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Polymeric Precursor Route for the Preparation of Calcium Phosphate Compounds

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Abstract: A polymeric combustion synthesis is described for the preparation of calcium phosphate compounds. The polymeric gel containing calcium and phosphate ions were synthesised by concentrating a solution of calcium nitrate and ethyl phosphate. When the above gel was introduced to a furnace kept at 500°C, a self combustion reaction was observed, leaving behind a calcium phosphate precursor powder. The above powder on heat treatment at 1000°C resulted in β-TCP, HAP or a mixture of the two phases depending on the Ca/P ratio in the gel. Dependence of Ca/P ratio on the composition of the calcium phosphate phase was studied by XRD. The morphological features of the precursor as well as the heat treated compounds were studied by SEM. The method offers an easy route for the preparation of β-TCP or HAP in the powder or in the porous form.

1 INTRODUCTION

Calcium phosphate is the main constituent of the bones and teeth of vertebrates. Pathological mineral deposits such as those that occur in dental calculus, bursitis, arthritis and other ectopic calcification also involve apatite-like minerals. In recent years, synthetic hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$, and β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$)] were the subject of extensive investigation as implant materials and coatings.[1–3] Today, these materials are available in the market as powders, dense, porous forms or as coatings over metallic implant for a variety of intended prosthetic applications. The preparation of the above compounds can be subdivided into three major headings, viz. dry process, wet process and hydrothermal process.[4,5] They include hydrolysis of calcium phosphates, hydrothermal synthesis, hydrothermal exchange, solid state mixing and heating, spray pyrolysis, sol–gel and wet precipitation methods etc. Variation in these routes lead to differences in morphology, crystallographic structure, stoichiometry and density. Even though the wet chemical method involving the precipitation of a required calcium phosphate phase by the addition of a phosphate solution into a calcium salt solution is the most commonly used method, there are difficulties associated in such methods like the control of stoichiometry, pH, volume of solvents etc. during the processing stages. To overcome these problems, Hattori *et al.* have suggested a polymeric route for the preparation of HAP.[6] Here, an organo phosphorous compound is mixed with calcium acetate and the resultant solution is freeze dried to get a dry polymeric complex. This complex is then heat treated to get HAP.

Here we are describing a new and simple polymeric combustion synthesis of HAP and β-TCP from a complex derived from triethyl phosphate and calcium nitrate. The calcium nitrate–triethyl phosphate complex initiates a self combustion reaction, when the complex is introduced into a

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preheated furnace. By selecting the appropriate Ca/P stoichiometry in the reactants, one can get HAP or β-TCP phase. The method offers a fairly easy way to prepare calcium phosphate porous samples also.

2 EXPERIMENTAL

Calcium nitrate $Ca(NO_3)_2{\cdot}4H_2O$ and triethyl phosphate $(C_2H_5O)_3$ PO which were used for the experiments were of analytical grade. Calcium nitrate was mixed with triethyl phosphate in varying quantities to have different Ca/P ratio in a Pyrex beaker. This mixture was heated with constant stirring. During the heating, calcium nitrate got slowly dissolved in ethyl phosphate. The solution was then concentrated further by continuous heating and stirring till a polymeric gel was formed. The beaker containing the gel was then introduced into a preheated furnace of 500°C. A sudden, vigorous, self-propagating combustion reaction was observed. The gel was first foamed up and later caught fire with the evolution of oxides of nitrogen and carbon. The decomposed gel appeared as a porous aggregate (Fig. 1).

The decomposed polymeric gel was powdered and was heat treated in an alumina crucible at 1000 and 1100°C in air. A flow sheet of the experimental run is illustrated in Fig. 2. The products obtained were characterised using X-ray diffraction (D/max, Rigaku, Japan). The morphology of the heat treated gel was observed under scanning electron microscope (Hitachi S 2400).

Fig. 1. Morphology of the precursor material.

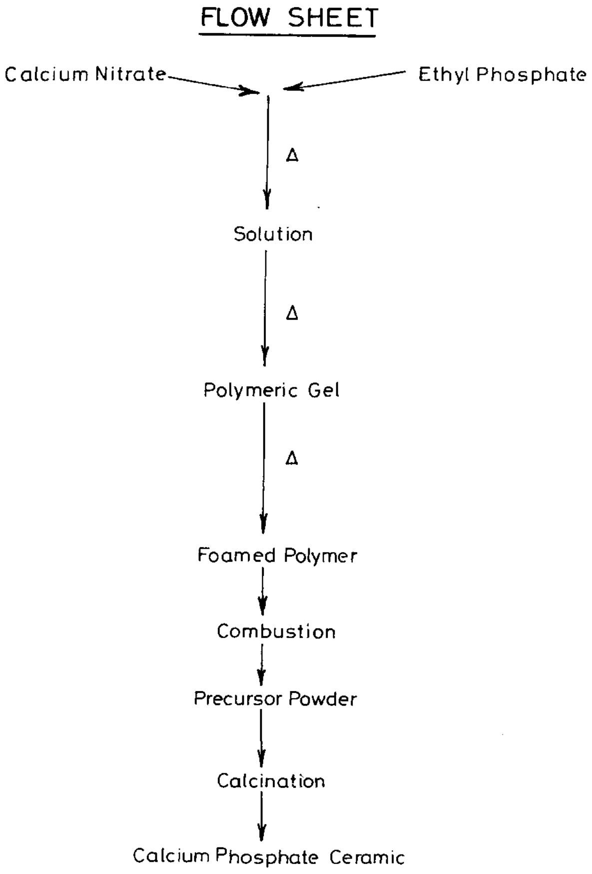


Fig. 2. Polymer precursor route.

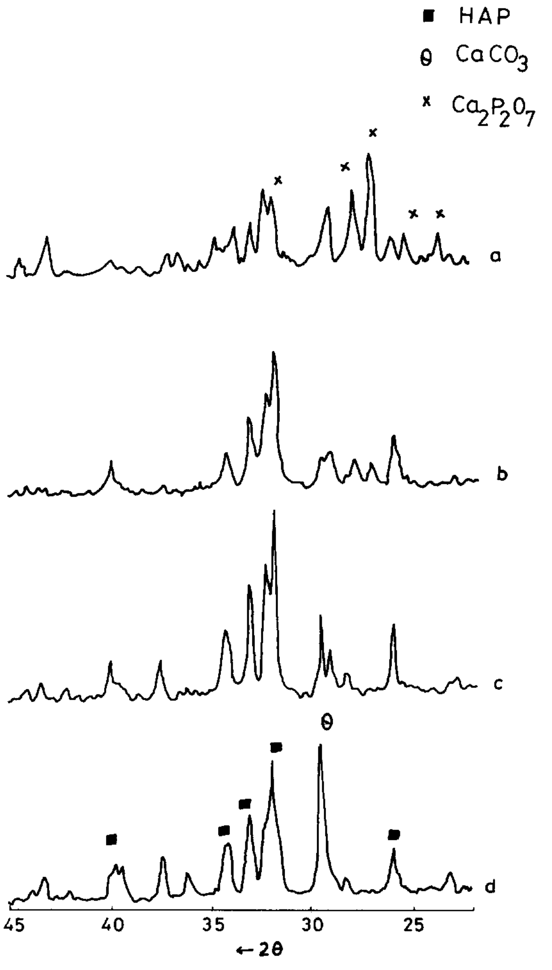


Fig. 3. XRD patterns of calcined powder (500°C for 1 h) derived from polymer gels having different Ca/P ratios. (a) Ca/lP = 1.0; (b) Ca/P = 1.3; (c) Ca/P = 1.6; (d) Ca/P = 1.9.

3 RESULTS

The powder derived by the combustion of polymer gels having different Ca/P ratios were subjected to the XRD analysis. The patterns are provided in Fig. 3. As seen from the patterns, the major phase is HAP in the powders except for the one derived from the gel having Ca/P ratio 1. The other phase is $CaCO_3$ ($2\theta = 29.5°$), and its intensity increases as the Ca/P ratio in the gel increases. In the case of powder derived from the gel having Ca/P ratio = 1, the phases identified are HAP, $Ca_2P_2O_7$ and $CaCO_3$. No β-TCP formation was observed.

The XRD patterns of the powder which were calcined at 1000°C for 2 h are reproduced in Fig. 4. The constituents of the powders are β-TCP, HAP and CaO depending on the initial Ca/P ratio in the gel. It is interesting to observe that there is a progressive transition from β-TCP to HAP as the Ca/P ratio increases in the reactant polymeric gel. Ca/P ratio of 1 is required for complete β-TCP formation and 1.4 is required for HAP. Further increase in the Ca/P ratio resulted in the excess formation of CaO phase along with HAP phase. So by judicious selection of the initial stoichiometry of the polymeric gel, one can generate the required calcium phosphate phase.

Figures 5 and 6 are the scanning electron micrographs of the two representative β-TCP and HAP samples heated at 1100°C for 2 h. The β-TCP samples are more porous than the HAP samples.

4 DISCUSSION

The calcium nitrate–ethyl phosphate mixture on concentrating transforms into a gel. This facilitates uniform mixing of the two components at the molecular level. This gel on further heating initiates an exothermic self combustion reaction with the decomposition reaction of NO_3^- and $-OC_2H_5$ groups. This type of self combustion reactions are

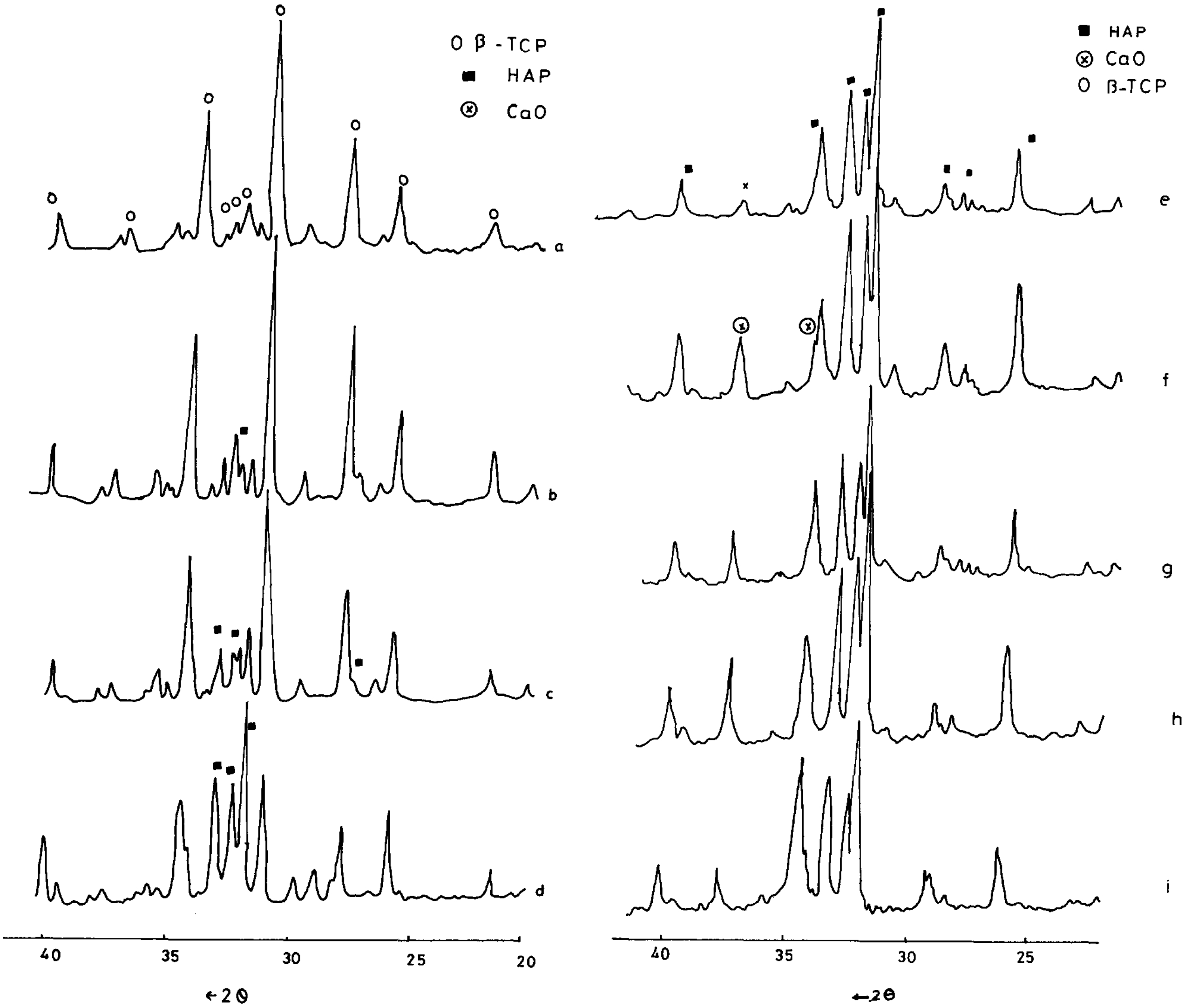
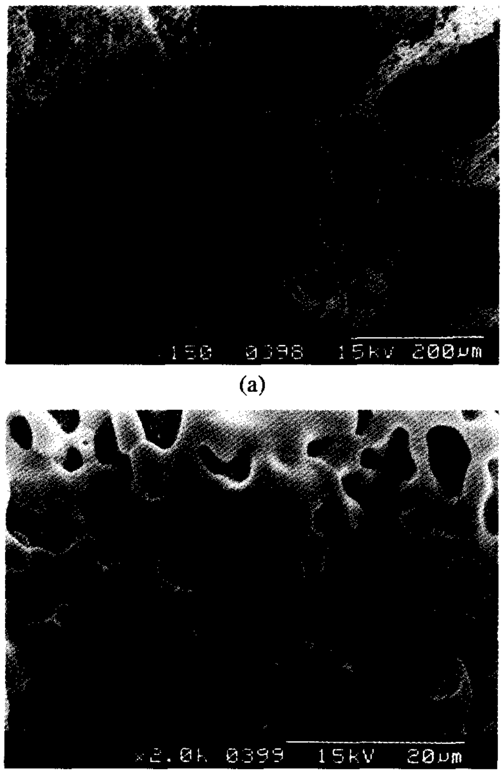


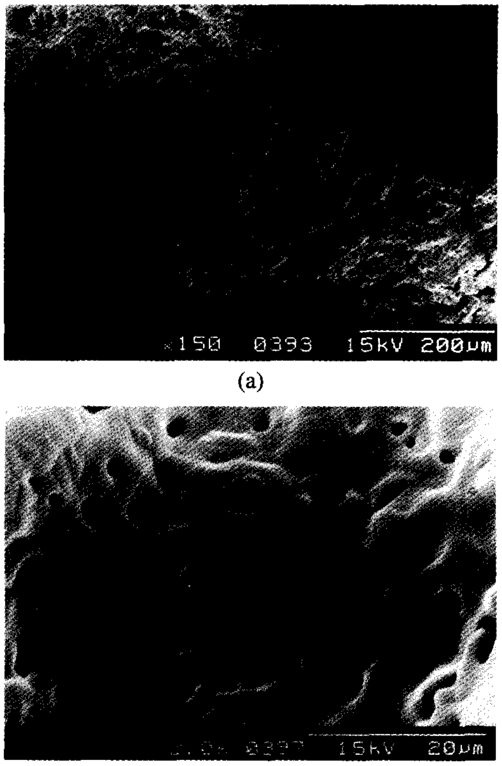
Fig. 4. XRD patterns of heat-treated powders (1000°C for 2 h) derived from polymer gels having different Ca/P ratios. (a) Ca/P = 1.0; (b) Ca/P = 1.1; (c) Ca/P = 1.2; (d) Ca/P = 1.3; (e) Ca/P = 1.4; (f) Ca/P = 1.5; (g) Ca/P = 1.6; (h) Ca/P = 1.8; (I) Ca/P = 1.9.



(a)

(b)

Fig. 5. Low and high magnification scanning electron micrographs of the calcined precursor (1100°C/2 h) derived from the polymeric gel having initial Ca/P = 1.0. The phase has been identified as β-TCP.



(a)

(b)

Fig. 6. Low and high magnification scanning electron micrographs of the calcined precursor (1100°C/2 h) derived from the polymeric gel having initial Ca/P = 1.4. The phase has been identified as HAP.

reported for urea–metal nitrate mixtures.[7] In the present experiment there is a loss of ethyl phosphate during the combustion due to evaporation. That may be the reason for the variation of Ca/P ratio of the reactants and products. An interesting observation in these experiments is that there are only two calcium phosphate phases formed ie. β-TCP and HAP. When the Ca/P ratio of reactants is 1 the product is β-TCP and when Ca/P is 1.4, the product is HAP. In general the products show a trend as given below depending on the Ca/P in the polymeric gel:

$$\beta\text{-TCP} \rightarrow \beta\text{-TCP} + \text{HAP} \rightarrow \text{HAP} \rightarrow \text{HAP} + \text{CaO}$$

So by judiciously selecting the initial ratio of the reactants one can get the required calcium phosphate phase.

5 CONCLUSION

A polymeric precursor route has been developed for the preparation of calcium phosphate ceramic compounds. β-TCP and HAP powders can be obtained by this simple process. This process can also be extended for the development of porous calcium phosphate bioceramics.

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