

Effect of a polymer addition on the crystallite size and sinterability of hydroxyapatite prepared with CaO powder and phosphoric acid

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Highly sinterable hydroxyapatite (HAp) ceramics were fabricated by the addition of polyethylene glycol (PEG) to a slurry consisting of CaO powder and phosphoric acid. The morphology of the synthesized powder was changed to a more porous structure and the particles showed a finer crystallite size by the addition of PEG in the solution process. The synthesized HAp powder employing PEG showed a higher surface area of 34.0 m²/g and a denser sintered microstructure in comparison with that prepared without PEG. The porous and soft agglomerated powders prepared by the application of the PEG polymer were easily dispersed to nano-sized powders of about 80~100 nm by an ultrasonic process and the powder compacts were well densified at 1300 °C for 1 h showing a fine grain size of 1.2 μm.

Key words: PEG polymer, Hydroxyapatite, Sintering, Powder.

Introduction

Synthetic HAp (Ca₁₀(PO₄)₆(OH)₂) materials can be fabricated via several ceramic and chemistry-based processing routes, such as sol-gel techniques [1], hydrothermal reactions [2], emulsion or microemulsion syntheses [3,4] and thermal plasma processing [5]. Since HAp is used mostly as powders and its usefulness depends on the powder properties such as particle size, surface area and morphology, it is believed that making nanostructure HAp can improve the properties of synthetic bone, such as its bioactivity and densification kinetics due to its higher surface area than the bulk form [6,7]. So, synthesis of ultra-fine HAp powders becomes an important step in processing parts. In addition, good biocompatibility and excellent densification behavior of synthesized powders, and easy processing for fabrication are also necessary. Layrolle *et al.* have synthesized HAp powders with an average particle size of 200 nm with a strongly agglomerated morphology having an average agglomerate size of 45.0 μm [8]. Lim *et al.* have reported synthesis of HAp powders with particle sizes between 0.5 and 1.0 μm with an agglomerated morphology [9]. As another useful method, recently HAp powders were successfully synthesized by using re-cycled eggshell or other natural materials [10,11]. In the process, the calcined eggshell or nature materials, such as oyster shell, were used as a CaO source. The crystalline

calcium phosphate phases were dependant on the mixing content of phosphoric acid and the calcination temperature.

Chemical processing routes based on organic/inorganic complexation in solution have recently been used to produce pure and homogeneous ceramic powders [12-16]. In the process, polymeric long chains in the mixture ensures the homogeneous distribution of the metal ions in its polymeric network structure and inhibits their segregation and/or precipitation from the solution. Polyethylene glycol (PEG) is one of the polymeric carriers for the polymer complexation process [17]. The polymer surrounds and covers the cations or sol particles, which decreases their mobility and constrains the system to reduce premature agglomeration. The process also produces porous materials through the oxidation reaction in the decomposition of the polymer, so that soft, fine and single-phase powders can be formed at a relatively low external temperature [18-21].

In this study, the HAp powders are synthesized by a wet-chemical method using CaO powder and phosphoric acid employing PEG as an organic carrier. The mixing effects of PEG on the powder properties and crystallite size are examined in comparison with the process without PEG. In addition, the sintering behavior of the synthesized HAp powders is also examined.

Experimental Procedure

Powder synthesis and densification

Calcined eggshell was used for the source of CaO powder. Washed raw eggshell was calcined in an air atmosphere at 800 °C for 1 h. The calcined eggshell

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showed a pure CaO phase with uniform particle size [10]. To synthesize HAp powders, phosphoric acid was mixed with the calcined eggshell. The mixing ratio (wt%) of the CaO powder and phosphoric acid was 1.0 : 1.2 [10]. The mixtures were ball milled with zirconia (Y-TZP) milling media under isopropyl alcohol solvent for 12 h, for homogeneous mixing and to break up the agglomeration of the calcined eggshell. After mixing in the wet system, the organic carrier, PEG (Aldrich, M.W.: 2000) was added, and the mixture was stirred for several hours and heated to elevate the temperature for drying. The amount of PEG was calculated using a ratio of total weight of phosphor ions from phosphoric acid to weight of PEG [11]. In this experiment, a mixing ratio of 1:1 was used. As the viscosity increased by evaporation of the isopropyl alcohol, the sol turned to a crispy gel. For comparison, a precursor gel without PEG was also prepared. Finally, the dried gels were heated to various temperatures at 4 K minute⁻¹ heating rate, in an air atmosphere. The heated powders were sieved to remove agglomeration and then uni-axially pressed at 10 MPa pressure. The powder compacts were sintered at 1300 °C for 1 h in an air atmosphere.

Characterization

Development of crystalline phases of the dried gels was studied using an X-ray diffractometer (Rigaku D/Max 2200) with CuK α radiation (40 kV, 30 mA). The measurements were made with a scanning speed of 8° minute⁻¹ and a sampling interval of 0.02°, over a range

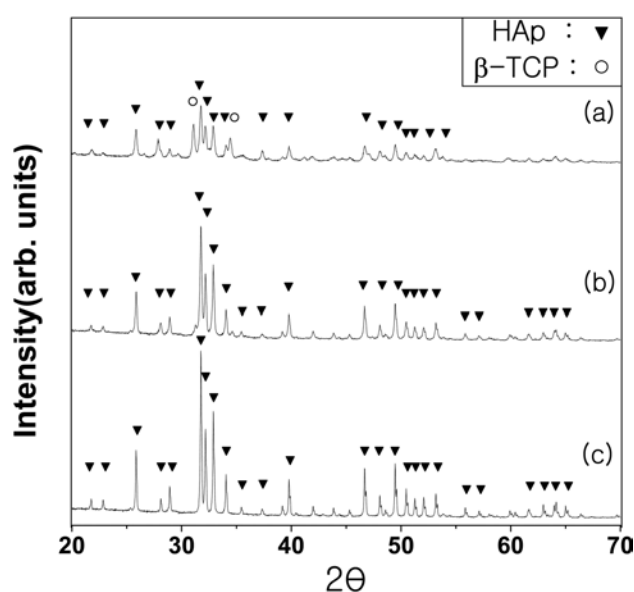


Fig. 1. XRD patterns of synthesized calcium phosphate powder employing PEG calcined at (a) 700 °C (b) 800 °C and (c) 900 °C for 1 h.

of 20–70° at room temperature. The morphological characteristics of the calcined eggshell, synthesized powders, and sintered samples were examined by scanning electron microscopy (SEM, Hitachi, S-3500N) and transmission electron microscopy (TEM, Jeol, JEM-2100F). The Ca/P molar ratio of the synthesized powders was examined by chemical analysis using ICP AES

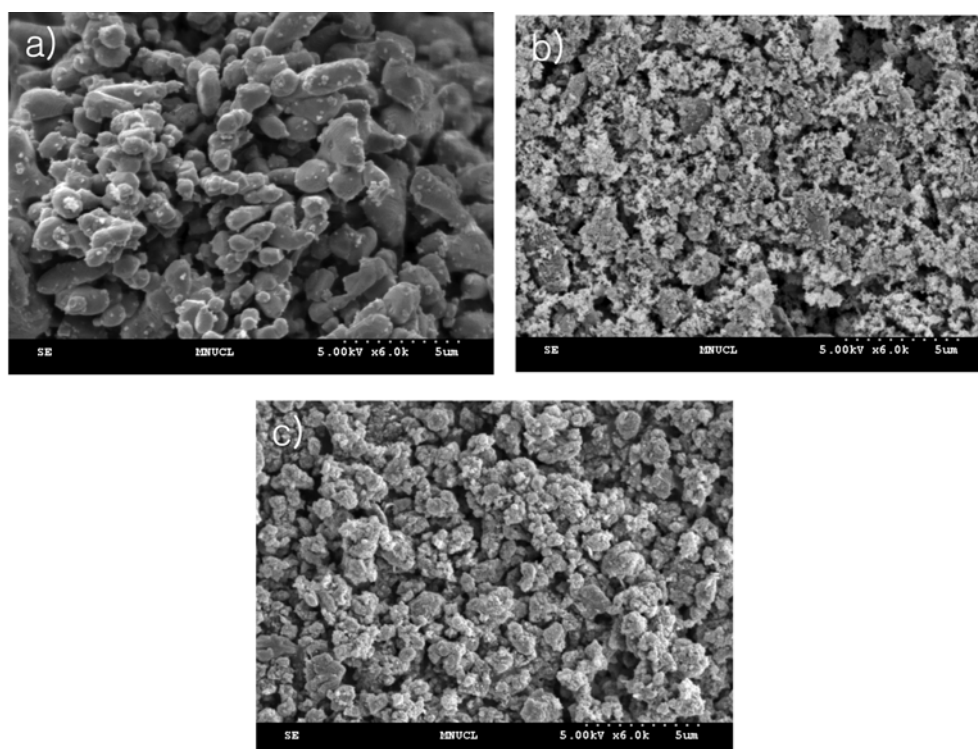


Fig. 2. SEM morphologies of (a) calcined eggshell and dried HAp precursor powders prepared (b) without PEG and (c) with PEG.

(Spectroflame EOF). The particle size distribution of the HAp powder employing PEG was measured by an electrophoretic light scattering spectrophotometer (Photal, ELS-8000). The 0.1 vol% powder was dispersed in de-ionized water with 0.3 wt% polyacrylic acid ammonium salt (Rock Chemie Co., DW-30) as a dispersant. The sample cell was ultrasonicated for 20 minutes and directly measured. The BET specific surface area of the powder was measured by nitrogen gas adsorption (Quantachrome Co., Autosorb-3B). The average grain sizes of sintered microstructures were analyzed according to the Jeffries-Saltykov method [22].

Results and Discussion

The XRD patterns of the synthesized calcium phosphate powders according to the heating temperature are presented in Fig. 1. In the case of employing PEG, the first HAp phase was observed at 700 °C and was the β -TCP phase. The fully developed HAp phase was observed at 800 °C and continued above this temperature. The Ca/P ratio was determined by ICP analysis with the fully-crystallized HAp powder heated at 900 °C. The result was 1.64, which is close to the Ca/P ratio (1.66) of

stoichiometric HAp.

The morphologies of the calcined eggshell and the dried HAp precursor powders are shown in Fig. 2. The particle sizes of the precursors notably decreased through the mixing process with the ball-milling process. This means that the calcined eggshell is soft enough to be ground to fine powders for making homogeneous mixing with phosphoric acid. In the morphology of the dried precursor without PEG, irregular agglomerations involving large-size, hard agglomerated particles were observed. The precursor including PEG was agglomerated with a granular-type, soft morphology. After calcination at 900 °C, the morphologies of synthesized HAp powders are presented in Fig. 3. In the synthesized HAp prepared with a PEG addition, the powder was also agglomerated showing a granular-type morphology with an ultra-fine, sub-micrometer particle size. In particular, the powder was quite soft in comparison with the HAp powder synthesized without PEG. The TEM morphologies of the synthesized HAp powders are shown in Fig. 4. The primary crystallite size of the powder employing PEG (Fig. 4 (b)) was finer and less agglomerated than the HAp powder formed without PEG. The difference in crystallite size means that the long chain PEG polymer contributed to the homogenous dispersion of the CaO powder and phosphor cations and limited their agglomeration and precipitation in the slurry solution process [18,19].

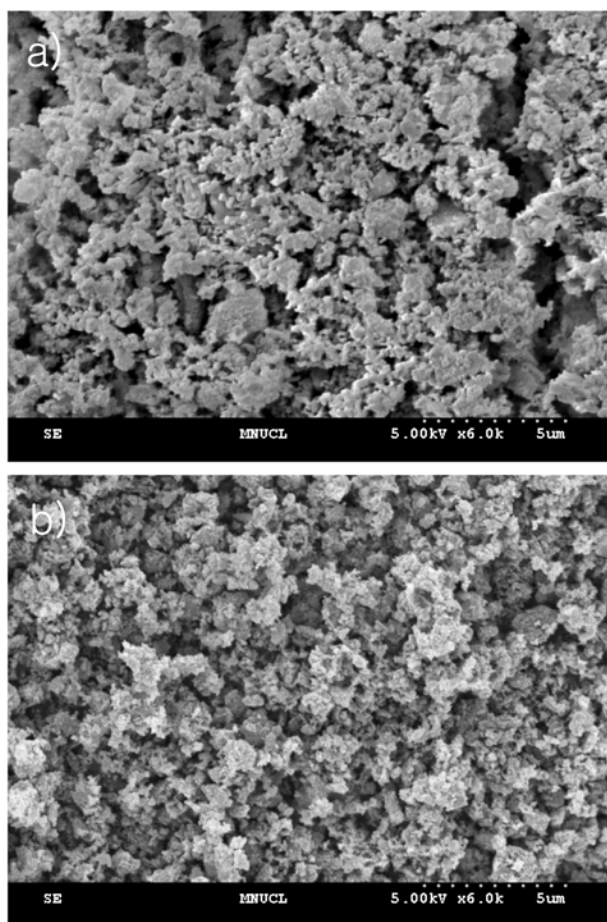


Fig. 3. SEM morphologies of synthesized HAp powders prepared (a) without PEG and (b) with PEG.

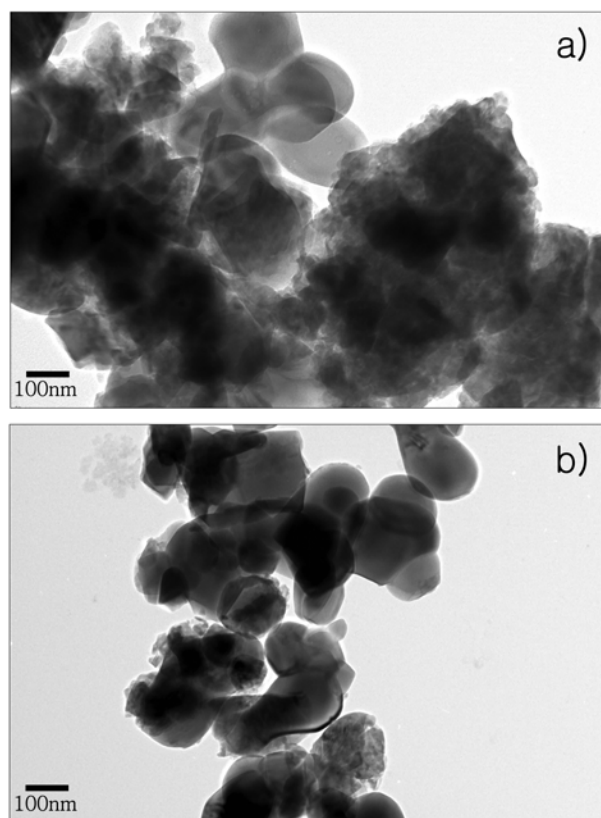


Fig. 4. TEM morphologies of synthesized HAp powders prepared (a) without PEG and (b) with PEG.

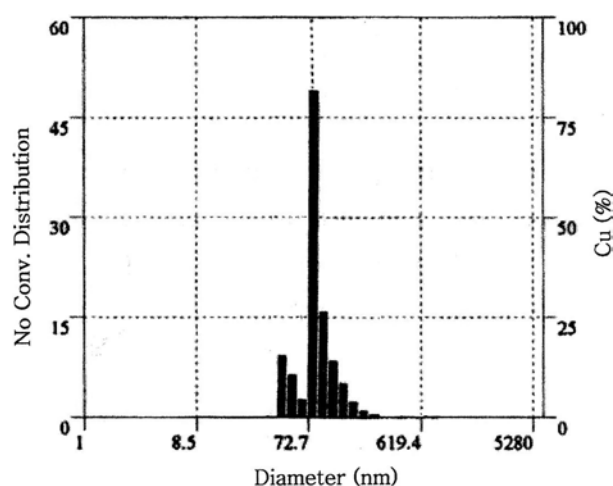


Fig. 5. Particle size analysis of HAp powder derived from the PEG addition.

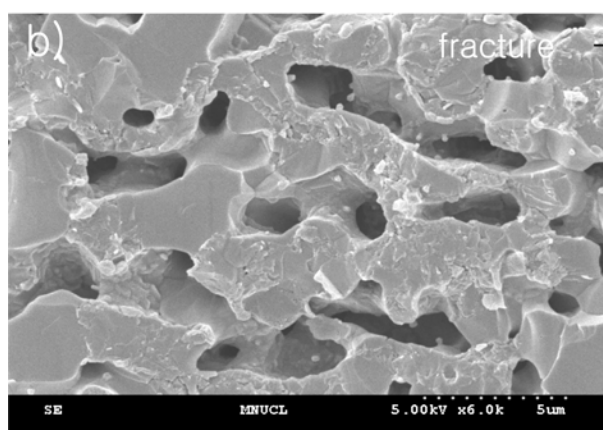
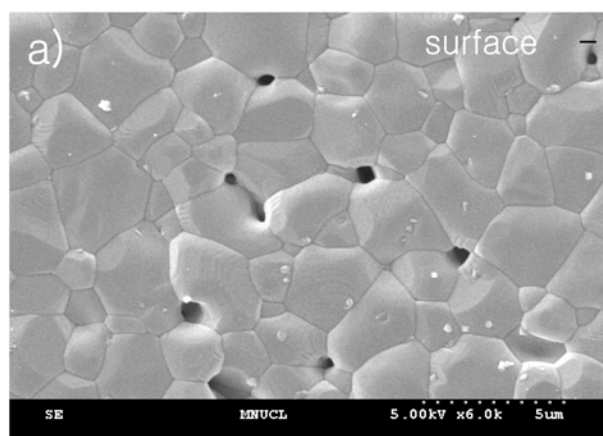


Fig. 6. SEM micrographs of sintered HAp samples prepared without PEG : (a) sample surface and (b) fracture surface sintered at 1300 °C for 1 h.

The particle size distribution of the HAp powder prepared with PEG is presented in Fig. 5. The powder was well dispersed by the addition of the dispersant and the ultrasonication process. The powder showed an average particle size of about 80~100 nm with a high specific surface area of 34.0 m²/g. The measured particle size distribution was quite wide. However, a high

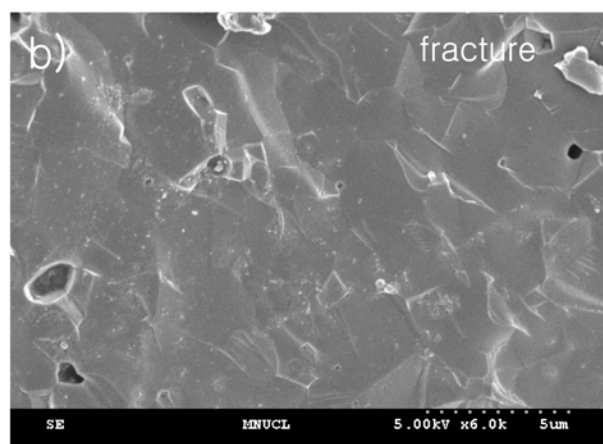
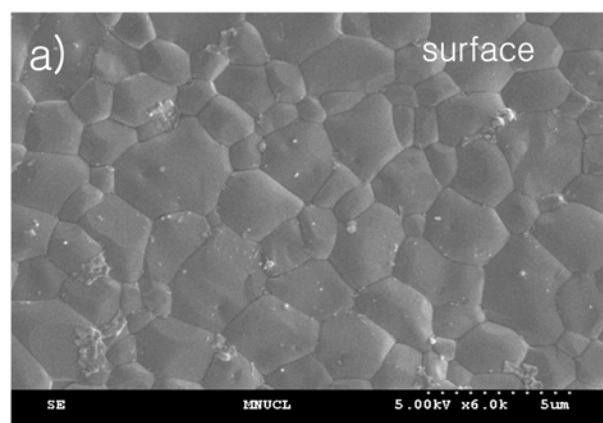


Fig. 7. SEM micrographs of sintered HAp samples prepared with PEG (a) sample surface and (b) fracture surface sintered at 1300 °C for 1 h.

fraction of measured particles belonged to the size range of 80~100 nm as shown in Fig. 5.

In the study of the sintering behavior, the densification of the as-calcined HAp powders (with and without PEG) was notably different. SEM micrographs of the sintered samples are presented in Figs. 6 and 7. In all samples, sintering shrinkage began at 1100 °C and the main shrinkage was observed above 1200 °C. In the densified samples sintered at 1300 °C, intra-granular fracture was observed in the all microstructures. The HAp prepared with the PEG polymer was nearly fully densified showing an average grain size of 1.2 μm (Fig. 7). The HAp prepared without the PEG polymer showed a coarse surface microstructure and large pores in its fracture surface (Fig. 6).

The improved densification behavior in the synthesized HAp powder prepared with PEG is due to the finer particle size and less agglomeration caused by the homogeneous precursor. Moreover, the soft agglomeration could be easily broken in the powder compacting process. In this slurry solution process with PEG, the polymer ensured the homogeneous distribution of the CaO powder and phosphoric acid in the slurry. Furthermore, the highly viscous slurry by the polymer addition prevents

sedimentation of the CaO powders during the drying process. In addition, the soft agglomerated powder by the polymer decomposition, in contrast with premature agglomeration in the case of without PEG, was easily broken to fine particles.

Conclusions

The particle size of HAP ceramic powder and its sintering behavior were studied in a special synthesis route using a slurry containing CaO powder, phosphoric acid and PEG polymer. The addition of PEG had an influence on the homogeneity of precursor and it resulted in a fine powder with a nano-scale particle size. Furthermore, the porous and soft agglomerated powder caused by the polymer burn-out during the calcination process resulted in an improvement of sinterability giving a denser powder compact. Finally, the application of PEG polymer in the synthesis process of HAP using CaO slurry with phosphoric acid made it possible to fabricate nano-sized HAP powders and improve the sinterability.

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