

EFFECT OF MOLAR RATIO IN FORMATION OF BIPHASIC HYDROXYAPATITE/ α -TRICALCIUM PHOSPHATE BIOCERAMICS

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Abstract

Biphasic Hydroxyapatite/ α -Tricalcium Phosphate (HAP/ α -TCP) with three Ca : P molar ratios of 1.60 : 1, 1.57 : 1 and 1.54 : 1 were prepared by precipitation method. The filtrated white paste samples were analysed by Thermogravimetric and Differential Thermal Analysis (TG / DTA)) to determine the weight loss %, and to enable the qualification of endothermic energy changes. After heat-treatment at 1200°C for biphasic HAP / α -TCP, the powder samples were characterized by X-ray Diffraction (XRD) and the lattice parameters, volume of the unit cell, the crystallite sizes, and weight percent ratios were evaluated. The morphology of biphasic HAP/ α -TCP powder was studied by using the Scanning Electron Microscopy (SEM).

Keywords: Hydroxyapatite, α -tricalcium phosphate, Ca: P molar ratios, precipitation.

Introduction

Hydroxyapatite (HAP), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and other calcium phosphates such as α -TCP, $\text{Ca}_3(\text{PO}_4)_2$, have been utilised extensively as implant materials because of their compositional similarity to that of the mineral phase of hard tissue in human bones [Juliana, M.,2009]. The main difference between HAP and α -TCP is the resorption rate when they are implanted in the body. HAP resorbs very slowly and most stable, while α -TCP dissolves 10 times faster in the body than HAP [Klein, C.P., 1983]. To control their resorption rates, currently there is an increasing interest on the preparation of mixtures of two or more calcium phosphates. When they combine each other, the formed biphasic HAP/ α -TCP ceramic controls the resorbability of TCP and maintains the osteoconductive property of HAP [Klein, C.P., 1983]. Moreover, biphasic calcium phosphates have more reliable bioactivity on physical and chemical properties [Caroline, V., 2002].

Materials & Methods

Diammonium hydrogen phosphate, $(\text{NH}_4)_2\text{HPO}_4$ and calcium nitrate tetra hydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved individually in distilled water and stirred for 10 minutes at 37°C to obtain two clear solutions. Then, calcium nitrate solution was slowly added to phosphate solution and concentrated ammonium hydroxide solution was also added and stirred for 2 hours at 37°C. The reaction temperature was controlled by water bath. The milky solution was filtered and the precipitate was washed with distilled water and aged for 24 hours to get the white paste sample. Then the paste was dried at 60°C for 24 hours and the dried solids were made into powder and calcined for 12 hours (soaking time) at 850°C to get biphasic HAP/ β -TCP. Then, this biphasic HAP/ β -TCP sample was heated again at 1200 °C with the soaking time of 3.5 hours and the biphasic HAP/ α -TCP was obtained.

Characterization

By using the DTG-60H, the thermal analysis for white paste samples was carried out. The powder x-ray diffraction (XRD) was performed for biphasic HAP/ α -TCP powder by Cu-K α

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radiation. The morphology and grain size of biphasic HAP/ α -TCP powder samples were observed by employing the Scanning Electron Microscopy (SEM).

Results and Discussion

Thermal analysis of the white paste samples was carried out by using Simultaneous TG/DTA Analyser (Shimadzu DTG-60/60H). The enthalpy change (ΔH) was calculated by the following equation,

$$\Delta H = (k/m) \int_{t_1}^{t_2} \Delta T dt \quad (1)$$

Where, ΔH is the enthalpy change, $\int_{t_1}^{t_2} \Delta T dt$ is the area enclosed by a curve, m is mass and k is thermal conductivity.

The area enclosed of endothermic curve was calculated by the trapezoid rule with the equation;

$$\text{Area of Trapezium} = [(b_1 + b_2) h] / 2 \quad (2)$$

Where, b_1 , b_2 are the bases of the trapezium and h is the height of the trapezium

Figure 1, 2 and 3 are the graphs of TG/DTA analysis of three white paste samples. In these graphs, each DTA curve contains one broad peak with endothermic nature and it indicates that the absorption of heat of the reacting substances during the phase change process.

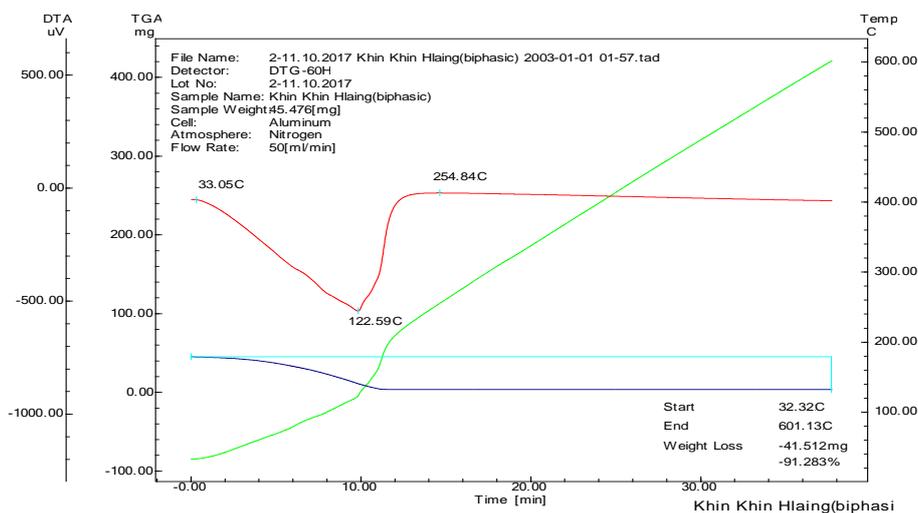


Figure 1 TG/DTA analysis of white paste sample S1

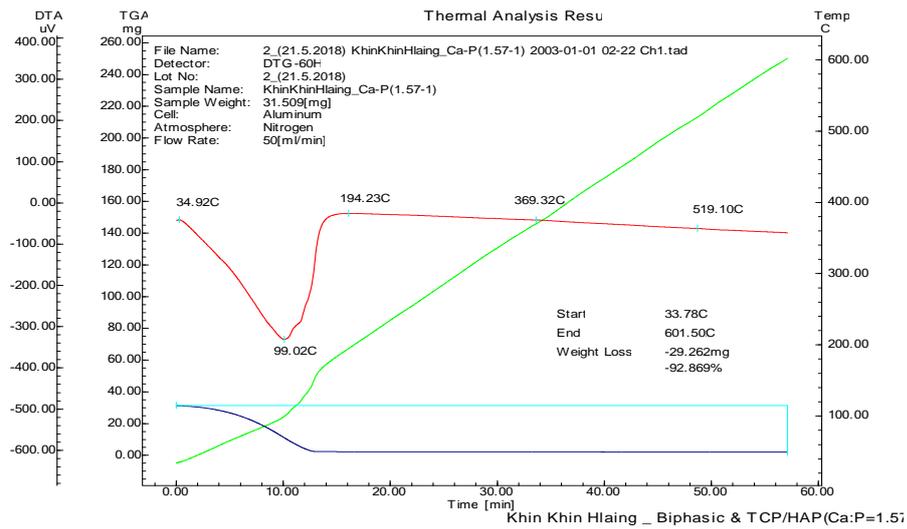


Figure 2 TG/DTA analysis of white paste sample S2

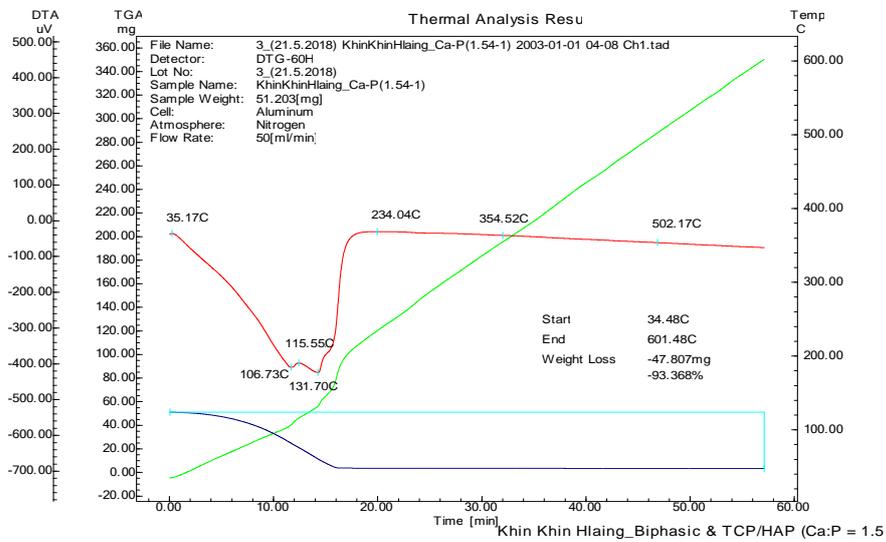


Figure 3 TG/DTA analysis of white paste sample S3

Table 1 shows the comparison of the decomposition temperatures of the reacting substances, $(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ obtained from DTA analysis and their literature values. It is worth to note that the peak decomposition temperatures from the DTA analysis agree well with the literature values of the reactants.

Table 2 shows the values of the thermal parameters of each endothermic reaction from DTA analysis for three white paste samples. During the phase change process, the temperature range increase from sample S1 to S3 when their Ca: P molar ratios decrease.

Table (3) shows the area enclosed of endothermic peak and enthalpy values in DTA analysis of three white paste samples. The sample S2 exhibits the smallest area enclosed and enthalpy while the sample S3 possesses the greatest values and the sample S1 remain between them.

Table 4 shows the values of the weight loss % of three white paste samples calculated from TG analysis. It can be observed that the weight loss % of the samples increase when the Ca : P molar ratios decrease.

Table 1 Comparison of the decomposition temperatures of $(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ from DTA analysis and their literature values

Sample	Ca : P	Reacting Substance	Decomposition Temperature ($^{\circ}\text{C}$)	
			DTA Result	Literature Value
S1	1.60 : 1	$(\text{NH}_4)_2\text{HPO}_4$	158	155
		$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	130	132
S2	1.57 : 1	$(\text{NH}_4)_2\text{HPO}_4$	150	155
		$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	135	132
S3	1.54 : 1	$(\text{NH}_4)_2\text{HPO}_4$	150	155
		$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	120	132

Table 2 Thermal parameters of endothermic reactions from DTA analysis of three white paste samples S1, S2 and S3

Sample	Ca : P Molar Ratio	Starting Temperature ($^{\circ}\text{C}$)	Ending Temperature ($^{\circ}\text{C}$)	Temperature Range ($^{\circ}\text{C}$)
S1	1.60: 1	40	230	190
S2	1.57: 1	35	232	197
S3	1.54: 1	38	240	202

Table 3 Area of Endothermic Peak and Value of Enthalpy change calculated from DTA analysis of three white paste samples

Sample	Process	A ($\mu\text{V min}$)	A (V sec)	I (A)	W (J)	ΔH (cal)
S1	Endothermic	3901.33	0.2341	13.64	3.194	0.76
S2	Endothermic	2757.33	0.1654	13.64	2.256	0.54
S3	Endothermic	4406.80	0.2644	13.64	3.606	0.86

Table 4 Loss of weight % of three white paste samples from TG analysis

Sample	Ca : P	Initial weight (mg)	Final weight (mg)	Weight loss (%)
S1	1.60:1	45.476	4.0	91.283
S2	1.57:1	31.509	2.5	92.870
S3	1.54:1	51.203	3.0	94.140

XRD Analysis

Phase composition of biphasic HAP/ α -TCP powder samples were examined by X-ray diffraction (XRD) by the Cu-K α radiation. The mean crystallite size (L) was calculated from Scherrer equation,

$$L = \kappa \lambda / \beta \cos \theta \tag{3}$$

Where, L is crystallite size, k is Scherrer’s constant, λ is X-ray wavelength, β is line broadening at half the maximum intensity and θ = Diffraction angle.

Reference Intensity Ratio (RIR) value and weight % of the HAP and α-TCP were determined by using the following formulae.

$$RIR_{\alpha\text{-TCP}} = I_{\alpha\text{-TCP}} / (I_{\alpha\text{-TCP}} + I_{\text{HAP}}), \tag{4}$$

$$RIR_{\text{HAP}} = I_{\text{HAP}} / (I_{\alpha\text{-TCP}} + I_{\text{HAP}}) \tag{5}$$

$$\text{Weight \%} = (RIR \times 100) \% \tag{6}$$

Where, I_{α-TCP} and I_{HAP} are maximum intensities of phase α-TCP and HAP.

Volume of unit cell of Hexagonal and Orthorhombic crystal systems were calculated by

$$V = a^2c \sin 60^\circ \tag{7}$$

$$V = a b c \tag{8}$$

Where, a, b, c are the lattice parameters of a unit cell

Figures 4, 5 and 6 represent the XRD patterns of three powder samples heated at 1200°C. The patterns of HAP and α-TCP phases are matched with reference files from ICDD (PDF-2 Release 2015 RD). All diffraction peak positions of the samples agree well with the standard XRD patterns of HAP and α –TCP and revealed the formation of biphasic HAP/ α -TCP after heating at 1200°C.

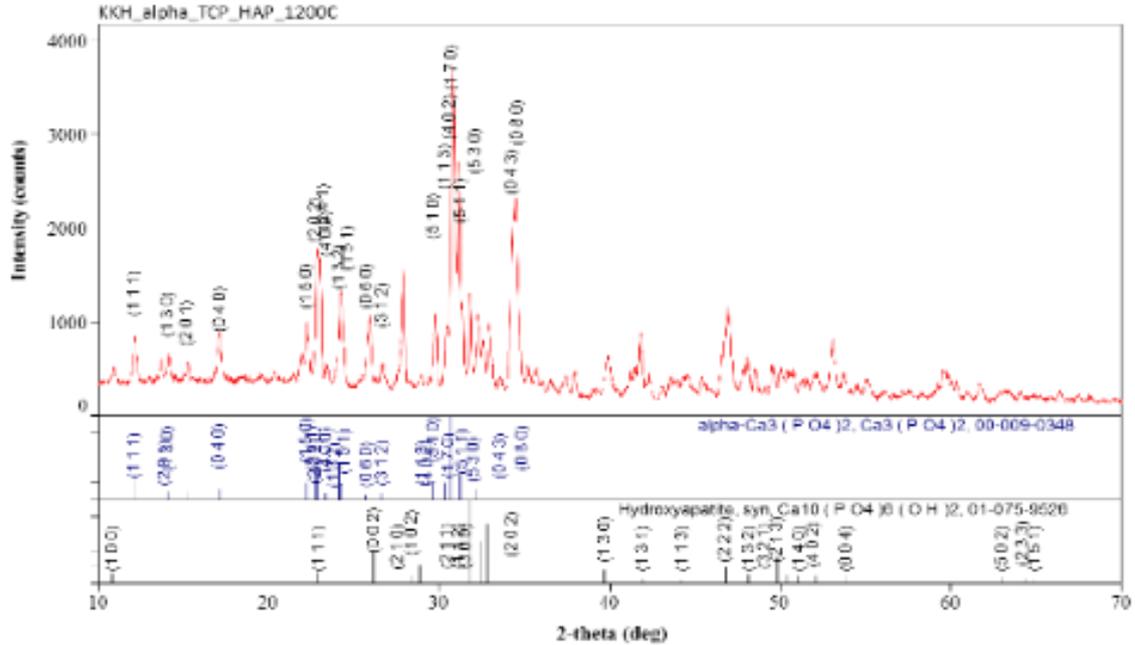


Figure 4 XRD pattern of biphasic HAP/α-TCP (Sample S1)

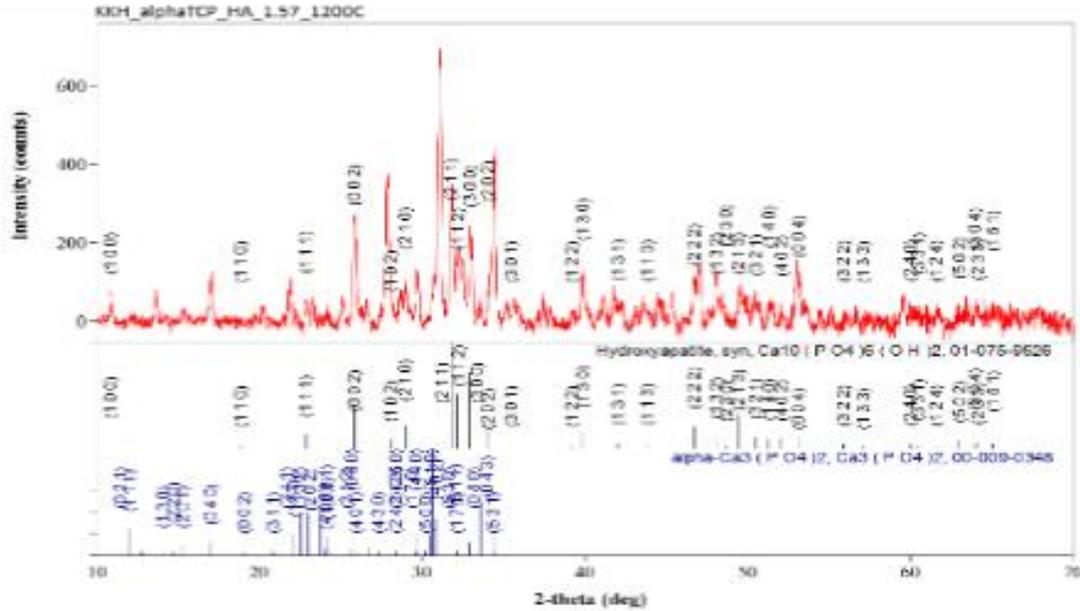


Figure 5 XRD pattern of biphasic HAP/ α -TCP (Sample S2)

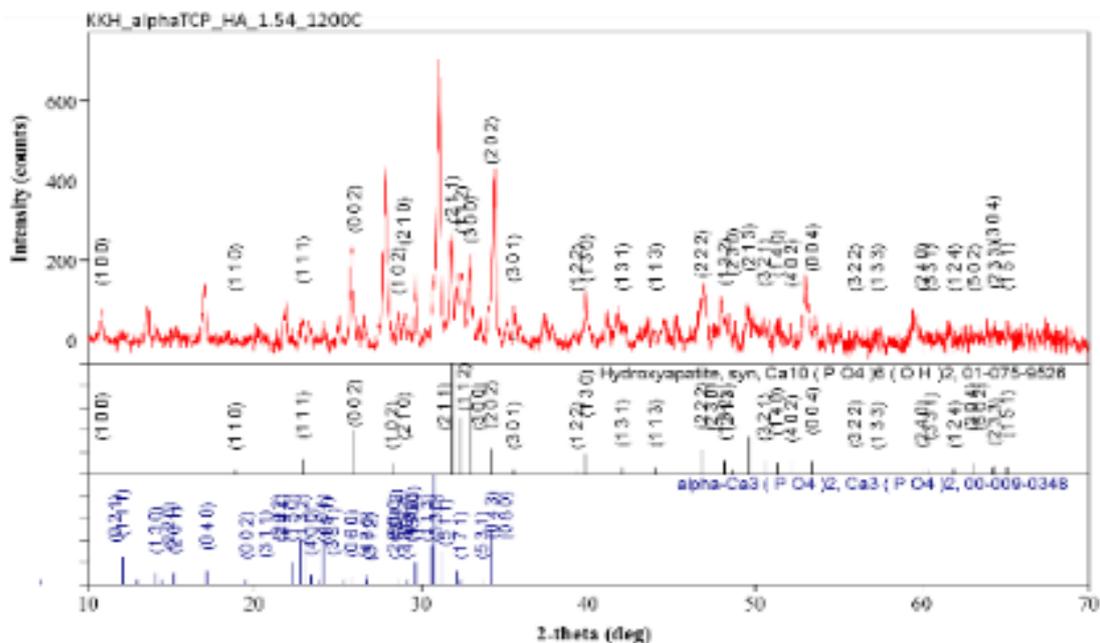


Figure 6 XRD pattern of biphasic HAP/ α -TCP (Sample S3)

Table 5 shows the comparison of the values of the lattice parameters and volumes of unit cells of the HAP and α -TCP in three biphasic HAP/ α -TCP samples. The values of the lattice parameters of HAP and α -TCP are agreed with their literature values. In both phases of HAP and α -TCP, the values of a, b and c increase with the decrease in Ca: P molar ratio (except the value of 'a' in sample S2 in α -TCP). It has been observed that with the increasing of the lattice parameter, the volumes of a unit cell also increase in both HAP and α -TCP. Moreover, the unit cell volume of α -TCP is always larger than that of HAP in every sample.

Table 6 shows the comparison of the Reference Intensity Ratio (RIR) and weight % of HAP and α -TCP in biphasic HAP/ α -TCP. When the weight % of HAP and that of α -TCP are

compared for each ratio, the weight % of α -TCP is nearly 5 times larger than that of HAP for Ca : P of 1.60 : 1 but 2 times for 1.57 : 1 and 3 times for 1.54 : 1.

Table 7 shows the comparison of the crystallite sizes of HAP and α -TCP in three biphasic HAP/ α -TCP powder samples. The crystallite sizes of HAP and α -TCP increase when the Ca: P molar ratio of each sample decreases. And, the crystallite size of α -TCP is always larger than that of HAP in every sample.

Table 5 Comparison of the lattice parameters and unit cell volume of HAP and α -TCP in three biphasic HAP/ α -TCP samples

Phase	Crystal system /Space group	Ca : P	Lattice parameter			Volume (\AA^3)
			a (\AA)	b (\AA)	c (\AA)	
HAP	Hexagonal / 176:P63/m	1.60 : 1	9.382	9.382	6.810	519.1
		1.57 : 1	9.396	9.396	6.856	524.2
		1.54 : 1	9.400	9.400	6.914	529.1
α -TCP	Orthorhombic / 47:Pmmm	1.60 : 1	15.171	20.700	9.071	2848.7
		1.57 : 1	14.760	20.800	9.311	2858.6
		1.54 : 1	15.222	20.830	9.316	2953.9

Table 6 Comparison of the RIR value and weight % of HAP and α -TCP in biphasic HAP/ α -TCP sample

Ca : P	Relative Intensity		RIR value		Weight (%)	
	HAP	α -TCP	HAP	α -TCP	HAP	α -TCP
1.60:1	19.64	100	0.16	0.84	16	84
1.57:1	40.19	67.52	0.37	0.63	37	63
1.54:1	31.96	100	0.24	0.76	24	76

Table 7 Comparison of the average crystallite size of HAP and α -TCP

Sample	Ca : P	Crystallite size (nm)	
		HAP	α -TCP
S1	1.60 :1	36.23	38.13
S2	1.57 :1	37.42	40.72
S3	1.54 :1	39.65	53.14

SEM Analysis

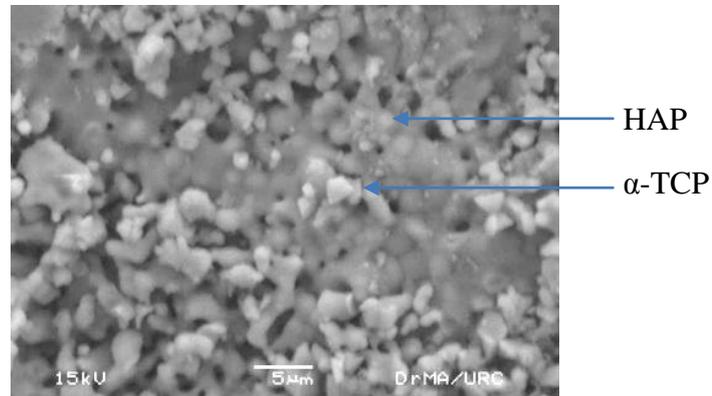
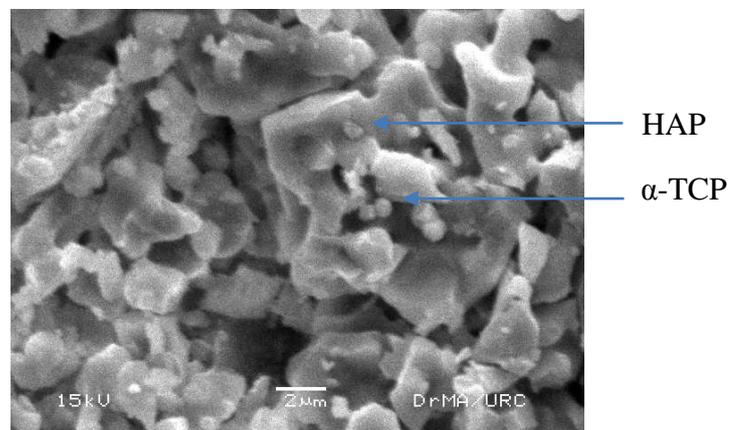
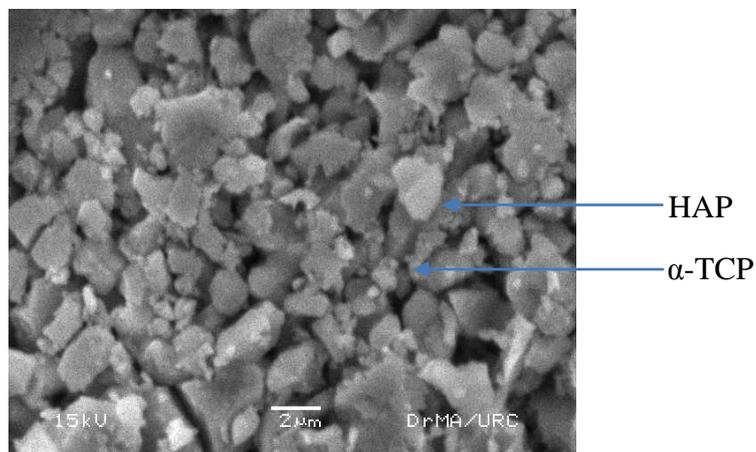
The surface morphology of biphasic HAP/ α -TCP power samples was observed by Scanning Electron Microscopy (SEM). Figures 7, 8 and 9 show the SEM images of surfaces of three biphasic HAP/ α -TCP powder samples. The average particle sizes of HAP and α -TCP were calculated by Eq (9),

$$\text{Particle sizes} = \text{Total length of the particles} / \text{Number of particles} \tag{9}$$

Table 8 shows the comparison of the average particle sizes of HAP and α -TCP calculated from SEM analysis for three biphasic HAP/ α -TCP samples. The smaller the Ca: P molar ratio of the samples, the smaller the particle size of HAP and the larger the size of α -TCP. Moreover, the particle size of α -TCP is always larger than that of HAP in each sample.

Table 8 Comparison of the average particle size of HAP and α -TCP from SEM analysis

Sample	Ca : P	Particle size (μm)	
		HAP	α - TCP
S1	1.60 :1	0.83	0.91
S2	1.57 :1	0.58	1.20
S3	1.54 :1	0.31	1.46

**Figure 7 SEM image of biphasic HAP/ α -TCP (S1)****Figure 8 SEM image of biphasic HAP/ α -TCP (S2)****Figure 9 SEM image of biphasic HAP/ α -TCP (S3)**

Conclusion

The three biphasic HAP/ α -TCP samples with Ca: P molar ratio of 1.60: 1, 1.57:1 and 1.54:1 were prepared via precipitation method by using Ca (NO₃)₂.4H₂O and (NH₄)₂HPO₄ as precursors. The decomposition temperatures of the reacting molecules obtained from the DTA analysis well agree with the literature values. It has been proved that when the amount of Ca decreases in Ca: P molar ratio, the temperature range in which endothermic reaction occurred increases (DTA analysis), the value of % weight loss increases (TG analysis). Importantly, the values of lattice parameters (except 'a' in sample S2 in α -TCP phase), the volume and crystallite sizes in both HAP and α -TCP become larger with the decrease in the amount of Ca in Ca: P molar ratio. The SEM analysis prove that the particle size of α -TCP is always larger than that of HAP and it well agrees with the XRD results. Therefore, this research reveals that the molar ratio of Ca: P does effect the formation of biphasic hydroxyapatite/ α -tricalcium phosphate bioceramics in structural and thermal behaviors.

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