

The effect of calcium carbonate particle size on the formations β -tricalcium phosphate

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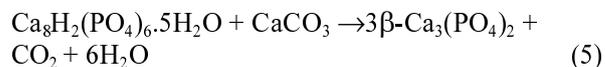
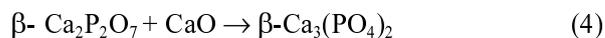
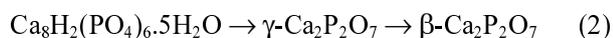
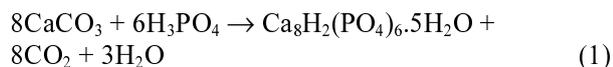
β -tricalcium phosphate (β -TCP) powder was synthesized using various calcium carbonate (CaCO_3) particles sizes (40 nm-780 μm) with phosphoric acid (H_3PO_4) at room temperature (25 °C). CaCO_3 was first dissolved in deionized water at room temperature followed by the addition of H_3PO_4 . The mixture was stirred until reaching a stable pH between 5.5-6.5 for 1 hour. The time taken to reach pH 5.5 increased from 12.5 minutes to 1140 minutes as the CaCO_3 particle size increased from 40 nm to 780 μm . The slurry was filtered, dried in oven at a temperature of 80 °C for 24 hours then crushed with an agate mortar and calcined at a temperature of 850 °C to form the β -TCP phase. XRD quantitative analysis showed that the amount of the β -TCP synthesized from CaCO_3 as the starting material decreased from 81.9% to 20.3% as the CaCO_3 particle size increased from 40 nm to 780 μm . FESEM analysis showed that the morphology of CaCO_3 as the starting material was not maintained after it was synthesized to β -TCP powder.

Key words: Particle size, calcium carbonate, β -TCP, morphology, XRD quantitative analysis.

Introduction

Tricalcium phosphate (TCP) with the chemical formula $\text{Ca}_3(\text{PO}_4)_2$ is a bioceramic that has Ca/P ratio of 1.50 [1]. TCP can exist as two polymorphs such as β -TCP and α -TCP. β -TCP is stable below 1120 °C with a density equal to 3.07 gm/cm³, α -TCP is stable between 1120 °C and 1470 °C with a density equal to 2.86 gm/cm³ [2]. In contrast to α -TCP, β -TCP is thermodynamically stable in a biological environment. Despite a similar degree of solubility, the biodegradation of β -TCP is faster than that of α -TCP mainly because the latter form hydrolyses either partially or completely to hydroxyapatite. The resulting crystals have a non-physiological morphology, are not re-adsorbed due to their very low level of solubility and may enter the lymphatic system by phagocytosis [3].

Conventionally, β -TCP powders are synthesized via a solid state process and a wet chemistry method [4-7]. The latter method is used to form the octacalcium phosphate (OCP) with the chemical formula of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$. OCP is usually calcined above 850-1100 °C to obtain β -TCP, as described by the following equations:



In this study, various particle sizes (40 nm-780 μm) were used to synthesize β -TCP powders via a wet chemistry method of the CaCO_3 - H_3PO_4 system [8]. This system is able to produce β -TCP with minimum impurities, by a fast reaction and it is easy to filter the synthesized products. The aim of this investigation is to study the effect of various CaCO_3 particle sizes as the starting raw material on the purity of synthesized β -TCP powders.

Materials and Method

CaCO_3 particles with various sizes were obtained from Nanomaterials Technology Pte. Ltd., Singapore (40 nm), the Mineral and Geoscience Department of Malaysia, Malaysia (780.0, 162.5 and 6.10 μm) and the CSI Corporation Sdn. Bhd., Malaysia (593.24 μm). A particle size analyzer (Rodas), X-ray fluorescence (XRF) (Rigaku Rix 3000), an X-ray diffractometer (XRD) (Bruker AXS D8 Advance) and a field emission scanning electron microscope (FESEM) (LEO VPFESEM SUPRA 35 VP) were used to characterize the particle size, the chemical composition, the mineral composition and morphology of CaCO_3 , respectively.

Each CaCO_3 powder batch was first dissolved in 100 ml deionized water at room temperature followed by the addition

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of H_3PO_4 (Merck, 85%) according to a Ca/P ratio of 1.50. The mixture was stirred until the reaction completed at pH 5.5-6.5 and stirring was maintained for 1 hour. The slurry was filtered, washed with deionized water and finally dried in an oven at 80 °C for 24 hours.

Dried synthesized powders were subjected to particle sizes analysis, XRD analysis and morphological assessment. Quantitative XRD analysis was performed to determine the percentage of each phase that was presence in the dried synthesized powders. β -TCP powders were obtained when the synthesized powders were calcined at 850 °C for 2 hours. The same analyses were repeated for the calcined powders. Fig. 1 shows a flow chart for the study of the effect of various $CaCO_3$ particle sizes on the purity of synthesized β -TCP powders.

Results and Discussion

The reaction between $CaCO_3$ - H_3PO_4 can be monitored by measuring the pH of the slurry. Based on a previous study, the reaction is assumed to be completed when the pH of the slurry reaches between pH 5.5-6.5 [8]. Fig. 2 shows the time taken to reach a completed reaction for different particle sizes of $CaCO_3$.

When the $CaCO_3$ particle size is increased from 40 nm to 780 μm , the mixing time also is increased. This is due to the larger $CaCO_3$ particle size which has a lower total surface area. The frequency for a phosphorus atom to collide with a calcium atom would be reduced. Therefore, reaction rate was very low and a longer mixing duration was needed. In this study, the finest $CaCO_3$ particle size (40 nm) needed only 12.5 minutes to reach pH 5.5

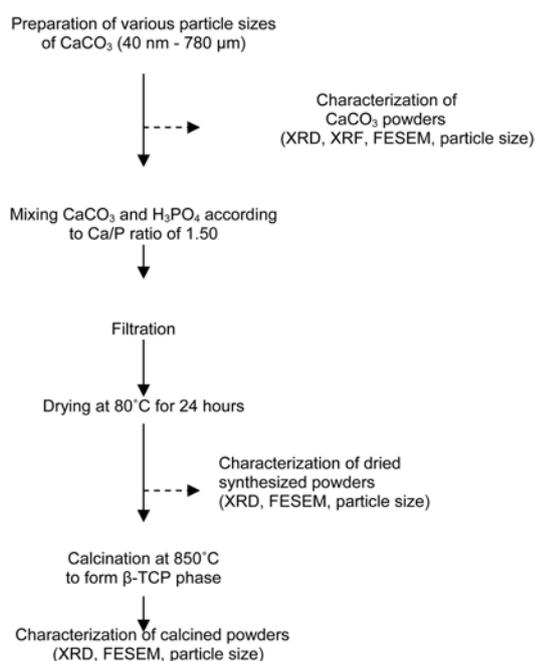


Fig. 1. A flow chart for the study of the effect of various $CaCO_3$ particle sizes on the purity of synthesized β -TCP powders.

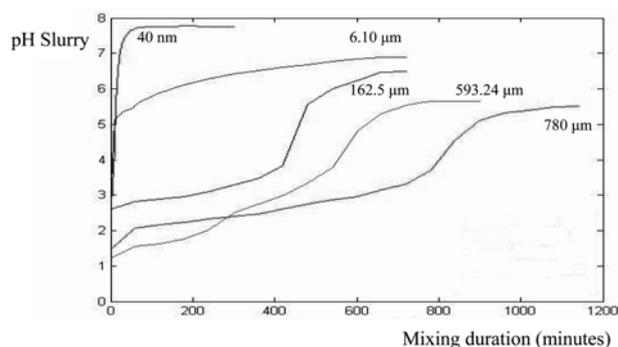


Fig. 2. The effect of particle size and pH on the reaction time.

while the largest $CaCO_3$ particle size (780 μm) needed 1140 minutes. The effect of particle size on the efficiency of the reaction is very clear since the chemical composition of each starting $CaCO_3$ powder is almost the same as shown by the XRF analysis given in Table 1.

Based on Equations 1-5, the conversion from $CaCO_3$ to β -TCP with the presence of H_3PO_4 occurred after the dried slurry was calcined at 850 °C for 2 hours. XRD was employed to monitor the reaction that took place. Fig. 3 shows the XRD analyses for the starting raw materials, $CaCO_3$, which indicated the presence of very high purity $CaCO_3$ (ICDD 85-1105).

Table 1. Result of XRF analysis for the starting $CaCO_3$ materials

Composition (wt%)	40 nm	*6.10 μm	162.5 μm	*593.2 μm	*780.0 μm
Al_2O_3	0.1	0.2	0.06	0.2	0.2
SiO_2	0.2	0.3	0.1	0.3	0.3
SO_3	0.01	-	-	-	-
CaO	55.6	54.5	54.4	54.5	54.5
Fe_2O_3	0.08	0.08	0.06	0.08	0.08
NiO	-	0.02	-	0.02	0.02
SrO	0.01	0.03	0.04	0.03	0.03
MgO	-	0.8	1.3	0.8	0.8
P_2O_5	-	0.04	0.04	0.04	0.04
K_2O	-	0.03	-	0.03	0.03
@LOI	44.0	44.0	44.0	44.0	44.0

*Sample taken from the same source

@ LOI – Lost on Ignition

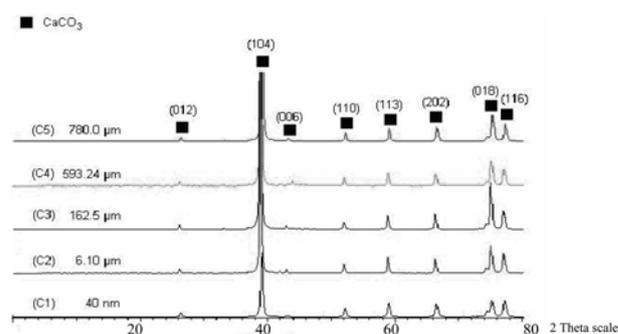


Fig. 3. XRD patterns for different sizes of $CaCO_3$ particles as the starting raw materials.

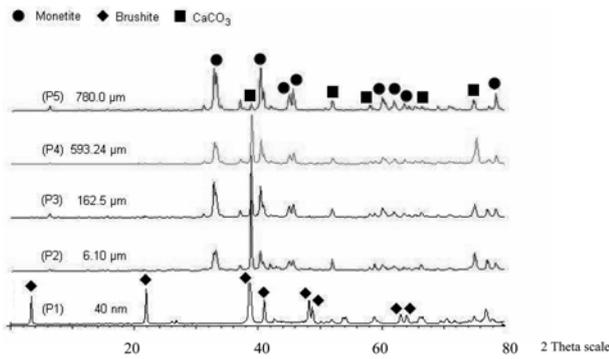


Fig. 4. XRD patterns for reaction products between different sizes of CaCO_3 particles with H_3PO_4 .

Fig. 4 shows the XRD analysis for the conversion of CaCO_3 phase to other phases after the CaCO_3 reacted with H_3PO_4 . There are 3 different phases detected in these reacted products i.e. brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (ICDD 72-713), monetite, CaHPO_4 (ICDD 70-360) and CaCO_3 (ICDD 85-1108).

The brushite phase is only detected for the sample synthesized using 40 nm CaCO_3 . Other samples contain monetite and CaCO_3 phases. Therefore, the products for the reaction between CaCO_3 and H_2PO_4 are also dependent on the particle size of the starting raw materials.

Brushite has been reported to form at around pH 6.5 and remain stable above this pH [9]. The sample with a particle size of 40 nm, the finest particle size, needed only 12.5 minutes for the mixing process to achieve pH 6.5 and completed the reaction at pH 7.8. Other samples, 6.10 μm , 162.5 μm , 593.2 μm and 780.0 μm , took 60 minutes, 480 minutes, 720 minutes and 1140 minutes, respectively to achieve their maximum pH.

Brushite was easily formed in the 40 nm sample since the slurry becomes saturated and the reaction was completed in a very short time. Therefore, the hydrolysis process was only limited to the formation of brushite. For the remaining samples, the monetite phase was present in every sample. Monetite was formed from hydrolyzed brushite according to equation 6. Brushite that formed initially has enough time to be hydrolyzed to the monetite phase.



Besides the presence of brushite and monetite, the CaCO_3 phase is also present in each sample. The CaCO_3 here was from the starting material that did not completely react with H_3PO_4 and remains in the samples. Calcined powder samples were analyzed by XRD to determine the presence of the β -TCP phase after calcination at 850 °C. The results are shown in Fig. 5.

From the results, β -TCP [ICDD 70-2065], β -calcium pyrophosphate, β - $\text{Ca}_2\text{P}_2\text{O}_7$ (β -CPP) [ICDD 81-2257] and calcium oxide, CaO (ICDD 74-1226) phases were present in each sample. From the XRD analysis, β -TCP was the major phase in the 40 nm sample and β -CPP was the minor phase. However, as the starting raw material CaCO_3 ,

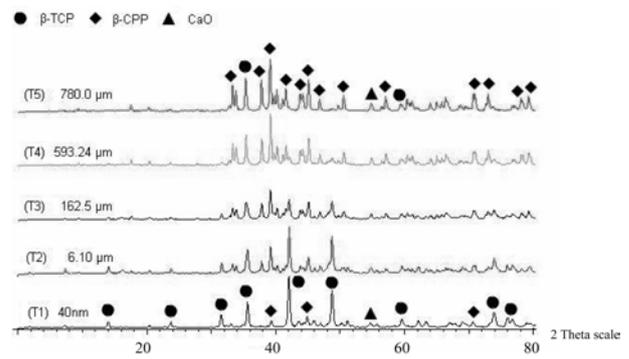


Fig. 5. XRD pattern for the calcined reaction products between different sizes of CaCO_3 particles with H_3PO_4 at 850 °C for 2 hours.

particle size increases, the formation of the β -TCP phase decreases and the β -CPP phase increases.

The reason is that when the finest particle size (40 nm) of the starting raw material CaCO_3 was used, the reaction between CaCO_3 and H_3PO_4 was very effective and the mixing process was homogeneous. Most of the CaCO_3 particles are able to transform to brushite. When brushite was calcined at a temperature of 850 °C, the transformation of brushite to β -CPP was also very effective. At the same time, the remaining CaCO_3 will also transform into CaO. When β -CPP is combined with CaO, β -TCP is produced. When coarse particles (6.10 to 780.0 μm) of the starting material CaCO_3 were used, the reaction between CaCO_3 and H_3PO_4 was not that efficient and the mixing process was not homogeneous. This is due to the formation of monetite found together with β -TCP. When monetite was calcined at a temperature of 850 °C, the transformation of monetite to β -CPP was also not effective. At the same time, the remaining CaCO_3 will also transform into CaO. Some of the monetite phase will combine with CaO and form β -TCP phase but most of it cannot combine with CaO. Therefore, the monetite phase remained after calcination and become the major phase. The overall calcination process can be represented by Equations 1 to 6. The amount of each phase in the calcined powders was determined using XRD quantitative analysis. The data is given in Table 2.

From the results, the amount of β -TCP synthesized using CaCO_3 (40 nm) is 81.9% with other phases present, β -CPP (14.3%) and CaO (3.7%). As the particle size of CaCO_3 increases to 780 μm , the amount of β -TCP decreases

Table 2. Percentages of each phase in the calcined powders

Samples	% Composition		
	β -TCP	β -CPP	CaO
40 nm	81.9	14.3	3.8
6.10 μm	65.1	31.5	3.4
162.5 μm	44.6	51.3	4.1
593.2 μm	27.4	67.9	4.7
780.0 μm	20.3	74.8	4.9

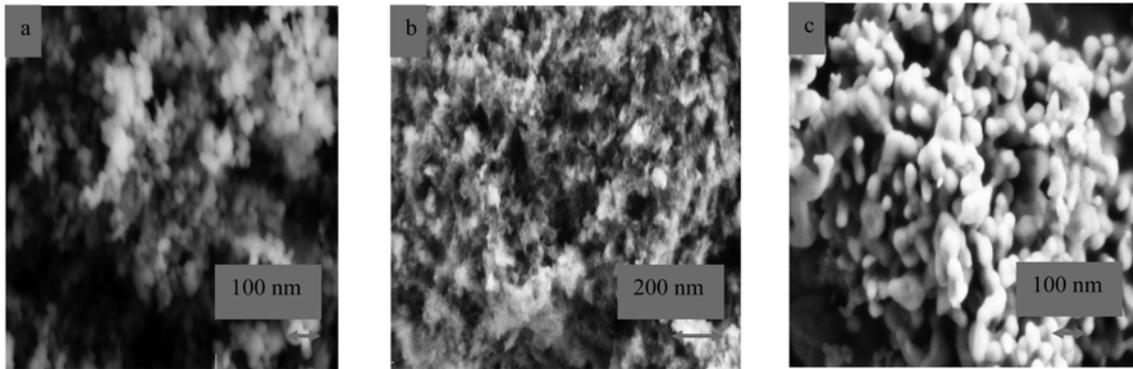


Fig. 6. (a) The changes of CaCO_3 morphology (40 nm) as starting raw material, (b) after reaction with H_3PO_4 and (c) reaction product after calcination at 850°C for 2 hours.

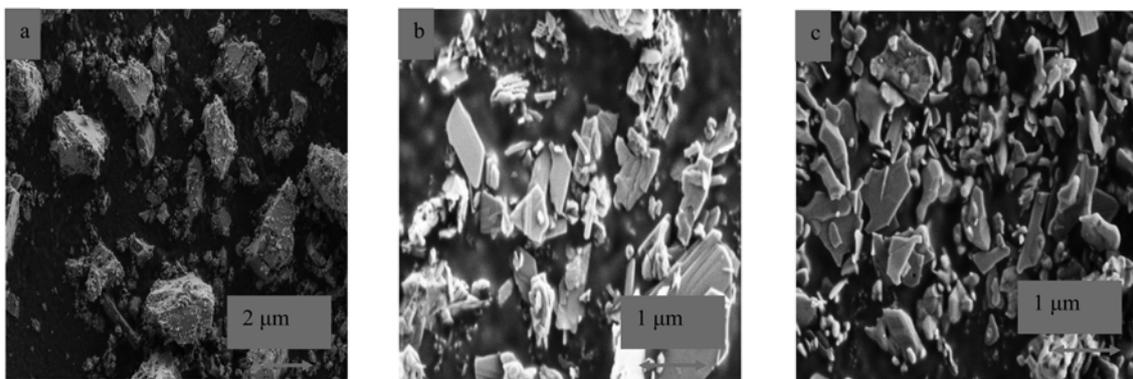


Fig. 7. (a) The changes of CaCO_3 morphology ($6.10\ \mu\text{m}$) as starting raw material, (b) after reaction with H_3PO_4 and (c) reaction product after calcination at 850°C for 2 hours.

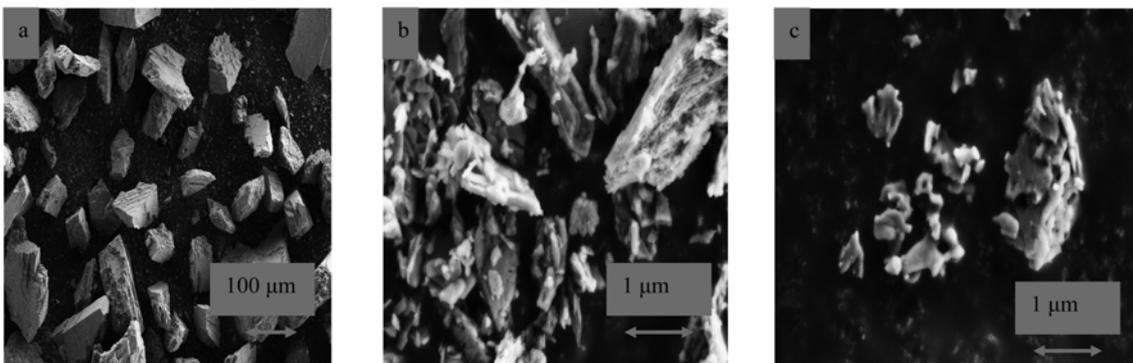


Fig. 8. (a) The changes of CaCO_3 morphology ($162.5\ \mu\text{m}$) as starting raw material, (b) after reaction with H_3PO_4 and (c) reaction product after calcination at 850°C for 2 hours.

(20.3%) with β -CPP (74.8%) and CaO (4.9%). This can obviously be seen from the XRD spectrum, the peak intensity of β -TCP decreases while the peak intensity of β -CPP increases. This is due to the increase in particle size of CaCO_3 .

The morphology of the starting CaCO_3 powders, reaction products and powders of the calcined reaction products, can be seen in Figs. 6-10. The 40 nm sample was produced via a process of precipitating calcium carbonate (PCC) which means its shape is different from the other samples which originated from natural calcium carbonate (NCC). NCC is irregularly rhombohedral in shape whilst the

PCC are very fine particles with a more uniform and regular shape. It is obvious that the particle size and shape of each powder did not remain the same after the reaction and calcination processes.

Particle size has an important influence on the rate of calcination of calcium carbonate. For very small particles (nano size), heat transfer becomes very efficient for conversion to the β -TCP phase. For micrometre sizes, the chemical reactions and internal mass transfer are the main resistances that control the calcination. After the calcination, the morphology of β -TCP becomes flakier.

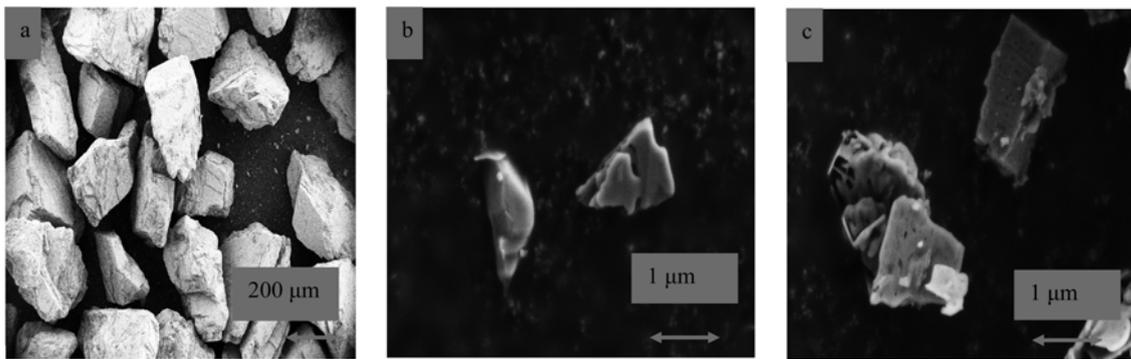


Fig. 9. (a) The changes of CaCO_3 morphology ($593.24 \mu\text{m}$) as starting raw material, (b) after reaction with H_3PO_4 and (c) reaction product after calcination at 850°C for 2 hours.

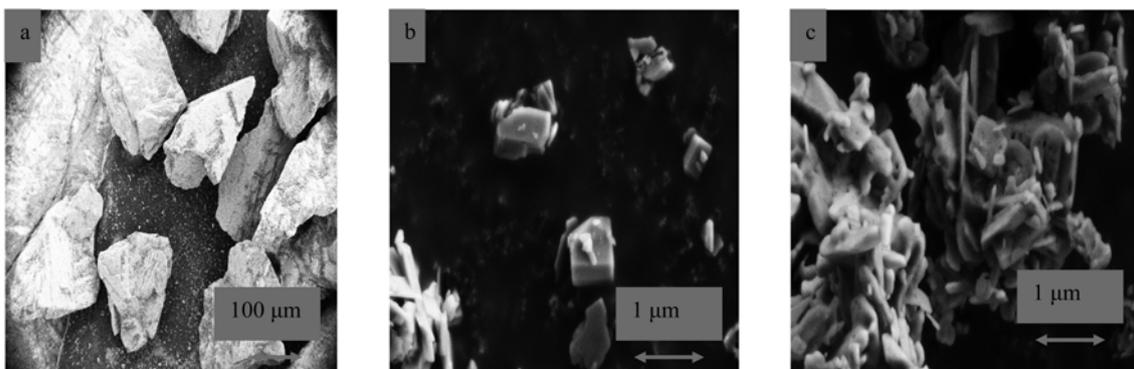


Fig. 10. (a) The changes of CaCO_3 morphology ($780 \mu\text{m}$) as starting raw material, (b) after reaction with H_3PO_4 and (c) reaction product after calcination at 850°C for 2 hours.

Conclusions

The time taken to complete the reaction increases from 12.5 minutes to 1140 minutes, when the CaCO_3 particle size was increased from 40 nm to $780 \mu\text{m}$. Also as the starting material CaCO_3 particle size increases from 40 nm to $780 \mu\text{m}$, the amount of synthesized β -TCP powders decreases from 81.9% to 20.3%. The particle size and shape of each powder did not remain the same after the reaction and calcination processes to synthesized β -TCP powders.

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References

1. M. Vallet-Regi, J. Pena and Izquierdo, *Solid State Ionics*, 172 (2004) 445-449.
2. M. Descamps, J.C.Harnaz and A. Leiricho, *J. Euro. Ceram Soc.* 27(2007) 2401-2410.
3. H.H. Horch, R. Sader, C. Pautke, A. Neff, H. Deppe and A. Kolk, *Int. J. of Oral & Maxillofacial Surgery*, 35 (2006) 708-713.
4. J.S. Bow, S.C. Liou and S.Y. Chen, *Biomaterials*, 25[6] (2004) 3155-3161.
5. D. Choi and Kumta, *Mat. Sc. Eng.* 27[3] (2007) 377-381.
6. S.J. Lee, Y.S. Yoon, M.H. Lee and N.S. Oh, *Mat. Lett.* 61[6] (2007)1279-1282.
7. K. Yoshida, M. Kobayashi, H. Hyuga, N. Kondo, H. Kita, K. Hashimoto and Y. Toda, *J. Euro. Ceram Soc.* 27 (2007) 3215-3220.
8. Y. Zhang, G. Yin, S. Zhu, D. Zhou, Y. Wang, Y. Li and L. Luo, *Current App. Physics*, 5 [5] (2005) 531-534.
9. S.M. Arifuzzaman and S. Rohani, *J. Cryst. Growth* 267 [3-4] (2004) 624-634.