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A study on thermal behavior of uncalcined $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaCO_3$ mixtures

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Abstract

Biphase composites of hydroxyapatite (HA) and β-tricalcium phosphate (TCP) with various phase compositions have been obtained by controlling the molar ratio of $Ca(HPO_4) \cdot 2H_2O$ and $CaCO_3$ at an appropriate value between 1.5 and 2.0. In this work, biphase composites of HA and β-TCP with various phase compositions were prepared from the uncalcined $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaCO_3$ mixtures. The thermal properties of uncalcined raw materials were investigated using DTA/DSC/TG. The kinetic parameters of dehydration and decomposition for uncalcined $Ca(H_2PO_4)_2 \cdot H_2O/CaCO_3$ mixtures were also evaluated by non-isothermal differential thermal analysis (DTA) techniques.

Keywords: Uncalcined $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaCO_3$ mixtures; DTA; TG; Dehydration; Decomposition; Non-isothermal DTA kinetics

1. Introduction

Ceramics are historically the oldest of the synthetic uncalcined materials. Hydroxyapatite (HA) and tricalcium phosphate (TCP) are the most commonly used phosphate ceramics for bone replacement due to their biocompatibility [1–5]. It is well known that the mineral constituent of human hard tissues generally shows a porous biphase (HA + TCP) structure after being sintered at high temperature. Artificially sintered porous biphase or multiphase (HA + β- or α-TCP) bioceramics, which are analogous to bone material, are found to have good bone-bonding ability. Accordingly, an implant with desired biodegradability can be obtained by controlling the content of β-TCP in HA-β-TCP biphase composite and the pore size of the implant. Therefore, many studies focus on the synthesis of these biphase ceramics through various raw materials and processes [6]. In our previous study [7], the thermal properties and the phase changes at certain temperatures of dibasic calcium hydrogen phosphate and monobasic calcium phosphate were investigated using non-isothermal differential thermal analysis (DTA) techniques and X-ray powder diffraction patterns. We observed CaP_2O_6 and CaP_2O_7 phases after the dehydration and decomposition process of $Ca(H_2PO_4)_2 \cdot H_2O$ and $Ca(HPO_4) \cdot 2H_2O$, respectively. In the present work, variations in atomic Ca/P ratios between 0.75 and 1.00 among the uncalcined $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaCO_3$ mixtures were first prepared, then the kinetic parameters of dehydration and decomposition for these uncalcined mixtures were evaluated by thermal analysis techniques.

2. Experimental

Calcium phosphate ceramics in atomic Ca/P ratios varying between 0.7 and 1.0 were mixed by agitation in ethanol (250 ml) for 24 h. The compositions of uncalcined raw materials listed in Table 1 were

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Table 1
Composition of uncalcined raw materials

Uncalcined mixture powder	$Ca(H_2PO_4)_2 \cdot H_2O$ (g)	$CaCO_3$ (g)	Mole ratio of Ca/P
A	126	25	0.75
B	94.53	25	0.83
C	63.62	25	1.0

obtained after drying at 80 °C for 6 h. For studying the thermal properties of uncalcined materials, samples of approximately 5.0 mg were used with a Universal V 2.5H TA Instrument at a heating rate of 5–30 °C/min under static air atmosphere. The kinetic parameters of dehydration and decomposition can be calculated from a series of DTA curves.

3. Results and discussion

A single kinetic expression is not feasible for a wide range of decompositions that follow first-order kinetics. In thermogravimetry (TG) one can make an assumption that the values of the calculated activation energy (E_a) are independent of the reaction mechanism. This approach is not valid for later stages in the process and the independence of E_a should be used carefully. An upper limit of 10% decomposition is suggested, although in certain cases 20% is justified. It is strongly recommended that E_a calculations should be conducted at different levels of decomposition [8]. The DTA/TG curves of calcium carbonate are shown in Fig. 1. The DTA curves have two endothermic peaks. The peak temperatures varied with heating rate from 44 to 153 °C for the first peak,

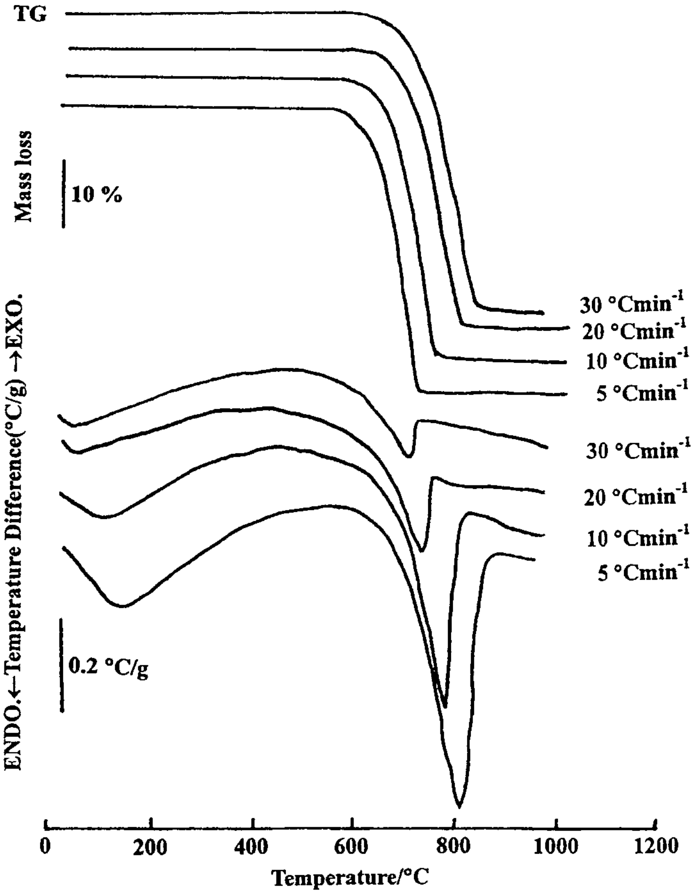

Fig. 1. DTA/TG of calcium carbonate at a heating rate of 5–30 °C/min under static air atmosphere.

Table 2
Activation energy of dehydration and decomposition for $CaCO_3$ and $Ca(H_2PO_4)_2{\cdot}H_2O$

	E_a (kJ mol^{-1})	$-\gamma_b$[a]	E_a, kJ mol^{-1} (mass loss %)							
			1	3	5	7	9	15	20	30
$CaCO_3$										
First endothermic peak (44–153 °C)	19.8	0.976	98.5 (1.00)	96.1 (0.995)	92.6 (1.00)	92.6 (1.00)	91.7 (1.00)	90.7 (1.00)	99.5 (0.987)	71.0 (0.975)
Second endothermic peak (710–815 °C)	190.4	0.996								
$Ca(H_2PO_4)H_2O$[b]										
First endothermic peak (139–155 °C)	154.51	0.997	214 (0.958)		201 (0.996)				245 (0.972)	
Second endothermic peak (259–284 °C)	164.27	0.998								

[a] $-\gamma_b$ is the correction coefficient for linear regression analysis.

[b] The kinetic parameters were selected from Ref. [7].

and from 710 to 815 °C for the second peak. The first peak corresponds to the loss of water and the second to the decomposition of calcium carbonate. The kinetic parameters calculated by the non-isothermal TG/DTA technique are listed in Table 2. The E_a analysis based on non-isothermal TG for $CaCO_3$ decomposition closely approximates the mass loss at 20%. These results are in agreement with the American Society for Testing Materials, Committee E37 on Thermal Measurements.

Fig. 2 illustrates the DTA and TG curves for the three uncalcined mixed powders with a heating rate of 10 °C/min under static air atmosphere. For the DTA curve of uncalcined mixture powder A, three endothermic peak maxima are observed at 52, 431 and 695 °C. These peaks correspond to the dehydration and decomposition processes. In the uncalcined mixture powder B, four endothermic peak maxima are observed below 400 °C at 52, 123, 253, and 310 °C. A small endothermic peak also occurred at 590 °C for mixture B. The DTA curve for uncalcined mixture powder C also had three endothermic peaks at 53, 346 and 413 °C. The activation energies corresponding to dehydration and decomposition for uncalcined mixture powders by non-isothermal DTA techniques is summarized in Table 3.

The TG curves for uncalcined mixture powder A had two stages of mass loss below 800 °C and an 80.6 wt.% residue at 1200 °C. Uncalcined mixture powder B also exhibited two stages of mass loss below 500 °C and an 85.4 wt.% residue at 1200 °C. The uncalcined mixture powder C had only one stage of

Table 3
The activation energy of dehydration and decomposition for three uncalcined mixture powders

Uncalcined mixture powders	E_a (kJ mol^{-1})	$-\gamma_a$	Mass loss % (experimental)	Mass loss % (theoretical)
A				
First endothermic peak (311–373 K)	21.7	0.994	19.4%	$19.2\% = \frac{(126/252) \times 2 \times 18 + (25/100) \times 44}{126 + 25}$
Second endothermic peak (699–726 K)	209.4	0.998		
Third endothermic peak (942–1016 K)	191.4	0.985		
B				
Second endothermic peak (387–405 K)	135.1	0.972	14.6%	$14.9\% = \frac{(94.53/252) \times 18 + (25/100) \times 44}{94.53 + 25}$
Third endothermic peak (522–535 K)	343.9	0.995		
Fourth endothermic peak (570–602 K)	161.3	0.998		
C				
Second endothermic peak (599–630 K)	177.2	0.981	11.7%	$12.4\% = \frac{(25/100) \times 44}{63.62 + 25}$
Third endothermic peak	208.5	0.933		

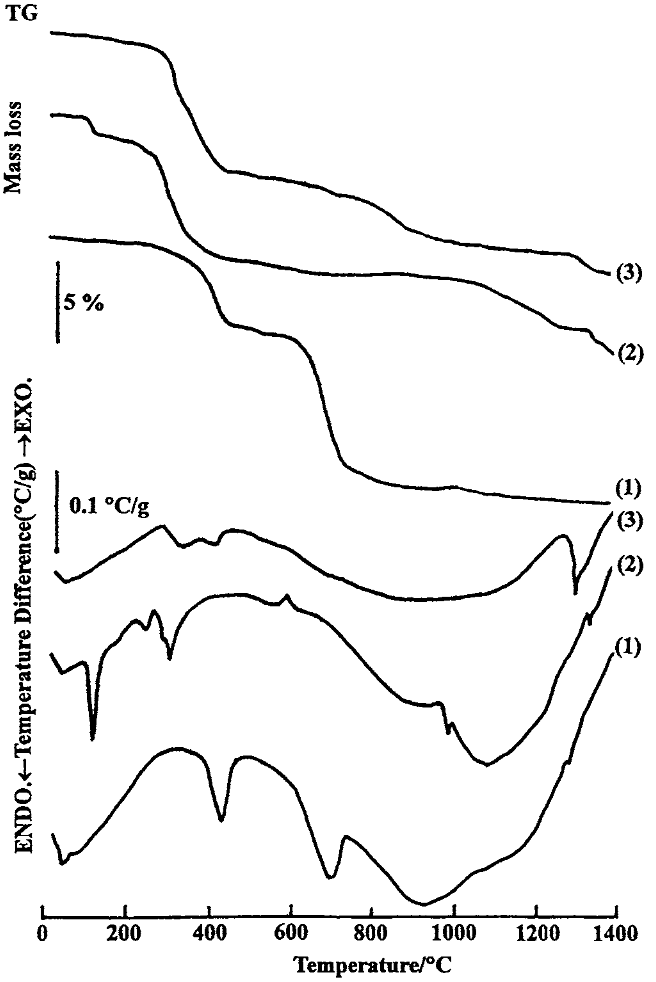

Fig. 2. DTA/TG of uncalcined mixtures at a heating rate of 10 °C/min under static air atmosphere: (1) uncalcined mixture A, (2) uncalcined mixture B, (3) uncalcined mixture C.

mass loss below 500 °C and an 88.3 wt.% residue at 1200 °C.

According to the composition of raw materials and by comparing the residue of TG analysis, we propose the following decomposition equations:

$$x\mathrm{Ca(H_2PO_4)_2 \cdot H_2O} + y\mathrm{CaCO_3} \rightarrow \text{uncertain calcium phosphate} + 2x\mathrm{H_2O} + y\mathrm{CO_2} \quad (1)$$

$$x\mathrm{Ca(H_2PO_4)_2 \cdot H_2O} + y\mathrm{CaCO_3} \rightarrow \text{uncertain calcium phosphate} + x\mathrm{H_2O} + y\mathrm{CO_2} \quad (2)$$

$$x\mathrm{Ca(H_2PO_4)_2 \cdot H_2O} + y\mathrm{CaCO_3} \rightarrow \text{uncertain calcium phosphate} + y\mathrm{CO_2} \quad (3)$$

By comparing the equations and the mass residue of TG analysis, the uncalcined mixture powders can yield HA with the proper heat treatment. This is especially the case for uncalcined powders B and C. These observations will be examined in a future study.

4. Conclusions

The thermal properties of dehydration and decomposition of $CaCO_3$ and three uncalcined mixture powders were determined in this study. Kinetic parameters evaluated by non-isothermal DTA techniques were also reported. Decomposition equations were derived to predict the high temperature behavior of calcium carbonate and calcium hydrogen phosphate hydrate to form water, carbon dioxide and an undefined calcium phosphate. The uncalcined mixture powder B and C can yield HA with the proper heat treatment.

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