SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE 
\(\beta\)-TCP AND CDHAp NANO Particles

Bersu Baştuğ\(^1\)

\(^1\)Department of Metallurgical and Materials Engineering, METU, 06800 Ankara, Turkey

ABSTRACT

Bioceramics are used in different applications due to their high surface-to-volume ratio, reactivity, etc. Moreover, nano-sized calcium orthophosphates have an important role in the hard tissue-engineering field and they revolutionize this field starting from bone graft applications to the controlled drug delivery systems. Therefore, nanodimensional calcium orthophosphates are the important topics in material science and engineering. This paper reports the synthesis and characterization of the most widely used calcium orthophosphates such as hydroxyapatite (HAp), \(\beta\)-Tricalcium phosphate (\(\beta\)-TCP) and calcium-deficient hydroxyapatite (CDHAp). X-ray diffraction (XRD) techniques and Fourier transform infrared analyses (FTIR) were used to understand chemical and structural characteristics of the as-synthesized powders. The critical parameters affecting the synthesis processes of the calcium phosphates were also investigated.

Keywords: Bioceramics, Nanoparticles, Calcium orthophosphates

INTRODUCTION

During the past 30 - 40 years, the use of biomaterials has extensively increased with the evolution of innovated fields such as tissue engineering and bone regeneration applications. Bioceramics, in this sense, are preferred to be used in the class of medical implants. Throughout the body, bioceramics are used in a lot of different applications now. Some applications include dental implants, percutaneous devices, and use in periodontal treatment, alveolar ridge augmentation, orthopedics, maxillofacial surgery, otolaryngology, and spinal surgery [1]. These bioceramics are classified as either “bioinert” or “bioactive” and bioactive ceramics are categorised as resorbable or non-resorbable. The type of materials used as bioactive ceramics include polycrystalline materials such as bioglasses, glass ceramics and ceramic-filled bioactive composites. All of these materials are commonly produced in either porous or bulk form, granular form and in the form of coatings [2]. Nano-sized particles and crystals play an important role in the formation of calcified tissues of various organisms. The most important nano-sized and nanocrystalline calcium orthophosphates are present in natural bone, teeth, deer antlers and tendons of mammals in order to make these organs stable and hard. The most common calcium orthophosphates with their chemical formula and their Ca to P ratio are listed in Table 1 [3].

Table 1. Most common calcium orthophosphates with their chemical formula and Ca/P molar ratio.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Chemical formula</th>
<th>Ca/P molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite (HA, HAp or OHAp)</td>
<td>Ca(_{10})(PO(_4))(_6)(OH)(_2)</td>
<td>1.67</td>
</tr>
<tr>
<td>(\alpha)-Tricalcium phosphate ((\alpha)-TCP)</td>
<td>(\alpha)-Ca(_3)(PO(_4))(_2)</td>
<td>1.5</td>
</tr>
<tr>
<td>(\beta)-Tricalcium phosphate ((\beta)-TCP)</td>
<td>(\beta)-Ca(_3)(PO(_4))(_2)</td>
<td>1.5</td>
</tr>
<tr>
<td>Calcium-deficient hydroxyapatite (CDHA or Ca-def HA)</td>
<td>Ca(_{2n})(HPO(_4))(<em>n)(PO(<em>4))(</em>{3-n})(OH)(</em>{2n})</td>
<td>1.5 – 1.67</td>
</tr>
<tr>
<td>Amorphous calcium phosphates (ACP)</td>
<td>Ca(_{2n})H(_n)(PO(_4))(<em>n)(</em>{2n})H(_2)(_O), n = 3 – 4.5; 15 – 20% H(_2)(_O)</td>
<td>1.2 – 2.2</td>
</tr>
</tbody>
</table>

\(^1\) Senior Undergraduate student at Middle East Technical University, Ankara, Turkey

Email Address: e188026@metu.edu.tr
Hydroxyapatite Synthesis

In the synthesis of the hydroxyapatite, calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$•4H$_2$O) and ammonium hydrogenphosphate ((NH$_4$)$_2$HPO$_4$) are used as precursors. During the synthesis Ca/P molar ratio is kept 1.67. The precursors are dissolved in 100 ml distilled water. At the beginning of the process, the pH of the phosphate solution is slowly added into the phosphate solution. This process is done in the open atmosphere. The pH of the solution is kept at 10 by controlled addition of (NH$_4$)OH. After this process, the precipitated solution is left for 12 hours at 60°C. In order to obtain the particles, this precipitated solution is centrifuged. This process is followed by ultrasonic treatment in distilled water and ethanol. The collected particles are finally left in a drying furnace at 90°C for 18 hours.

8-Tricalcium Phosphate Synthesis

In the synthesis of tricalcium phosphate Ca(NO$_3$)$_3$H$_2$O and (NH$_4$)$_2$HPO$_4$ aqueous solutions are used. In order to obtain the Ca/P molar ratio 1.5, 2.125 grams of Ca(NO$_3$)$_3$H$_2$O and 0.792 grams of (NH$_4$)$_2$HPO$_4$ are dissolved in 100 ml distilled water. Calcium nitrate solution is slowly added to the diammonium hydrogen phosphate solution maintained at 60°C. While adding, the solution is mixed with 1000 rpm. In addition to the temperature, pH of the solution should also be maintained at 7 by addition of NH$_3$ during the synthesis. After all Ca-nitrate solution is added to the di-ammonium hydrogen phosphate solution, the solution is kept at 1000°C for 1.5 hours.

Chemical characterizations of both hydroxyapatite and β-TCP are carried out by using energy dispersive X-Ray spectroscopy (EDS, Nova Nano430-FeI). Fourier transform infrared radiation (FTIR, Frontier—Perkin Elmer) is used to find out the alterations in the chemical structure of both hydroxyapatite and β-TCP. Moreover, X-Ray diffraction analysis (XRD—Rigaku D/max 2000 PC diffractometer) is done to determine the crystallinity properties such as crystallite size and phase determination. Cu K$_\alpha$ (λ = 1.54 Å) radiation is carried out as x-ray source.

RESULTS AND DISCUSSIONS

The experiment is conducted using calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$•4H$_2$O) and ammonium hydrogenphosphate ((NH$_4$)$_2$HPO$_4$) as precursors. For synthesis of hydroxyapatite, Ca/P molar ratio is 1.67. After hydroxyapatite is synthesized, the characterization is done by XRD and FTIR analysis. HAp particles are obtained in two routes: centrifuged and filtered.

All of the XRD patterns were plotted between 20° to 40°. Because, the specific peaks of XRD patterns of each calcium orthophosphates are obtained at this interval.

The aim of producing HAp by two different routes; filter and centrifuge, is to see the effect of producing way on the HAp particles. From XRD results it can be understood form the broadening values that the HAp synthesized by centrifuge has smaller grain size compared to HAp synthesized by filter.
Synthesized β-TCP is also characterized by XRD pattern. Before keeping the solution at 1000°C for 1.5 hours, Ca-deficient apatite (CDHA) is produced. Since the molar ratio of CDHA is the same as the TCP, in order to distinguish β-TCP and CDHA XRD analysis is done. These XRD patterns are then compared with the literature studies. The difference of β-TCP and CDHA is observed by XRD pattern. Figure 3 and Figure 4 shows their difference. Therefore, it can be said that CDHA is calcined above 700 – 800°C to transform into to β-TCP.

From XRD patterns of synthesized calcium orthophosphates which are HAp, CDHA and β-TCP are all nanosized particles, around 20 nm. However, the HAp obtained by filter is not in nanosized.

Figure 5 and Figure 6 shows the FTIR analysis of HAp which are synthesized by centrifuge and filter respectively. It can be said from these analysis, when the particles size decreases, the absorbed carbonate increases.

Synthesized β-TCP is produced by heating the CDHA to 1000°C for 1.5 hours, the carbonate peak in the pattern is disappeared due to the effect of heating. Moreover it can be said that β-TCP does not absorb so much water due to the effect of heating again.
Finally, from the website of Sigma-Aldrich Distributor, 10 grams of β-TCP (>98% purity, unsintered powder) is 215.50 Euro. 10 grams of HAp nanopowder (>97% purity, <200 nm particle size) is 81.90 Euro [7].

CONCLUSION

The synthesis of most important calcium orthophosphates which are HAp, β-TCP and CDHA, is explained. The optimum Ca/P molar ratio, pH and temperature are given for each calcium orthophosphates. These parameters are very important for the synthesis and the effect the final products excessively. The most important effect of these parameters on the final product is its size. Finally, the characterization of each HAp, β-TCP and CDHA are done by XRD and FT-IR analysis. Nowadays, more efforts are focused on combining these important calcium orthophosphates with cells, drugs and other active biological substances for lots of purposes.

REFERENCES


AUTHOR INFORMATION

Bersu Baştuğ is a senior from METU, TURKEY majoring in metallurgical and materials engineering. Her advisor for this project is Professor Dr. Caner Durucan, METU Metallurgical and Materials Engineering Department. Her academic interests include bioceramics. In her free time, she likes to read, listen music.