Effects of heat treatment temperature and atmosphere on the morphology and structure of calcium phosphate

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Abstract. Calcium phosphate can exist as several phases including hydroxyapatite (HA) and β-tricalcium phosphate (βTCP). Both HA and βTCP are chemically similar to calcified tissue, resulting in high biocompatibility. In this study, we investigated the effects of heat treatment temperature (800 °C and 900 °C) and atmosphere (ambient air and argon) on the morphology, crystalline structure, and functional groups of calcium phosphate powder. Calcium phosphate without heat treatment was evaluated for comparison. The powders were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, and transmission electron microscopy. Under both atmospheric conditions, the effect of heat treatment at 800 °C led to the formation of both HA and βTCP, which was caused by the reduction of CO$_3^{2-}$ bond in calcium phosphate. In contrast, the heat treatment of calcium phosphate at 900 °C generated C–H and C=O groups, resulting in βTCP alone.

Keywords: β-tricalcium phosphate, functional group bonds, calcium phosphate, crystalline structure, hydroxyapatite, morphology

1. Introduction
Nanotechnology involves the process of manipulating, controlling, and integrating of atoms and molecules in the formation of nanoscale materials, structures, components, devices, and systems [1]. Nanosized calcium particles have become additives to food products since they can help absorb calcium in the body, especially its absorption by bone, have no effect on the appearance and taste of food.

The calcium phosphate phases hydroxyapatite (HA) and β-tricalcium phosphate (βTCP) have similar chemical structures as the inorganic components of teeth and bones, resulting in good biocompatibility [2]. HA and βTCP play significant roles in the formation of biphasic calcium phosphate (BCP), which has the ability to form strong bonds with the host bones that form a fibrous interface, resulting in bioinertness in bones [3].

Previous studies have evaluated how temperature and other conditions affect the transformation of calcium phosphate powder into different phases. This study will focused on the morphology, crystallinity, and functional groups of calcium phosphate after the heat treatment. The treatment was done at temperature of 800 °C and 900 °C under air and argon atmospheres. Therefore, this study can provide the proper method in obtaining each phase of hydroxyapatite, β-tricalcium phosphate or BCP.

2. Experimental
2.1. Preparation of calcium phosphate
Commercial calcium phosphate powder was purchased from CV Surchana Agung. Five calcium phosphate samples were evaluated in this study: calcium phosphate without heat treatment (WH),
Figure 1. TEM images of calcium phosphate samples: (a) WH, (b) 800°C, (c) 800°C–Ar, (d) 900°C, and (e) 900°C–Ar.

calcium phosphate heated at 800 °C in ambient air (800 °C), calcium phosphate heated at 800 °C in argon atmosphere (800 °C–Ar), calcium phosphate heated at 900 °C in ambient air (900 °C), and calcium phosphate heated at 900 °C in argon atmosphere (900 °C–Ar). The masses of calcium phosphate heated in ambient air were about 5 g and meanwhile the masses of calcium phosphate heated in argon atmospheres were about 3 g.

2.2. Heat treatment of calcium phosphate
Heat treatment was performed at either 800 °C or 900 °C [3,4] in a Nobertherm P330 furnace for 4 h at a heating rate of 30 °C/min under ambient air or argon atmosphere. For heat treatment in argon atmosphere, the furnace was flushed with argon eight times followed by vacuuming for 10 min.

2.3. Characterization of calcium phosphate
The calcium phosphate samples were examined before heat treatment and thereafter by using transmission electron microscopy (TEM; Tecnai 200 kV D2360 SuperTwin) with an emitted electron current of 2.94 µA. X-ray diffraction (XRD) was carried out using a Rigaku Miniflex 600 with operating power at 40 kV and 1 kV/step control mode with CuKα radiation at a wavelength of 1.54 Å. Diffraction lines were recorded in the 2θ range of 5°–90°. The percentages of HA and βTCP phases and full width at half maximum (FWHM) were determined from the XRD data using X’Pert HighScore Plus. Fourier transform infrared (FTIR) spectroscopy was carried out according to ASTM E168 standards in the wavenumber range 450–4000 cm⁻¹.

3. Results and discussion
The TEM image of the WH sample (figure 1a) shows agglomerated calcium phosphate nanoparticles with sizes of ~20 nm. In the TEM images of the 800 °C and 800 °C–Ar samples (figures 1b and figure 1c), respectively, the nanoparticles exhibited necking resulting from the heat treatment, and the
particle size was \( \sim 50–100 \) nm. This necking phenomenon was attributed to agglomeration and densification in volume or grain boundary of calcium phosphate particles, in agreement with the findings of Bernache-Assollant et al. [5]. Otherwise, heat treatment under argon atmosphere resulted in increased particle size and prevented necking. Figures 1d and figure 1e show TEM images of the 900 °C and 900 °C–Ar samples, respectively. Under ambient air, the particles exhibited necking and were \( \sim 60–110 \) nm in size. The increase in particle size can be attributed to the high temperature, as reported by Zhou [4]. The particle microstructure exhibited densification, due to heat treatment of 900 °C in ambient air. The particles in the 900 °C–Ar sample were spherical with sizes of \( \sim 20 \) nm, and grains were clearly formed. The grains indicated a microstructure with poor densification that was marked by the pores. Thus, high crystallization was caused by argon atmosphere during heating.

Figure 2 shows the XRD patterns of the WH, 800 °C, and 800 °C–Ar samples. Peaks corresponding to the (002), (211), (112), (310), and (004) planes of HA were observed in the spectrum of WH, with the (211) peak having the highest intensity. Heat treatment at 800 °C led the formation of HA and \( \beta \)TCP phases, as noted by Victoria [3]. The refinement results from X'Pert High Score Plus software denoted the percentage of relative intensity of calcium phosphate, which heated in ambient air, comprised HA phases as much as 23.1% and \( \beta \)TCP phases as much as 76.9% respectively. Meanwhile, the heat treatment of calcium phosphate using argon atmosphere resulted in the changes in the relative intensity of HA into 42.7% and \( \beta \)TCP into 57.3%.
Table 1. XRD refinement data of all samples for (220) peak

|                | 2θ (°) | FWHM | Crystallite size (Å) |
|----------------|--------|------|----------------------|
| 800°C          | 34.49  | 0.24 | 383.22               |
| 800°C-Ar       | 34.43  | 0.25 | 180.48               |
| 900°C          | 34.52  | 0.20 | 496.65               |
| 900°C-Ar       | 34.51  | 0.19 | 537.50               |

Heat treatment at 900 °C led to the formation of βTCP alone (figure 3). The low FWHM values of the 900 °C and 900 °C–Ar samples indicate that the high temperature led to good crystallinity [6], in agreement with the TEM image in figure 1e.

Table 1 shows the FWHM values of all samples for the (220) peak, which corresponds to βTCP [6]. The (220) peak was not observed in the XRD spectrum of the WH sample, which contained only HA.

Figure 4 shows the FTIR spectra of the WH, 800 °C, and 800 °C–Ar samples. Peaks corresponding to the bonds of various functional groups including OH, PO₄, and CO₃²⁻ were identified in the spectra [3,7]. OH bond peaks appeared at 3386, 3572 and 3571 cm⁻¹ in the WH, 800 °C, and 800 °C–Ar samples, respectively. Peaks corresponding to CO₃²⁻ bonds were observed in the spectrum of the WH
sample at 1029, 1023, and 1025 cm$^{-1}$. Meanwhile, peaks of CO$_2$ disappeared in both 800 °C and 800 °C-Ar samples due to heat treatment temperature. We concluded that the condensation CO$_2$ occurred and BCP that comprised HA and βTCP phases were formed [3].

Figure 5 shows the FTIR spectra of the WH, 900 °C, and 900 °C–Ar samples. Peaks of OH, PO$_4^{3-}$, and CO$_2$ bonds were identified [4]. The peak associated with OH stretching at 3386 cm$^{-1}$ was found only in the spectrum of the WH sample. The high temperature of 900 °C reduced –OH bond at the wave number of 3386 and 630 cm$^{-1}$ in both 900 °C and 900 °C–Ar samples, corresponded to Victoria [3]. The C–H groups of alkenes were indicated by peaks at 945 and 946 cm$^{-1}$ in the spectra of the 900 °C and 900 °C–Ar samples, respectively. CO$_2$ bonds were indicated by a peak at 1116 cm$^{-1}$ in the spectrum of the 900 °C sample and by peaks at 1118 and 1217 cm$^{-1}$ in the spectrum of the 900 °C–Ar sample. Heating under argon atmosphere resulted in the formation of new bonds, as indicated by peaks corresponding to the C–H and C=O groups of alkenes and esters at 1366 and 1739 cm$^{-1}$, respectively.

4. Conclusions
Before heat treatment, the agglomerated HA particles were ~20 nm in size and exhibited poor crystallinity. Heating in air atmosphere caused the HA particles to undergo necking, resulting in increased particle size. Heating under argon atmosphere might reduce the necking of the calcium phosphate particles compared with ambient air. Both HA and βTCP phases formed after heat treatment at 800 °C. Heating at 900 °C resulted in the formation of only βTCP. Heating at this temperature under argon atmosphere resulted in the formation of alkene and ester functional groups.

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