RESEARCH ON THE PRODUCTION OF POROUS HYDROXYAPATITE CERAMICS FROM COCKLE SHELLS OF LANGCO, THUATHIEN-HUE PROVINCE

NGHIÊN CỨU CHẾ TẠO GỐM XỐP HYDROXYAPATIT TỪ VỎ SÒ LĂNG CÔ, THỪA THIÊN-HUẾ

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Abstract - The study dealed with the process of producing hydroxylapatite (HA) powder and porous hydroxylapatite ceramics. The raw material, cockle shell from Lang Co (Thua Thien-Hue Province) was thermally decomposed into CaO and then the obtained CaO reacted hydrothermally with a $(NH_4)_2HPO_4$ solution. The hydrothermal process was carried out in a autoclave equipment at 180-220^{o}C. Some characteristics of the obtained hydroxyapatite powder as phase content, bonding, particle shape and size were determined by X-ray Diffraction (XRD), Infrared Spectrometry (FT-IR) and Scanning Electron Microscopy (SEM). The results showed that the reaction temperature did not affect the phase content but HA crystalline shapes and sizes. The study also dealed with the impact of slurry water content and firing temperature on the HA ceramics properties. As the result, the porous HA ceramics having good compressive strength (261 MPa) was obtained, and it had the slurry water content of 35% and the firing temperature of 1250^{o}C.

Key words - hydroxyapatite; hydroxyapatite ceramics; cockle shell; hydrothermal reaction; autoclave

Tóm tắt - Bài báo này nghiên cứu chế tạo bột hydroxyapatit (HA) và gốm xốp hydroxyapatit. Nguyên liệu là vỏ sò Lăng Cô (Thừa Thiên-Huế) được chuyển hóa thành CaO, sau đó thực hiện phản ứng thuỷ nhiệt với dung dịch $(NH_4)_2HPO_4$ trong khoảng nhiệt độ từ 180-220^{o}C trong autoclave. Bột hydroxyapatit thu được được xác định thành phần pha, đặc trưng liên kết, hình dạng và kích thước hạt bằng các phương pháp nhiễu xạ tia X (XRD), hồng ngoại biến đổi Fourier (FT-IR) và hiển vi điện tử quét (SEM). Kết quả cho thấy, nhiệt độ của phản ứng thủy nhiệt không ảnh hưởng đến thành phần pha nhưng ảnh hưởng đến hình dạng và kích thước hạt khoáng HA. Đối với quá trình chế tạo gốm xốp, đã nghiên cứu ảnh hưởng của độ ẩm hồ đổ rót và nhiệt độ nung đến tính chất của gốm HA. Kết quả với độ ẩm tạo hình 35%, nhiệt độ nung 1250^{o}C thì gốm xốp HA đạt được cường độ chịu nén khá cao (261 MPa).

Từ khóa - hydroxyapatit; gốm hydroxyapatit; vỏ sò; phản ứng thủy nhiệt; autoclave

1. Introduction

Hydroxyapatite (HA), which has the chemical composition of $Ca_{10}(PO_4)_6(OH)_2$, is the main inorganic mineral in human or animal bone and teeth. Artificial porous HA ceramics is non-toxic material with no known allergic reaction to human body, has good bioactivities and could make good bonding with host bone tissue [1-6]. Due to above mentioned advantages, artificial HA ceramics is commonly used as bone graft and substitute material in recent decades. HA could be prepared from natural or artificial raw material sources in different ways such as wet method, solid reaction, hydrothermal method etc…[2, 6]. The main purpose of these methods is making HA powder that has required technical properties. And then HA powder will be used as raw material to produce porous HA ceramics.

Besides having a similar composition and characteristics to natural bone, porous HA ceramics has structure with interconnected pores enabling fibrous tissues and blood vessel easily penetrate. For this reason, HA material has high biocompatibility with cells and tissues, has good bone conduction, ability to bond directly to immature bone and then rapid bone generation without elimination [7].

Currently around the world, the research on manufacturing and applying HA has been developed quickly. Some researches on manufacturing HA from animal bone, corals, cockle shell were published [8-11]. In Vietnam, researches on producing and using HA materials for medical and biological purposes are gaining interests. There are studies on HA materials using many different methods of synthesis such as precipitation, hydrothermal, sol-gel etc… from 2003 [7, 12-14]. In this work, we present results of the synthesis of HA powder and porous HA ceramics from cockle shells of Lap An lagoon, Lang Co Town, Thua Thien-Hue Province.

2. Experiments

Raw materials were cockle shells obtained from Lap An Lagoon, Lang Co Town, Thua Thien-Hue Province and pure ammonium hydophosphate $(NH_4)_2HPO_4$ (China).

First, the cockle shells were cleaned by mechanical (scrubing) and chemical methods (cleaning the surface with HCl solution 0,5 M). Then they were washed many times with distilled water, dried at 105^{o}C and were crushed into pieces smaller than 5×5 mm.

The cockle shells then were calcited at 850^{o}C for one hour in order to convert $CaCO_3$ completely to CaO. We obtained CaO in fine powder after grinding and sieving through a 0.063 mm sieve.

HA was formed according to the following reaction of CaO and $(NH_4)_2HPO_4$:

$$10CaO + 6(NH_4)_2HPO_4 + 4H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12NH_4OH$$

The reaction was performed in autoclave at the temperatures of 180, 200 and 220^{0}C, corresponding to pressure from 10-15 at, the reaction time was 24 hours.

Water in the above mentioned reaction played the role

as a reactant and simultaneously as a solvent which dissolved and diffused $(NH_4)_2HPO_4$ salt in a heterogeneous reaction [14].

Obtained HA powder was washed and filtered many times by boiled distilled water in order to eliminate residual salts. The following process was drying at 105^{o}C and grinding the powder into particles smaller than 0.063 mm. HA powders were characterized by XRD on Siemens D5005, by SEM on Hitachi S4800 and by Infrared Spectrometry on FT-IR-8700 Shimadzu equipment (Japan).

HA powder then was shaped by slip casting method and firing at 1200 or 1250^{o}C with 1 hour of soaking time to make porous HA ceramics.

3. Results and discussion

3.1. Effect of washing and filtering process on mineral composition of HA powder

The effect of washing and filtering process on mineral composition of HA powder was determining by XRD in order to know HA content. XRD diagram of HA powder, which was synthesized at 200^{o}C without washing and filtering, was presented in Figure 1. The results showed that HA, $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$ contents were approximately 65.27%; 29.52% and 5.21%, respectively.

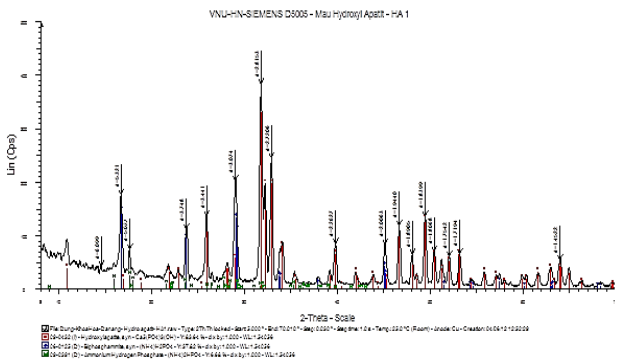

Figure 1. *XRD diagram of HA powder synthesized at 200^{o}C without washing and filtering*

XRD diagram of HA powder that was synthesized at 200^{o}C, washed and filtered many times by boiled distilled water, dried at 105^{o}C to constant weight was presented in Figure 2. The result showed that HA content was 100%.

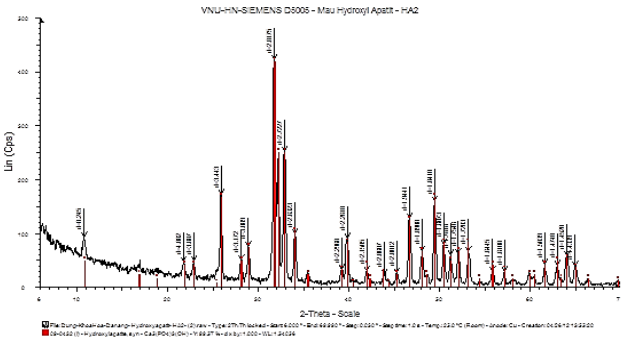

Figure 2. *XRD diagram of HA powder synthesized at 200^{o}C after washing and filtering*

It could be seen that washing and filtering processes after the synthesis had a great effect on the purity of the HA powder. For this reason, there must be washing and filtering processes by boiled distilled water in experimental procedure to obtain HA powder with high purity, to remove residual $(NH_4)H_2PO_4$ or such salts as $NH_4(OH)$, $(NH_4)_2HPO_4$ that were byproducts of the reaction.

3.2. Effect of synthesized temperature on mineral composition of HA powder

HA powder was synthesized by the above hydrothermal reaction carrying out at the temperatures of 180, 200 and 220^{o}C. The obtained HA powders after washing, filtering, drying, grinding were characterized by XRD for determining phase composition. XRD patterns showed only the peaks characterizing for HA phase. There were no peaks characterizing other phases, so that meaned the HA powder samples were monophase (see Figure 2).

Synthesized temperature thus did not affect the mineral composition of HA powder in the range of the experimental temperatures.

3.3. Effect of synthesized temperature on particles size of HA powder

After synthesizing at different reaction temperatures, the HA powders were washed, filtered, dried, ground and characterized by SEM. SEM images of the HA powders at different synthesized temperatures were presented in Figures 3a), 3b) and 3c).

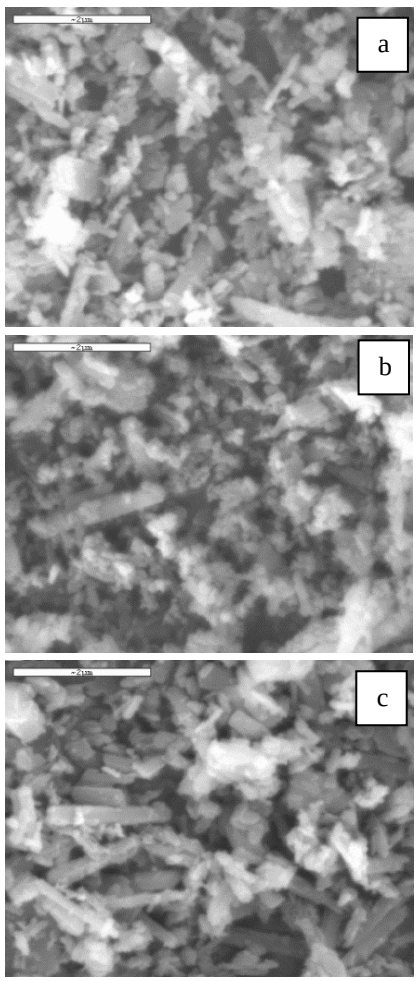

Figure 3. *SEM images of HA powder synthesized at a) 180^{o}C; b) 200^{o}C and c) 220^{o}C*

The SEM images showed that the synthesized temperature affected the shape, size and the aggregation form of the HA particles. At the synthesized temperature of 180^{o}C, the HA particles mainly existed as debrises, some had cylindrical shape or small particles linking together as aggregrations with different forms. At the synthesized temperature of 200^{o}C, some cylindrical particles that were 0.4 µm in diameter, 2 µm in length appeared. At the synthesized temperature of 220^{o}C, the HA particles mainly existed in cylindrical shape which was 0.1-0.3 µm in diameter and 1.8 µm in length, the number of particles in debris decreased, that made the more homogeneous structure of HA powder.

3.4. FT-IR characterisation

FT-IR spectrum of HA powder synthesized at 200^{o}C was presented in Figure 4.

In the spectrum, it could be seen absorption bands characterized for HA material. Absorption bands at 633.4 and 3571.6 cm^{-1} corresponding to vibration of OH^- group in structure. Bands at 1100 to 900, 603, 568.1 cm^{-1} could be assigned to vibrations of PO_4^{3-} group. The intension of bands at 603 and 568.1 cm^{-1} could be seen indicating the crystallinity level of HA powder.

It could be seen from the spectrum that there were relatively low intense bands at 1409.7 to 1550 cm^{-1}. These bands were assigned to CO_3^{2-} group in material structure (indicating the substitution of CO_3^{2-} group to OH^- or PO_4^{3-} group). There was difference in result in comparison with XRD characterisation. In the XRD pattern peaks corresponding to $CaCO_3$ were not appeared most likely due to small amount of existed $CaCO_3$. The reason of the presence of CO_3^{2-} ion maybe due to an incomplete decomposition of the cockle shell during the calcination to make CaO or due to an absorption of CO_2 from the air during the synthesis procedure [5, 14].

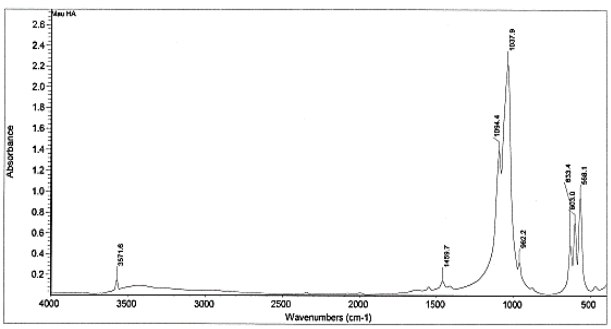

Figure 4. *FT-IR spectrum of HA powder synthesized at 200^{o}C*

3.5. Effect of slurry water content on HA ceramics properties

Shaping process of HA ceramics was carried out by the slip casting method in gypsum mould with the slurry water content of 35, 40 and 45%. The sintering process was carried out in experimental furnace at 1250^{o}C. The physical and mechanical properties of the HA ceramics were determined, and the results were presented in Table 1.

It could be seen that as the slurry water content increased, the water absorption, the apparent and total porosity increased but the bulk density and compressive strength of the HA ceramics decreased. The reason was that when slurry water content increased, the density of the green body decreased. Furthermore, water was removed during the drying process and left pores in the material. Thus, appropriate slurry for the slip casting process had to have the water content as small as possible.

Table 1. *Effect of the slurry water content on physical and mechanical properties of HA ceramics*

Slurry water content (%)	H (%)	X_{bk} (%)	X_t (%)	ρ_v (g.cm^{-3})	ρ (g.cm^{-3})	σ_n (MPa)
35	8.52	22.43	23.22	2.63	3.43	261.0
40	15.02	31.22	39.37	2.08	3.43	260.0
45	20.29	39.86	42.70	1.97	3.43	258.2

With: H-water absorption, X_{bk}-apparent porosity, X_t-total porosity, ρ_v-bulk density, ρ- specific density, σ_n-compressive strength.

3.6. Effect of firing temperature on HA ceramics properties

The green body was shaped from the slurry with the water content of 35% and then was firing at 1200^{o}C and 1250^{o}C. Table 2 presented the comparison of the HA ceramics properties at two different firing temperatures.

Table 2. *Physical and mechanical properties of the HA ceramics fired at 1200 and 1250^{o}C*

Firing temperature (^{o}C)	H (%)	X_{bk} (%)	X_t (%)	ρ_v (g.cm^{-3})	ρ (g.cm^{-3})	σ_n (MPa)
1200	30	50	51.4	1.67	2.99	189.0
1250	8.5	22.4	23.2	2.63	3.43	261.0

The result showed that if the firing temperature increased from 1200^{o}C to 1250^{o}C then the water absorption, apparent porosity, total porosity declined, but the bulk density, specific density and compressive strength increased. The reason was that when the firing temperature increased, the sintering level of the material increased too.

It could be seen that these parameters such as the slurry water content and the firing temperature greatly affected the HA ceramics properties. In comparison with the other HA ceramics [7] our HA ceramics, which was shaped with the slurry water content of 35% and fired at 1250^{o}C had a relatively good compressive strength (261 MPa).

4. Conclusion

The synthesis of monophase HA powders from cockle shells of Lang Co (Thua Thien-Hue province) and $(NH_4)_2HPO_4$ via hydrothermal method at 180, 200 and 220^{o}C was carried out successfully. Some characteristics of the obtained hydroxyapatite powders as phase content, bonding, particles shape and size were determined by X-ray Diffraction (XRD), Infrared Spectrometry (FT-IR) and Scanning Electron Microscopy (SEM).

The results showed that the synthesized temperature did not affect the mineral composition of the HA powder but affected the shape and size of the HA particles. At the synthesized temperature of 220^{o}C, the HA particles

mainly existed in cylindrical shape with 0.1-0.3 μm in diameter and 1.8 μm in length, and the number of particles in the debris decreased, that made the structure of HA powder more homogeneous.

For making ceramics, we have investigated the production of porous HA ceramics which was shaped at different slurry water contents and fired at different temperatures. As a result, a porous HA ceramics having good compressive strength (261 MPa) was produced with the conditions of 35% of slurry water content and 1250^{o}C of firing temperature.

The results mentioned above are preliminary but very important for further investigations into using Lang Co cockle shells to produce HA powder and porous ceramics with the goal of increasing the effective application of this local raw material.

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