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Preparation and Characterization of Apatitic Biphasic Calcium Phosphate

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Abstract

The apatitic biphasic calcium phosphate (ABcp) consisting of hydroxyapatite (HA) and β-tricalcium phosphate (β-Tcp) has been prepared by precipitation technique using slaked lime and orthophosphoric acid. The X-ray diffraction analysis of the product I (hydroxyapatite) revealed that ABcp was partially crystalline state. However, on heating at 800° C for 8 hrs, XRD pattern indicated a perfectly crystalline form of ABcp. This observation was supported by FT-IR measurement. The change in morphology regarding in the functional nature was infered by the shift in the FT-IR frequency. The optimization of the apatitic biphasic calcium phosphate was done by the variation of disodium hydrogen phosphate concentration, setting time, hardening time as well as compressive strength. The prepared cement may be used as an artificial substitution bone.

Key words : Hydroxyapatite, β-tricalcium phosphate, precipitation technique, apatitic biphasic calcium phosphate

Introduction

Bioceramics fulfil a unique function as biomedical materials. The development of biomaterials and manufacturing techniques has broadened the diversity of applications within the human body (Brown, 1999). Ceramics employed within the body can fall into all three biomaterial classifications i.e, inert, resorbable and active, meaning they can either remain unchanged, dissolve or actively take part in physiological processes. Bioceramics satisfy need as diverse as low co-efficients of friction for lubricating surfaces in joint prostheses, surfaces on heart valves that avoid blood clotting, materials that stimulate bone growth and those that can harness radioactive species for therapeutic treatments. From the point of view of biocompatibility, apatitic biphasic calcium phosphate seems to be the most suitable ceramic material for bone replacement implants. The calcination of biphasic apatitic calcium phosphate was obtained by aqueous precipitation method. This method conserves the bioactivity and biodegradability, increases the purity of the ceramics and displays interesting mechanical properties. And in this study, a

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precipitation route has been used to prepare biphasic apatitic calcium phasphate. Its evoluation and characteristics are also discussed.

Materials and Methods

Chemicals employed in this study were of reagent grade (BDH) and deionized water was used as the common diluent for all solutions prepared (Kivrak, 1998).

The apparatus used consist of a muffle furnace (England), a vacuum pump (Central Scientific Co., Chicago, USA), a digital corning Model 7020 pH meter, Mettler balance.

The apatitic biphasic calcium phosphate with a higher amount of hydroxyapatite and β-tricalcium phosphate was prepared by a precipitation method using slaked lime and orthophosphoric acid. The precipitate was aged for 48 hrs, filtered, washed with water, oven dried and heated at 800° C for 8 hrs. The phase purity and constitution of the prepared dried and calcined samples were characterized by the powder X-ray diffraction (XRD) using Cu-K_α radiation and the Fourier Transform Infrared (FT-IR) spectrometry using KBr pellet technique. And then, the setting time, compressive strength, porosity and change in dimensions of the set cement were also assessed using standard moulds.

Results and Discussion

Crystal Phase Analysis

The phase purity and constitution of prepared (ABcp) composite bioceramic powders was checked by X-ray diffraction (Komath, 2000). The XRD spectra of the composites are shown in Figures 1 and 2. Two phases can be identified from these reflection pattern. The first phase (shown in Figure 1) that can be deduced from the pattern was that of hydroxy apatite (HA), which was partially crystalline as evidenced by the broad peaks located in the region of the HA reflection. When it was calcined at 800°C for 8 hours, (shown in Figure 2) it showed biphasic nature with hydroxy apatite and β-tricalcium phosphate (β-tcp) which was the main crystalline phase present, identified by the sharp, narrow reflections.

The relative intensity ratio of biphasic composite samples of 75%, 65%, 60%, 50% and 40% HA is shown in Table 1. These data showed that as the concentrationof orthophosphoric acid increased, the intensity of HA characterstic peaks gradually decreased and □-tcp peaks increased progressively. When the concentration of the acid solution was in the range of 0.62-0.68 M, the XRD patterns showed a biphasic nature where the crystalline phase was composed by HA and β-tcp. The acid concentration was increased to 0.66 M, the ABcp formed a 50% HA and 50 β-tcp composite structure. When the acid concentration was over 0.68 M, the biphasic structure would completely transform into β-tcp, where all the characterized peaks of HA would disappear. The relative intensity ratio (RIR) of HA to β-tcp can be calculated by the formula, RIR = I β -tcp / (I β-tcp + I HA) using intenstiy peak of HA (1 2 2) ,and β-tcp (0 2 10).

FTIR - Spectra Analysis

To further understand the phase transformation of biphasic composite of apatitic biphasic calcium phosphate (ABcp) it can be verified by means of FT-IR spectroscopy. The result of FT-IR analysis showed the absorption band of phosphate stretching at 1027, 962, 603, 564 and 471 cm^{-1}, CO shoulder of C-O vibration mode of carbonate hydroxy apatite at 1423 and 1455 cm^{-1}, OH^- band of HA at 3433 and 1638 cm^{-1} and HPO^{2-} band at 874 cm^{-1} in the spectra as shown in Figures 3 and 4.

The data of the FT-IR spectra of the dried sample and calcined sample is shown in Table 3. Trace amount of carbonate absorption band showed up in the spectra which might be a result of atmospheric carbondioxide contamination. Carbonate group present in the sample was not considered as impurity because the bone material was basically a CO_3^{2-} substituted hydroxy-apatite. HPO_4^{2-} band of DCPD is observed at 874 cm^{-1} for the dried sample (before calcined at 800°C). When calcined at 800°C for 8 hr, this band was disappeared and so it could be concluded that the condensation of HPO_4^{2-} was complete and biphasic character was formed at 800°C for 8 hours. The broad stretching band of OH^- was drastically reduced when calcined at 800°C.

Optimization of the prepared cements for orthopedic and dental applications

The properties of set cement are to be manipulated and optimized for a particular application. The particle sizes are already fixed to <150 μm and wetting ratio is selected to be 0.65 ml of distilled water and Na_2HPO_4 solution to 1g of sample. The setting characteristics and strength of the cement are controlled by the amount of accelerator added. The setting times and compressive strength of the cement at different concentrations of Na_2HPO_4 solution are shown in Figures 5 and 6. From these results, a linear decrease in setting time and compressive strength with increase in concentration can be observed. Thus, for optimizing the cement, the accelerator (Na_2HPO_4) concentration has to be selected 0.2 M. The initial and final setting times of the cement at this concentration are 10 min and 15 min respectively, and the corresponding compressive strength is 10 ± 2 MPa.

Conclusion

Apatitic biphasic calcium phosphate has been prepared from slaked lime and orthophosphoric acid using a precipitation technique. From XRD pattern, dried sample (product I) showed a broad peak indicating that partially crystalline state and product II showed a biphasic nature after heating at 800°C for 8 hours. From FT-IR spectrum of product I showed HPO_4^{2-} band (874 cm^{-1}); when calcined, this peak was disappeared due to the formation of biphasic nature. The optimization of the cement for orthopedic filling application was done by adjusting the concentration of the accelerator. It was found that the setting time and hardening time decrease on increasing the accelerator (Na_2HPO_4) concentration. The optimum concentration of Na_2HPO_4 was decided to be 0.2 M, compromising setting properties and strength. At this value, the setting and hardening times (10 and 15 min, respectively) and compressive strength (11.15 MPa) satisfy the clinical requirements of filling.

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Table 1 - Various relative intensity ratios of hydroxy apatite and β-tricalcium phosphate composite (ABcp) by varying the concentration of orthophosphoric acid solution

H_3PO_4 (M)	Ca(OH)2 (M)	relative intensity ratios of HA to β - tcp (%)
0.62	1	25% β-tcp : 75% HA
0.63	1	35% β-tcp : 65% HA
0.65	1	40% β-tcp : 60% HA
0.66	1	50% β-tcp : 50% HA
0.68	1	60% β-tcp : 40% HA

Table 2 - Data of mechanical test for prepared sample

Properties / Feature	Annotation
Chemical composition	$Ca_{10}(PO_4)_6(OH)_2$ - β - $Ca_3(PO_4)_2$
Particle size (μm)	< 150
Liquid to solid ration (ml / g)	0.65
Paste consistency	Soggy, syrupy
Setting time (min) - Initial	10
- Final	15
Average diameter (mm)	12
Average height (mm)	15.98
Compressive strength (MPa)	10 ± 2

Table 3 - Data of the FT-IR spectra of the dried sample and calcined sample

No.	Functional group	Related wavenumber (cm^{-1})	
		dried sample (product I) $Ca_{10}(PO_4)_6(OH)_2$	calcined sample (product II) $Ca_{10}(PO_4)_6(OH)_2$ - β - $Ca_3(PO_4)_2$
1.	υ_{OH}	3433 (very broad and strong)	3421 (very small and weak)
2.	δ_{OH}	1638 (medium intensity)	1634 (very weak intensity)
3.	υ_{P-O} of PO_4^{3-}	1027 (very broad and strong)	1065 (very broad and strong)
4.	υ_{P-O} of HPO_4^{2-}	874 (medium intensity)	
5.	$\upsilon_{CO_3}2-$	1423 (medium intensity)	1438 (weak intensity)

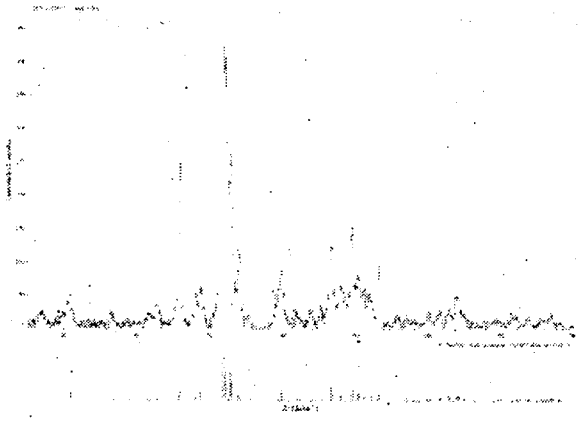

Figure 1. XRD diffractogram of the apatitic biphasic calcium phosphate (dried sample, product - I)

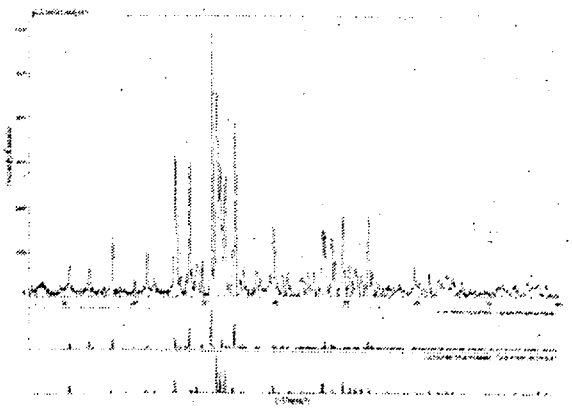

Figure 2. XRD diffractogram of the apatitic biphasic calcium phosphate (calcined sample, product-II)

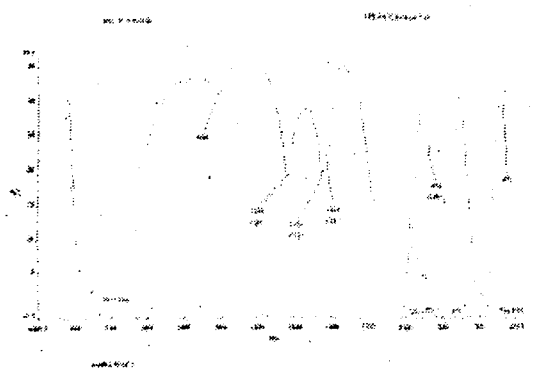

Figure 3. FT-IR spectrum of the apatitic biphasic calcium phosphate (dried sample - product - I)

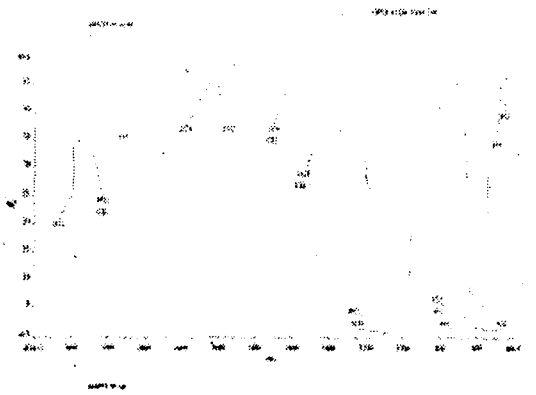

Figure 4. FT-IR spectrum of the apatitic biphasic calcium phosphate (calcined sample - product - II)

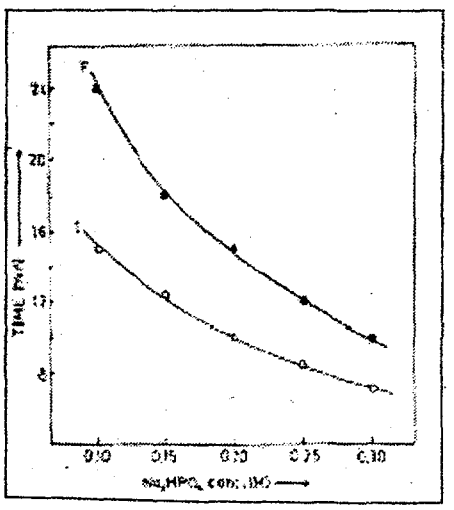

Figure 5 The setting times of cement at different concentrations of Na_2HPO_4

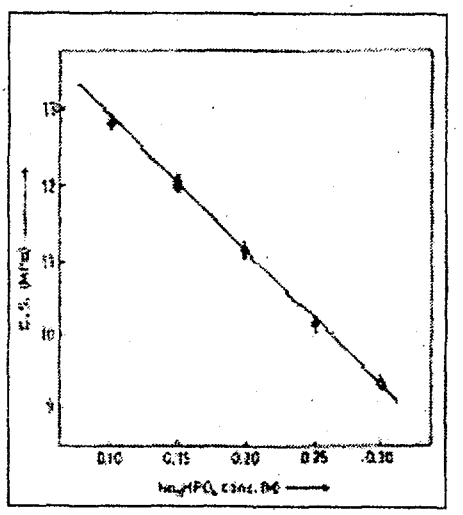

Figure 6 The compressive strength of cement at different concentrations of Na_2HPO_4

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