972, 1003, 1080	632, 3572
6	M1-1000-2	540, 586, 941, 1003, 1118	648, 3572
7	M1-1000-4	570, 594, 979, 1041, 1072	632, 3572
8	M1-1100-2	578, 594, 979, 1041, 1072	632, 3580
9	M1-1200-2	540, 601, 941, 1026, 1057	640, 3580
10	M1-1300-2	532, 609, 949, 1010, 1141	648, 3572
	Ref. [15], Ref. [40]	557, 604, 945, 1087	630, 3571

After heat treatment, peaks of the phosphate group at 532 – 609 and 941 – 1141 cm^{-1} are observed which can be assigned to the β-TCP and HA. The peaks of the hydroxyl group are slightly shifted to 632 and 3572 cm^{-1}, matching well with those in the HA and proving the formation of HA with good crystallinity. These results correspond well with the findings of Gibson et al., Xidaki D. et al. and Hayashi K. et al. [15, 30, 40] (Table 2). It is found that the FTIR spectra of Ca-deficient apatite have two peaks of υ^3 band at 1088 and 1029 cm^{-1} [30]. The pure β-TCP is characterized by two sharp peaks of the phosphate (PO_4^{3-}) group at 604 and 544 cm^{-1}. While in the biphasic calcium phosphates, the peaks are mixed and slightly shifted at about 600, 570, and 540 cm^{-1} [15].

3.4. Quantitative analysis

The relative ratio of different phases in the crysttaline part of the studied powders depending on the heat treatment parameters, is shown in Fig. 9.

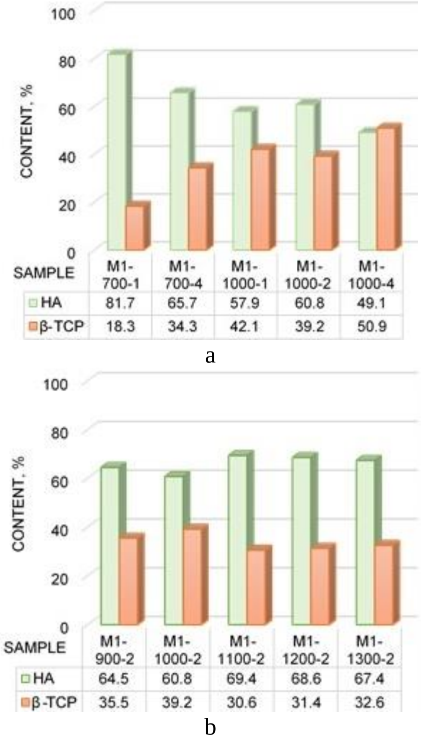


Fig. 9. Influence of the heat treatment parameters on the phase composition of BCP powders: a – duration; b – temperature

After 1 h calcination at 700 °C, the monophasic HA composition of the initial powder changes to biphasic, consisting of 81.7 % HA and 18.3% β-TCP (Fig. 9 a). Increasing the holding time until 4 hours leads to a decrease of the HA to 65.7 % and an increase of the β-TCP up to 34.3 %. After heat treatment in the temperature range 900 – 1300 °C, biphasic HA/β-TCP structure with a predominant HA phase is formed (Fig. 9 b).

A clear correlation between the calcination temperature and the phase ratio cannot be seen. The highest β-TCP amount of 39.2 % is found in calcination at 1000 °C, as the rest is HA (60.8 %). At the high temperature range (1100 – 1300 °C) the lower amount of β-TCP is observed (30.6 – 32.6 %) and the HA is in the range 69.4 – 67.4 %. It can be seen in Fig. 9 a that the calcination duration at 1000 °C temperature does not strongly influence the relative ratio of phases. The HA/β-TCP ratio changes from 57.9/42.1 % to 49.1/50.9 % in 1 h and 4 h calcination duration, respectively.

The composition of the precursors is crucial for the phase transformations during the heat treatment. It is found that BCPs are obtained when the pH of the solution is 8.0 and Ca/P ratio is between 1.5 – 1.67 [19, 20, 21]. It should be taken into account that at pH 8.0 the Ca/P is about 1.6. As the pH stability range of HA is between 6.5 – 9.5, it is expected that HA to be a predominant phase of the BCPs in this range [5].

In our study, phosphoric acid and calcium hydroxide with Ca/P ratio 1.5 are used as starting materials. The crystalline phase of the as-synthesized precursor consists only of HA (Fig. 5), which is may be due to the pH 10 of the initial solution which changes the Ca/P ratio until 1.59. As a result, a biphasic HA/β-TCP crystalline structure with predominant HA phase is obtained in the following heat treatment. Increasing the temperature up to 1000 – 1300 °C leads to lower β-TCP increase may be due to the reversible transformation of β-TCP into HA and stabilization of HA at higher temperatures [10, 42]. Transformation of β-TCP into α-TCP has not been observed, because β-TCP phase can remain thermally stable even up to 1300 °C [20]. The calcination time between 1 – 2 hours has low influence on the β-TCP formation. Its amount increases with about 10 % only at 4 hours of calcination. These results correspond well with findings in the works of [10, 41, 42].

4. CONCLUSIONS

Biphasic calcium phosphates, prepared via heat treatment of precipitated powders, are investigated in the present study. The precursor is prepared by wet-chemical precipitation using phosphoric acid and calcium hydroxide. The as-synthesized powder is subjected to calcination at different temperatures and durations.

New data about the quantitative and qualitative changes in the crystalline and amorphous phases of the investigated powders are found depending on the heat treatment parameters. The crystalline/amorphous phase ratio of the as-synthesized samples is 61.4/38.6 %. Linear tendencies of the crystalline phase increase and the amorphous phase decrease with increasing the calcination temperature are revealed.

The crystalline phase of the as-synthesized precursor consists only of HA. The phase transformations take place at 700 °C calcination, resulting in the formation of biphasic HA/β-TCP structure. Increasing the process duration leads to an increase of the β-TCP amount from 18.3 % in 1 h up to 34.3 % in 4 h process. Heat treatment in the temperature range 900 – 1300 °C leads to the formation of biphasic HA/β-TCP crystalline structure with HA as the predominant phase.

A clear correlation between the heat treatment parameters and the HA/β-TCP ratio is not observed. The highest β-TCP amount (39.2 %) is found at 1000 °C, while at high temperatures (1100 – 1300 °C) it is about 30.6 – 32.6 %. The HA amount is 60.8 % and in the range 69.4 – 67.4 % respectively. Increasing the duration from 1 h to 4 h leads to a slight increase of β-TCP and a change of the HA/β-TCP ratio from 57.9/42.1 % to 49.1/50.9 % respectively.

The newly obtained data on crystallinity and HA/β-TCP ratio in heat treatment with different parameters will be used for optimization of the processes in the design of new biofunctional materials with optimized resorbability and mechanical properties required for bone grafts and tissue engineering.

Acknowledgments

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